Insight into the origin of carbon matrix effects on the emission signal of atomic lines in inductively coupled plasma optical emission spectrometry

Raquel Serrano, Guillermo Grindlay^{*}, Luis Gras, Juan Mora

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

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ABSTRACT

In inductively coupled plasma optical emission spectrometry (ICP-OES), the presence of carbon in the matrix strongly affects (positively and negatively) the emission signal of atomic lines. However, the emission signal of ionic lines is mostly unaffected by this concomitant. The goal of this work is to gain insight into the origin of carbon matrix effects on the signal of atomic lines in ICP-OES. To this end, the emission signal of a total of 3608 lines (i.e., 1755 atomic and 1853 ionic lines) of 62 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Re, Rh, S, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn and Zr) were registered for carbon containing solutions (20 g L⁻¹) prepared from glycerol. Results were compared to those obtained operating a 1% w w⁻¹ HNO₃ solution. Compared to the HNO₃ reference solution, emission signals for As, B, Hg, I, P, Se and Te atomic lines were increased for the carbon containing solution. However, signal suppression was noticed for the signal emission of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cs, Eu, Fe, Ga, Ge, K, Ho, In, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pd, Pr, Pt, Re, Rh, S, Sb, Sc, Sn, Sr, Ti, Tm, V, Y and Zr atomic lines. No measurable matrix effects within experimental uncertainties were registered for Au, Cu, Ir, Gd and Zn atomic lines. As regards Ce, Dy, Er, Nd, Sm, Tb, Th, U and Yb no clear conclusion about matrix effects was feasible due to the limited atomic emission wavelengths monitored. Experimental results showed that the intensity of matrix effects depends on both analyte ionization energy and the energy of the electronic upper level involved in the electronic transition. Matrix effects on atomic emission lines can be explained by the simultaneous occurrence of different mechanisms: (i) charge transfer reactions; (ii) collisional ionization; and (iii) collisional excitation with carbon-based species. Because these mechanisms mostly affect analyte atomic population, carbon matrix effects are more significant on the emission signal of atomic lines rather than ionic ones. Finally, the judicious analyte wavelength selection is critical to minimize carbon matrix effects for those elements for which the most sensitive wavelength is atomic (i.e., Se and alkali elements). On this regard, the selection of the internal standard should consider both the ionization energy and the energy of the electronic upper level of the analyte.

1. Introduction

The analysis of carbon containing matrices by means of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) is challenging due to the occurrence of both spectral and non-spectral interferences [1,2]. The origin of spectral interferences is well understood and could be mitigated by means of different instrumental and non-instrumental approaches [1–4]. Carbon based non-spectral interferences (i.e., matrix effects) are, however, more complex since aerosol generation and transport to the plasma, plasma energy, analyte excitation and

ionization mechanisms and, as regards ICP-MS, ion extraction, can be simultaneously affected [1,2]. Most of the studies about carbon based non-spectral interferences have been focused on the influence of organic solvents on aerosol generation and transport, plasma characteristics and ion extraction. In general, organic solvents afford finer aerosol and higher aerosol transport than diluted acid solutions [5]. Consequently, analyte signal is expected to increase. Nevertheless, because of solvent load into the plasma also increases, plasma temperature may be deteriorated affecting negatively to the analyte signal (i.e., signal suppression) [6–9]. In general, the magnitude of carbon matrix effects in ICP-based techniques depends on several factors such as: (i) the element

^{*} Corresponding author.

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

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considered; (ii) the carbon matrix source and concentration; and (iii) the instrument characteristics and experimental conditions employed (i.e., r.f. power, nebulizer gas flow rate, etc.) [6–13]. More limited has been the number of works dealing with changes on analyte excitation/ionization mechanisms due to the presence of carbon in ICP-based techniques.

Allain et al. [14] first noticed that the ion signal for several hard-to-ionize elements in ICP-MS was selectively enhanced operating carbon-containing matrices (i.e., glycerol, methanol, methane, etc.). Thus, for instance, Hg signal was enhanced 5-fold in the presence of a 1 mol L⁻¹ glycerol solution regarding a non-carbon containing standard. Subsequent investigations demonstrated that analyte signal enhancement was related to the occurrence of a charge transfer (CT) mechanism between analyte atoms (M) and carbon charged species (i.e., mainly C⁺) that increases the production of excited ions from the original atom ((M⁺)^{*}) [6–9,15]:

This reaction is a two-electron transfer process, one electron from the analyte atom is transferred to the ion and another electron from the analyte atom is excited to a higher level. Unlike other mechanisms present in the ICP discharge, carbon-based CT reaction is highly specific since it requires minimum reaction energy defect (i.e., difference between carbon ionization energy and a given ionic electronic level of the analyte) and conservation of total electron spin [8,16–18]. This mechanism explains the rather limited number of elements affected by this interference (i.e., As, Au, Hg, I, P, Se, Sb and Te) [8]. Nevertheless, carbon-based CT reactions in ICP-MS are not yet fully understood since, despite reaction requirements are fulfilled, ionic signal for several hard-to-ionize elements (i.e., B, Os, Pt, Ir, Cd, Be and S) is not enhanced operating carbon containing matrices [8]. This interference does not affect the ionic signal of those elements with ionization energies below 8.0 eV since they are almost totally ionized under normal ICP experimental conditions.

Carbon-based CT reactions also affect the analyte emission profile in ICP-OES. It has been observed that the emission signal for As, Hg, I, P, Se and Te atomic lines is enhanced operating carbon containing matrices, regardless of the view mode employed [10–13]. Signal enhancement is more pronounced for those lines which electronic transitions involve the highest upper atomic energy levels. Thus, for instance, operating a 20 g L⁻¹ C solution, relative intensity of As I 173.950 nm (²D_{5/2} (8.48 eV) → ²D_{5/2} (1.35 eV)) and As I 249.294 nm (⁴P_{1/2} (6.28 eV) → ²D_{3/2} (1.31 eV)) were increased 1.56 and 1.27, respectively [12]. Carbon-induced signal enhancement on the emission of atomic lines has been successfully explained by means of a two-step mechanism based on carbon CT reactions followed by an ion-electron recombination process by which analyte ions ((M⁺)^{*}) are transformed in excited atoms (M^{*}) [10–12]:

Because the increase in the analyte excited ionic population ((M⁺)^{*}), higher ionic emission signals should be expected for As, Hg, I, P, Se and Te operating carbon-rich matrices but, except for Hg, it has not been feasible to check it due to several experimental constraints [12]. Our research group [10,12] and others [11,13,19] have previously reported that the emission signal for atomic lines of a significant number of elements (e.g. Ag, Al, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Ir, K, Li, Mg, Mn, Na, Ni, Pb, Pd, Pt, S, Sb, Sr and Zn) is suppressed when operating carbon containing solutions, particularly for those wavelengths with total emission line excitation energies lower than 4–5 eV [10,12]. Interestingly, the emission of ionic lines for these elements were unaffected by carbon. To explain signal suppression effects on the emission of atomic lines, different mechanisms, such as carbide formation or collisional deactivation by carbon atoms, have been proposed [10,11,19]. However, none of them successfully explain the different behavior shown by atomic and ionic lines in the presence of carbon

matrices in ICP-OES. Therefore, an extended and systematic study of the influence of carbon on the behavior of atomic lines in ICP-OES is strongly required to clarify this relevant subject.

The goal of this work was to gain insight into the origin of carbon matrix effects on the emission signal of atomic lines in ICP-OES. To this end, the emission signal of a total of 1755 atomic lines of 62 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Re, Rh, S, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn and Zr) were registered for carbon containing solutions (20 g L⁻¹ prepared from glycerol) and results were compared to those obtained for a 1% w w⁻¹ HNO₃ solution. For a better understanding of carbon matrix effects, the emission signal of a total of 1853 ionic lines for the above-mentioned elements was also monitored. Finally, considering the findings of this study, it was examined how to detect and mitigate carbon matrix effects on the emission of atomic lines.

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 to prepare the solutions employed throughout this work. Nitric acid (69% w w⁻¹) was employed to prepare the reference solution (Panreac, Castellar del Valles, Spain) whereas matrix-containing solutions were made from 86 to 88% w w⁻¹ glycerol (Scharlau, Sentmenat, Spain) and 99.95% w w⁻¹ calcium nitrate tetrahydrate (Merck, Darmstadt, Germany). Mono-elemental 1000 mg L⁻¹ analyte solutions (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, I, In, Ir, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Re, Rh, Sb, Sc, Se, Sn, Sr, Te, Ti, V, Y, Zn and Zr), lithium and caesium nitrates and lanthanide chloride salts (HoCl₃, TbCl₃, TmCl₃, PrCl₃) were purchased from Sigma-Aldrich (Schelldorf, Germany). A 10 mg L⁻¹ rare earth elements multielemental standard (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb, U) was obtained from High Purity Standards (North Charleston, SC, USA). Sulfuric acid 96% w w⁻¹ was purchased from Panreac (Castellar del Valles, Spain).

