

Accepted Manuscript

Carbon, sulfur and phosphorus-based charge transfer reactions in inductively coupled plasma atomic emission spectrometry

Guillermo Grindlay, Luis Gras, Juan Mora, Margaretha T.C. de Loos-Vollebregt

PII: S0584-8547(15)00262-1
DOI: doi: [10.1016/j.sab.2015.10.010](https://doi.org/10.1016/j.sab.2015.10.010)
Reference: SAB 4994

To appear in: *Spectrochimica Acta Part B: Atomic Spectroscopy*

Received date: 30 June 2015
Accepted date: 24 October 2015



Please cite this article as: Guillermo Grindlay, Luis Gras, Juan Mora, Margaretha T.C. de Loos-Vollebregt, Carbon, sulfur and phosphorus-based charge transfer reactions in inductively coupled plasma atomic emission spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy* (2015), doi: [10.1016/j.sab.2015.10.010](https://doi.org/10.1016/j.sab.2015.10.010)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Carbon, sulfur and phosphorus-based charge transfer reactions in inductively coupled plasma atomic emission spectrometry

Guillermo Grindlay^{#*}, Luis Gras[#], Juan Mora[#], Margaretha T.C. de Loos-Vollebregt^{\$}

[#]*University of Alicante, Department of Analytical Chemistry, Nutrition and Food Sciences, PO Box 99, 03080 Alicante, Spain.*

^{\$}Ghent University, Department of Analytical Chemistry, Krijgslaan 281 – S12, 9000 Ghent, Belgium.

E-mail: guillermo.grindlay@ua.es

Abstract

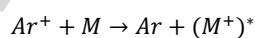
In this work, the influence of carbon, sulfur and phosphorus-based charge transfer reactions on the emission signal of 34 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, I, In, Ir, K, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, S, Sb, Se, Sr, Te and Zn) in axially-viewed inductively coupled plasma–atomic emission spectrometry has been investigated. To this end, atomic and ionic emission signals for diluted glycerol, sulfuric acid and phosphoric acid solutions were registered and results were compared to those obtained for a 1% w w⁻¹ nitric acid solution. Experimental results show that the emission intensities of As, Se and Te atomic lines are enhanced by charge transfer from carbon, sulfur and phosphorus ions. Iodine and P atomic emission is enhanced by carbon and sulfur-based charge transfer whereas the Hg atomic emission signal is enhanced only by carbon. Though signal enhancement due to charge transfer reactions is also expected for ionic emission lines of the above mentioned elements, no experimental evidence has been found with the exception of Hg ionic lines operating carbon solutions. The effect of carbon, sulfur and phosphorus charge transfer reactions on atomic emission depends on: (i) wavelength characteristics. In general, signal enhancement is more pronounced for electronic transitions involving the highest upper energy levels; (ii) plasma experimental conditions. The use of robust conditions (i.e. high r.f power and lower nebulizer gas flow rates) improves carbon, sulfur and phosphorus ionization in the plasma and, hence,

signal enhancement; and (iii) the presence of other concomitants (e.g. K or Ca). Easily ionizable elements reduce ionization in the plasma and consequently reduce signal enhancement due to charge transfer reactions.

Introduction

The excitation and ionization of analytes in the inductively coupled plasma (ICP) is a complex process due to the simultaneous occurrence of different mechanisms including: (i) collisional excitation; (ii) collisional ionization; (iii) radiative recombination; (iv) Penning ionization and excitation; and (v) charge transfer reactions[1]. A better understanding of these mechanisms is necessary to evaluate matrix effects due to sample concomitants as well as to obtain better insight in the underlying physical and chemical processes in inductively coupled plasma mass spectrometry (ICP-MS) and in inductively coupled plasma atomic emission spectrometry (ICP-AES).

Charge transfer reactions in the ICP are mainly based on the transfer of charge between Ar ions (Ar^+) and analyte atoms (M), resulting in an excited analyte ion ($M^+)^*$ [2,3]:

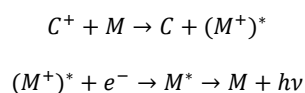


This type of reaction is highly specific and involves atomic and high-energy ionic levels of the analyte [4,5]. For appreciable charge transfer to occur, two requirements should be fulfilled: (i) the reaction energy defect (ΔE) should be minimum. This means that analyte ions should have an electronic level close in energy to the Ar ionization energy; and (ii) the total spin number of reactants and products should be conserved (Wigner spin rule). Nonetheless, observations suggest that, for some elements, Ar-based charge transfer reactions in ICP could even be produced without fulfilling the above mentioned criteria [6]. This type of reactions has been studied for a variety of elements [4-6], especially magnesium and transient metals.

The potential contribution of non-argon based charge transfer reactions to the signal in ICP-based techniques has been evaluated by several authors. The effect of carbon-based charge transfer reactions on analyte ionization in ICP-MS has been recognized for a long time [7-10]. Similarly, sulfur-based charge transfer reactions have also been noticed in ICP-MS [10]. Reaction requirements are similar to those previously outlined for Ar-based charge transfer

reactions (i.e. minimum energy defect of the reaction and conservation of the electron spin) and, as a consequence, non-argon based charge transfer reactions only affect certain elements [11,12]. It was found that As, P, Se and Te signals in ICP-MS are selectively enhanced by carbon and sulfur-based charge transfer reactions whereas Au, Hg, I, and Sb are only enhanced by carbon. It has also been suggested that P containing matrices could have similar effects in ICP-MS [10].

Studies about non-argon based charge transfer reactions in ICP-AES have been more limited so far [13-16] but it has already been demonstrated that certain emission lines are affected by this type of reactions. Chan and Hieftje [13] studied the influence of oxygen, hydrogen, nitrogen, krypton, methane, and carbon dioxide addition into the central channel on the emission intensity of atomic and ionic lines in ICP-AES for Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr and Zn. They found that relative intensities did not change for emission lines with excitation energies close to the ionization energies of the foreign gases and therefore concluded that the contribution of charge transfer from the selected foreign-gas ions did not have a significant contribution to the overall ionization and excitation process of the elements tested. However, Briker et al. [14] observed that the emission lines of Fe ions in a radially-viewed plasma were significantly affected when Xe was added into the plasma channel. The emission intensity of most Fe ionic lines was suppressed in the presence of Xe but for certain ionic Fe lines the emission signal was selectively enhanced. This anomaly was explained by near-resonant charge transfer reactions between Xe^+ and neutral Fe which overpopulates certain Fe^+ states (i.e. those close in energy to the Xe ionization energy). Machat et al. [15] reported that, when compared to aqueous standards, intensities of Se atomic emission lines were enhanced when glycerol, sulfuric acid and phosphoric acid solutions were introduced in the plasma. Signal enhancement for carbon containing solutions can be explained by means of a two-step mechanism where the analyte is ionized by carbon ions and, after an ion-electron recombination process, the population of excited analyte atoms is increased [15,16].



Similarly, it was suggested that sulfur and phosphorus-based charge transfer reactions could explain the matrix effects observed for Se, As and Te atomic emission lines. In our previous study of carbon-related matrix effects in axially-viewed ICP-AES, we found that, among 15 elements, As and Se atomic lines were enhanced (up to 30%) by carbon [16]. For the other analytes, the emission intensity of atomic lines was depressed whereas no changes were registered for the ionic emission lines.

Up to date, carbon-based charge transfer reaction studies in ICP-AES have focused on As, Se and Te [15,16] and no information is found for P, Hg or I, although these elements could theoretically also be affected by this type of interference [11]. Similarly, the influence of sulfur- and phosphorus-based charge transfer reactions on the analyte emission signal has not been studied systematically [15]. The goal of this work is to investigate the influence of carbon-, sulfur- and phosphorus-based charge transfer reactions on the analytical response of atomic and ionic emission lines of 34 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, I, In, Ir, K, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, S, Sb, Se, Sr, Te and Zn) in axially-viewed ICP-AES. To this end, atomic and ionic emission signals were registered for diluted glycerol, sulfuric acid and phosphoric acid solutions and results were compared to those obtained for a 1% w w⁻¹ nitric acid solution. The influence of experimental conditions, the cross-sectional emission profile, line characteristics and the presence of easily ionizable elements on atomic and ionic line intensities have been evaluated.

