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Signal Enhancement of Elements with Different Ionization Potential by Organic Solvent in ICP-MS

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Signal enhancement of elements with different ionization potential by organic solvent in inductively coupled plasma mass spectrometry was investigated. In the presence of the 3 % methanol or 4 % glycerol, the enhancement factors were in the range of 1.5 to 2.8 compared with the aqueous solution for high ionization potential elements (*e.g.*, As, Se *etc.*), while the factors were less than 1.5 for the low ionization potential elements (*e.g.*, Ce, In *etc.*). Signal enhancement caused by sample nebulization-transport efficiency improved was less than 1.5, which was obtained by detecting the sample aerosol collected with cold trap. The degrees of ionization of As and Se in organic solvent were increased to 69-71 and 56-58 %, respectively. However, In and Ce were only slightly increased with organic solvent. Our results demonstrated that signal enhancement of elements with high ionization potential was mainly attributed to the increased degree of ionization in plasma, while the low ionization potential elements were mainly attributed to the improved sample nebulization-transport efficiency.

Keywords: Signal enhancement, Organic solvent, Degree of ionization, ICP-MS.

INTRODUCTION

Inductively coupled plasma-mass spectrometry (ICP-MS) has been a preferred technique for analysis of trace elements owing to its excellent analytical capability. Sometimes, the direct determination of trace metals is difficult because of matrix interference problems and low concentration of metals in biological and environmental samples. The pre-concentration or separation techniques based on the organic solvent extraction have been widely used to improve the detection limit and selectivity. In particular, addition of organic compounds to the analyte solution could increase signal intensity of high ionization potential elements by ICP-MS detection¹⁻⁵. Rodushkin *et al.*⁶ had reported that the analytical performance of ICP-SFMS was significantly improved by addition of methane to the argon gas flow, the signal intensities of As, Te, Se and Sb were enhanced two- to four-fold. Kovacevic *et al.*⁷ studied the matrix effect of methanol on ICP-MS signals of phosphorus, a sevenfold increase in the phosphorus signal was observed when water and 2.5 mol L⁻¹ methanol were compared.

The enhancement effects of organic compounds on signal intensities could occur during the nebulization-transport process and ionization process in plasma⁸⁻¹⁰. The introduction of small amounts of organic solvents into the plasma modifies the physicochemical properties of the nebulized solution with regard to the aqueous sample, contributing to an overall smaller

droplet size, which favors nebulization efficiency and improves desolvation of the aerosol in the plasma, resulting in an improvement of signal intensity^{11,12}. Shuqin *et al.*¹³ observed the signal enhancement of Hg about ten times by adding small amount of ethylenediamine or triethanolamine, the signal enhancement was caused by improved sample nebulization-transport efficiency based on the experiment results that the enhancement of intensity of the atomic line and ionic line of Hg was the same in the presence of aqueous ammonia, ethylenediamine and triethanolamine did not increase. Allain *et al.*¹⁴ had reported signal enhancement of Hg, As, Te, Se and Au due to the presence of carbon-containing compounds in plasma, which could be attributed to the modification of the ionization equilibrium in the plasma. Larsen and Stürup¹⁵ had proposed that an increased population of carbon or carbon-containing ions in the plasma facilitates a more complete ionization of analytes. The degrees of ionization of As and Se would be enhanced by electron transfer from the analytes to the carbon or carbon-containing polyatomic ions. Similar charge transfer mechanism from C⁺-species to analyte atoms in the central channel of the plasma discharge had been provided by Campbell *et al.*¹⁶, Olivas *et al.*¹⁷ and Al-Ammar *et al.*¹⁸. Our group¹⁹ had demonstrated that the signal enhancement of As, Se and Te was not due to improvement in the nebulization transport of the sample by Carry-over effect experiments of volatile organic solvent. These results also suggest that

mechanism of carbon-induced signal enhancement varies with ionization potential and mass of elements. Kovacevic *et al.*²⁰ had further confirmed this results by using a modified thermostatted double pass spray chamber. Liu and Beauchemin²¹ investigated the radial profiles of some background and analytes ions by ICP-TOF-MS in recently studies. The similar distribution of several background ions (C^+ , CO^+ and ArC^+) was observed which further confirmed the suggestion that ionization predominantly occurs through charge transfer with carbon-containing ions.

