

## INVESTIGATIONS INTO NONSPECTROSCOPIC EFFECTS OF ORGANIC COMPOUNDS IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

**Polonca Kralj, Marjan Veber\***

*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia*

*Received 24-09-2003*

### Abstract

Organic compounds introduced into an ICP-MS (inductively coupled plasma mass spectrometry) system can affect analysis in several ways. In our work nonspectroscopic effects caused by moderate concentrations of different organic compounds (methanol, acetonitrile, tris (hydroxymethyl) aminomethane, glucose, and ammonium acetate) were evaluated. The effect of carbon originating from volatile organic compounds on different processes in the plasma was found to be the most important reason for analyte signal changes. By varying instrumental parameters and using a mixed oxygen-argon plasma, it was confirmed, that high signal enhancements of Zn, As, and Se can be ascribed to the more efficient ionization, caused by C<sup>+</sup> ions as modifiers.

### Introduction

Inductively coupled plasma mass spectrometric (ICP-MS) measurements are severely affected by nonspectroscopic (or matrix) effects, which are especially typical for elements with high masses and low first ionization energies. There are basically three types of matrix-induced interferences.<sup>1</sup> The first one is related to sample transport effects and is influenced by sample impact on droplet formation in the nebulizer or droplet-size selection in the spray chamber. The second one is caused by the influence of the matrix on ionization conditions in the plasma. The third type of interferences occurs in the ion optics region, where matrix-induced space charge effects influence ion transmission from the interface to the mass analyzer. The importance of the last two effects depends mostly on the first ionization energy and the mass of the element/isotope.

Organic compounds can be introduced into ICP-MS systems as a part of biological, clinical and nutritional samples (e.g. urine, blood, milk, wine, metal transport proteins,<sup>2</sup> etc.), oils, and fuels. Organic solvents are used in preconcentration and separation procedures based on solvent extraction and they are components of eluents in chromatographic separation techniques.

Carbon in the plasma affects ICP-MS measurements in several ways. It is deposited on the cooled sampling orifice resulting in the cone clogging. The presence of carbon can cause polyatomic interferences, e.g.  $^{40}\text{Ar}^{12}\text{C}^+$  on  $^{52}\text{Cr}^+$  and  $^{12}\text{C}^{14}\text{N}^+$  on  $^{26}\text{Mg}^+$ , when low-resolution ICP-MS instruments are applied. In many cases, however, these spectroscopic interferences can be successfully overcome by adding other gases to argon, for example Xe,<sup>3</sup> by mathematical correction methods,<sup>4</sup> by using collision/reaction cells,<sup>5</sup> or by application of cool plasma conditions.<sup>6</sup> On the other hand, the introduction of an organic solvent<sup>7</sup> or carbon-containing gas such as methane<sup>8</sup> in the nebulizer gas can serve as a chemical modifier and reduce other polyatomic interferences, e.g.  $^{40}\text{Ar}^{35}\text{Cl}^+$  on  $^{75}\text{As}^+$ .

The presence of organic solvents (1-5% (v/v) of ethanol, propanol, butanol, acetic acid) is reported to cause signal enhancements of elements with higher ionization potentials, e.g. arsenic and selenium. In the presence of different concentrations of organic solvents signal enhancement factors of 3 to 8 were observed for arsenic.<sup>9-11</sup> Signal enhancement was also dependent on the arsenic species analysed.<sup>9</sup> Signals for selenium were enhanced by factors of 2 to 6.<sup>12,13</sup> This phenomenon can be attributed to the modification of the ionization equilibrium in the plasma.<sup>10</sup> Under standard operating conditions the degree of ionization for carbon has been estimated to be 5% compared to 0.02 % for argon in the plasma. It is suggested that the introduction of organic compounds into the plasma results in the increased population of  $\text{C}^+$  (ionization energy 11.26 eV). The degree of ionization of the analytes is therefore improved by transfer of electrons to carbon ions from elements with ionization energy lower than carbon. An increase in the degree of ionization is typical for elements with high first ionization energy, which are not completely ionized.

In our work some aspects of nonspectroscopic effects of moderate concentrations of different organic compounds were studied and possible mechanisms, which would explain them, were proposed.

### Experimental

The quadrupole inductively coupled plasma mass spectrometer (ICP-MS) used in this work was Agilent (Palo Alto, USA) HP 4500. Operating conditions are given in Table 1.

