

## The influence of ethanol addition on the spatial emission distribution of traces in a vertical argon stabilized DC arc plasma

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*Abstract:* The plasma of a vertical argon stabilized DC arc at atmospheric pressure is applied as a spectrochemical source. The lateral distributions of relative spectral line intensities of some trace elements (Zn, Pt, Cd, Mg, Ca and Al) introduced into the plasma in the form of aqueous and ethanol–aqueous solutions were experimentally determined. These distributions were correlated with the calculated equilibrium plasma composition of the arc plasma. On the basis of the obtained results, an explanation of the influence of ethanol addition on the radiation densities from an arc plasma is given.

*Keywords:* vertical argon stabilized DC arc plasma, ethanol addition, spatial emission distribution.

### INTRODUCTION

Organic solvents, as well as their mixtures with water, are frequently applied in analytical atomic spectrometry. Their effect on trace element determination by different spectrochemical sources, mainly flames<sup>1,2</sup> and inductively coupled plasmas,<sup>3–5</sup> is often studied for practical reasons, while its mechanism has not been completely explained. The reference data concerning this subject are quite controversial probably due to the different experimental characteristics of the applied plasma sources and incomplete understanding of the effect.

The plasma of a vertical argon stabilized DC arc, burning at atmospheric pressure is one of the common spectrochemical sources used for the analysis of various samples.<sup>6–8</sup> The main characteristics of this arc with an aerosol supply are: long-term stability, relatively simple experimental set-up, good sensitivity and detectability and low consumption of the employed gas. Also, it is possible to

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change easily the plasma gas and the composition of the aerosol solution, as well as any construction detail of the arc device. In this way the excitation and analytical characteristics of a plasma can be changed over a wide range. The optimal conditions (arc current, concentration of spectroscopic buffer – KCl, argon flow rates and the observation position) for measurement of the spectral line intensities of analytes were previously examined when aqueous-ethanol solutions were introduced into the arc plasma.<sup>8,9</sup>

The aim of this study was to investigate the spatial distribution of the radiation densities of various plasma components of the above-mentioned arc plasma. Therefore, on the one hand, the lateral distributions of the spectral line intensities of several trace elements (Zn, Pt, Cd, Mg, Ca and Al), carbon as one of the main components and the intensity of the band head of the CN radical emitted from plasma loaded with an aqueous and ethanol–aqueous solutions were determined. On the other hand, the influence of ethanol addition on the equilibrium plasma composition in this arc was studied. The calculated values of the different plasma constituent densities were correlated to the experimentally measured spectral line distributions. The obtained results are important for the possible application of this arc source in analytical spectrometry and in the physical chemistry of plasmas.

## EXPERIMENTAL

### *Instrumentation and operation*

The essential parts of the arc device are given in detail in Ref. 6. A cylindrically symmetric 10 mm high arc plasma column was used as the analytical plasma zone. The analysed solutions were nebulized by means of a laboratory made pneumatic cross-flow nebulizer and a double pass spray chamber.

A spectrograph PGS-2 (Carl Zeiss, Jena) equipped with photoelectric detection was applied as the monochromator. The experimental equipment and operating parameters are listed in Table I.

TABLE I. Experimental equipment and operating conditions

Excitation source	Argon stabilized vertical DC arc
Arc current	7A
Spectrograph	PGS-2, Carl Zeiss Jena
Grating	651 grooves/mm
Entrance/Exit slit width	50/60 $\mu\text{m}$ (analytes), 90/80 $\mu\text{m}$ (Fe)
Detector	Hamamatsu R212 photomultiplier
Recorder	BIG 1, Carl Zeiss Jena
Nebulizer	Pneumatic Babington type
Spray chamber	double pass
Argon flow rate	2 L/min
Argon pressure	$3.72 \times 10^5$ Pa

In order to investigate the influence of ethanol vapor loads on the characteristics of the arc plasma emission, the lateral distributions of the spectral line intensities of the studied elements with different excitation potentials (Table II) were measured. For this purpose, the emission from different parts of the plasma were projected onto the monochromator entrance slit (in 1:1 ratio) by successive movement of the arc device along the direction orthogonal to the optical axis of the spectrometer. The lateral distributions of the emission of the trace and main plasma components, such as C and CN, were measured.

The enhancement factors of various analytes were calculated as the ratio of the relative spectral line intensity in the presence and in the absence of ethanol. These factors were calculated on the basis of the maximum intensity of a spectral line ( $F_1 = I_{al}/I_{aq}$ ) or the area under a spectral line lateral distribution ( $F_A = A_{al}/A_{aq}$ ).

The lateral distribution of the plasma excitation temperature was determined from the ratio of two atomic iron lines, Fe I 373.713 nm and Fe I 373.486 nm.

#### *Solutions and reagents*

Ethanol (redistilled before use), hydrochloric acid, potassium chloride of AR grade and deionized water were used for preparing of the solutions. The test solutions were prepared by adding the required volume of ethanol and stock solutions of Zn, Pt, Cd, Mg, Ca and Al (1000 mg/L) to a volumetric flask and making up to the final volume with 3 % (v/v) HCl.