The enhancement effects of organic compounds on signal intensities could occur during the nebulization-transport process and ionization process in plasma. However, which process was the major factor to improve the signal intensity of analyte in the presence of organic compounds? The aim of this work was to investigate the signal enhancement of elements with different ionization potential in organic solvent. To confirm the main factor that dominate the signal enhancement, the degrees of ionization of interested analytes and sample nebulization-transport efficiency were investigated by ICP-MS. The variations were used to distinguish the enhancement effects caused by improved sample nebulization-transport efficiency and/or ionization efficiency.

EXPERIMENTAL

A POEMS III Plasma Optical Emission Mass Spectroscopy (Thermo Jarrell Ash-VG Elemental Corporation, USA) instrument equipped with a pneumatic concentric glass nebulizer and a cyclonic spray chamber was used. The sample solution and the drain of the spray chamber were pumped. The instrument operating mode was set at "only MS" and the parameters were selected to maximize the sensitivity and minimize the variation coefficient by using 1 % HNO_3 solution containing 10 ng mL^{-1} of Be, Co, In, Tb and U. The signals of selected elements were acquired as in pulsed mode. The operating parameters are summarized in Table-1.

TABLE-1
ICP-MS OPERATING CONDITIONS

ICP-MS instrument	Thermo Jarrell Ash POEMS III
R.F. power	1350 W
Nebulizer gas	0.65 to 0.72 $L\ min^{-1}$ (variable)
Auxiliary gas	1.0 $L\ min^{-1}$
Plasma gas	14.0 $L\ min^{-1}$
Sampling depth	8 mm
Sampling cone	1.0 mm
Skimmer cone	0.7 mm
Sample uptake	1.0 $mL\ min^{-1}$
Data acquisition	Pulse mode
Integration time	2 s
Number of sweeps	10
Points/Amu	16
Analysis isotopes	9Be , ^{59}Co , ^{73}Ge , ^{75}As , ^{82}Se , ^{85}Rb , ^{114}Cd , ^{115}In , ^{133}Cs , ^{140}Ce and ^{209}Bi

Multi-element mixed stock solution was prepared from 1 mg mL^{-1} of single element standard solution (National Center for Analysis and Testing of Steel Materials, China). 10 ng mL^{-1} testing sample solutions were prepared by dilution of multi-element stock solutions with 2 % (v/v) nitric acid, 3 % (v/v)

methanol or 4 % (v/v) glycerol matrix. Solutions of 1×10^{-7} mol L^{-1} of As and Rb, Se and Rb, In and Cs, Ce and Cs were prepared by dilution of stock solutions with above organic matrix, respectively. In preparing each pair solution, a strict ratio of 1:1 between the molar ratios of two elements was necessary. Ultra pure nitric acid was prepared by sub-boiling distillation in commercial available quartz distillatory. Ultra pure water with resistivity of $18.2\ M\Omega\ cm^{-1}$ from a 4-module E-pure system (Barnstead Thermolyne Corporation, USA) was used throughout for preparing sample solutions.

Measuring the degree of ionization: For this work, the measurement of degree of ionization was performed according to the literature²² with slight modification. The elements (As, Se, Ce and In) and relatively easily ionized elements (Rb, Cs) were selected for the detection of degree of ionization. For instance, we obtained the ionization ratio for As in the plasma by introducing a solution of the same molar concentration As and Rb into the plasma. Rubidium has fairly low first ionization potential (4.117 eV), while the ionization potential of arsenic is 9.81 eV, both of these energies are lower than the ionization potential of argon at 15.755 eV. Because rubidium has such a low ionization potential it should be completely ionized in the plasma, whereas arsenic will not be. Thus, the ratio of As^+/Rb^+ should be equivalent to the degree of ionization for arsenic. The degree of ionization for analyte was calculated as the following formula:

$$\alpha_M = M_i / (M_i + M_\alpha) \times 100\% = N_M / N_{EIE} \times 100\% \quad (1)$$

where α_M is the degree of ionization for analyte (M), M_i and M_α are the ion and atom counts of M, N_M is the signal intensity of M, N_{EIE} is the signal intensity of the relatively easily ionization element, all the used values must be after blank and abundance of isotope corrections.