**Table 1.** ICP-MS operating conditions.

Nebulizer	Babington
High RF power	1500 W
Low RF power	1300 W
Argon coolant flow	15 L min <sup>-1</sup>
Argon auxiliary flow	0.7 L min <sup>-1</sup>
Argon nebulizer flow	1.00 to 1.05 L min <sup>-1</sup>
Sampling depth	5.5 mm
Measured time per peak	0.6 s
Spray chamber temperature	2 °C
Sampler and skimmer cones	Nickel

Stock element standard solutions were obtained from Merck (Darmstadt, Germany). Blank and multielement standard solutions containing elements listed in Table 2 at 100 µg/L in 1% (v/v) HNO<sub>3</sub> and with addition of different amounts of organic compounds were prepared. Nitric acid, methanol, and acetonitrile were of analytical grade from Merck. Tris (hydroxymethyl) aminomethane (TRIS), glucose, and ammonium acetate were of analytical grade from Fluka (Hanover, Germany). Pure water from a Milli-Q system (Millipore, Bedford, USA) was used throughout for preparing sample solutions. High purity oxygen for mixed gas plasma was obtained from Messer (Griesheim, Germany).

The criteria for the selection of measured elements/isotopes in this study were diversity of mass and first ionization energies and additionally, the absence of spectral interferences caused by carbon or other elements present in the solution. The selected elements/isotopes under investigation are listed in Table 2.

The procedure for the direct analyte transport rate ( $W_{\text{tot}}$ ) measurements described in the literature<sup>15</sup> was applied. To ensure effective trapping of the aerosol particles filters with pore size 0.3 µm were used. 5 µg/mL of Y, Ru, Ce, and Tl solutions containing carbon (originating from different organic compounds) at concentration of 10 mg/mL as well as 1% (v/v) HNO<sub>3</sub> solution were prepared. Aerosols from the spray chamber were collected in glass fiber filters (Macherey-Nagel, MN 85/70 BF, 47-mm diameter, pore size 0.3 µm, Germany) over 10 minutes. Filters were removed from the holder (made of acid resistant material), rinsed, and extracted with 40 mL of 3% (v/v) HNO<sub>3</sub> solution. After filtration of extracts Y, Ru, Ce, and Tl concentrations in each of the solutions were determined by ICP-MS using acid matched calibration. Standard solutions containing 0,

1, 5, 10, 20, 50, and 100 µg/L of elements were used. The analyte transport measurements were made in three replicates.

It was assumed that also particles with diameters smaller than 0.3 µm would be trapped on the filters due to droplet coagulation or accretion. To verify this assumption an additional filter was placed successively in the filter holder. No significant differences in concentrations of Y, Ru, Ce and Tl were observed for the resultant extract, which indicated that the above-mentioned procedure was appropriate for analyte transport measurements.

**Table 2.** First ionization energies of elements in the multielement standard solutions; measured isotopes are also specified.

Element	First ionization energy (eV) <sup>14</sup>
<sup>7</sup> Li	5.39
<sup>45</sup> Sc	6.54
<sup>66</sup> Zn	9.39
<sup>71</sup> Ga	6.00
<sup>75</sup> As	9.81
<sup>82</sup> Se	9.75
<sup>89</sup> Y	6.38
<sup>111</sup> Cd	8.99
<sup>115</sup> In	5.79
<sup>140</sup> Ce	5.47
<sup>205</sup> Tl	6.11
<sup>208</sup> Pb	7.42

#### *Mixed argon-oxygen plasma conditions*

Oxygen (from 0.01 to 0.05 L/min) was added to the argon carrier. The argon flow was diminished correspondingly so that the total carrier gas flow was kept constant at 1.05 L/min and transport efficiency was not changed. Multielement solutions containing 1% (v/v) HNO<sub>3</sub> and 10 mg/mL of carbon originating from acetonitrile were introduced to the system and signal intensities for selected elements measured.