2. Experimental

2.1. Reagents

High-purity water with a resistivity >18 MΩ.cm obtained from a Milli-Q water Direct-Q3 purification system (Millipore Inc., Paris, France) was used throughout this work. Nitric acid (69% w w⁻¹) was employed to prepare the reference solution (Merck, Darmstadt, Germany) whereas matrix-containing solutions were made from glycerol, 98% w w⁻¹ sulfuric acid and 65% w w⁻¹ phosphoric acid (Panreac, Castellar del Valles, Spain). Silver, Al, As, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, Ir, K, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, S, Sb, Se, Sr, Te and Zn

mono-elemental solutions (Merck, Darmstadt, Germany) were employed to prepare analyte test solutions.

2.2 Matrix and analyte solutions

Three different matrix solutions were employed in this work. Thus, 20 g L⁻¹ carbon (glycerol), sulfur (sulfuric acid) and phosphorus (phosphoric acid) solutions were used to study concomitant-based charge transfer reactions whereas 1% w w⁻¹ nitric acid was employed as the reference solution. Matrix effects were evaluated using 100 mg L⁻¹ mono-elemental analyte solutions. No multi-element standard was prepared to avoid the occurrence of spectral interferences (e.g. As I 228.812 nm and Cd I 228.802 nm).

2.3 ICP instrumentation

ICP-AES measurements were performed using an Agilent 720 ICP-AES (Agilent, Santa Clara, USA) with axial viewing. The sample introduction system consisted of a concentric pneumatic nebulizer (Seaspray, Glass Expansion, Australia) coupled to a cyclonic spray chamber (Cinnabar, Glass Expansion, Australia). Table 1 shows the operating conditions used with this instrument. The wavelengths of the emission lines selected for all analytes monitored in this work are shown in Table S1 (Appendix). Information about the energy of the electronic levels involved, E_{exc} (excitation energy) and E_{sum} (the sum of the excitation and ionization energy) is also included in this table. Spectroscopic data were mainly taken from the NIST database [17] but some other sources were also employed [18-21]. The spectral lines of each element were the most prominent with the exception of As, Hg, I, P, Se, Te where the pool of (atomic) lines selected was wider to enlarge insight in charge transfer reactions in ICP-AES. Emission signals for all the lines listed in Table S1 were strong enough (>2000 counts) to distinguish them from the background at a concentration of 100 mg L⁻¹.

3. Results

3.1. Matrix effects

Figures 1a-c show the relative ion intensities, I_{rel} , for different emission lines as a function of their E_{sum} values for matrix solutions containing 20 g L⁻¹ of carbon, sulfur and phosphorus, respectively. I_{rel} is defined as the net signal intensity of the analyte obtained in a matrix-containing solution relative to that in 1% w w⁻¹ nitric acid solution. In general, signal repeatability for atomic and ionic emission lines was ~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. Dashed lines in Fig. 1 represent this range. Thus, I_{rel} values higher than 1.04 indicate signal enhancement, whereas values lower than 0.96 indicate signal suppression. The vertical line in Fig 1 indicates the type of emission line (*i.e.* atomic vs ionic). Results in Fig. 1 point out that the presence of carbon, sulfur and phosphorus strongly affects the emission intensity of some of the lines tested. The magnitude of matrix effects (I_{rel}) depends on both the concomitant and line characteristics (E_{sum}).

3.1.1 Carbon

When introducing the carbon-containing matrix (Fig 1a), significant differences in I_{rel} values were noticed between ionic and atomic lines. In general, signal suppression was significant for atomic lines with E_{sum} values lower than 4-5 eV. Thus, for instance, signals for Na I 588.995 nm (E_{sum} 2.10 eV) and Li I 610.365 nm (E_{sum} 2.69 eV) were depressed up to 23% when compared to 1% w w⁻¹ nitric acid solution. On the other hand, signal enhancement was observed for all atomic emission lines of As, I, Se and Te as well as for several atomic lines of Hg and P. The magnitude of the carbon matrix effect for these elements depends on the emission line selected. Thus, for instance, I_{rel} values for Se I 185.883 nm (E_{sum} 6.67 eV) and Se I 241.424 nm (E_{sum} 5.14 eV) were 1.62 and 1.42, respectively. The behavior of As, Se and Te atomic emission lines is in agreement with previous observations using different instrumentation [15,16]. Finally, Fig. 1a revealed no matrix effects for ionic lines in the presence of carbon with the exception of Hg II 194.227 nm (E_{sum} 16.86 eV) for which I_{rel} was 1.21.

To explain the carbon-based matrix effects shown in Fig. 1, it should be taken into account that

carbon solutions may affect: (i) plasma excitation conditions; (ii) aerosol generation and transport; and (iii) analyte excitation-ionization mechanisms within the plasma when compared to a 1% w w⁻¹ nitric acid solution. Plasma energetic characteristics were evaluated using different methodologies such as: (i) the intensity of the Ar I line at 420.069 nm [22]; (ii) excitation energy by means of the Boltzmann plot using Fe atomic lines [23]; and (iii) the Mg II (280.270 nm)/Mg I (285.213 nm) line intensity ratio [24]. No significant differences were registered for these parameters between 1% w w⁻¹ nitric acid and 20 g L⁻¹ of carbon solution, with the exception of the Mg II/Mg I ratio, which was somewhat higher for the carbon matrix. The MgII/Mg I ratio for 1% w w⁻¹ nitric acid and 20 g L⁻¹ of carbon solutions was 4.0 and 4.8, respectively. Interestingly, the higher Mg II/Mg I ratio for the carbon matrix was related to suppression of the Mg I signal. These findings are in agreement with previous observations made by Grindlay et al. [16] and indicate that matrix effects are not related to changes in plasma excitation conditions. No significant differences in aerosol generation and transport have been observed for diluted nitric acid and 20 g L⁻¹ carbon solutions made from glycerol [16]. Therefore, no differences in the emission signals from nitric acid and the carbon containing solution are expected. This is indeed confirmed by the absence of matrix effects for most of the ionic lines. The above-mentioned considerations lead to the conclusion that signal enhancement shown in Fig 1a should be related to changes in the excitation-ionization mechanism. The signal reduction observed for some atomic lines can be related to different phenomena such as a lower population of excited atoms due to the deactivation of excited state atoms by collisions with elemental carbon or carbon radicals or the formation of stable carbide compounds [16,25]. The positive matrix effects registered for As, Hg, I, P, Se and Te lines can be explained by carbon-based charge transfer reactions followed by an ion-electron recombination process which enhances the population of excited atoms and, hence, the emission signal. This two-step mechanism has been previously proposed as an explanation for signal enhancement of As, Se and Te atomic emission lines [15,16]. In addition, and taking into account the observed influence of carbon on the behavior of hard-to-ionize elements in ICP-MS [11], it can be expected that the emission for Hg, I and P is also affected by carbon on a similar basis. According to the charge transfer mechanism just mentioned the analyte ion population for As,

Hg, I, P, Se and Te is enhanced and, therefore, increased emission signals for those ionic states directly affected by charge transfer reactions could be expected. Nonetheless, the potential effect of other mechanisms (e.g. electron impact) makes the picture more complex due to possible changes in the population of ionic states not directly affected by charge transfer reactions. For this reason, the spectrum covered by the ICP-AES instrument was checked for emission signals of As, Hg, I, P, Se and Te ionic lines. Unfortunately, with the exception of Hg, no emission from ionic lines of these elements was found with the instrument configuration employed in this work. Emission signals from the ionic levels directly excited by the charge transfer reactions radiate in the IR region (e.g. As II 799.820 nm, Se II 759.410 nm or P II 787,816 nm) and they could not be detected with our instrument. In addition, most of these electronic transitions are forbidden and they would only radiate weakly [17,18]. The sensitivity of ionic lines not directly involved in charge transfer reactions (e.g. As II 223.607 or Te II 179.360 nm) was also poor. As it has been pointed out previously, Hg II 194.227nm shows a positive matrix effect due to the presence of carbon in the plasma (Fig 1.a.) which means that both Hg atomic and ionic lines (Table S1) are positively affected by carbon charge transfer reactions. At this point, it is interesting to note that previous studies in ICP-MS have shown that Au and Sb ionization in the plasma is also enhanced by carbon-based charge transfer reactions [11]. However, none of the atomic and ionic lines of these elements showed signal enhancement in ICP-AES.