In degree of ionization determination, each pair elements are quite close in mass and the mass bias which might be present in the instrument is ignored. Further, rubidium acts as a form of internal standard for arsenic, the use of the ratio As^+/Rb^+ could compensate the single drift over narrow mass ranges.

Collecting sample aerosol by cold trap: To evaluate the change of sample nebulization-transport efficiency with or without adding organic reagents, the analyte aerosol from the spray chamber was collected by cold trap. Fig. 1 shows the schematic diagram of cold trap capturing system. This system was composed of a borosilicate glass capture and a steel dewar vessel equipped with a pneumatic concentric glass nebulizer and a cyclonic spray chamber. The capture was connected to outlet of the spray chamber with Tygon tube. The sample aerosol from the spray chamber was transported to the capture, where the aerosol was froze quickly and collected. The cryogen was prepared by mixing liquid nitrogen and ethanol, the temperature was at $-110\ ^\circ C$. After the cryogen was injected into the Dewar vessel and the captor was installed into it. The mixed solution of 2 mg mL^{-1} was nebulized continuously for 10 min and the aerosol formed from spray chamber was frozen. The sample aerosol collected was diluted to 25 mL by 2 % nitric acid and determined by ICP-MS. The residue of organic reagent (10^{-4} , v/v) did not influence on the determination by ICP-MS. Both the collection and quantification were carried out thrice to get more reliable values.

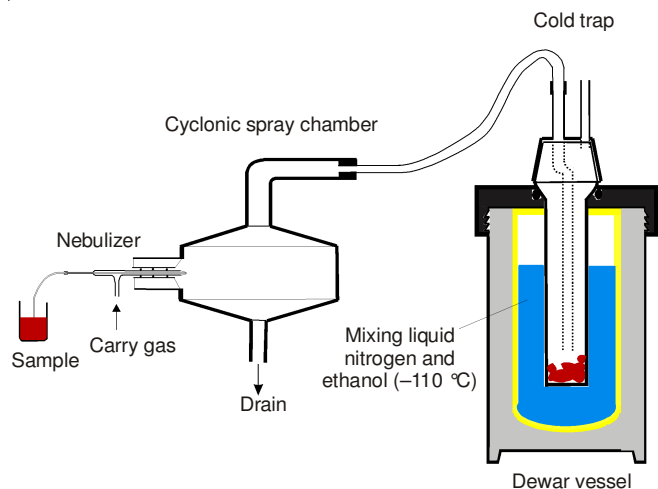


Fig. 1. Schematic diagram of cold trap capturing system for collecting the sample aerosol formed from spray chamber

RESULTS AND DISCUSSION

Signal enhancement effects of elements with different ionization potential: To investigate the signal enhancement effects of elements with differential ionization potential, the two organic solvents *i.e.*, methanol and glycerol were selected. The resultant signal intensities were normalized to values obtained with 2 % HNO_3 solutions. The enhancement factor was defined as the maximum normalized values and used to evaluate the effects of signal enhancement. Fig. 2 showed the

normalized signal intensities of selected elements as a function of methanol or glycerol concentrations. The maximum intensities for As, Se, Te and Be in organic solvent were higher than those in 2 % HNO_3 solution. The enhancement factors were in the range of 1.5 to 2.8 (Fig. 2a, 2b). This behaviour was contrast to other elements such as Co, Cd, Bi, In, Ce and Ge where the change in the signal intensity was less than 1.5 (Fig. 2c, 2d). Fig. 2 showed that the variation of signal enhancement was correlated to ionization potential of element. According to the values of enhancement factors, the interested elements could be separated into two groups. One group was As, Se, Te and Be, their first ionization potential are 9-11 eV, the enhancement factors were 1.5 to 2.8. Another group was Co, Cd, Bi, In, Ce and Ge, the first ionization potentials are less than 9 eV and the enhancement factors were less than 1.5. Fig. 3 showed the signal enhancement factors in methanol or glycerol solvent as a function of ionization potential. There was a trend of increasing enhancement factor with ionization potential. Comparison of the enhancement effects for different elements between methanol and glycerol solvents, the higher signal intensities of elements with high ionization potential were obtained in methanol than the glycerol solvent. However, signal intensities in the glycerol were higher than the methanol for elements of low ionization potential. This phenomenon can be explained using the surface tension and volatility of organic solvent. These results indicated that enhancement effect of element with different ionization potential were different,