## Results

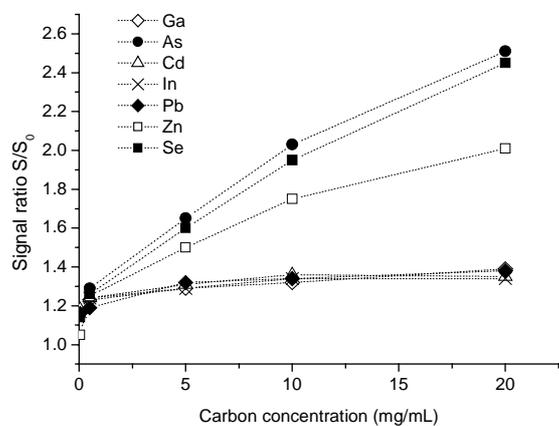
#### *Effect of organic compounds*

Addition of different concentrations of organic compounds influenced signals for all investigated elements. In Figure 1 results for glucose solutions are given as S/S<sub>0</sub> ratios (signal in the presence of matrix / signal in 1% HNO<sub>3</sub> solution). Enhancement

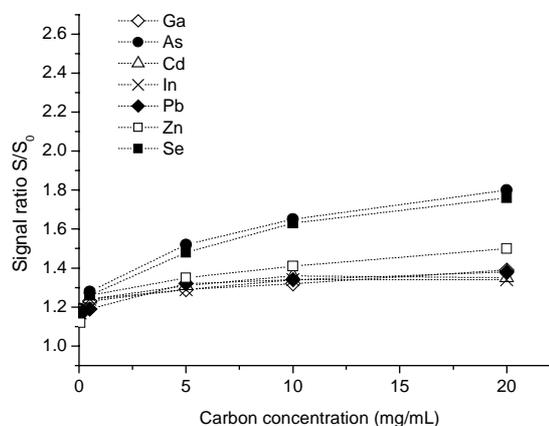
factors varied from 1.3 for elements with first ionization energy up to 9 eV (Li, Sc, Ga, Y, Cd, In, Ce, Tl, and Pb) to 2.5 for As and Se.

At a lower plasma power (1300 W) signal enhancement factors for the solution with the highest glucose concentration were found to be 1.5 for Zn and 1.8 for As and Se, as shown in Figure 2. Signals for other elements were comparable to those of the measurements at high plasma power.

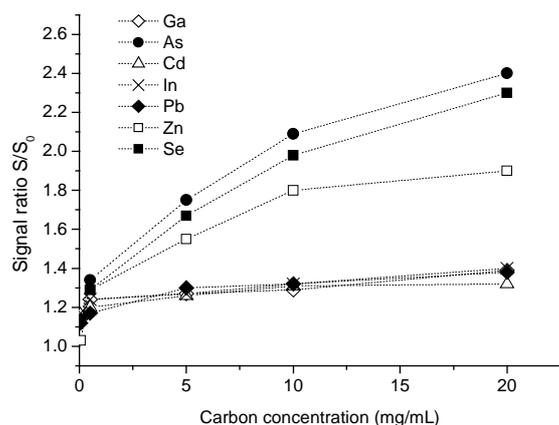
The same trends were observed also for solutions containing tris(hydroxymethyl) aminomethane (TRIS) and ammonium acetate (Figures 3 to 6). In Table 3 maximum enhancement factors of selected elements (carbon concentration of 20 mg/mL) at high and low plasma power are presented.



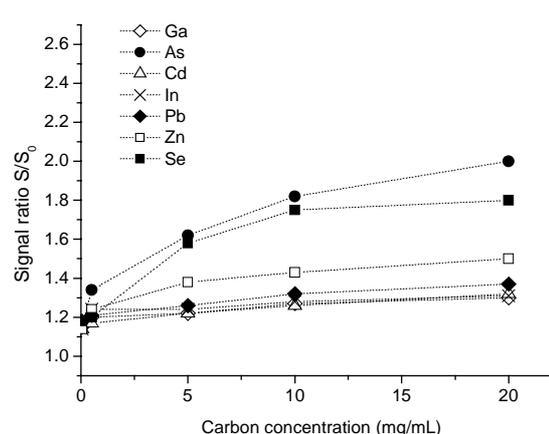
**Figure 1.** Signal change of selected elements in the presence of different concentrations of carbon (originating from glucose); plasma power was 1500 W.



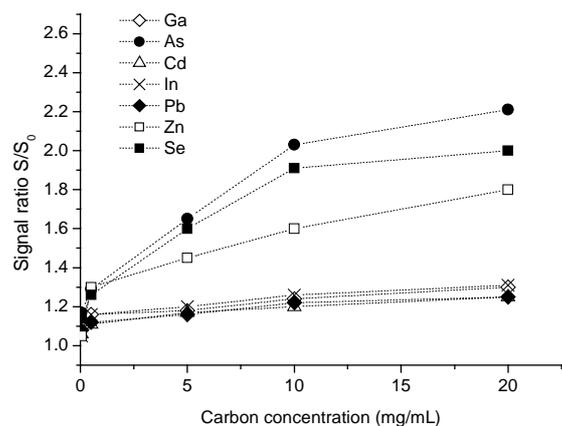
**Figure 2.** Signal change of selected elements in the presence of different concentrations of carbon (originating from glucose); plasma power was 1300 W.