3.1.2 Sulfur and phosphorus

For sulfur (Fig 1b) and phosphorus (Fig 1c.) matrices, it was observed that ionic emission lines and most of the atomic emission lines were suppressed on average 10% when compared to the nitric acid solution. Positive matrix effects ($I_{rel} > 1.04$) were registered for the atomic lines of As, I, P, Se and Te in the sulfur matrix whereas for the phosphorus matrix As, Se and some Te (e.g. 182.215 nm or 200.202 nm) lines were enhanced. It is interesting to note that, though P signals were enhanced by the sulfur matrix, the S signals were not enhanced by the phosphorus matrix. Finally, the magnitude of signal enhancement caused by each matrix was strongly dependent on the selected emission line.

Suppression of analyte emission for ionic and most of the atomic lines could be attributed to changes in the analyte transport rate. It is well-known that sulfuric and phosphoric acid solutions afford lower analyte transport rate values when compared to nitric acid solutions and, hence, lower signals are expected for these matrices [12,26]. Plasma energetic characteristics were not significantly modified by sulfur and phosphorus when compared to 1% w w⁻¹ nitric acid solution. Differences in the Mg II/Mg I ratio, the Ar I emission intensity and the excitation temperature between sulfur and phosphorus containing matrices and the corresponding nitric acid solution were less than 5%. Therefore, signal enhancement observed for the sulfur- and phosphorus-containing solutions must be related to the analyte atomization-ionization process. Previously published work [15] suggests that, similar to carbon, the origin of signal enhancement could be explained by a two-step reaction mechanism based on charge transfer reactions with sulfur and phosphorus ions, followed by an ion-electron recombination process that populates excited atom states.

Vanhaecke et al. [10] reported that a 0.5 M H₃PO₄ matrix increased the ionization of As, Se and Te in ICP-MS when compared to a 0.14 M nitric acid solution. However, the topic was not covered in detail in their paper and the number of analytes studied was very limited. In a recently published systematic study of non-spectral interferences in ICP-MS due to the presence of sulfuric acid, Garcia-Poyo et al. [12] demonstrated that As, P, Se and Te ionization is significantly enhanced by sulfur-based charge transfer reactions. To better understand sulfur and phosphorus-based charge transfer reactions in ICP-based techniques and to complete our previous study [12], additional experiments were carried out in ICP-MS. First, it was investigated whether I is affected by sulfur-based charge transfer reactions since this element was not included in the work of Garcia-Poyo et al. [12]. Second, the potential influence of phosphorus on the ion signals of Ag, Al, As, Au, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, Ir, Li, Mn, Ni, P, Pb, Pd, Pt, S, Sb, Se, Sr, Te and Zn was also investigated. Ca, K, Mg and Na were not measured because of high background signals (e.g. ⁴⁰Ar⁺). Instrumentation and operating conditions for these experiments were similar to those described elsewhere [12]. Signals obtained in ICP-MS for 20 g L⁻¹ sulfur and phosphorus solutions were compared to the corresponding signals in nitric acid 1% w w⁻¹ solution. Signal repeatability was on average 2% (10 replicates). Therefore,

I_{rel} values higher than 1.04 indicate signal enhancement, whereas values lower than 0.96 indicate signal suppression. Positive matrix effects were observed for I operating the sulfur matrix (I_{rel} :1.17) and, hence, it can be considered that this element is also affected by charge transfer reactions. As regards the phosphorus matrix (see Supplementary material, Figure S1), it was observed that the ion intensities for most elements were depressed on average 7% when compared to the 1% w w⁻¹ nitric acid solution. Positive matrix effects were registered for As, Se, Sb, Te (I_{rel} values 1.48, 1.30, 1.12 and 1.22, respectively). The observed signal enhancement in ICP-MS clearly supports the previously discussed occurrence of phosphorus-based charge transfer reactions in ICP-AES and the corresponding atomic emission signal enhancement for As, Se and Te caused by the phosphorus matrix. Interestingly, Sb signals behave differently. In ICP-AES, none of the atomic and ionic lines of Sb show a positive matrix effect whereas the ¹²¹Sb⁺ signal is enhanced in ICP-MS.

Finally, similar to the carbon matrix, potential changes in the emission intensity of ionic lines for elements affected by sulfur- and phosphorus-based charge transfer could not be investigated due to instrumental limitations and poor sensitivity.

3.2. Influence of experimental conditions (r.f. power and nebulizer gas flow rate)

Matrix effects in ICP-AES strongly depend on the plasma operating conditions [26,27]. For this reason, the influence of the nebulizer gas flow rate (Q_g) and plasma r.f. power on I_{rel} values has been studied. Figure 2 shows the influence of Q_g on I_{rel} values for Se I 196.090 nm, Mg I 285.213 nm and Cd II 214.439 nm operating carbon, sulfur and phosphorus matrices at different r.f. power values (i.e. 1400 and 1100 W). These emission lines were selected to represent the group of elements exhibiting different behavior in the presence of the concomitants studied. Thus, Se I 196.090 nm was selected as an atomic emission line affected by charge transfer reactions due to the presence of carbon, sulfur and phosphorus, whereas Mg I 285.213 nm and Cd II 214.439 nm were selected to represent the groups of atomic and ionic lines not affected by charge transfer reactions, respectively. As shown in Figure 2, for a given concomitant solution, matrix effects depend on both r.f. power and Q_g . When operating the carbon matrix (Fig 2a.) at 1400 W, I_{rel} values for atomic lines (Se I 196.026 nm and Mg I 285.213 nm) are almost

independent of Q_g up to 0.9 L min^{-1} . Above this gas flow, I_{rel} values decreased but Se I 196.090 nm still shows a positive matrix effect. Cd II 214.439nm shows no matrix effects at the selected nebulizer gas flows. When the power was adjusted to 1100 W, I_{rel} values for all the lines decreased for $Q_g > 0.7 \text{ L min}^{-1}$ and at Q_g of 1 L min^{-1} even Se I 196.090 nm would exhibit signal suppression due to the presence of carbon. From the results shown in Fig 2a, it is clear that positive matrix effects for Se I 196.090 nm are more significant at 1400 W than at 1100 W. Interestingly, in our previous study on carbon matrix effects in axial-viewed ICP-AES [16] no significant influence of Q_g and r.f. power on I_{rel} was observed. The influence of experimental conditions on sulfur (Fig 2b) and phosphorus (Fig 2c) matrix effects was rather similar to carbon. Nonetheless, when increasing Q_g at 1100 W signal suppression was more significant, especially for sulfuric acid.

Matrix effects shown in Fig 2 for Cd II 214.439 and Mg I 285.213 nm can be explained taking into account that concomitants negatively affect plasma energetic conditions under non-robust conditions (i.e. low r.f power and high Q_g) and, hence, emission intensity is reduced in the presence of the carbon, sulfur and phosphorus matrix [27,28]. In fact, it was observed that all parameters employed in this work to assess plasma energetic conditions (i.e. Ar I 420.069 nm, Mg II/Mg I ratio and excitation temperature) decreased when increasing Q_g and this effect was indeed more significant at 1100 W than at 1400 W. Regarding the matrix effects on Se I 196.090 nm emission it should be taken into account how plasma experimental conditions affect charge transfer reactions. This type of reaction involves the concomitant ion population (i.e. C^+ , S^+ and P^+) and, hence, it is favoured under robust conditions where atomization and ionization are more efficient. Thus, it was observed that the emission signals for C I 193.090 nm, S I 181.917 nm and P I 213.618 nm increased under robust conditions. Carbon, sulfur and phosphorus ion population in the plasma could not be estimated due to lack of sensitive ionic lines for these elements. Nevertheless, experiments carried out in ICP-MS using similar experimental conditions have shown that $^{12}C^+$, $^{33}S^+$ and $^{31}P^+$ signals increased under robust conditions.