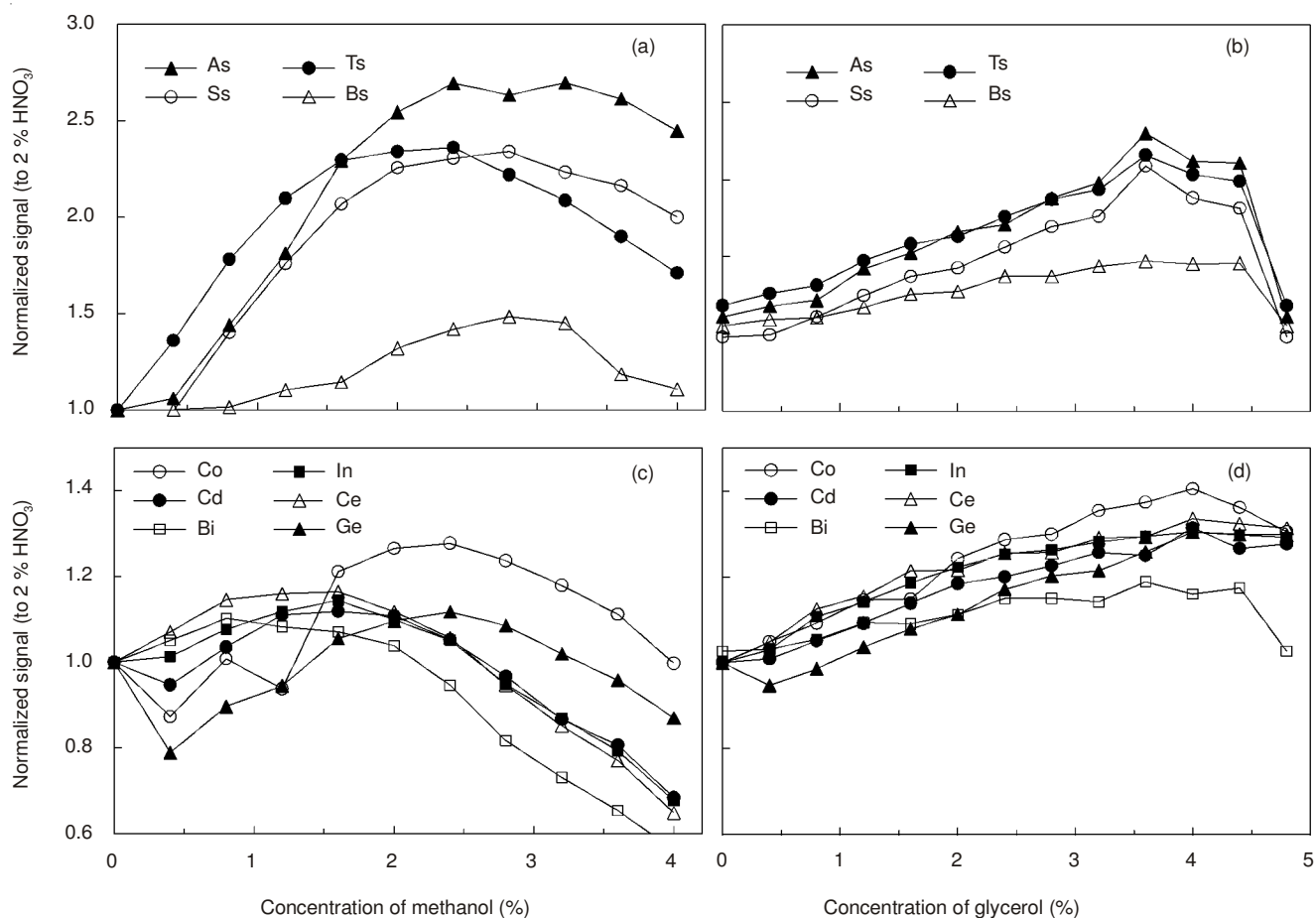


Fig. 2. Analyte signals normalized to values in 2 % HNO_3 matrix as a function of methanol (a and b) or glycerol (c and d) concentrations. Analyte concentrations are constant at 10 ng mL^{-1}

