



A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma–mass spectrometry

Guillermo Grindlay^{a,b,*}, Juan Mora^a, Margaretha de Loos-Vollebregt^{b,c}, Frank Vanhaecke^b

^a Department of Analytical Chemistry, Nutrition and Food Sciences, University of Alicante, PO Box 99, 03080-Alicante, Spain

^b Ghent University, Department of Analytical Chemistry, Krijgslaan 281-S12, 9000 Ghent, Belgium

^c Delft University of Technology, Faculty of Applied Sciences, Analytical Biotechnology, Julianalaan 67, 2628 BC Delft, The Netherlands

ARTICLE INFO

Article history:

Received 7 March 2013

Accepted 12 May 2013

Available online 19 May 2013

Keywords:

Carbon
Matrix effect
Ionization energy
Charge transfer
ICP-MS

ABSTRACT

A systematic study on the influence of carbon on the signal of a large number of hard-to-ionize elements (*i.e.* B, Be, P, S, Zn, As, Se, Pd, Cd, Sb, I, Te, Os, Ir, Pt, Au, and Hg) in inductively coupled plasma–mass spectrometry has been carried out. To this end, carbon matrix effects have been evaluated considering different plasma parameters (*i.e.* nebulizer gas flow rate, r.f. power and sample uptake rate), sample introduction systems, concentration and type of carbon matrix (*i.e.* glycerol, citric acid, potassium citrate and ammonium carbonate) and type of mass spectrometer (*i.e.* quadrupole filter vs. double-focusing sector field mass spectrometer). Experimental results show that P, As, Se, Sb, Te, I, Au and Hg sensitivities are always higher for carbon-containing solutions than those obtained without carbon. The other hard-to-ionize elements (Be, B, S, Zn, Pd, Cd, Os, Ir and Pt) show no matrix effect, signal enhancement or signal suppression depending on the experimental conditions selected. The matrix effects caused by the presence of carbon are explained by changes in the plasma characteristics and the corresponding changes in ion distribution in the plasma (as reflected in the signal behavior plot, *i.e.* the signal intensity as a function of the nebulizer gas flow rate). However, the matrix effects for P, As, Se, Sb, Te, I, Au and Hg are also related to an increase in analyte ion population caused as a result of charge transfer reactions involving carbon-containing charged species in the plasma. The predominant specie is C^+ , but other species such as CO^+ , CO_2^+ , C_2^+ and ArC^+ could also play a role. Theoretical data suggest that B, Be, S, Pd, Cd, Os, Ir and Pt could also be involved in carbon based charge transfer reactions, but no experimental evidence substantiating this view has been found.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Carbon is a concomitant matrix element in many applications of inductively coupled plasma–mass spectrometry (ICP-MS) [1]. It can be found at significant levels in environmental, nutritional, clinical and petrochemical samples. In addition, organic solvents are sometimes employed during the sample preparation step (*e.g.*, extraction/preconcentration) or as eluent in hyphenated techniques.

The presence of carbon in the plasma is a source of spectral and non-spectral interferences in ICP-MS [2]. Several authors have reported that signal intensities for hard-to-ionize elements are significantly enhanced in a carbon-containing matrix in comparison with the corresponding solution without carbon [3–7]. It has been demonstrated that the magnitude of this interference depends on: (i) the element, (ii) the experimental conditions employed (*i.e.* r.f. power, nebulizer gas flow rate, sample uptake rate) [5,6,9,11]; and (iii) the carbon matrix source

[3–6,13]. There is a general observation that signals for As, Se, Te, Au and Hg are enhanced in the presence of carbon [3–13]. Thus, Allain *et al.* [3] reported that As, Au and Hg signal intensities obtained in 1M glycerol were about 2.4, 3.2 and 6.0 times higher than in water, respectively. Other authors have suggested that the signal intensity for Be [6,14], B [14] and Sb [4] can also be increased as a result of the presence of carbon, but contradictory statements can be found for other hard-to-ionize elements, such as P [15,16], Zn [5,6,8,17] and I [3,4]. Despite belonging to the group of hard-to-ionize elements, no signal enhancement due to carbon has been reported for Pt [3], Ir [8] and Cd [5,17]. Signal enhancement reaches a maximum at a matrix concentration that depends on the carbon source. Such matrix effects have been observed for both inorganic (as a carbonate salt) [4,12] and organic carbon sources (*e.g.*, alcohols, organic acids, amines, surfactants, *etc.*) [5,6,9,17]. In addition, selective signal enhancement for hard-to-ionize elements was also observed for aqueous solutions when a volatile organic solvent [7] or methane [18] was added externally to the nebulizer gas flow.