2.2. Matrix and analyte solutions

To evaluate the influence of carbon on the analytical signal, a 20 g L⁻¹ carbon containing solution prepared from glycerol was employed whereas a 1% w w⁻¹ HNO₃ was used as the reference matrix solution. Glycerol was used as carbon source since a 20 g L⁻¹ carbon solution from this compound affords similar aerosol and plasma characteristics than those from a 1% w w⁻¹ HNO₃ one because both solutions present similar physical properties (i.e., surface tension, density, and volatility) [10]. Thus, it is easier to study the influence of carbon on the mechanisms responsible of analyte emission in ICP-OES [10,12]. On this regard, to gain insight into carbon matrix effects, additional experiments were performed with both matrices spiked with calcium at two concentration levels (2000 and 20,000 mg L⁻¹).

The analyte concentration employed in this work was selected according to the sensitivity of the emission lines of the elements evaluated. Thus, mono-elemental solutions containing 200 mg L⁻¹ of analyte were prepared for most of the elements (Ag, Al, As, Au, B, Be, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, I, In, Ir, Mn, Mo, Nb, Ni, P, Pb, Pd, Pt, Re, Rh, Sb, Sc, Se, Sn, Te, Ti, V, Y, Zn and Zr), while for those elements whose emission lines are more sensitive, solutions containing 100 mg L⁻¹ (Ho, Pr, Tm and Tb) and 50 mg L⁻¹ (Ba, Ca, Cs, K, Li, Mg Na and Sr) were prepared. Matrix effects for La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu, Th and U were investigated using 1 mg L⁻¹ standard due to the concentration constraints imposed by the standard available. Finally, due to the limited sensitivity of the atomic lines of S in ICP-OES, a solution containing 1000 mg L⁻¹ of this element made from sulfuric acid was used.

2.3. ICP instrumentation

ICP-OES measurements were performed using an Agilent 720 ICP-OES (Agilent, Santa Clara, USA) with axial viewing. The sample introduction system consisted of a OneNeb® concentric pneumatic nebulizer (Ingeniatics, Sevilla, Spain) coupled to a cyclonic spray chamber (Cinnabar, Glass Expansion, Australia). Table 1 shows the operating conditions used. Under these experimental conditions (i. e. high r.f. power and low nebulizer gas flow rate), it is easier to evaluate carbon influence on analyte excitation/ionization mechanisms since plasma temperature is hardly affected by the introduction of glycerol solutions [10,12].

All the (ionic and atomic) wavelengths investigated throughout this work are included in the Appendix (Tables S1 and S2, respectively). Spectroscopic data were obtained from the NIST database [20] and some other sources [21–23]. For those elements present in the rare earth elements multielemental standard (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu, Th and U), and given the impossibility to measure emission lines for the different element independently, wavelengths were carefully selected to avoid potential spectral interferences after a thoroughly revision of spectral database [20–23]. Wavelengths not totally resolved by ICP-OES spectrometer were discarded.

No significant carbon-based spectral interferences were found for the (ionic and atomic) wavelengths monitored operating the 20 g L⁻¹ carbon containing solution prepared from glycerol. In all cases, raw emission signals were corrected with a blank solution using ICP-OES instrument software. Signal-to-background ratios were, for all the lines tested in this work, above 10 to clearly distinguish analyte emission signal from the background at the concentrations employed.

2.4. Determination of carbon concentration in real samples

To evaluate the impact of the carbon-based matrix interferences from a practical point of view, different real samples were considered: mussel tissue (BCR-278R), fly ash (BCR-176R), polyethylene (high level) (ERM-EC681K) and seagrass samples (i.e., *Cymodocea nodosa* (Ucria) Aschers and *Posidonia oceanica* (L.) Delile). All samples were digested using a microwave oven (model Start D, Milestone, S.r.l., Sorisole, Italy) using a mixture of HNO₃ (69% w w⁻¹) and H₂O₂ (30% w v⁻¹) and the different programmes recommended by the manufacturer (Table S3, Appendix). Carbon content in the digested samples were determined by ICP-OES using the C I 193.030 nm line and glycerol standards (i.e., 2–20 g L⁻¹C) [10].

3. Results

3.1. Carbon matrix effects

To investigate carbon matrix effects in ICP-OES, ionic and atomic analyte emission signals for a 20 g L⁻¹ carbon containing solution were registered and results were compared to those obtained for a 1% w w⁻¹ HNO₃ one (reference solution). Relative emission intensity, I_{rel} , defined

as the net signal intensity of the analyte obtained in the carbon-containing solution relative to that in the 1% w w⁻¹ HNO₃ one, was calculated for a total of 3608 emission lines (1853 ionic and 1755 atomic) of 62 elements (Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Re, Rh, S, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn and Zr). It is important to point out that no ionic emission lines were monitored for As, I, P, Se and Te because their very low sensitivity in the operating wavelength range of the instrument employed [12]. Taking into account the average precision of the emission signal for all emission lines tested (approximately 2%), it can be considered that I_{rel} values between 0.96 and 1.04 range indicate no measurable matrix effects within experimental uncertainties. For I_{rel} values outside this range, the carbon containing solution gives rise to matrix effects (signal enhance for $I_{rel} > 1.04$, or signal depression for $I_{rel} < 0.96$) [10,12].

In general, no measurable matrix effects within experimental uncertainties were noticed for most (> 90%) of the ionic lines studied in this work (Table S1, Appendix). For those ionic lines showing matrix effects, slight signal suppression (i.e., $0.91 < I_{rel} < 0.95$) was registered with some few exceptions (e.g. Al II 176.334 nm, $I_{rel} 0.76 \pm 0.03$). Ionic lines showing signal suppression correspond to Al, Cr, Fe, Ge, Mg, Ni, Pb, Rh, Sc and Ti. Nevertheless, the number of ionic lines showing no measurable matrix effects for these elements was higher than those showing signal suppression. These results are in agreement with previous data in the literature [10,12] and are the expected since neither analyte transport nor plasma temperature are significantly affected by the 20 g L⁻¹ carbon containing solution made from glycerol regarding 1% w w⁻¹ HNO₃. In this work, the Ar I 430.010 nm line to Ar continuum ratio was employed as an indicator of plasma electron temperature [24]. No significant differences in this ratio were noticed between the glycerol and the reference solution (i.e., Glycerol: 15.5 ± 0.3 ; 1% w w⁻¹ HNO₃: 15.6 ± 0.2). Finally, signal enhancement was just found for a single Hg wavelength (i.e., Hg II 194.227 nm, $I_{rel} 1.20 \pm 0.03$). This behavior has been previously attributed to changes on Hg ionic population by carbon-based CT reactions [12].

The behavior of atomic lines was, however, more complex since most of the wavelengths monitored shown matrix effects (Table S2, Appendix). Signal enhancement (i.e., $I_{rel} > 1.04$) was registered for As, B, Hg, I, P, Se and Te atomic lines. For these elements, the highest I_{rel} values were afforded by Se (e.g. Se I 199.446 nm, $I_{rel} 1.56 \pm 0.02$). Negative matrix effects (i.e., signal suppression) were observed for Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cs, Eu, Fe, Ga, Ge, K, Ho, In, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pd, Pt, Pr, Re, Rh, S, Sb, Sc, Sn, Sr, Ti, Tm, V, Y and Zr atomic lines. Among them, the lowest I_{rel} values were shown by La I 510.624 nm ($I_{rel} 0.63 \pm 0.02$) and Pr I 492.460 nm ($I_{rel} 0.62 \pm 0.02$). No carbon matrix effects were registered for Au, Cu, Gd, Ir and Zn atomic lines. Finally, no clear conclusion about matrix effects was feasible for Ce, Dy, Er, Nd, Sm, Tb, Th, U and Yb atomic lines since the most sensitive emission wavelengths for these elements were ionic and the number of atomic lines available in the ICP-OES employed in this work was rather limited (or even inexistent). Consequently, these elements were not further investigated. Fig. 1 summarizes the influence of the carbon matrix on the signal of the atomic emission lines for the 62 elements investigated.