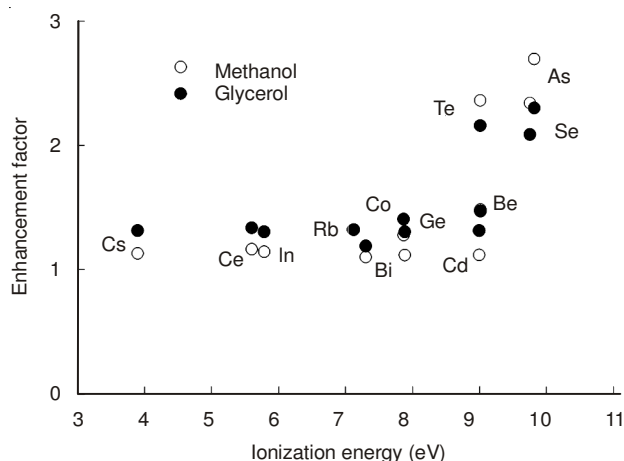


Fig. 3. Enhancement factor as a function of ionization potential

the element with higher ionization potential was of higher enhancement factor in the organic solvent.

Influence of organic solvent on the degree of ionization:

To evaluate the relation of the signal enhancement and the degree of ionization in the presence of organic solvent, the degree of ionization for As, Se, Ce and In were detected directly by ICP-MS. In present experiment, the same molar concentration of As and Rb solution was introduced into ICP-MS and the signal intensities of As and Rb were recorded. After blank and abundance of isotope corrections, the degree of ionization of As was calculated using the above formula (1). Similarly, the degree of ionization for Se, Ce and In were calculated by introducing every pair solution of Se and Rb, Ce and Cs, In and Cs solutions. The degree of ionization for the interested elements in the organic solvent and the nitric acid solution were summarized in Table-2. The degree of ionization of As was 33 % (nitric acid), 71 % (methanol) and 58 % (glycerol), while the degree of ionization of Se was 35 % (nitric acid), 69 % (methanol) and 56 % (glycerol). The degree of ionization for elements with high ionization potential (As and Se) was increased obviously. In contrast, the degree of ionization for elements with a lower ionization potential (In and Ce) were only slightly changed by the presence of organic compounds, since their ionization rate were close to 100 %. Further, the degree of ionization of As was enhanced by a factor of 2.2 (methanol) and 1.7 (glycerol), while Se was enhanced by a factor of 2.0 (methanol) and 1.6 (glycerol). The values of the improved degree of ionization were close to the signal enhancement factors in the presence of organic compounds (Fig. 2). Thus, the results indicated that elements with high ionization potential such as As and Se, the signal enhancement effect could be mainly attributed to the increase

of the degree of ionization due to an improvement of the ionization efficiency of aerosol in the plasma.

Influence of organic solvent on the nebulization-transport efficiency: Just as the above statement, the signal enhancement effect for elements with the high ionization potential was mainly attributed to increase of the degree of ionization. However, the degree of ionization for elements with low ionization potential (In and Ce) were only slightly changed by the presence of organic compounds, so the signal enhancement effect of Ce and In could not be attributed to improved the degree of ionization. To investigate the signal enhancement effect of organic solvent on the nebulization-transport efficiency, we designed an experiment for collecting the sample aerosol online from spray chamber by cold trap. 2 mg mL⁻¹ mixed solution was nebulized continuously for 10 min and the sample aerosol formed from spray chamber was frozen. The sample collected was dissolved and diluted to 25 mL by 2 % nitric acid and determined by ICP-MS. Signal intensities of analytes in organic solvent and nitric acid solution were shown in Fig. 4. The signal intensities of all interested elements in the presence of methanol or glycerol, were higher than that of 2 % HNO₃ solution. Fig. 5 showed the enhancement factors caused by improved nebulization-transport efficiency as function of mass. The enhancement factors were lower than 1.5. This indicated that the enhancement effect caused by improved sample nebulization-transport efficiency was to a limit extent. For elements with low ionization potential such as Co, Cd, Bi, In, Ce and Ge, the values were in accordance with the enhancement factors above describing the effects of organic compounds present in the sample. Hence, the signal enhancement effects of elements with low ionization potential were mainly attributed to an improvement of the nebulization-transport efficiency.