3.3. Cross-sectional emission profile.

Chan and Hieftje highlighted that matrix effects show a strong spatial dependence and, hence, plasma spatial profiling is a useful tool to flag matrix effects for both radially [28-30] and axially-viewed ICP-AES [31,32]. Although a specific instrument configuration is required to obtain a detailed cross sectional emission profile, our instrument can provide some limited plasma spatial profiling to check charge transfer reactions. The ICP-AES instrument is equipped with a software tool that allows optimization of the plasma viewing position by controlling two mirrors between the plasma and the monochromator. One of these mirrors is located just in front of the plasma and can be mechanically moved along the horizontal plasma axis to view off axis positions in the plasma. The cross-sectional spatial emission profiles for Se I 196.090 nm, Mg I 285.213 nm and Cd II 214.439 nm have been measured for carbon, sulfur and phosphorus (20 g L⁻¹) containing solutions. A bell-shaped centered distribution of emission intensities was observed for each emission line, regardless the matrix employed (Fig. S2, Appendix) and, as expected, the magnitude of the emission signal depends on the matrix. Figure 3 shows the corresponding I_{rel} values for the above mentioned lines at different plasma locations along the horizontal plasma axis. As it can be observed in this figure, for each concomitant, matrix effects depend on the selected plasma position. Thus, for instance, carbon matrix effects for the atomic lines of Se and Mg (Fig 3a) are more significant in the region close to the plasma central axis, probably due to the higher carbon ion concentration in this region. Liu and Beauchemin [33] reported that the C⁺ ion signal is indeed higher close to the plasma central axis. As already pointed out before, no direct C⁺ ion emission signal measurements were feasible but the atomic carbon emission was higher close to the plasma central axis (Figure S3) which also confirms the presence of more carbon. In agreement with analyte transport data, no matrix effects on Cd II 214.439 nm were registered. Results for sulfur (Fig 3b) and phosphorus (Fig. 3c) matrices could be explained on a similar basis taking into account both changes in aerosol transport and analyte excitation/ionization mechanism due to more sulfur and phosphorus present in the central channel (Figure 3S). Interestingly, the I_{rel} values for Se I 196.090 nm measured in the phosphorus matrix were positive at positions close to the plasma central channel but signal suppression was observed at positions 2.0 mm off axis.

Finally, it is worth to mention that results in Fig 3 confirm that the occurrence of charge transfer

reactions in the plasma could be flagged similar to other plasma-related interferences [31,32].

3.4. Influence of analyte line characteristics

As discussed in section 3.1 (Fig. 1), signal enhancement for some elements due to the presence of carbon, sulfur and phosphorus depends on the selected emission line. In previous studies of carbon-based charge transfer reactions, it has already been noticed that signal enhancement for As and Se atomic emission lines was more significant for electronic transitions involving the highest upper energy levels, irrespective of the corresponding lower energy levels [15,16]. The overpopulation of the high energy levels was explained by means of a recombination process between electrons and the analyte ions generated by the charge transfer reaction. To check the validity of these observations for more elements and matrices, I_{rel} values for atomic lines are presented in the order of increasing analyte upper electronic energy level (see Fig. 4) for carbon, sulfur and phosphorus solutions. Spectroscopic information on the atomic lines employed for each element are found in Table S1. When operating the carbon matrix (Fig. 4a) and the sulfur matrix (Fig. 4b), I_{rel} values for As, P, Se and Te atomic lines increase with the energy of the upper energy level involved in the electronic transition. Thus, for instance, I_{rel} values for As atomic lines range from 1.56 (As I 173.950 nm; $E_{upper\ level}$ 8.48 eV) to 1.27 (As I 197.263 nm and 249.294 nm; $E_{upper\ level}$ 6.28 eV) for the carbon matrix. Similar results have been obtained in the presence of phosphorus (Fig. 4c) for As and Se atomic lines. No relationship was found between I_{rel} enhancement and analyte upper electronic energy level for Hg atomic lines operating the carbon matrix as well as for I atomic lines operating the carbon or the sulfur matrix. Finally, the number of Te atomic lines exhibiting signal enhancement for the phosphorus matrix was rather limited and therefore no conclusion could be derived.

3.5. Influence of easily ionizable elements on charge transfer reactions.

Signal enhancement for the elements affected by charge transfer from carbon, sulfur and phosphorus depends on the ion population within the plasma and, hence, the magnitude of this interference can be changed by modifying the plasma ion-atom equilibrium. This fact is evident when looking at the influence of ICP experimental conditions on matrix effects (section 3.2.).

Alternatively, ion-atom equilibrium could be modified introducing easily ionizable elements into the plasma. The presence of these elements affords higher electron density and lower ion population [27] and, hence, charge transfer reactions should be reduced.

To evaluate the influence of easily ionizable elements on carbon, sulfur and phosphorus charge transfer reactions, both the reference (1 % w w⁻¹ nitric acid) and the matrix containing solutions (carbon, sulfur and phosphorus 20 g L⁻¹) were spiked with a certain amount of potassium for a final concentration of 1000 and 10000 mg L⁻¹. I_{rel} values were measured relative to 1% w w⁻¹ nitric acid solution containing the same amount of potassium. Fig. 5 and Fig. 6 show the influence of the upper electronic energy level on I_{rel} for Se and As atomic lines (Table S1), respectively. As it can be observed in these figures, I_{rel} values for all Se (Fig. 5) and As (Fig. 6) atomic emission lines decreased with increasing potassium concentration, regardless of the concomitant selected. Interestingly, the reduction of I_{rel} values was more significant for electronic transitions involving the highest upper energy levels. Thus, for instance, when increasing the potassium concentration up to 10000 mg L⁻¹ for the carbon matrix, I_{rel} values for As I 173.950 nm ($E_{upper\ level}$ 8.48 eV) decreased from 1.56 to 1.23 (i.e. 22%). However, I_{rel} for As I 249.294 nm ($E_{upper\ level}$ 6.28 eV) decreased from 1.28 to 1.10 (i.e. 14%). Similar findings were observed for P and Te atomic lines. As regards Hg and I atomic lines, I_{rel} values decreased with potassium concentration but no mutual differences were observed between the atomic lines selected. These results point out that charge transfer reactions in the plasma depend on the sample composition. The above mentioned experiments were also carried out using calcium instead of potassium as easily ionizable element. Findings were similar for carbon and phosphorus matrices in the presence of potassium. No conclusion was feasible for the sulfur matrix in the presence of calcium due to the formation of calcium sulfate precipitation.

Conclusions

From the results obtained in the present work it can be concluded that charge transfer reactions due to carbon, sulfur and phosphorus exert a significant influence on the atomic emission signal of some elements in ICP-AES. Arsenic, Se and Te atomic emission is enhanced by carbon-, sulfur- and phosphorus-based charge transfer reactions. Iodine and P atomic emission is also

enhanced by carbon- and sulfur-based charge transfer reactions whereas Hg atomic emission is only enhanced by carbon. Though this type of reaction is also expected to affect the emission signal of ionic lines, no experimental evidence was found with the exception of Hg ionic emission when operating carbon-containing solutions. The influence of charge transfer reactions on atomic emission strongly depends on the experimental conditions and, to a lesser extent, on the presence of easily ionizable elements (e.g. K or Ca). Further research on this topic is required to explain why atomic emission signal enhancement is not registered for some elements (e.g. Au or Sb) despite they do have atomic energy levels that fulfill the requirements for charge transfer reactions and experiments in ICP-MS suggest that they are indeed affected by charge transfer.