All the solutions contained the same concentration of spectroscopic buffer, *i.e.*, KCl (0.5 % m/v)

#### *Theoretical*

The equilibrium plasma composition of the different components formed in the arc plasma by various elementary processes were calculated by the method of minimizing the Gibbs free energy function in conjunction with the mass action law and the charge conservation relationship. By assuming the plasma was in chemical equilibrium, the processes of dissociation, ionisation and radiative capture were included. The plasma was regarded as a single-phase system with a constant ratio of the main and added components, in the stationary state.<sup>10</sup>

## RESULTS AND DISCUSSION

The main characteristic of a vertical argon stabilized DC arc as a spectrochemical source is its inhomogeneous spatial radiation field. In order to investigate the changes in radiation arising from ethanol addition, the lateral distribution of the spectral line intensity of several analytes were recorded and compared to atomic, ionic and molecular components of the same analyte (when possible) in the presence and in the absence of ethanol. Elements with different ionisation potentials were chosen.

The influence of the content of ethanol on the signal-to-background ratio (SBR) of various analytes was investigated previously.<sup>8,9</sup> It was shown that this vertical argon stabilized low current arc was more tolerant to an ethanol load than a horizontal U-shaped arc.<sup>11</sup> Namely the arc burns steadily with ethanol concentrations up to 40 % (v/v) but the SBR decreases with increasing ethanol concentration due to the significant increase in the background emission. With increasing quantities of ethanol in the arc, the amount of carbon extracted from the electrodes increases, causing increasing background emission. Therefore all investigations were performed with 20 % (v/v) aqueous-ethanol solution.

The relative intensities of the spectral lines of atomic and ionic Ca and the intensity of the band head of CaO as a function of the distance from the arc axis are

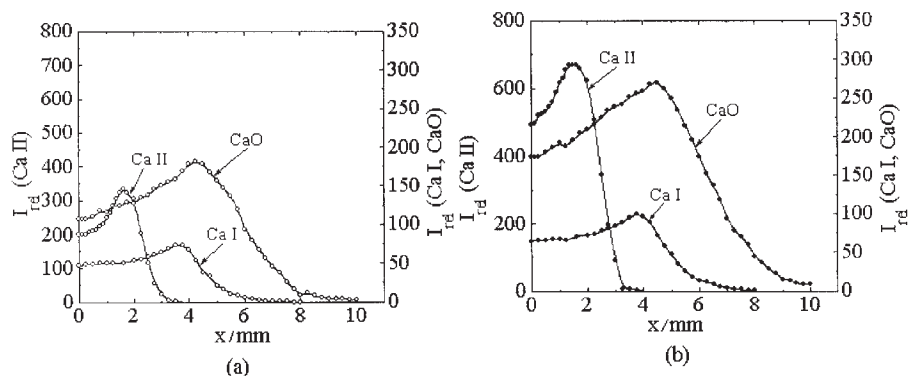


Fig. 1. Lateral distributions of the relative intensities of Ca I 422.673 nm, Ca II 396.847 nm and CaO band head at 609.700 nm (a) in aqueous and (b) in ethanol–aqueous solutions.

presented in Fig. 1, as an example. It can be noticed that ethanol addition increases the densities of all the Ca components. However, due to the formation of CaO, the intensity increase of atomic Ca is less expressed than that of ionic Ca. The same behavior of atomic and ionic line intensities in the presence of ethanol is observed in the case of other elements, such as Mg, which easily form oxides. The distributions of the relative intensity of Mg components are similar to those of Ca.

In the case of Cd, which does not readily form oxide, both the atomic and ionic spectral line intensities are enhanced in the presence of ethanol but the enhancement factor is a little bit higher for the ionic than for the atomic component. This is illustrated in Fig. 2 where the lateral distributions of the intensities of the atomic (a) and ionic (b) spectral lines are presented for Cd. All other elements investigated show enhancement of the intensities of the spectral lines in the presence of ethanol. This is demonstrated by the lateral distributions of the intensities of the Al and Pt atomic lines with and without ethanol, Figs. 3 and 4, respectively. A similar behaviour was shown by Zn.

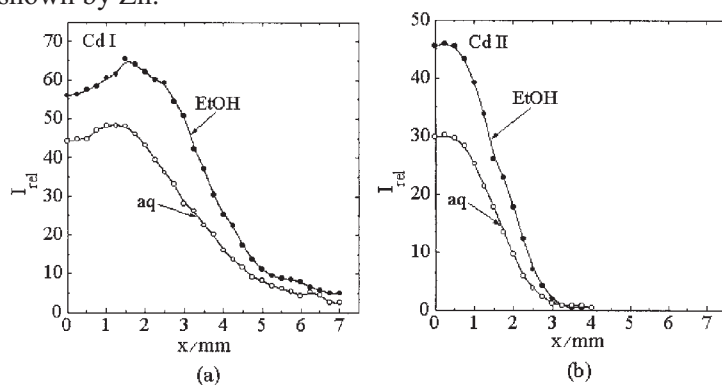


Fig. 2. Lateral distributions of the relative intensities of (a) Cd I 228.801 nm and (b) Cd II 226.502 nm in aqueous and ethanol–aqueous solutions.