3.1.1. Influence of atomic emission line properties on matrix effects

Previous works by Machat et al. [6], and by our research group [10,12] pointed out that signal enhancement for As (as well as for elements such as P, Se and Te) operating carbon containing solutions strongly depends on the energy of the electronic upper level ($E_{upper\ level}$) involved in the electronic transition. Therefore, it would be interesting to check whether the emission of atomic lines for other elements behaves similarly. Fig. 2 shows I_{rel} values for As, V and Zn atomic lines according to their $E_{upper\ level}$. These elements were selected to represent the groups of elements exhibiting different matrix effects in the presence of carbon (Fig. 1) and attending to their high number of atomic lines

Table 1
ICP-OES operating conditions.

Plasma forward power (W)	1400
Argon flow rate (L min ⁻¹)	
Plasma	15
Auxiliary	1.5
Nebulizer (Q _g)	0.7
Sample uptake rate (Q _l) (mL min ⁻¹)	0.6
Sample introduction system:	
Nebulizer	OneNeb®
Spray chamber	Cyclonic
View mode	Axial
Integration time (s)	1
Replicates	3

H																			He
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rd		
Fr	Ra																		

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 1. Response of the atomic lines of the different elements to carbon matrix effects in ICP-OES.

Fig. 2. Relative signal intensity (I_{rel}) obtained for a glycerol solution ($20 \text{ g L}^{-1}\text{C}$ solution) in comparison to $1.0\% \text{ w}^{-1}$ nitric acid for atomic lines according to their electronic upper energy level ($E_{upper \text{ level}}$). I_{rel} values among horizontal dotted lines indicate no measurable matrix effects within the experimental uncertainties.

available. Thus, As was selected as an element showing signal enhancement, whereas V and Zn were selected to represent those elements affording signal suppression and no-matrix effects, respectively. Results for the remaining elements investigated in this work can be found in the Appendix (Fig. S1-S3). As expected [10,12], matrix effects for As atomic lines increase with $E_{upper \text{ level}}$ (i.e., higher I_{rel} values). Similar findings were also observed for P, Se and Te atomic lines. However, no influence of $E_{upper \text{ level}}$ on I_{rel} were registered for B, Hg and I (Fig. S1, Appendix). On the other hand, it was also noticed that matrix effects for V atomic lines decreased with the $E_{upper \text{ level}}$. For this element, the higher the $E_{upper \text{ level}}$, the higher I_{rel} values obtained. Similar behavior is shown by Ba, Ca, Cr, Ho, In, Li, Mg, Mn, Mo, Nb, Pd, Re, Rh,

Sb, Sc, Sr, Ti, Tm, V, Y and Zr atomic lines (Fig. S2.A, Appendix). Interestingly, there were 13 elements belonging to the V group (i.e., Ag, Al, Be, Cd, Co, Fe, Ga, Ge, Ni, Pb, Pt, S and Sn) that did not show this trend. Atomic emission lines intensity for these elements was suppressed by carbon but no influence of $E_{upper \text{ level}}$ on I_{rel} was noticed (Fig. S2-B, Appendix). Finally, because the limited number of atomic lines available, no conclusion about the influence of $E_{upper \text{ level}}$ on matrix effects was feasible for Cs, Eu, K, La, Lu, Na, and Pr (Fig. S2-C, Appendix). No measurable matrix effects within experimental uncertainties were registered for Zn atomic lines, regardless the atomic line tested. Similar findings were observed for Au, Cu, Ga and Ir (Fig. S3, Appendix).

3.1.2. Influence of element ionization energy on matrix effects

It has been previously reported in ICP-MS that the magnitude of carbon matrix effects is somehow related to analyte E_{ion} [8]. Data in Fig. 2 also suggest such relationship, the lowest I_{rel} values (0.76–0.99) were observed for V (E_{ion} 6.7 eV) and the highest I_{rel} values (1.03–1.16) were registered for As (E_{ion} 9.8 eV). To validate this hypothesis, the influence of E_{ion} on I_{rel} values was examined using a box plot graph for all the elements investigated (Fig. 3) but Ce, Dy, Er, Nd, Sm, Tb, Th, U and Yb due to carbon matrix effects ambiguity. Data in Fig. 3 shows that strongest signal suppression corresponded to elements with low E_{ion} values (i.e., those that are almost completely ionized in the plasma). When increasing E_{ion} , signal suppression was less severe and either positive or no measurable matrix effects within experimental uncertainties was found among hard-to-ionize elements (i.e., those present in the plasma with low ionization degree, e.g. 52% for As, 33% for Se, etc.) (Fig. S4, Appendix) [25]. It is important to note that, irrespective of the element considered, the maximum and upper outliers in the box plot corresponded to those wavelengths involving electronic levels with the highest $E_{upper \text{ level}}$ studied. Because I_{rel} values for those electronic transitions involving the highest $E_{upper \text{ level}}$ were significantly different from the average behavior shown by the remaining transitions, matrix effects were indeed related to analyte ionic and atomic population abundance

Fig. 3. Relative signal intensity (I_{rel}) obtained for a glycerol solution (20 g L⁻¹ C solution) in comparison to 1.0% w w⁻¹ nitric acid for atomic lines according to analyte ionization energy (E_{ion}). I_{rel} values among horizontal dotted lines indicate no measurable matrix effects within the experimental uncertainties.

in the plasma.

3.2. Origin of carbon matrix effects

Matrix effects due to carbon in ICP-OES has been attributed to changes in: (i) aerosol generation, (ii) aerosol and analyte transport; (iii) plasma characteristics (e.g. electron temperature, etc.); and (iv) excitation/ionization mechanisms in the plasma [1,4,5,10–13]. As it has been previously pointed out, when operating 20 g L⁻¹ carbon containing solutions made from glycerol, neither factors (i), (ii) nor (iii) are significantly modified regarding the 1.0% w w⁻¹ HNO₃ solution [10]. Therefore, and attending to the results previously discussed, carbon matrix effects in atomic lines must be related to changes in analyte excitation and ionization mechanisms.

3.2.1. Signal enhancement

The origin of carbon matrix effects for As-like elements in ICP-OES has been previously investigated by our research group [10,12] and others [11,13]. Under given ICP operating conditions, analyte ionic and atomic population for any element relies on the simultaneous occurrence of different mechanisms. Thus, for a given plasma excitation conditions, ionic population depends on electron-impact ionization as well as Ar-based CT and the collision with metastable argon atoms [16,18,26]. On the other hand, atomic levels are mostly populated by two different mechanisms, electronic impact and ion-electron recombination [16,27]. The former depends on the population of the atom ground level and mostly affects the low energy atomic levels, whereas the later relies on the ionic population affecting atomic levels of high energy. In the case of As, given its high E_{ion} , the population of atomic levels is higher (black levels in Fig. 4.A) than that of the ionic ones (grey levels in Fig. 4.A). Hence, electronic impact excitation is the main mechanism controlling excited As atomic levels. In addition, considering Maxwell electronic distribution and the large energy gaps between As electronic levels, the overall efficiency to promote electrons through climbing the energy-level ladder (i.e., a bottom-up energy flow) is not expected to be high. When carbon is introduced into the plasma, analyte ionization is enhanced by carbon-based CT reactions thus favouring the

ion-electron recombination pathway and the population of high energy atomic levels (i.e., top-down energy flow). This mechanism simultaneously explains: (i) the signal enhancement reported for As-like elements (i.e., As, Hg, I, P, Se and Te) in ICP-MS when operating carbon-containing matrices [8]; and (ii) the increase in the I_{rel} values observed for atomic lines in ICP-OES with $E_{upper\ level}$ (Fig. 2) [10–12] and, as regards Hg, signal enhancement of the Hg II 194.227 nm line.