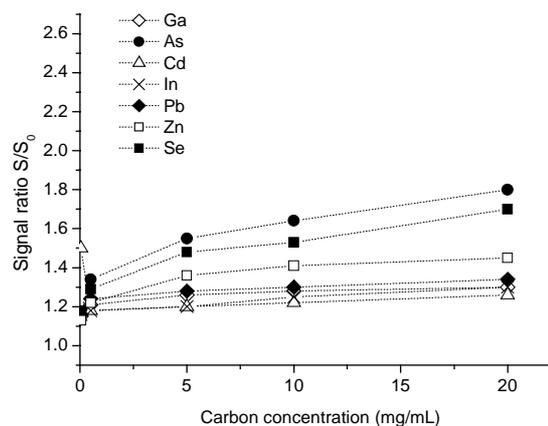
**Figure 3.** Signal change of selected elements in the presence of different concentrations of carbon (originating from ammonium acetate); plasma power was 1500 W.



**Figure 4.** Signal change of selected elements in the presence of different concentrations of carbon (originating from ammonium acetate); plasma power was 1300 W.



**Figure 5.** Signal change of selected elements in the presence of different concentrations of carbon (originating from TRIS); plasma power was 1500 W.

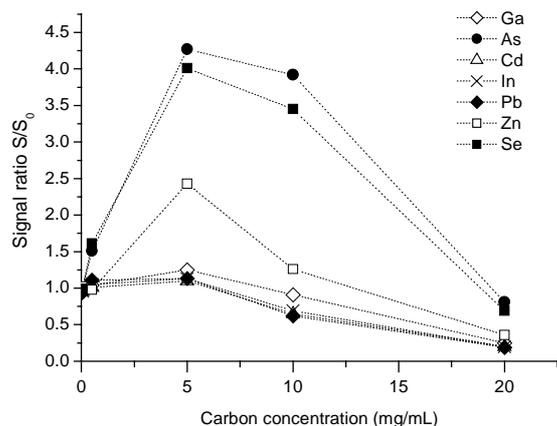


**Figure 6.** Signal change of selected elements in the presence of different concentrations of carbon (originating from TRIS); plasma power was 1300 W.

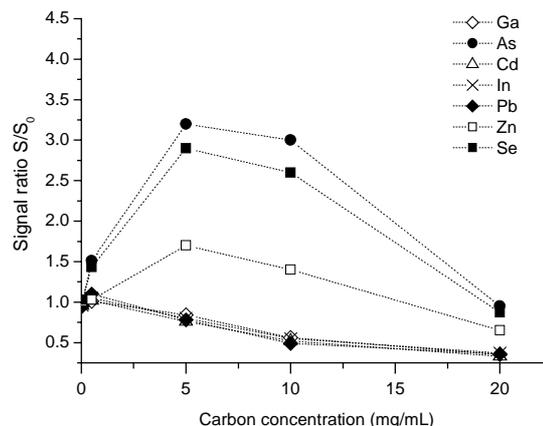
**Table 3.** The summary of maximum enhancement effects of selected elements in glucose, ammonium acetate, and TRIS solutions observed at 1500 and 1300 W.

	Glucose		Ammonium acetate		TRIS	
	1500 W	1300 W	1500 W	1300 W	1500 W	1300 W
Ga	1.4	1.4	1.4	1.3	1.3	1.3
Cd	1.3	1.3	1.3	1.3	1.2	1.2
In	1.3	1.3	1.4	1.3	1.3	1.3
Pb	1.4	1.4	1.4	1.4	1.2	1.3
As	2.5	1.8	2.4	2.0	2.2	1.8
Se	2.4	1.7	2.3	1.8	2.0	1.7
Zn	2.0	2.0	1.9	1.5	1.8	1.4