Signal enhancement in the presence of volatile carbon-containing compounds (*e.g.* methanol or ethanol) or surfactants has been partially attributed to changes in the nebulization process and, thus, in the

* Corresponding author at: Department of Analytical Chemistry, Nutrition and Food Sciences, University of Alicante, PO Box 99, 03080-Alicante, Spain.

E-mail address: guillermo.grindlay@ua.es (G. Grindlay).

amount of analyte reaching the plasma [4,6,9,13]. On the other hand, organic solvents also have a cooling effect on the plasma and, as a consequence, the zone of maximum ion density in the plasma could be shifted downstream [6,8,13]. However, these mechanisms do not explain the different magnitudes of the carbon matrix effect for various hard-to-ionize elements and they also do not support the observation that the signal for these elements is enhanced by carbon while at the same time the signal intensity for elements with low ionization energies is not influenced. Alternatively, signal enhancement has been attributed to changes in the ion population through a charge transfer reaction mechanism between C^+ and analyte atoms in the central channel of the plasma [4–6,12,13,19]. The degree of ionization for hard-to-ionize elements is relatively low under normal ICP-MS conditions (*i.e.* 52% for As and 33% for Se, as estimated from the Saha equation) [20] and therefore, improved ionization efficiency by charge transfer from C^+ ions would affect their signal intensities. Elements with low ionization energies are almost completely ionized in the plasma and no such signal enhancement can therefore be expected. Up to now, the carbon charge transfer process has not been studied in depth. First reports pointed out that the charge transfer reaction was possible due to the proximity of the ionization energy of carbon (11.26 eV) and that of hard-to-ionize elements. However, the hypothesis fails to explain why the signal of some hard-to-ionize elements is not enhanced in the presence of carbon (*e.g.*, Cd, Pt, Ir, *etc.*) [3,7,8,21]. Abou-Shakra et al. [19] studied carbon charge transfer reactions for As and Se and concluded charge transfer is possible when the ionization energy of carbon matches the energy of one of the electronic energy levels of the analyte ion. However, the validity of this conclusion was not checked for other hard-to-ionize elements. Some authors [6,17] have suggested the possibility that other carbon-based species in the plasma (*e.g.*, CO^+) could also play a role in charge transfer processes with hard-to-ionize elements. The ionization energies of these carbon species are higher than that for C^+ and they could therefore also improve the ionization efficiency of hard-to-ionize elements. Nonetheless, the potential contribution of such carbon-containing charged species has not been evaluated so far.

In this work, a systematic study on the influence of carbon on the signal of hard-to-ionize elements in ICP-MS is reported. The influence of experimental conditions (*i.e.* nebulizer gas flow rate, r.f. power and sample uptake rate), sample introduction system, type and concentration of carbon matrix (*i.e.* glycerol, citric acid, potassium citrate and ammonium carbonate), as well as mass spectrometer characteristics (*i.e.* quadrupole filter vs. double-focusing sector field mass spectrometer) on variation in the signal intensity due to concomitant C has been evaluated for a large number of hard-to-ionize elements (*i.e.* B, Be, P, S, Zn, As, Se, Pd, Cd, Sb, I, Te, Os, Ir, Pt, Au, and Hg). Hard-to-ionize elements were selected to cover a wide range of ionization energies (8.2–10.5 eV) and *m/z* (9–202 u). For comparison, also the potential effect on several easily ionizable elements (*i.e.* K, Sc, Mn, Co, Rb, Mo, In, Ba, W, Pb, and U) was studied.