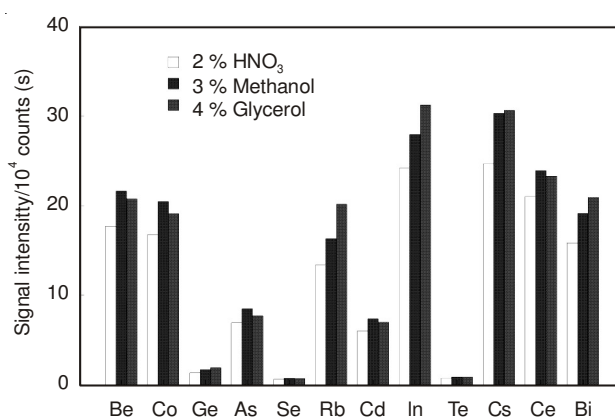


Fig. 4. Signal intensities of sample aerosol collected by cold trap

TABLE-2
DEGREE OF IONIZATION BY ICP-MS DETERMINATION

Element	Ionization potential (eV)	Degree of ionization (%)			Literature ^a
		2 % HNO ₃	3 % Methanol	4 % Glycerol	
As	9.810	33	71	58	52
Se	9.752	35	69	59	37
In	5.786	95	95	93	99
Ce	5.470	96	99	98	98

^aValues in this column were calculated values by Houk²³

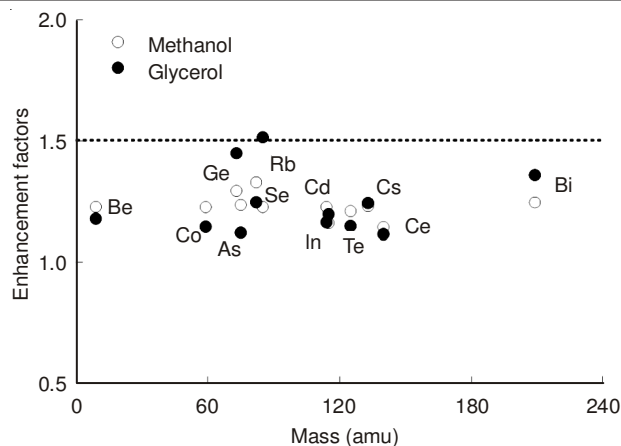


Fig. 5. Enhancement factors caused by improved nebulization-transport efficiency as a function of mass. The enhancement factor was the normalized intensities of the organic solvents to the value with 2 % HNO₃ in sample aerosol collected by cold trap

Conclusion

The signal enhancement effects in the presence of organic compounds were dependent upon the ionization potential. Compared with commonly used 2 % HNO₃ solution, the signal intensities of elements with high ionization potential (ionization potential, 9-11 eV) were enhanced by the factor of 1.5 to 2.8 in 3 % methanol or 4 % glycerol solvent. In contrast to the low ionization potential elements (IP < 9 eV), the enhancement factors were less than 1.5. The degrees of ionization of elements with high ionization potential were improved obviously, while the low ionization potential elements were slightly changed. The signal intensities of all the elements caused by improved sample nebulization-transport efficiency were to a limit extent and lower than 1.5. The experiment had demonstrated the mechanism of signal enhancement in the presence of the organic solvent, elements with high ionization potential (IP, 9-11 eV) was mainly contributed to the increase of the degree of ionization in the plasma and the low ionization potential elements (IP < 9 eV) was mainly attributed to the improvement of sample nebulization-transport efficiency.

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