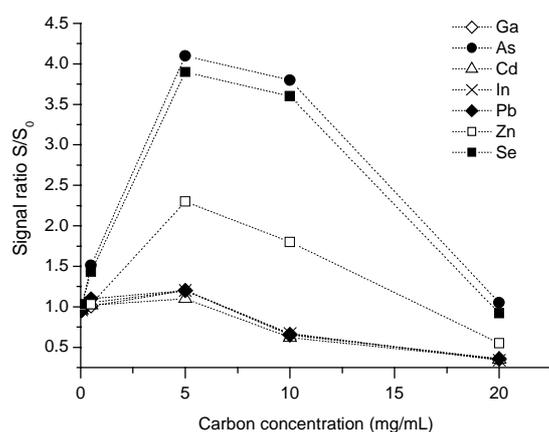
Signals in the presence of acetonitrile and methanol show different behavior. The effect of acetonitrile is presented in Figures 7 and 8. As and Se signals, which differed substantially from other analytes, increased with increasing acetonitrile concentration and attained a maximum enhancement of 4–4.5 at carbon concentration of 5–10 mg/mL followed by a sharp decrease at higher concentrations. Zn signals were intermediate in behavior with an enhancement factor of 2.5, which then decreased at high concentrations. The effect of acetonitrile on other elements was less pronounced. At 1300 W the signal patterns for As, Se, and Zn were similar with lower maximum enhancements. Similar behaviors for all elements were obtained also in the presence of methanol. The highest enhancement factors for As and Se were again around 4 at high plasma power (Figure 9) and around 3 at low plasma power (Figure 10). Effects ( $S/S_0$  ratios) of acetonitrile and methanol solutions (containing 5 mg/mL of carbon) observed at 1500 and 1300 W are summarized in Table 4.



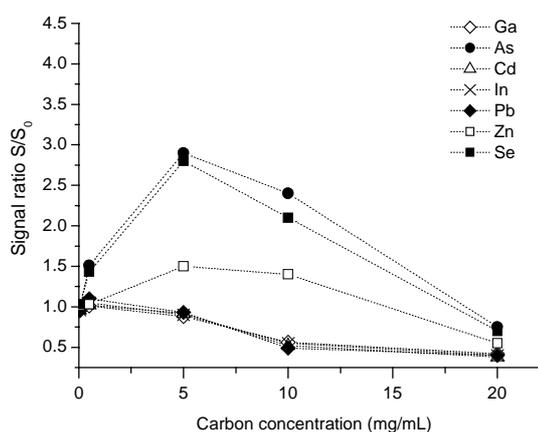
**Figure 7.** Signal change of selected elements in the presence of different concentrations of carbon (originating from acetonitrile); plasma power was 1500 W.



**Figure 8.** Signal change of selected elements in the presence of different concentrations of carbon (originating from acetonitrile); plasma power was 1300 W.



**Figure 9.** Signal change of selected elements in the presence of different concentrations of carbon (originating from methanol); plasma power was 1500 W.



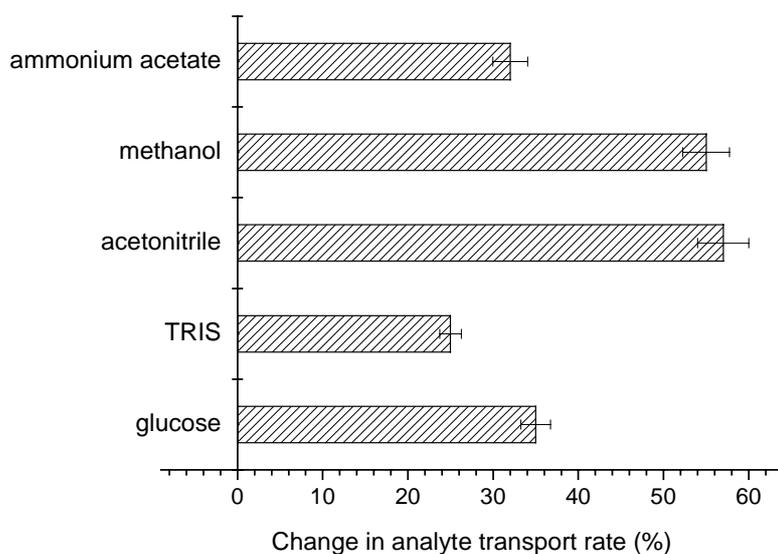
**Figure 10.** Signal change of selected elements in the presence of different concentrations of carbon (originating from methanol); plasma power was 1300 W.