References

1. M.W. Blades, Excitation mechanisms and discharge characteristics – Recent developments, in: P.W.J.M. (ed.), *Inductively coupled plasma emission spectroscopy*, Ch. 11, Wiley, 1987, p. 387.
- 2 J.A.M. Van der Mullen, I.J.M.M. Raaijmakersw, A.C.A.P Van Lammeren, D.C. Schram, B. Van der Sijde, H.J.W. Schenkelaars, On the charge transfer in an inductively coupled argon plasma, *Spectrochim. Acta Part B* 42 (1987) 1039-1051.
- 3 L.L. Burton, M.W. Blades, Charge transfer between Ar and Mg in an inductively coupled plasma, *Spectrochim. Acta Part B* 46 (1991) 819-830.
- 4 P.B. Farnsworth, A. Woolley, N. Omenetto, O. Matveev, Experimental studies of charge transfer reactions between argon and the third row metals calcium through copper in the inductively coupled plasma, *Spectrochim. Acta Part B* 54 (1999) 2143-2155.
- 5 G.C.Y. Chan, G.M. Hieftje, Using matrix effects as a probe for the study of the charge-transfer mechanism in inductively coupled plasma-atomic emission spectrometry, *Spectrochim. Acta Part B* 59 (2004) 163-183.
- 6 G.C.Y. Chan, G.M. Hieftje, Experimental evidence of state-selective charge transfer in inductively coupled plasma-atomic emission spectrometry, *Spectrochim. Acta Part B* 59 (2004)

1007-1020.

- 7 P. Allain, L. Jaunault, Y. Mauras, J.-M. Mermet, T. Delaporte, Signal enhancement of elements due to the presence of carbon-containing compounds in inductively coupled plasma mass spectrometry, *Anal. Chem.* 63 (1991) 1497-1498.
- 8 F.R. Abou-Shakra, M.P. Rayman, N.L. Ward, V. Hotton, G. Bastian, Enzymatic digestion for the determination of trace elements in blood serum by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 9 (1997) 429-433.
- 9 Z. Hu, S.H.S. Gai, Y. Liu, S. Lin, Volatile organic solvent-induced signal enhancements in inductively coupled plasma-mass spectrometry: a case study of methanol and acetone, *Spectrochim. Acta Part B* 59 (2004) 1463-1470.
- 10 F. Vanhaecke, J. Riondato, L. Moens, R. Dams, Non-spectral interferences encountered with a commercially available high resolution ICP-mass spectrometer, *Fresenius J. Anal. Chem.* 355 (1996) 397-400.
- 11 G. Grindlay, J. Mora, M.T.C. de Loos-Vollebregt, F. Vanhaecke, A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma-mass spectrometry, *Spectrochim. Acta Part B* 86 (2013) 42-49.
- 12 M.C. García Poyo, G. Grindlay, L. Gras, M.T.C. de Loos-Vollebregt, J. Mora, Non-spectral interferences due to the presence of sulfuric acid in inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 105 (2015) 71-76.
- 13 G.C.Y. Chan, G.M. Hieftje, Investigation of charge transfer with non-argon gaseous species in mixed-gas inductively coupled plasma-atomic emission spectrometry, *Spectrochim. Acta Part B* 62 (2007) 196-210.
- 14 T.M. Briker, F. G. Smith, R.S. Houk, Charge transfer reactions between xenon ions and iron atoms in an argon-xenon inductively coupled plasma, *Spectrochim. Acta Part B* 50 (1995) 1325-1335.
- 15 J. Machat, V. Otruba, V. Kanicky, Spectral and non-spectral interferences in the determination of selenium by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 17 (2002) 1096-1102.
- 16 G. Grindlay, L. Gras, J. Mora, M.T.C. de Loos-Vollebregt, Carbon-related matrix effects in

- inductively coupled plasma atomic emission spectrometry, *Spectrochim. Acta Part B* 63 (2008) 234-243.
- 17 NIST atomic spectradatabase (version 5), <http://www.nist.gov/pml/data/asd.cfm> (last access June 2015).
- 18 Atomic Line List (Version 2.05b18), <http://www.pa.uky.edu/~peter/newpage/> (last access June 2015).
- 19 Atomicspectral line database, <http://www.pmp.uni-hannover.de/cgi-bin/ssi/test/kurucz/sekur.html> (last access June 2015).
- 20 J. E. Sansonetti and W. C. Martin, Handbook of Basic AtomicSpectroscopic Data, *J. Phys. Chem. Ref. Data* 34 (2005) 1559-2259.
- 21 J.R. Platt, R. A. Sawyer, New Classifications in the Spectra of Au I and Au II, *Phys. Rev.* 60(1941) 866-876.
- 22 A. Batal, J. Jarosz, J.M. Mermet, A spectrometric study of a 40 MHz inductively coupled plasma-VI. Argon continuum in the visible region of the spectrum, *Spectrochim. Acta Part B* 36 (1981) 983-992.
- 23 J.F. Alder, R. M. Bombelka, G.G. Kirkbright, Electronic excitation and ionization temperature measurements in a high frequency inductively coupled argon plasma source and the influence of wáter vapour on plasma parameters, *Spectrochim. Acta Part B* 35 (1980) 163-175.
- 24 J.M. Mermet, Use of magnesium as a test element for inductively coupled plasma atomic emission spectrometry diagnostics, *Anal. Chim. Acta* 250 (1991) 85-94.
- 25 G.L. Long, J.S. Bolton, The effect of propane on atomic spectrometric signals in the inductively coupled argon plasma, *Spectrochim. Acta Part B* 42 (1987) 581-589.
- 26 J.L. Todolí, J.M. Mermet, Acid interferences in atomic spectrometry: analyte signal effects and subsequent reduction, *Spectochim. Acta Part B* 54 (1999) 895.
- 27 J.L. Todolí, V. Hernandis, L. Gras, J. Mora, Elemental matrix effects in ICP-AES, *J. Anal. At. Spectrom.* 17 (2002) 142-169.
- 28 G.C. Y. Chan, G.M. Hieftje, Warming indicators for the presence of plasma-related matrix effects in inductively coupled plasma-atomic emission spectrometry, *J. Anal. At. Spectrom.* 23 (2008) 181-192.

- 29 G.C. Y. Chan, G.M. Hieftje, Use of vertically resolved plasma emission as an indicator for flagging matrix effects and system drift in inductively coupled plasma-atomic emission spectrometry, *J. Anal. At. Spectrom.* 23 (2008) 193-204.
- 30 G.C. Y. Chan, G.M. Hieftje, Fundamental characteristics of plasma-related matrix-effects cross-over points in inductively coupled plasma-atomic emission spectrometry, *J. Anal. At. Spectrom.* 24 (2009) 439-450.
- 31 G.C. Y. Chan, G.M. Hieftje, Spatial emission profiles for flagging matrix interferences in axial-viewing inductively coupled plasma-atomic emission spectrometry: 1. Profile characteristics and flagging efficiency. *Anal. Chem.* 85 (2013) 50-57.
- 32 G.C. Y. Chan, G.M. Hieftje, Spatial emission profiles for flagging matrix interferences in axial-viewing inductively coupled plasma-atomic emission spectrometry: 2. Statistical protocol, *Anal. Chem.* 85 (2013) 58-65.
- 33 S. Liu, D. Beauchemin, Effect of metanol and sodium dodecylsulfate on radial profiles of ion abundance in inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 61 (2006) 319-325.

Figure captions

Fig 1. Relative signal intensity (I_{rel}) obtained for a 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus containing solution in comparison to $1\% \text{ w w}^{-1}$ nitric acid for lines of different E_{sum} values. I_{rel} values among dotted lines indicate no matrix effects. r.f. power 1400 W ; Q_g 0.7 L min^{-1} ; Q_l 1.0 mL min^{-1} .

Fig 2. Influence of Q_g on I_{rel} for Se I 196.090 nm , Mg I 285.213 nm and Cd II 214.439 nm operating 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus solutions at different r.f. powers. (—) 1400 W ; (---) 1100 W . Q_l 1.0 mL min^{-1} .

Fig 3. Relative signal intensity (I_{rel}) values for Se I 196.090 nm , Mg I 285.213 nm and Cd II 214.439 nm operating 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus solutions as a function of plasma viewing location. r.f. power 1400 W ; Q_g 0.7 L min^{-1} ; Q_l 1.0 mL min^{-1} .

Fig. 4. Influence of the analyte upper electronic energy level on I_{rel} obtained for a 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus containing solution. r.f. power 1400 W ; Q_g 0.7 L min^{-1} ; Q_l 1.0 mL min^{-1} .

Fig. 5. Influence of the Se upper electronic energy level on I_{rel} obtained for a 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus solutions containing different amounts of potassium. r.f. power 1400 W ; Q_g 0.7 L min^{-1} ; Q_l 1.0 mL min^{-1} .