Carbon-based CT reactions in ICP-MS have been previously examined from a theoretical point of view by our research group considering both spin conservation (Wigner's rule) and reaction energy defect (ΔE) [8]. According to Wigner's rule [28], the total spin angular momentum of the reactants and products are vector sums of the individual particles spin numbers and, hence, CT successfully occurs when a common spin state is found between the reactants and products. For instance, CT between C⁺ and As atoms is feasible due to the availability of a singlet close to C⁺ ionization energy and the presence of a common spin state (1) between the reactants and products [8]:

$$S_i = |S_i| = (s_{C^+} + s_{As}), (s_{C^+} + s_{As} - 1) \dots, |s_{C^+} - s_{As}| = 2 \& 1$$

$$S_f = |S_f| = (s_C + s_{As^+}), (s_C + s_{As^+} - 1) \dots, |s_C - s_{As^+}| = 1$$

Reaction energy defect (ΔE) is defined as the difference between the ionization energy of the particle which transfers the charge (C⁺) and the sum of the ionization and excitation potentials of the product ion ((M⁺)^{*}). For appreciable CT to occur, species affected by this type of reaction should have at least one ionic electronic level close to the ionic ground state of the particle transferring the charge (C⁺_{energy} ≈ (M⁺)^{*}_{energy}). Based on previous works about Ar-based CT reactions in ICP-OES [18,29,30], the feasibility of carbon-based CT was high when 1.00 eV < ΔE < -0.50 eV (where the negative sign indicates that the ionization energy of (M⁺)^{*} exceeds that of C⁺). According to these criteria, As, Hg, I, P, Se and Te fulfill CT reaction requirements with C⁺. In the case of B, its high ΔE (i.e., -1.67 eV) does not explain a CT reaction with C⁺ although a CO₂⁻-based CT reaction would be feasible [8]. The significance of the latter

Fig. 4. Simplified ionic and atomic energy level diagrams for (A) As and (B) V showing potential excitation and ionization pathways operating with 1.0% w w⁻¹ nitric acid and a glycerol solution (20 g L⁻¹C solution). Electronic levels in black are expected to be more populated than those in grey.

mechanisms is, however, less likely considering that CO₂⁺ levels in the plasma are 1000-fold lower than those of C⁺ [8]. Nevertheless, that previous study about carbon-based CT fundamentals in ICP-MS shows several shortcomings. First, the above-mentioned interpretation of the Wigner's rule predicts high CT probability even when there is a very large change in the electronic configuration (e.g., a three-electron transfer reaction). Several authors have pointed out that experimental data about CT reactions are better explained considering a strictest interpretation of the Wigner spin rules [17,18,31]. According to them, the total spin before and after the charge exchange should remained the

same. This means that, since C⁺ gains one spin-state during CT (from a doublet, ²P, to a triplet, ³P), the metal atom undergoing CT must upon ionization loses one spin-state.

$$S_i = s_{C^+} + s_M = s_C + s_{(M^+)^*} = S_f$$

$$S_i = 2 + s = 3 + (s - 1) = S_f$$

Interestingly, other authors have proposed a different interpretation of this rule suggesting that the spin multiplicity of the analyte can increase or decrease by one spin multiplicity after CT. For instance, an

atomic doublet can be transformed into either an ionic singlet or triplet after the CT [18,32,33]. Second, the ΔE range assume for successful CT between C^+ and analyte atoms is probably too conservative. Experimental data in ICP-OES suggest that Ar-based CT reactions could even proceed with ΔE larger than ± 1.00 eV (e.g., Pt, Sn) [16,18]. Finally, it is usually considered that CT involves the ground state of the charge acceptor atom (M) but experimental evidences suggest that this process might be also feasible from low-lying atomic levels (M^*) when their population density is significant [16]. Therefore, the feasibility of carbon-based CT reactions for As, Hg, I, P, Se and Te have been reexamined considering: (i) the different interpretations of Wigner spin rule (i.e., strictest version: analyte undergo a spin change of -1 ; intermediate version: analyte undergo a spin change of ± 1); (ii) a larger ΔE range (-1.25 eV $< \Delta E < 1.25$ eV). Charge transfer reactions within this range are expected to proceed faster than those outside this range; and (iii) the involvement of both ground and low-lying electronic levels of analyte atoms. For low-lying electronic levels, because the lower abundance of the species involved, CT reaction rate should proceed slower than those involving ground electronic levels. Table 2 shows the spectroscopic data for the most likely analyte electronic levels of As, B, Hg, I, P, Se and Te involved in CT reactions with C^+ . For electronic levels of high population density fulfilling reaction requirements, CT feasibility is classified as high. Conversely, CT feasibility is low when: (i) the population density of a given electronic state is limited (i.e., Boltzmann-Maxwell distribution); (ii) the Wigner's rule in its most strictest or intermediate interpretation are not fulfilled; or (iii) ΔE is not within -1.25 eV $< \Delta E < 1.25$ eV.

As it is shown in Table 2, the closest ionic electronic level to the C^+ ground state (i.e., 11.26 eV) for Se ($^2D_{3/2,5/2}$; $E = 11.38/11.55$ eV) and Te ($^2P_{1/2,3/2}$; $E = 11.55/11.98$ eV) fulfills CT reaction requirements and, hence, they are likely to participate in such reactions. This conclusion agrees with that obtained in our previous study about carbon-based CT requirements [8]. Interestingly, when using the strictest version of Wigner spin conservation rule, it is observed that total spin is not preserved for those ionic electronic levels of As (1D_2) and P (1D_2) previously proposed to react with C^+ [8]. Thus, for instance, when considering the As ground state term ($^4S_{3/2}$), CT would successfully proceed if the As^+ state is a triplet. However, the closet ionic level to C^+ ground state is a singlet (1D_2 at 11.04 eV). In fact, this specific reaction requires from spin flipping.

$$S_i = s_{C^+} + s_{As} = 2 + 4 = 6$$

$$S_f = s_C + s_{(As^+)^*} = 3 + 1 = 4$$

Though there are literature examples showing that spin-forbidden reactions are feasible, they proceed with a slower rate than those spin-allowed, and, hence, carbon matrix effects are not expected to be

related to electronic levels involved in such reactions [17,18]. Therefore, the feasibility of CT reactions for other electronic levels for the above-mentioned elements was checked. Because the presence of low-lying atomic levels for As ($^2D_{3/2,5/2}$; $E = 1.31/1.35$ eV), CT could successfully proceed with a singlet ionic state (1S_0) at 12.59 eV. From the Boltzmann-Maxwell distribution, and considering an average plasma temperature of 7600 K (See Section 3.3.1, Table 6), the population density of the low-lying atomic level of As is significant (i.e., approximately one third of that of the ground state). An alternative pathway could involve As^+ triplet ($^3P_{0,1,2}$; $E = 9.79-10.10$ eV) since CT reaction requirements are also fulfilled assuming the strictest interpretation of Wigner's spin rule. Following the same reasoning for P, the most likely candidate is P^+ triplet ($^3P_{0,1,2}$; $E = 10.48/10.53$ eV). Finally, as regards Hg and I, a close inspection of spectroscopic data suggest that carbon-based CT could only occur assuming the intermediate interpretation of Wigner's spin rule with a Hg^+ doublet ($^2S_{1/2}$; $E = 10.44$ eV) and I^+ singlet ($^2P_{2,1,0}$; $E = 10.45/11.33$ eV). Signal enhancement observed for the Hg II 194.227 nm emission wavelengths partially supports this mechanism ($^2P_{1/2}$ (16.82 eV) $\rightarrow$ $^2S_{1/2}$ (10.44 eV)). Nevertheless, in the case of I, CT reactions could also proceed with a different electronic level (1D_2 ; $E = 12.15$ eV) assuming the strictest interpretation of Wigner's spin rule.

Special mention deserves the behavior of B. Charge transfer probability between B ground state and C^+ is expected to be low due to the absence of an appropriate electronic level (Table 2). Nakazawa et al. [15] have shown that, under conventional plasma conditions, BO^+ population in the plasma is significant ($\approx 4\%$) due to the high energy of boron oxide bond (809 kJ mol $^{-1}$). It is expected that, because of carbon introduction into the plasma, boron oxide levels would be reduced due to the higher affinity of carbon to oxygen (1076 kJ mol $^{-1}$), thus increasing B atomic population and atomic emission [15]:

Nevertheless, if signal enhancement would be related to this mechanism, the emission signal for atomic lines of other elements showing high oxygen bond strengths (e.g. La, 799 kJ mol $^{-1}$; Zr, 776 kJ mol $^{-1}$) should have also been enhanced in the presence of carbon but no experimental evidences were noticed (Table S2, Appendix). From the above-mentioned discussion and given the experimental data obtained in this work, it is not feasible to determine unambiguously the origin of matrix effects for B atomic lines.

A close inspection of carbon atomic levels (Fig. 4.A) suggest that an additional mechanism based on carbon species could also play a significant role on matrix effects for As-like elements. Most of the electronic states for C atoms lies between 7.48 and 11.26 eV and, hence, they have enough energy to ionize and excite As-like elements.

Table 2

Feasibility of charge transfer reaction requirements between C^+ and As-like elements. C ground state: 3P ; C^+ ground state 2P , 11.26 eV. ΔE is defined as the energy defect between the particle that transfer the charge (C^+) and the sum of the ionization and excitation potentials of the analyte ion generated ($(M^+)^*$).