**Table 4.** Effects of acetonitrile and methanol solutions (containing 5 mg/mL of carbon) observed at 1500 and 1300 W.

	Acetonitrile		Methanol	
	1500 W	1300 W	1500 W	1300 W
Ga	1.3	0.8	1.2	0.9
Cd	1.1	0.7	1.1	0.9
In	1.1	0.8	1.2	0.9
Pb	1.1	0.8	1.2	0.9
As	4.3	3.2	4.1	2.9
Se	4.0	2.9	3.9	2.8
Zn	2.4	1.7	2.3	1.5

### Analyte transport rate

The effect of different organic compounds containing 10 mg/mL of carbon on changes in analyte transport rate ( $W_{\text{tot}}$ ) is presented in Figure 11. Changes are given relative to 1% (v/v)  $\text{HNO}_3$  solution. It is evident that the presence of organic compounds significantly improved the analyte transport rate. The highest increases were observed for acetonitrile and methanol solutions.

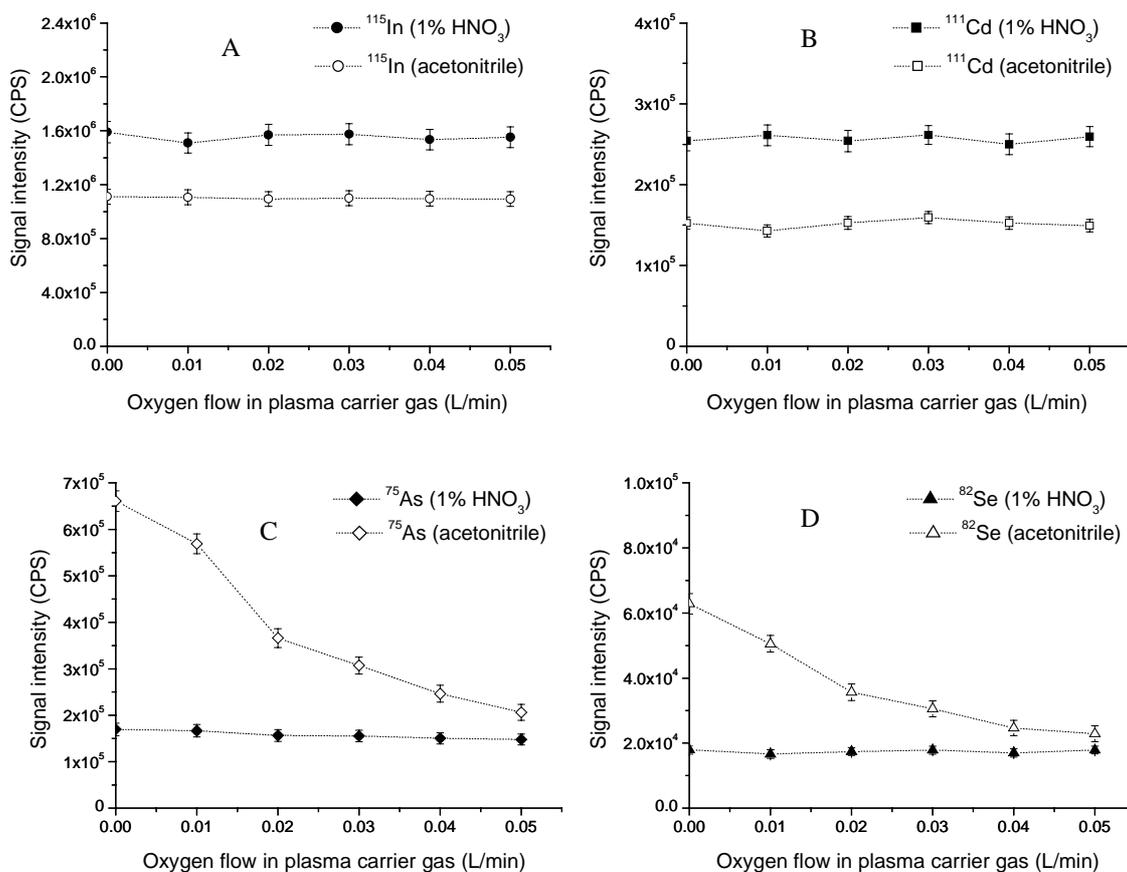


**Figure 11.** Changes in analyte transport rate ( $\Delta W_{\text{tot}}$ ) in the presence of 10 mg/mL of carbon originating from different organic compounds.