Fig. 6. Influence of the As upper electronic energy level on I_{rel} obtained for a 20 g L^{-1} (a) carbon, (b) sulfur and (c) phosphorus solutions containing different amounts of potassium. r.f. power 1400 W ; Q_g 0.7 L min^{-1} ; Q_l 1.0 mL min^{-1} .

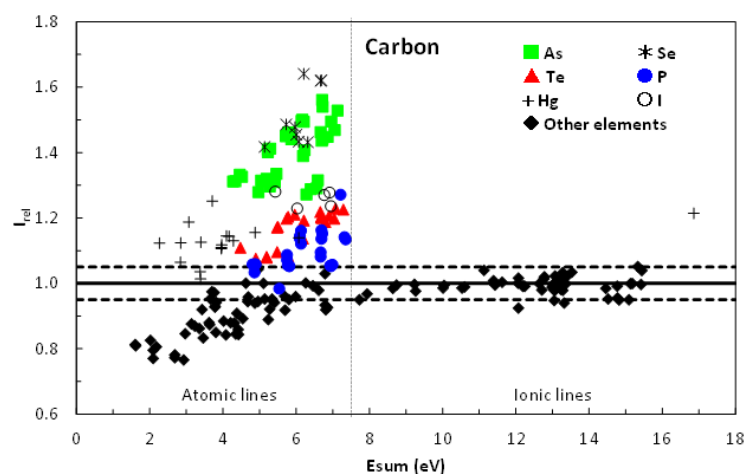


Figure 1A

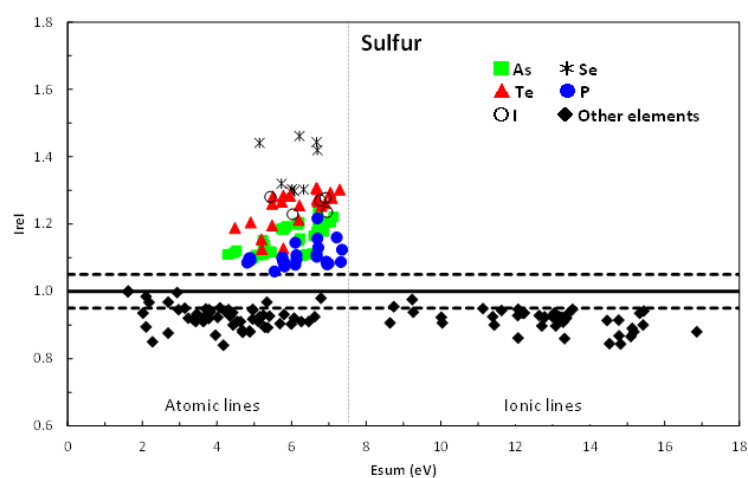


Figure 1B

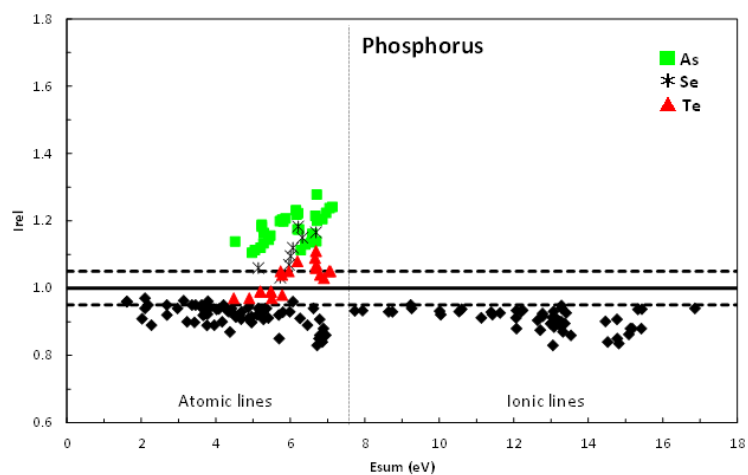


Figure 1C

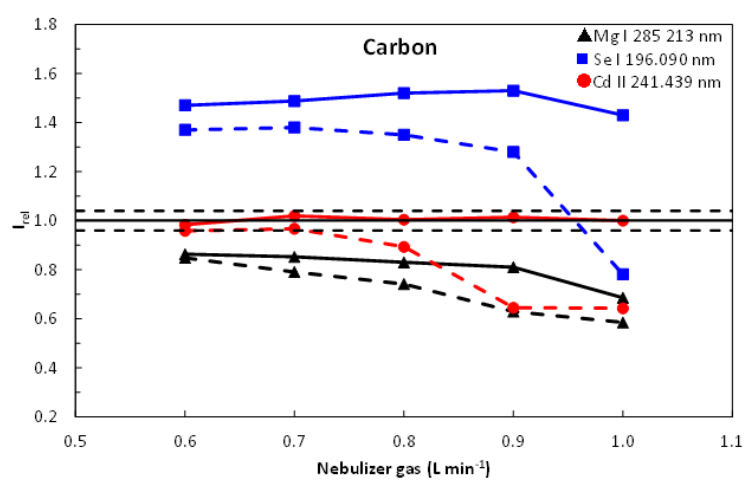


Figure 2A

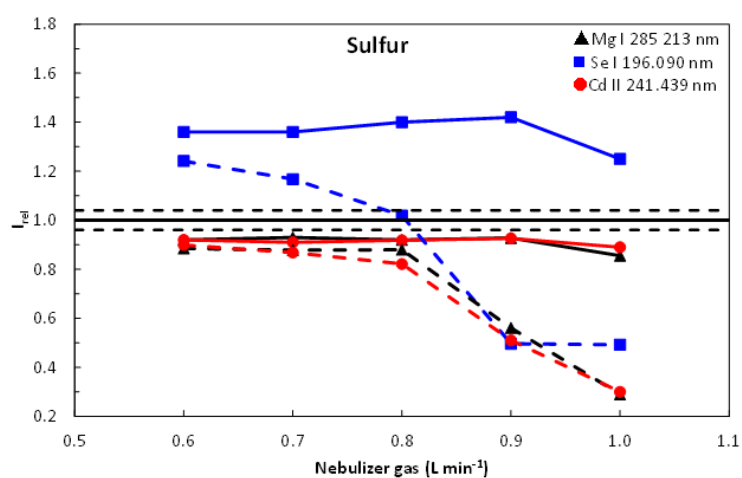


Figure 2B

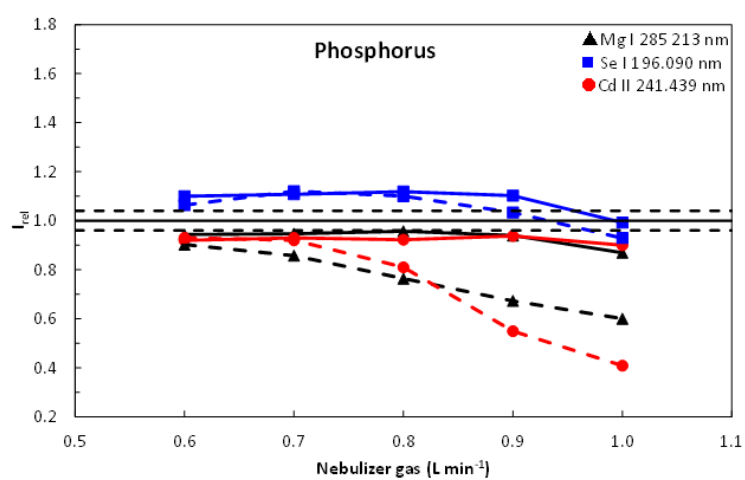


Figure 2C

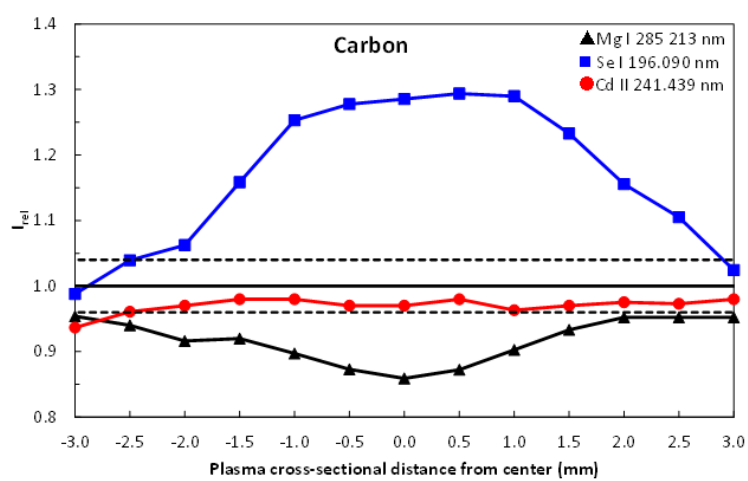


Figure 3A