Analyte	Atom electronic level		Ion electronic level		ΔE (eV)	Spin conservation	CT probability
	Term	Energy (eV)	Term	Energy (eV)			
As	$^4S_{3/2}$	0.00	1D_2	11.04	0.22	No	Low
	$^4S_{3/2}$	0.00	$^3P_{0,1,2}$	9.79/10.10	1.16/1.47	Yes	High
	$^2D_{3/2,5/2}$	1.31/1.35	1S_0	12.59	-0.02/0.02	Yes	High
B	$^2P_{1/2,3/2}$	0.00	$^3P_{0,1,2}$	12.93	-1.67	Yes*	Low
	$^2P_{1/2,3/2}$	0.00	1S_0	8.30	2.96	Yes	Low
Hg	1S_0	0.00	$^2S_{1/2}$	10.44	0.82	Yes*	High
I	$^2P_{3/2,1/2}$	0.00/0.94	$^3P_{2,0,1}$	10.45/11.33	-0.07/1.75	Yes*	High
	$^2P_{3/2,1/2}$	0.00/0.94	1D_2	12.15	-0.89/0.05	Yes	High
P	$^4S_{3/2}$	0.00	1D_2	11.60	-0.34	No	Low
	$^4S_{3/2}$	0.00	$^3P_{0,1,2}$	10.48/10.53	0.73/0.78	Yes	High
Se	$^3P_{2,1,0}$	0.00/0.31	$^2D_{3/2,5/2}$	11.38/11.45	-0.19/0.19	Yes	High
Te	$^3P_{2,0,1}$	0.00/0.59	$^2P_{1/2,3/2}$	11.55/11.98	-0.72/0.30	Yes	High

* Intermediate interpretation of Wigner's spin rule.

According to this scheme, the high energy atomic levels might be populated by two different pathways: (i) analyte ionization (Penning-like ionization) followed by an ion-electron recombination process; and/or, (ii) directly by collision with carbon excited species. Unlike carbon-based CT reactions, energetic differences between analyte atomic levels and excited carbon species are less critical since any energy mismatch between both species could be accommodated by means of the kinetic energy of the particles involved [26]. Because collisional ionization is also dependent on plasma electron density, it is compatible with previous experiments by our research group in which carbon-based matrix effects on atomic emission for As-like elements decreased in the presence of easily ionizable elements (i.e., K and Ca) [12]. Nevertheless, according to this scheme, other hard-to-ionize elements (e.g. Au, Zn, etc.) should behave similarly but no experimental evidences of signal enhancement on the emission of atomic lines have been found. Unfortunately, to gain insight into the occurrence of all the mentioned mechanisms, a detailed study of the population of all the species involved in these mechanisms (e.g. C*, C⁺, C, M, M*, M⁺, etc.) would be needed but such study requires a complex setup based on lasers that cannot be employed with commercial ICP-OES instruments [17].

3.2.2. Signal suppression

Signal suppression induced by carbon on atomic emission has been previously attributed to the formation of stable carbide compounds as well as to collisional deactivation of the excited analyte states but experimental evidences supporting them are scarce and limited to a very few elements and lines [10,11,19]:

In the present work, the potential influence of the above-mentioned mechanisms on the atomic emission signal has been systematically investigated. First, it has been checked whether carbide formation is responsible of signal suppression for atomic lines. To this end, data about C-element bond formation energy available in the literature [34] was collected and compare to experimental I_{rel} values (Table 3). For each element, the wavelength showing the strongest signal suppression (i.e., lowest I_{rel} values) was selected. Results showed that there were no correlation between carbide bond strength energy and signal suppression. For instance, despite the carbide bond energy for S (714 kJ mol⁻¹) is 2.8-fold higher than that for Al (255 kJ mol⁻¹), no differences in matrix effects are observed between both species (S: I_{rel} 0.92 ± 0.02; Al: I_{rel} 0.90 ± 0.01). Similarly, the carbide bond energy for Zr (561 kJ mol⁻¹) was lower than that for S but signal suppression was more

Table 3

Relative signal intensity (I_{rel}) obtained for a 20 g L⁻¹ carbon-containing solution (glycerol) in comparison to 1.0% w w⁻¹ nitric acid for atomic lines and the corresponding carbon-analyte bond energy. Wavelengths included corresponds to those atomic lines showing the lowest I_{rel} values. Uncertainties for I_{rel} values are presented as the standard deviation of 3 replicates.

Element	Wavelength (nm)	$E_{\text{upper level}}$ (eV)	I_{rel}	M-C (kJ mol ⁻¹)
Al	394.401	3.143	0.90 ± 0.01	255
Ni	346.165	3.606	0.88 ± 0.01	337
Fe	385.991	3.211	0.85 ± 0.01	376
Y	668.757	1.853	0.72 ± 0.01	418
Ti	521.039	2.427	0.74 ± 0.01	423
V	486.473	2.565	0.76 ± 0.01	427
Pd	379.919	4.224	0.87 ± 0.01	436
Sc	404.779	3.083	0.83 ± 0.01	444
Ge	323.949	4.674	0.93 ± 0.01	460
La	510.624	2.758	0.63 ± 0.01	462
Mo	390.295	3.176	0.76 ± 0.01	481
Zr	612.748	2.177	0.74 ± 0.01	561
Nb	509.529	2.519	0.77 ± 0.04	569
Rh	369.236	3.357	0.73 ± 0.01	580
Pt	340.813	3.739	0.95 ± 0.01	598
S	181.972	6.860	0.92 ± 0.01	714

significant for the former element (I_{rel} 0.74 ± 0.02). As regards collisional deactivation hypothesis, this mechanism would be likely for those excited species that possess an excited atomic-state energy close to that of carbon atoms (e.g. ¹D 1.26 eV; ¹S 2.68 eV, ⁵S 4.18 eV, ³P 7.48 eV, ³D 8.65 eV, etc.) and, for this reason, higher matrix effects (i.e., signal suppression) should be expected for them [20]. A close inspection of experimental data reveals that there was not any specific trend in I_{rel} values for those analytes with excited atomic states near to the carbon ones. Therefore, it can be derived that the origin of the carbon-induced signal emission suppression cannot be attributed to neither carbide formation nor collisional deactivation mechanisms. In fact, if the above mechanisms would be correct, similar reactions are expected for the ionic population of the analyte. As a result, analyte ionic population would also have been affected and, hence, the emission signal of ionic lines. However, emission signal for ionic lines was unaffected in the presence of carbon matrix (Table S1, Appendix).

Since both carbon-based CT reactions and collision with excited atomic carbon seem to be the main responsible of the matrix effects observed for As-like elements, we have investigated whether these mechanisms were also responsible of signal suppression. The hypothesis is based on the observation that the atomic lines showing signal suppression correspond to analytes that were almost completely ionized in the plasma (e.g. 99% for V) (black levels in Fig. 4.B) and, hence, the above-mentioned mechanisms would have a great impact on the (limited) analyte atomic population present in the plasma (grey levels in Fig. 4.B). For this kind of elements, because the high ionic population and the small energy gaps between atomic levels, changes on the overall mechanisms populating atomic levels of high energy (i.e., bottom-up vs top-down energy flow) by carbon is marginal with regard As-like elements. However, this is not true for low energy electronic levels since carbon-based CT transfer affects (the limited) analyte ground state population and, hence, the population of (low energy) excited states. These carbon-based mechanisms would simultaneously explain the lack of matrix effects on the emission of ionic lines (i.e., ionic populations remain mostly unaltered) and matrix effects dependence on atomic lines with $E_{\text{upper level}}$.

To evaluate the potential occurrence of the aforementioned carbon-based mechanisms, carbon matrix effects were investigated under the presence of easily ionizable elements since these species affects discharge electron density and ion-atom equilibrium [12]. To this end and given the high number of ionic and atomic lines available in ICP-OES, V was selected as model analyte. A 200 mg L⁻¹ V reference solution (1% w w⁻¹ HNO₃) and the C-containing solution (20 g L⁻¹C) were spiked with different amounts of calcium (2000 and 20,000 mg L⁻¹). For each carbon solution, I_{rel} for V atomic lines was calculated relative to 1% w w⁻¹ HNO₃ solution containing the same amount of calcium. As expected from previous works in the literature, and irrespective of the matrix considered (20 g L⁻¹C or 1.0 w w⁻¹ HNO₃), it was observed that both atomic and ionic emission signal decreased with Ca concentration [26,35,36]. Fig. 5 shows the I_{rel} values obtained for V atomic and ionic lines operating a 20 g L⁻¹ carbon solution for different Ca levels. In agreement with previous experiments for non-Ca containing solutions, no measurable matrix effects within experimental uncertainties were registered for V ionic lines operating the carbon matrix with regard the reference solution. However, I_{rel} values for V atomic lines increased in the presence of Ca. Interestingly, the increase in I_{rel} was more significant for the atomic lines with the lowest $E_{\text{upper level}}$ values. For instance, I_{rel} values for V emission lines with $E_{\text{upper level}}$ values about 2.5 eV increased from 0.79 ± 0.02 to 0.95 ± 0.02 (i.e., 20%), whereas I_{rel} raise for emission lines with higher $E_{\text{upper level}}$ values (i.e., 4.5 eV) was from 0.84 ± 0.02 to 0.95 ± 0.02 (i.e., 13%). According to these data, the observed net matrix effects diminished in the presence of Ca. This behavior is easily explained by considering that the higher electronic density afforded by Ca: (i) increases analyte atomic population; (ii) reduces carbon-charged species population; and (iii) favours electron collision with regard ion-electron recombination [10,12]. Matrix effects

Fig. 5. Relative signal intensity (I_{rel}) obtained for V atomic and ionic emission lines operating a glycerol solution (20 g L⁻¹C solution) with different amounts of calcium in comparison with the equivalent solution in 1.0% w w⁻¹ nitric acid. I_{rel} values among horizontal dotted lines indicate no measurable matrix effects within the experimental uncertainties.

reduction for V-like elements operating carbon/calcium-matrices was analogous to those previously registered for As-like ones [12] thus suggesting that both carbon-based CT reactions and collision with excited atomic carbon play indeed a simultaneous role on both signal enhancement and signal suppression of atomic emission.