### Effect of oxygen

Signal intensities for elements in the presence of oxygen were measured for 1% (v/v)  $\text{HNO}_3$  and acetonitrile solution. The behavior of  $^{115}\text{In}$  (as a representative of elements with low first ionization energies),  $^{111}\text{Cd}$  (with first ionization energy slightly less than 9 eV) and  $^{75}\text{As}$  and  $^{82}\text{Se}$  (as representatives of elements with high first ionization energies) are shown in Figure 12.

For both solutions, In and Cd signal intensities did not significantly change with increase of oxygen flow. The same was observed for As and Se in 1% (v/v)  $\text{HNO}_3$  solution. However, the addition of oxygen substantially decreased the signal intensities of  $^{75}\text{As}$  and  $^{82}\text{Se}$  in the presence of acetonitrile.



**Figure 12.** Signal intensities for 100  $\mu\text{g/L}$  of  $^{111}\text{Cd}$  and  $^{115}\text{In}$  (A) and  $^{75}\text{As}$  and  $^{82}\text{Se}$  (B) at different oxygen flow in plasma carrier gas for the solutions containing 1% (v/v)  $\text{HNO}_3$  or 10 mg/mL of carbon originating from acetonitrile.

## Discussion

Regarding low mass and high first ionization energy of carbon, organic compounds should be considered as relatively simple matrices in ICP-MS measurements. However, the results in the presence of low and moderate concentrations of organic compounds in the analyte solutions show the opposite behavior.

With the exception of Zn, As, and Se, small signal enhancements observed in the presence of 10 mg/mL carbon originating from solid organic compounds (glucose, TRIS, ammonium acetate), can be correlated with transport efficiency data. Thus, signal increases of 20-40% can be ascribed to sample transport. Since signals behave in a similar way, this effect can be compensated by internal standardization.

Large signal enhancement for Zn, As, and Se in the presence of glucose, TRIS, and ammonium acetate cannot be attributed only to transport phenomena, but mostly to changes in the ionization equilibrium in the plasma. Improved ionization is achieved by transfer of electrons to carbon ions from elements with ionization energy lower than carbon. Transfer of electrons occurs if the difference between their first ionization energies is less than 2 eV.<sup>16</sup> This is true for Zn, As, and Se. Therefore, high signal enhancement factors for these elements support the above-mentioned mechanism. No significant signal enhancement is observed for cadmium, which is also an element with relatively high first ionization energy, since the difference between first ionization energies is too high (2.27 eV). Measurements at low plasma power resulted in lower signal enhancement for Zn, As, and Se as a consequence of the smaller population of carbon ions due to the lower plasma temperature and less pronounced transfer of electrons.

In comparison to glucose, TRIS, and ammonium acetate, volatile organic compounds (acetonitrile and methanol) cause even more pronounced effects on signals. Although the content of carbon in the analyte solutions was the same for all matrices studied, significantly higher amounts of acetonitrile and methanol vapors entered the plasma together with sample aerosol, altering the properties of plasma and thus lowering the ionization temperature.<sup>17</sup>

Increase in transport in the presence of methanol and acetonitrile results in no enhancement of elements with first ionization energy lower than 9 eV, since the effect described above clearly prevails over the other matrix effects. It is also reasonable to assume that transport cannot account for the effect of methanol and acetonitrile on As, Se, and Zn signals at both power levels. Signal enhancements can be therefore ascribed to the ionization conditions in the plasma. Since more carbon is introduced into the plasma, higher population of carbon ions is present. Consequently, for As, Se, and Zn substantially higher signal enhancements in acetonitrile and methanol solutions are observed. When lower plasma power is applied, the population of carbon ions is diminished and therefore the enhancement factors are lower.

The addition of small amounts of oxygen to the carrier gas did not significantly effect analyte signals. Therefore it can be concluded that these small low amounts of oxygen did change plasma temperature, which is also in accordance with data reported

by Lam and Horlick<sup>18</sup>. The authors observed no effect on analyte sensitivity when up to 5% (v/v) of oxygen was introduced into the plasma.

Smaller signals for As, Se, and Zn in acetonitrile solution in the presence of oxygen can be explained by formation of  $\text{CO}^+$  and  $\text{CO}_2^+$  ions in the plasma, which diminished the population of  $\text{C}^+$  ions. The first ionization energies of  $\text{CO}^+$  (14,01 eV) and  $\text{CO}_2^+$  ions (13,77 eV)<sup>14</sup> are too high to efficiently promote the ionization of elements with high first ionization energy. These observations additionally confirm the electron transfer mechanism.

