



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



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## ABSTRACT

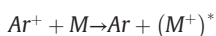
In this work, the influence of carbon-, sulfur-, and phosphorus-based charge transfer reactions on the emission signal of 34 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, I, In, Ir, K, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, S, Sb, Se, Sr, Te, and Zn) in axially viewed inductively coupled 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<sup>-1</sup> 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.

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## 1. 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<sup>+</sup>) and analyte atoms (M), resulting in an excited analyte ion (M<sup>+</sup>)<sup>\*</sup> [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 ( $\Delta E$ ) 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 reaction has been studied for a variety of elements [4–6], especially magnesium and transition metals.

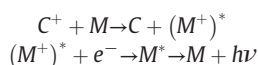
The potential contribution of non-argon-based charge transfer reactions to the signal in ICP-based techniques has been evaluated by several authors. The effect of carbon-based charge transfer reactions on analyte ionization in ICP-MS has been recognized for a long time [7–10]. Similarly, sulfur-based 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

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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 gasses 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<sup>-1</sup> 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<sup>-1</sup>) was employed to prepare the reference solution (Merck, Darmstadt, Germany) whereas matrix-containing solutions were made from glycerol, 98% w w<sup>-1</sup> sulfuric acid and 65% w w<sup>-1</sup> phosphoric acid (Panreac, Castellar del Valles, Spain). Silver, 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 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<sup>-1</sup> carbon (glycerol), sulfur (sulfuric acid), and phosphorus (phosphoric acid) solutions were used to study concomitant-based charge transfer reactions whereas 1% w w<sup>-1</sup> nitric acid was employed as the reference solution. Matrix effects were evaluated using 100 mg L<sup>-1</sup> 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<sup>-1</sup>.

## 3. Results

### 3.1. Matrix effects

Fig. 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<sup>-1</sup> 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<sup>-1</sup> nitric acid solution. In general, signal repeatability for atomic and ionic emission lines was

**Table 1**  
ICP operating conditions.

|  | ICP-AES   |
|--|-----------|
| Plasma forward power/ W                            | 1100–1400 |
| Argon flow rate/ L min <sup>-1</sup> :             |           |
| Plasma   | 15        |
| Auxiliary  | 1.5       |
| Nebulizer ( $Q_g$ )                                | 0.5–1.0   |
| Sample uptake rate ( $Q_s$ )/ mL min <sup>-1</sup> | 1.0       |
| Injector diameter / mm                             | 2.4       |
| Sample introduction:                               |           |
| Nebulizer  | Seaspray  |
| Spray chamber                                      | Cyclonic  |
| View mode  | Axial     |
| Integration time/ s                                | 1         |
| Replicates   | 5         |

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