From a theoretical point of view (Table 4), carbon-based CT reaction might be expected for Ag, Al, Ba, Ca, Co, Cr, Eu, Fe, Ga, In, La, Lu, Mg, Mn, Mo, Nb, Ni, Pd, Pt, Re, Rh, S, Sb, Sc, Sr, Ti, V, Y and Zr. For these elements, potential electronic states are significantly populated and fulfill spin conservation (either strictest or intermediate interpretation) and ΔE requirements. However, CT probability for Be, Cd, Cs, Ge, K, Li, Na, Pb and Sn is expected to be low due to the most likely states do not fulfill all the CT requirements, particularly ΔE . For instance, among alkali elements, ΔE for Li, Na and K is 5.87, 6.12 and 6.92 eV, respectively. No conclusion was feasible for Pr, Ho and Tm due to the limited spectroscopic information available for these species [20–23]. As regards the collisional mechanisms based on excited atomic carbon, all the elements might be theoretically involved due to requirements are less demanding than with CT reactions (i.e., ΔE and spin conservation) and they show several (ionic and atomic) electronic levels with energies matching those of carbon atoms. Nevertheless, it is important to remark that, for some elements (Ag, Al, Be, Cd, Cs, Ga, Ge, In, K, Li, Mg, Na, Pb, Pd, Pt, S, Sb, Sn and Sr), the number of ionic levels is rather limited between 7.48 and 11.26 eV (<3 levels) and, therefore, the pathway based on excited atomic carbon is expected to be more significant.

3.2.3. No measurable matrix effects within experimental uncertainties

The lack of matrix effects on the atomic emission signal for Zn-like elements (i.e., Au, Cu, Gd, Ir and Zn) was striking considering the previous findings for As and V-like elements. In fact, the lack of matrix effects shown by Au atomic lines was remarkable since several works have previously shown that Au ionization in ICP-MS is enhanced by carbon-based CT reactions [8,14]. Just as V-like elements, the potential occurrence of carbon-based CT reaction was examined (Table 5). With the exception of Zn, all the elements in this group (i.e., Au, Cu, Gd and Ir) have an electronic state fulfilling carbon-based CT reaction requirements (either assuming the strictest or the intermediate version of Wigner's spin rule) so, a priori, atomic emission should have shown a similar behavior to As- and V-like elements. As regards Zn, the lack of matrix effects on atomic emission could be explain by the high ΔE for those electronic levels potentially involved in CT reactions with C⁺. On the other hand, all the above-mentioned elements have both ionic and atomic levels close to those of carbon and, hence, they could be involved in collisional (excitation/ionization) processes with atomic carbon.

Further insight on the lack of matrix effects for these elements requires to measure the population of the different analyte and carbon species present in the discharge. Unfortunately, as it has been previously mentioned, it is not feasible with commercial instruments.

3.3. Practical considerations derived from carbon matrix effects in ICP-OES

Because carbon matrix effects exert a strong influence on the emission signal for atomic lines in ICP-OES, it is expected that elemental analysis for carbon-rich matrices are biased. Therefore, it has been examined how to detect and mitigate carbon matrix effects in ICP-OES.

3.3.1. Plasma characterization

To evaluate the existence and magnitude of non-spectral interferences in ICP-OES, different plasma parameters could be monitored such as plasma electron and excitation temperatures (T_{exc}) [37]. Though several plasma parameters could be directly measured using the emission of Ar atomic lines or plasma background (e.g., electronic temperature and electron density) [24,38], some strategies rely on the use of the ionic and/or atomic emission of a given element introduced into the plasma as analytical probe. Thus, for instance, T_{exc} may be estimated by means the Boltzmann plot using Fe atomic lines [37,39] or by means the line pair intensity ratio using Ti II lines (e.g. Ti II 322.284 nm/Ti II 322.424 nm) [37]. Because carbon matrix effects, biased results in plasma parameters might be obtained operating the emission of atomic lines when compared to the ionic ones. In fact, contradictory results have already been reported about carbon influence on plasma characteristics regarding acidic solutions [10,12]. Therefore, given the new findings presented in this work about carbon matrix effects, several plasma characterization methodologies based on analyte (ionic and atomic) emission were reexamined to determine their strengths and weakness when operating carbon rich matrices. To evaluate both wavelength and analyte characteristics on plasma excitation temperature estimates afforded by the Boltzmann plot, ionic and atomic lines of Fe and Ti were employed. Wavelengths and transition probability values for Fe and Ti emission lines were obtained from different database [23,40,41]. In addition, due to its wider use for assessing plasma robustness, the Mg II 280.270 nm/Mg I 285.213 nm ratio was also employed [37,42]. Because differences in instrument response, the Mg II 280.270 nm/Mg I 285.213 nm ratio was corrected using the nearby background emission [37,42,43].

The results obtained using the above-mentioned methodologies operating both the 20 g L⁻¹ carbon and the reference matrix solution are summarized in Table 6. As it can be derived from data in Table 6, the T_{exc} afforded by the different methodologies was similar (average T_{exc} 7600 K). Interestingly, irrespective of the probe employed, no differences on T_{exc} were observed between the glycerol and the reference solution. Similar findings were obtained using the line pair intensity ratio for atomic and ionic emission lines of Fe and Ti (data not shown) [37]. The lack of change on T_{exc} when using ionic lines was not surprising considering that carbon does not affect ionic emission intensity. For atomic lines, however, it should be considered that excitation temperature is deduced from the plot of:

$$\ln \frac{I\lambda}{gA} \text{ vs } E_{exc}$$

where λ is analyte wavelength, I wavelength intensity, g is the statistical weight ($g = 2J + 1$, J being the total electronic angular momentum quantum number), A is electronic transition probability factor and E_{exc} is excitation energy. Because differences on atomic emission were not so large (<20% for Fe and Ti), and the damping effect of the $\ln$ term, no changes on plasma temperature were observed within experimental uncertainties. From these results, it is obvious that T_{exc} obtained by means the Boltzmann plot using the emission of atomic lines was not

Table 4

Feasibility of charge transfer reaction requirements between C^+ and V-like elements. C ground state: 3P ; C^+ ground state 2P , 11.26 eV. ΔE is defined as the energy defect between the particle that transfer the charge (C^+) and the sum of the ionization and excitation potentials of the analyte ion generated ($(M^+)^*$).