2. Experimental

2.1. Reagents

Carbon-containing solutions were made from glycerol, citric acid, potassium citrate and ammonium carbonate (Merck, Darmstadt, Germany). High-purity water with a resistivity > 18 M Ω ·cm was obtained from a Milli-Q water Direct-Q3 purification system (Millipore Inc., France). Li, Be, B, P, S, Sc, Mn, Co, Zn, As, Se, Rb, Mo, Pd, Cd, In, Sb, I, Te, Ba, W, Os, Ir, Pt, Au, Hg, and Pb and U mono-elemental solutions (Merck, Germany) were employed to prepare multi-element test solutions.

All glassware and polypropylene flasks were soaked in 1.4 M HNO_3 overnight and rinsed with Milli-Q water prior to use. Test solutions were freshly prepared daily.

2.2. ICP-MS instrumentation

A quadrupole-based Xseries 2 ICP-MS instrument and an Element XR sector field instrument (both from Thermo Scientific, Germany) were employed throughout this work. The operating conditions for both instruments are listed in Table 1. The sample introduction system of the Xseries 2 instrument consisted of a conical nebulizer (AHF Analysentechnik AG, Germany) mounted onto a single-pass spray chamber with impact bead (inner volume 23 cm³). Additionally, a PFA single-pass spray chamber (inner volume 43 cm³) was employed to evaluate the possible influence of the sample introduction system characteristics on carbon matrix effects. The sample introduction system of the Element XR instrument consisted of a MicroMist nebulizer mounted onto a cyclonic spray chamber (both from Glass Expansion Ltd, Australia). The nuclides monitored with both instruments together with their respective ionization energies and ionization degrees (estimated via Saha equation) [20] are listed in Table 2. In order to monitor the plasma conditions and the matrix load of the plasma, the signals of $^{13}C^+$, $^{13}C_2^+$, $^{13}C^{16}O^+$, $^{13}C^{16}O_2^+$, $^{38}Ar^+$ and $^{40}Ar^{13}C^+$ were registered.

2.3. Aerosol drop size distribution measurements

To evaluate the influence of carbon on aerosol generation and transport, aerosol drop size distributions for carbon-containing solutions and the corresponding solutions without carbon were measured by means of a laser Fraunhofer diffraction system (Model 2600c, Malvern Instruments Ltd., Malvern, UK). Description of the instrument setup and experimental details can be found elsewhere [22].

3. Results and discussion

3.1. Carbon matrix effects

Fig. 1 shows the relative ion intensities, I_{rel} for different elements as a function of their ionization energy for solutions containing carbon 5 and 30 g L⁻¹ made from glycerol as observed using the quadrupole-based ICP-MS (Q-ICP-MS) instrument. I_{rel} is defined as the net signal intensity of the analyte obtained in a carbon-containing solution relative to that in the reference solution, *i.e.* high-purity water. Signal repeatability is ~2% RSD (10 replicates). Therefore, it can be considered that I_{rel} values below 0.96 or higher than 1.04 (*i.e.* exceeding an uncertainty range of $\pm 4\%$) indicate matrix effects. This range is represented by dashed lines in Fig. 1. I_{rel} values higher than 1.04 indicate signal enhancement, whereas values lower than 0.96 indicate signal suppression.

Fig. 1 shows that I_{rel} values strongly depend on the carbon concentration and the ionization energy of the element considered. In the presence of a carbon concentration of 5 g L⁻¹, no matrix effects were observed for most of the nuclides monitored, with the exception

Table 1
ICP-MS operating conditions.

ICP-MS instrument	Q-ICP-MS Xseries 2	SF-ICP-MS Element 2
Plasma forward power(W)	1100–1400	1100–1300
Argon flow rate (L min ⁻¹)		
Plasma	13	16
Auxiliary	0.7	0.8
Nebulizer	0.65–1.00	0.81–0.91
Sample introduction system		
Nebulizer	Conical	Micromist
Spray chamber	Single-pass with and without impact bead	Cyclonic spray chamber
Sample uptake rate (mL min ⁻¹)	0.2–1.0	0.2–1.0
Dwell time (ms)	10	50
Sweeps	100	100
Replicates	5	5

Download English Version:

<https://daneshyari.com/en/article/1239845>

Download Persian Version:

<https://daneshyari.com/article/1239845>

[Daneshyari.com](https://daneshyari.com)