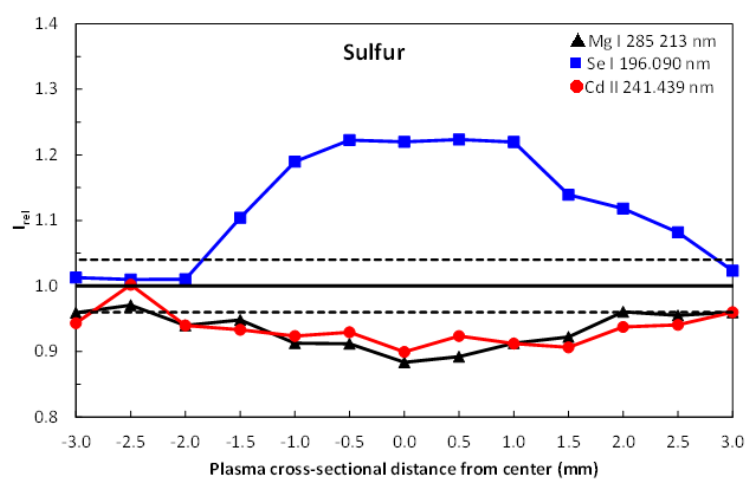


Figure 3B

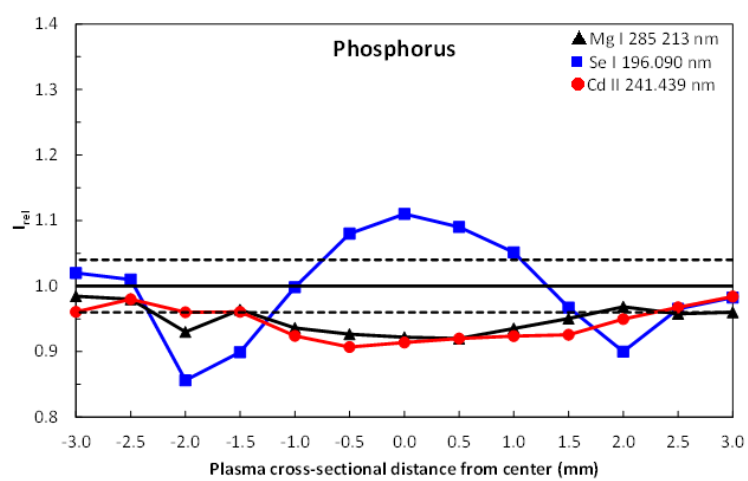


Figure 3C

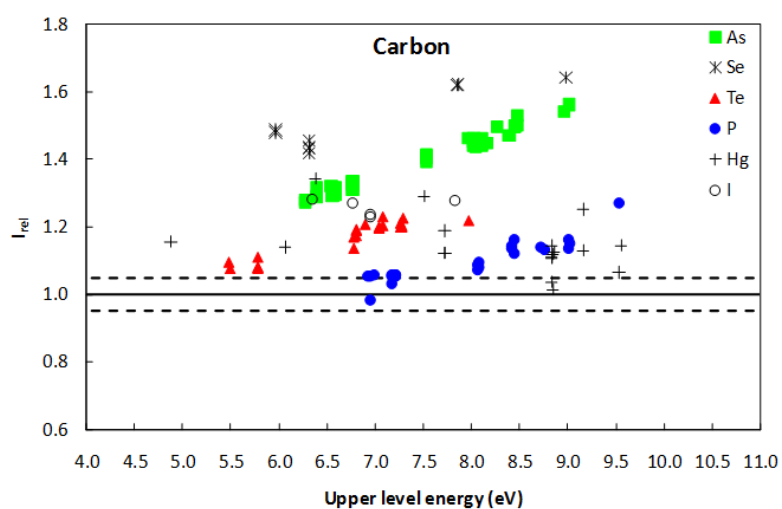


Figure 4A

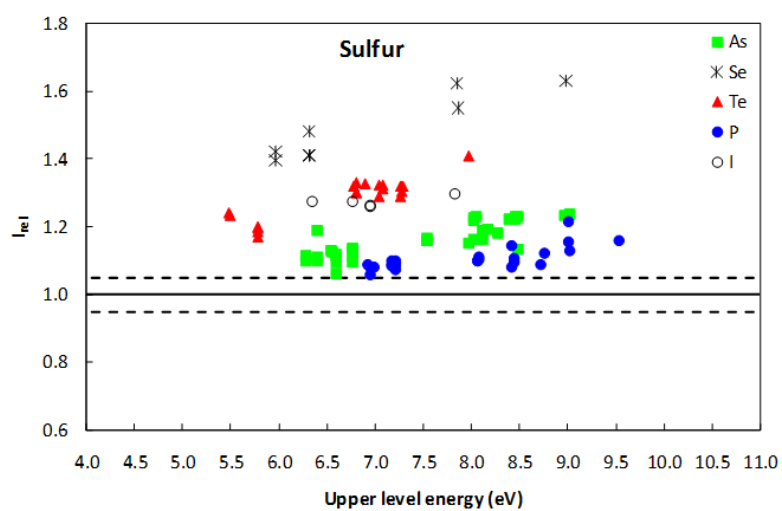


Figure 4B

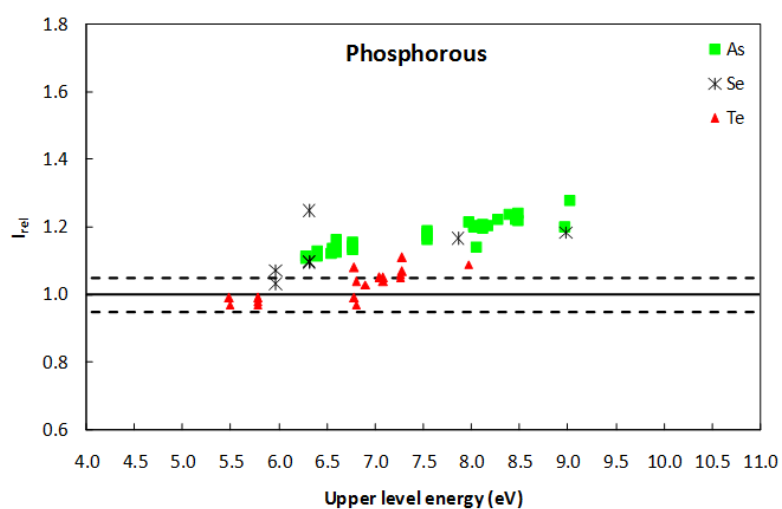


Figure 4C

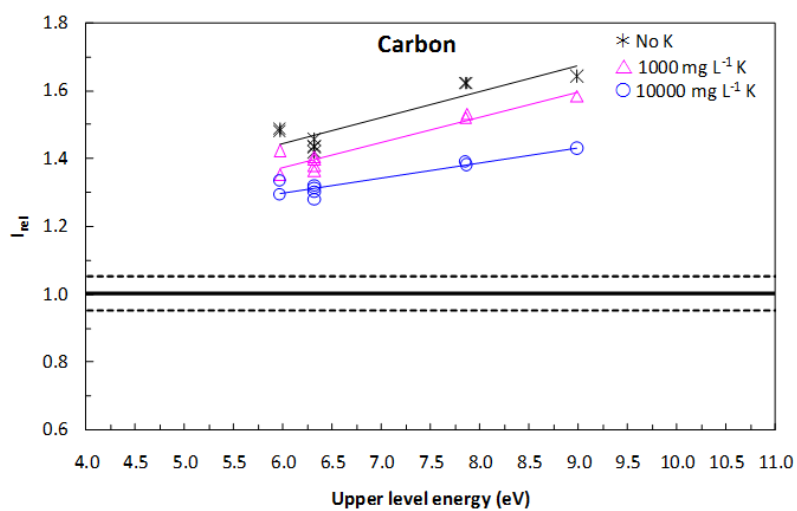


Figure 5A

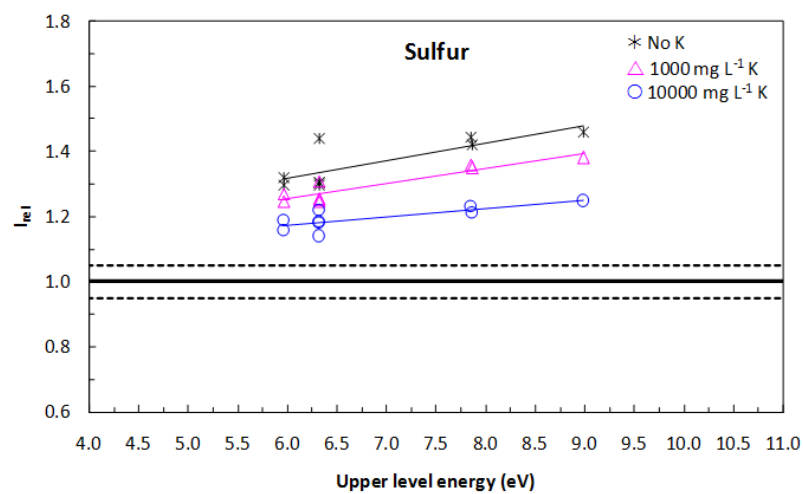


Figure 5B

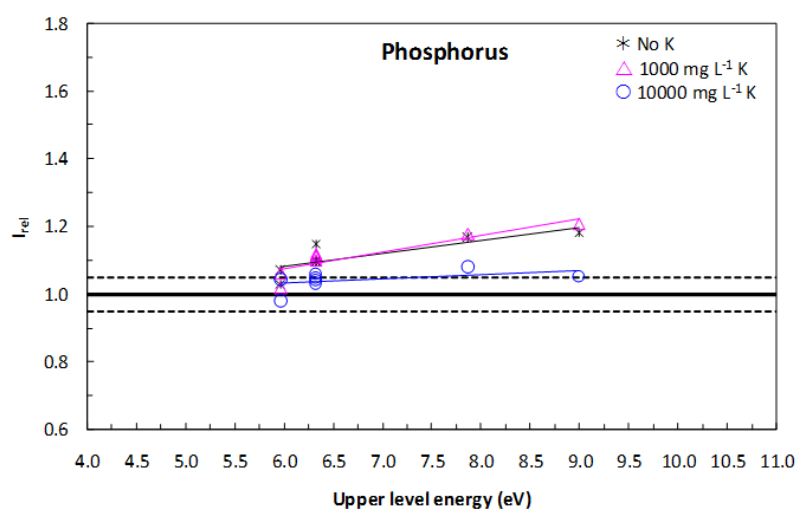


Figure 5C

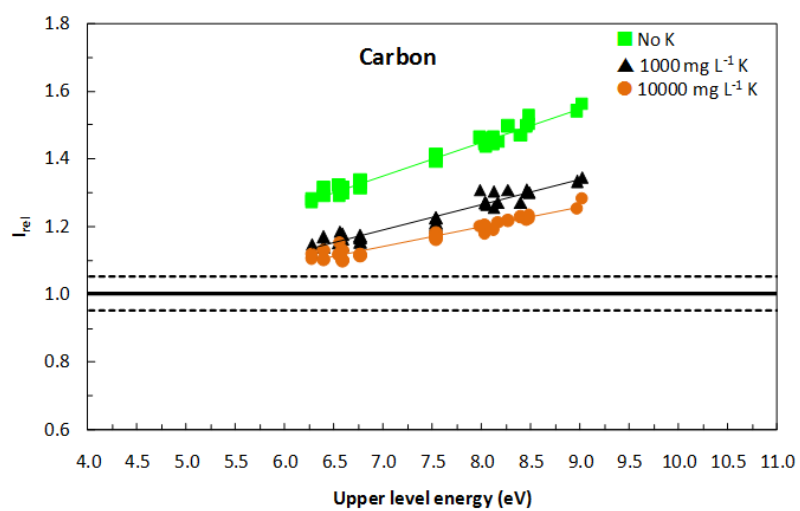


Figure 6A

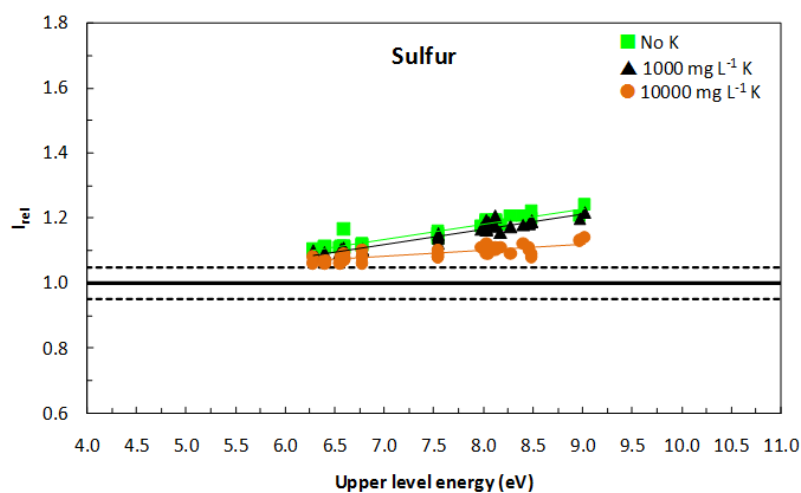


Figure 6B

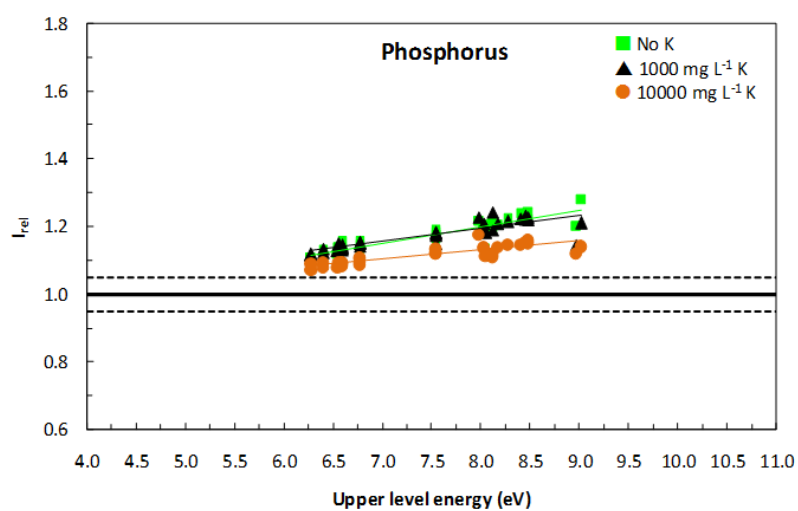


Figure 6C

Table 1.ICP operating conditions

	ICP-AES
Plasma forward power/ W	1100-1400
Argon flow rate/ L min ⁻¹ :	
Plasma	15
Auxiliary	1.5
Nebulizer (Q _g)	0.5-1.0
Sample uptake rate (Q _i)/ mL min ⁻¹	1.0
Injector diameter / mm	2.4
Sample introduction:	
Nebulizer	Seaspray
Spray Chamber	Cyclonic
View mode	Axial
Integration time/ s	1
Replicates	5

Highlights

- Atomic emission for some elements in ICP-AES is enhanced by C, S and P-containing matrices
- Carbon, sulfur and phosphorus-based charge transfer reactions in ICP-AES are thoroughly studied
- Atomic signal enhancement due to charge transfer reactions depend on analyte wavelength, plasma conditions and the presence of easily ionizable elements.