Analyte	Atom electronic state		Ion electronic level		ΔE (eV)	Spin conservation	CT probability
	Term	Energy (eV)	Term	Energy (eV)			
Ag	$^2S_{1/2}$	0.00	1S_0	7.57	3.69	Yes	Low
	$^2S_{1/2}$	0.00	$^2[5/2]_{3,2}$	12.43/12.62	-1.17/-1.36	Yes	High
Al	$^2P_{1/2,3/2}$	0.00/0.01	1S_0	5.98	5.28/5.29	Yes	Low
	$^2P_{1/2,3/2}$	0.00/0.01	$^3P_{0,1,2}$	10.61/10.64	0.62/0.65	Yes*	High
Ba	1S_0	0.00	$^2P_{1/2,3/2}$	11.33/11.41	-0.07/-0.15	Yes*	High
	$^3D_{1,2,3}$	1.12/1.19	$^2S_{1/2}$	12.40	-0.02/0.05	Yes	High
Be	1S_0	0.00	$^2S_{1/2}$	9.32	1.94	Yes*	Low
Ca	1S_0	0.00	$^2S_{1/2}$	12.57	-1.31	Yes*	Low
	$^3P_{0,1,2}$	1.88/1.90	$^2D_{3/2,5/2}$	13.16	-0.02/0.00	Yes	High
Cd	1S_0	0.00	$^2S_{1/2}$	8.99	2.27	Yes*	Low
Co	$^4F_{9/2,3/2}$	0.00/0.22	$^3D_{3,2,1}$	11.29/11.51	-0.25/0.19	Yes	High
Cr	7S_3	0.00	$^6F_{1/2-11/2}$	12.57/12.69	-1.31/-1.43	Yes	Low
	5S_2	0.94	$^6F_{1/2-11/2}$	12.57/12.69	-0.37/-0.49	Yes*	High
Cs	$^2S_{1/2}$	0.00	1S_0	3.89	7.37	Yes	Low
Eu	$^8S_{7/2}$	0.00	$^7S_{1,2,3}$	11.82/11.98	-0.56/-0.72	Yes	High
Fe	$^5D_{4,3,2,1,0}$	0.00/0.12	$^4G_{11/2-5/2}$	11.05/11.13	0.13/0.33	Yes	High
Ga	$^2P_{1/2,3/2}$	0.00/0.10	$^3P_{0,1,2}$	11.87/12.04	-0.78/-0.51	Yes*	High
Ge	$^3P_{0,1,2}$	0.00/0.17	$^2P_{1/2,3/2}$	7.90/8.12	3.14/3.53	Yes	Low
In	$^2P_{1/2,3/2}$	0.00/0.27	$^3P_{0,1,2}$	11.03/11.47	-0.21/0.50	Yes*	High
K	$^2S_{1/2}$	0.00	1S_0	4.34	6.92	Yes	Low
La	$^2D_{3/2,5/2}$	0.00/0.13	1P_1	11.24	0.02/0.15	Yes	High
Li	$^2S_{1/2}$	0.00	1S_0	5.39	5.87	Yes	Low
Lu	$^2D_{3/2,5/2}$	0.00/0.25	1D_2	11.05	0.21/0.46	Yes	High
Mg	1S_0	0.00	$^2P_{1/2,3/2}$	12.07/12.08	-0.81/-0.82	Yes*	High
Mn	$^6S_{5/2}$	0.00	$^5D_{4,0,1,3,2}$	11.50/11.51	-0.24/-0.25	Yes	High
	$^6S_{5/2}$	0.00	$^7P_{2,3,4}$	12.19/12.24	-0.93/-0.98	Yes*	High
Mo	7S_3	0.00	$^6F_{1/2-11/2}$	12.77/13.16	-1.51/-1.90	Yes	Low
	5S_2	1.34	$^6F_{1/2-11/2}$	12.77/13.16	-0.17/-0.56	Yes*	High
	5S_2	1.34	$^4P_{1/2-5/2}$	12.94/13.15	-0.34/-0.55	Yes	High
Na	$^2S_{1/2}$	0.00	1S_0	5.14	6.12	Yes	Low
Nb	$^6D_{1/2-9/2}$	0.00/0.13	$^5F_{1,2,3,4,5}$	11.31/11.47	-0.21/0.08	Yes	High
Ni	$^3F_{4,3,2}$	0.00/0.27	$^2P_{3/2,1/2}$	11.24/11.31	-0.05/0.29	Yes	High
Pb	3P_0	0.00	$^2P_{1/2,3/2}$	7.42/9.16	3.84/2.10	Yes	Low
Pd	1S_0	0.00	$^2F_{7/2,5/2}$	12.34/12.61	-1.35/-1.08	Yes*	High
Pt	$^3D_{3,2,1}$	0.00/1.26	$^2F_{7/2,5/2}$	11.20/11.87	-0.61/1.32	Yes	High
Re	$^6S_{5/2}$	0.00	5S_2	9.96	1.30	Yes	Low
	$^6S_{5/2}$	0.00	$^5P_{3,2,1}$	10.51/10.77	0.75/0.49	Yes	High
Rh	$^4F_{9/2-3/2}$	0.00/0.43	$^3G_{5,4,3}$	11.39/11.66	-0.40/0.30	Yes	High
S	$^3P_{2,1,0}$	0.00	$^2D_{3/2,5/2}$	12.20	-0.94	Yes	High
Sb	$^4S_{3/2}$	0.00	$^3P_{0,1,2}$	8.60/9.30	1.96/2.66	Yes	Low
	$^2D_{3/2,5/2}$	1.05/1.22	1S_0	11.57	0.74/0.91	Yes	High
Sc	$^2D_{3/2,5/2}$	0.00/0.02	1F_3	10.57	0.69/0.71	Yes	High
Sn	$^3P_{0,1,2}$	0.00/0.42	$^4P_{1/2,3/2,5/2}$	13.10/13.63	-2.37/-1.42	Yes*	Low
Sr	1S_0	0.00	$^2S_{1/2}$	11.60	-0.34	Yes*	High
Ti	$^3F_{2,3,4}$	0.00/0.05	$^2G_{7/2,9/2}$	11.11/11.14	0.12/0.20	Yes	High
V	$^4F_{3/2-9/2}$	0.00/0.07	$^3F_{2,3,4}$	11.45/11.52	-0.26/-0.12	Yes	High
Y	$^2D_{3/2,5/2}$	0.00/0.07	1F_3	10.35	0.91/0.98	Yes	High
Zr	$^3F_{2,3,4}$	0.00/0.15	$^2G_{7/2,9/2}$	10.91/10.99	0.27/0.50	Yes	High

* Intermediate interpretation of Wigner's spin rule.

Table 5

Feasibility of charge transfer reaction requirements between C^+ and Zn-like elements. C ground state: 3P ; C^+ ground state 2P , 11.26 eV. ΔE is defined as the energy defect between the particle that transfer the charge (C^+) and the sum of the ionization and excitation potentials of the analyte ion generated ($(M^+)^*$).

Analyte	Atom electronic level		Ion electronic level		ΔE (eV)	Spin conservation	CT probability
	Term	Energy (eV)	Term	Energy (eV)			
Au	$^2S_{1/2}$	0.00	1D_2	12.89	-1.63	Yes	Low
	$^2S_{1/2}$	0.00	$^3D_{3,2,1}$	11.08/12.66	-1.4/0.18	Yes*	High
Cu	$^2S_{1/2}$	0.00	1D_2	10.99	0.27	Yes	High
Gd	$^9D_{2,3,4,5,6}$	0.00/0.21	$^8P_{9/2,7/2,5/2}$	12.23/12.29	-0.76/-1.03	Yes	High
Ir	$^4F_{9/2,3/2,5/2,7/2}$	0.00/0.78	$^3P_{2,1}$	11.32/11.50	-0.24/0.72	Yes	High
Zn	1S_0	0.00	$^2S_{1/2}$	9.39	1.87	Yes*	Low

* Intermediate interpretation of Wigner's spin rule.

sensitive enough for detecting changes in analyte excitation and ionization mechanisms by carbon.

When operating the Mg II 280.270 nm/Mg I 285.213 nm ratio, however, a 10% increase in the Mg II 280.270 nm/Mg I 285.213 nm

ratio was obtained for the carbon matrix regarding the 1.0% w w⁻¹ HNO₃ solution. Consequently, the Mg II 280.270 nm/Mg I 285.213 nm ratio is highly sensitive to carbon matrix effects, but care must be taken to interpret the changes produced in this parameter. The increase in the

Table 6

Influence of the matrix composition on the values of different plasma excitation-related parameters. Uncertainties for I_{rel} values are presented as the standard deviation of 3 replicates.

Parameter	Matrix	
	HNO ₃ 1% w w ⁻¹	Carbon 20 g L ⁻¹
Excitation temperature (T_{ex})(K):		
Fe atomic lines	7800 ± 200	7600 ± 200
Fe ionic lines	8300 ± 200	8400 ± 200
Ti atomic lines	7500 ± 300	7800 ± 300
Ti ionic lines	7100 ± 300	7200 ± 300
Ionic to atomic ratio		
Mg II (280.270 nm)/Mg I (285.213 nm)	5.20 ± 0.03	5.70 ± 0.02

ionic to atomic line intensity ratio would suggest that plasma excitation conditions are enhanced due to the presence of carbon (i.e., higher plasma temperature). However, the higher Mg II 280.270 nm/Mg I 285.213 nm ratio observed for the glycerol solutions was due to signal suppression of atomic lines rather than an increase on ionic emission. It should be kept in mind that neither the shape and position of the discharge (i.e., *thermal pinch* [44]) nor the Ar I 430.010 nm line to Ar continuum ratio were affected by glycerol introduction.