### Conclusions

Due to their high volatility acetonitrile and methanol have a significant effect on analyte signals in comparison to glucose, TRIS, and ammonium acetate. Signal enhancements for As, Se, and Zn can be mostly attributed to more efficient ionization, caused by  $\text{C}^+$  ions as modifiers.

The most effective approach to control nonspectroscopic interferences caused by carbon-containing compounds are the use of matrix-matched calibration standard solutions, internal standard correction methods and the addition of oxygen to the plasma gas.

It should be emphasised that volatile organic compounds can be successfully used as modifiers for Zn, As, and Se, as described in the literature<sup>12-14</sup>. Higher degree of ionization for these elements can be achieved by adding small amounts of carbon containing compounds to calibration standard solutions and samples, which results in the improvement of sensitivity in ICP-MS measurements.

The described matrix effects of organic compounds should not be overlooked only in direct ICP-MS analysis, but also when ICP-MS is coupled as a detector to high performance liquid chromatography, especially when gradient elution is applied.

### Acknowledgements

The financial support of the Ministry of Education, Science and Sport of Republic Slovenia (contract no. PN P0-504) is gratefully acknowledged.

### References

1. R. Thomas, *Spectroscopy* **2002**, *17*, 24–31.
2. M. Patriarca, N. A. Kratochwil, P. J. Sadler, *J. Anal. At. Spectrom.* **1999**, *14*, 633–637.

3. F. G. Smith, D. R. Wiederin, R. S. Houk, *Anal. Chem.* **1991**, *63*, 1458–1462.
4. D. Ashley, *At. Spectrosc.* **1992**, *13*, 169–173.
5. I. Feldmann, N. Jakubowski, C. Thomas, D. Stuewer, *Fresenius' J. Anal. Chem.* **1999**, *365*, 422–428.
6. F. Vanhaecke, S. Saverwyns, G. De Wannemacker, L. Moens, R. Dams, *Anal. Chim. Acta* **2000**, *419*, 55–64.
7. I. Llorente, M. Gómez, C. Cámara, *Spectrochim. Acta, Part B* **1997**, *52*, 1825–1838.
8. S. J. Hill, M. J. Ford, L. Ebdon, *J. Anal. At. Spectrom.* **1992**, *7*, 1157–1165.
9. E. H. Larsen, S. Stürup, *J. Anal. At. Spectrom.* **1994**, *9*, 1099–1105.
10. P. Allain, L. Jaunault, Y. Mauras, J. M. Mermet, T. Delaporte, *Anal. Chem.* **1991**, *63*, 1497–1498.
11. C. J. Amarasiriwardena, N. Lupoli, V. Potula, S. Korrick, H. Hu, *Analyst* **1998**, *123*, 441–445.
12. R. M. Olivas, C. R. Quetel, O. F. X. Donard, *J. Anal. At. Spectrom.* **1995**, *10*, 865–870.
13. B. Gammelgaard, O. Jøns, *J. Anal. At. Spectrom.* **1999**, *14*, 867–874.
14. D. R. Lide, *Handbook of chemistry and physics, 71<sup>st</sup> edition*; CRC Press, Boston, 1990, pp 10–210/211.
15. A. Montaser, *Inductively coupled plasma mass spectrometry*; Wiley-VCH, New York, 1998, pp 377–378.
16. P. B. Farnsworth, A. Woolley, N. Omenetto, O. Matveev, *Spectrochim. Acta, Part B* **1999**, *54*, 2143–2155.
17. A. Montaser, *Inductively Coupled Plasma Mass Spectrometry*; Wiley-VCH, New York, 1998, p 171.
18. J. W. H. Lam, G. Horlick, *Spectrochim. Acta, Part B* **1990**, *45*, 1313–1325.

### Povzetek

Preučevali smo nespektroskopske (matrične) vplive različnih organskih spojin. Najbolj je bil izrazit vpliv hlapnih organskih spojin na različne procese v plazmi. Do povečanja intenzitet signalov za elemente z visoko prvo ionizacijsko energijo naj bi prišlo zaradi prenosa naboja na C<sup>+</sup> ione. Predpostavljeni mehanizem smo poskušali potrditi s spreminjanjem instrumentalnih pogojev in dodajanjem kisika k nosilnemu plazemskemu plinu.