3.3.2. Influence of the carbon source on matrix effects

Unlike glycerol at the concentration level employed in this work, most of the carbon-rich matrices analysed in ICP-OES strongly affect, in addition, both aerosol and plasma characteristics (e.g. acetic acid, ethanol, xylene, etc.) [1,4–7]. Therefore, when using this kind of organics, the magnitude of carbon matrix effects may vary significantly with regard glycerol solutions. To investigate carbon matrix effects on the emission of atomic lines operating such kind of matrices, analyte emission signals for a 20 g L⁻¹C solution made from acetic acid were compared with those obtained with 1.0% w w⁻¹ HNO₃. Fig. 6 shows I_{rel} values obtained for different Mg and As atomic emission lines according to their $E_{\text{upper level}}$ for both acetic and glycerol solutions. It is observed that, regardless the matrix considered, I_{rel} values for Mg and As atomic lines increased with $E_{\text{upper level}}$. Nevertheless, due to the lower surface tension of the acetic acid, [5] I_{rel} values for this matrix were significantly higher than those obtained with glycerol, irrespective of the analyte and line tested. Similar findings were observed for all the elements and lines studied in this work. From data shown in Fig. 6 for acetic acid, it could be concluded that the emission of Mg atomic lines was not affected by carbon whereas As atomic lines showed higher (positive) matrix effects. According to these results, when other factors come into play (e.g. aerosol generation, etc.), the influence of carbon on the analyte atomic

Fig. 6. Relative signal intensity (I_{rel}) obtained for Mg and As atomic lines operating a 20 g L⁻¹ carbon containing solution prepared with acetic acid or glycerol. I_{rel} values among horizontal dotted lines indicate no measurable matrix effects within the experimental uncertainties.

population (and hence, on the emission signal) might be challenging to notice unless plasma robustness is checked (i.e., Mg II 280.270 nm/Mg I 285.213 nm).

3.3.3. Analyte emission wavelength selection

In some cases, carbon matrix effects in ICP-OES would not present a serious problem for metal analysis since ionic lines are usually selected to maximize detection capabilities due to its higher sensitivity against the atomic ones. Nevertheless, Ag, Al, As, Au, B, Cs, Cu, Ga, Ge, Hg, I, In, K, Li, Na, P, Pb, Pd, Rh, S, Sb, Se, Sn, Te and Zn constitutes the exception of this rule. For these elements, atomic lines are most sensitive than the ionic ones and, then, the presence of carbon might significantly affect the accuracy of the results.

To evaluate carbon matrix effects on the emission signal of the most sensitive wavelength for the above-mentioned elements in real sample analysis, different carbon-containing samples (e.g., mussel tissue, fly ashes, polyethylene and seagrasses) were digested (Table S3, Appendix) to know the carbon concentration levels present in the final sample solution. The amount of carbon was estimated by measuring the C I 193.030 nm emission line signal in sample digests using glycerol standards (i.e., 1–20 g L⁻¹C). The carbon content found in the different samples ranges from 0.2 g L⁻¹ (polyethylene) to 5 g L⁻¹ (*Posidonia oceanica* (L.) Delile). Therefore, the latter carbon concentration was selected to evaluate matrix effects on the most sensitive wavelength of Ag, Al, As, Au, B, Cs, Cu, Ga, Ge, Hg, I, In, K, Li, Na, P, Pb, Pd, Rh, S, Sb, Se, Sn, Te and Zn (Table 7). In general, no measurable matrix effects within the experimental uncertainties were noticed for Ag, Al, As, Au, B, Cu, Ga, Ge, Hg, I, In, P, Pb, Pd, Rh, S, Sb, Sn, Te and Zn. However, significant signal suppression (>10%) was observed for Cs, K, Li and Na atomic lines. Also, a signal enhancement of about 12% was observed for Se. From these results, it can be concluded that accuracy for alkali elements and Se can be compromised due to presence of residual carbon after acid digestion treatments. Nevertheless, these conclusions should be revised when the residual carbon concentration would be higher than 5 g L⁻¹, since matrix effects for a higher number of elements would be expected. To mitigate carbon matrix effects on elemental analysis by means of ICP-OES, different approaches are feasible: (i) matrix

Table 7

Relative intensity ratio (I_{rel}) for atomic emission lines of the elements selected operating a Carbon 5 g L⁻¹ solution. Wavelengths included correspond to the most sensitive line of each element. Uncertainties for I_{rel} values are presented as the standard deviation of 3 replicates.

Element	Wavelength (nm)	$E_{\text{upper level}}$ (eV)	E_{ion} (eV)	I_{rel}
K	766.491	1.62	4.34	0.90 ± 0.02
Na	588.995	2.10	5.14	0.88 ± 0.02
In	451.131	3.02	5.79	0.96 ± 0.03
Al	396.152	3.14	5.98	0.95 ± 0.02
Cs	672.328	3.23	3.89	0.82 ± 0.03
Rh	343.488	3.61	7.46	0.95 ± 0.03
Ag	328.068	3.78	7.58	0.97 ± 0.03
Cu	327.395	3.79	7.73	1.01 ± 0.04
Li	610.365	3.88	5.39	0.90 ± 0.01
Ga	294.363	4.31	6.00	0.97 ± 0.02
Pb	283.305	4.37	7.41	0.99 ± 0.03
Pd	340.458	4.45	8.34	1.04 ± 0.02
Sn	283.998	4.79	7.34	1.00 ± 0.01
Ge	265.117	4.85	7.90	0.98 ± 0.03
Hg	253.652	4.89	10.44	1.03 ± 0.02
B	249.772	4.96	8.29	1.02 ± 0.02
Au	242.794	5.10	9.22	1.01 ± 0.02
Sb	217.582	5.70	8.61	0.98 ± 0.03
Te	217.582	5.70	8.61	0.98 ± 0.03
Zn	213.857	5.80	9.39	0.99 ± 0.01
Se	196.026	6.32	9.75	1.12 ± 0.03
As	188.980	6.56	9.78	1.03 ± 0.03
S	181.972	6.86	10.36	1.01 ± 0.02
I	178.215	6.95	10.45	0.99 ± 0.03
P	213.618	7.21	10.49	1.01 ± 0.02

matching; (ii) buffering matrix effects with the addition of a high carbon concentration to both standard and samples [10]; (iii) internal standardization; and (iv) standard addition calibration method. In this case, internal standard wavelength should be carefully selected according to both analyte E_{ion} and atomic wavelength $E_{upper\ level}$ (Table S2, Appendix). Nevertheless, given the potential influence of other concomitants present in the sample, the suitability of a given internal standard should be checked for any specific application.

4. Conclusions

Results in this work clearly show that carbon matrix effects on the emission signal of atomic lines in ICP-OES are rather complex. In general, signal enhancement effects occur for atomic lines of As, B, Hg, I, P, Se and Te whereas signal suppression prevails among atomic lines of Ag, Al, Be, Ba, Ca, Cd, Co, Cr, Cs, Eu, Fe, Ga, Ge, K, Ho, In, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pd, Pr, Pt, Re, Rh, S, Sb, Sc, Sn, Sr, Ti, Tm, V, Y and Zr. No measurable matrix effects within experimental uncertainties are registered for Au, Cu, Ir, Gd and Zn atomic lines. As regards Ce, Dy, Er, Nd, Sm, Tb, Th, U and Yb no clear conclusion about matrix effects is feasible due to the limited atomic emission wavelengths monitored. Experimental data suggest that the presence of carbon in the sample matrix affects both analyte ionic and atomic populations through different carbon-based mechanisms: (i) CT reactions; (ii) collisional ionization; and (iii) collisional excitation. To further insight into the specific contribution of each of the above-mentioned to matrix effects as well as the discrepancies observed on matrix effects for some elements between ICP-AES and ICP-MS (e.g. Au), additional experiments using an ad hoc (i.e., custom made) experimental setup would be required [35]. Some practical considerations can be derived from these findings. First, the use of Mg II/Mg I to evaluate plasma robustness is highly sensitive to carbon non-spectral interferences due to the different matrix effects affecting atomic and ionic lines of a given element. Carbon source also plays an important role in the intensity of matrix effects, since the emission of atomic lines could be affected by changes on the excitation and ionization mechanisms but also on the aerosol generation and transport to the plasma. Finally, a judicious selection of the analyte wavelength must be performed to avoid carbon-based matrix effects, particularly for Se and alkali elements. On this regard, the selection of the internal standard is not a trivial task since it must take into account both analyte and wavelength characteristics (i.e., E_{ion} and $E_{upper\ level}$).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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