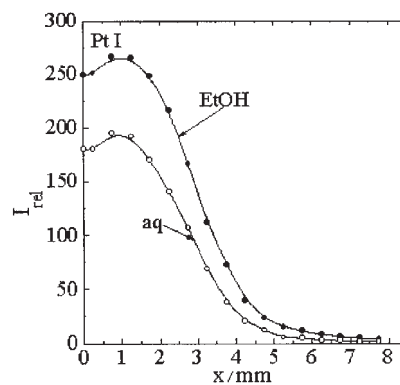
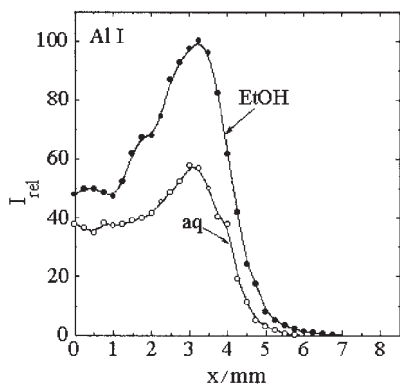


Fig. 3. Lateral distributions of the relative intensities of Al I 396.153 nm in aqueous and ethanol-aqueous solutions. Fig. 4. Lateral distributions of the relative intensities of Pt I 306.471 nm in aqueous and ethanol-aqueous solutions.

Besides the spectral lines of the trace elements, a strong continuum emission and emission of atoms and radicals of the main plasma components (Ar, H, O, C and N) characterize the spectra of this arc. The lateral distributions of the intensity of the carbon atomic spectral line from arc both in the presence and absence of ethanol are presented in Fig. 5b. This line is obviously strongly increased when ethanol is introduced into the plasma. This plasma component takes part in a reaction with nitrogen from environment forming CN radicals. The lateral distributions of the intensity of the CN band head, presented in Fig. 5a, also shows enhancement of the emission of this species after ethanol addition. The shape of this lateral distribution is characterized by a strong continuum emission from the plasma center. In this case there was no possibility for background correction.

A list of the enhancement factors of the analytes and plasma constituents together with their relevant physical parameters are given in Table II. These data con-

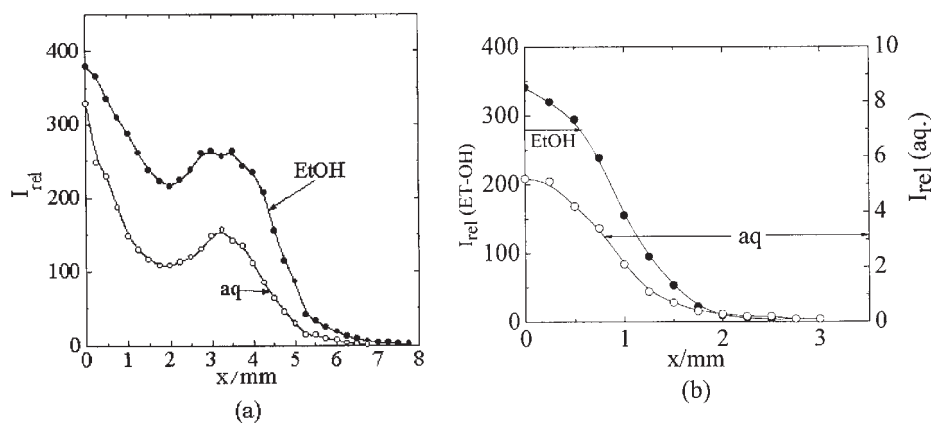


Fig. 5. Lateral distribution of the relative intensities of (a) the band head of CN at  $\lambda = 421.600$  nm and (b) spectral line of C I at  $\lambda = 247.857$  nm in aqueous and ethanol-aqueous solutions.

firm the conclusions about the influence of the ethanol load on the emission of various species more obviously than their later distributions.

TABLE II. Spectral lines and their characteristics

Element	Wavelength/nm	Ionisation potential/eV	Excitation potential/eV	$P_{al}/P_{aq}$	$I_{al}/I_{aq}$
Ca I	422.673	6.11	2.93	1.40	1.34
Ca II	396.847	–	3.12	2.31	2.01
CaO	609.700	–	–	1.66	1.47
Al I	396.153	5.98	3.14	1.64	1.75
Pt I	306.470	9.00	4.04	1.50	1.37
Cd I	228.801	8.99	5.41	1.45	1.30
Cd II	226.502	–	5.47	1.49	1.52
Mg I	285.210	7.65	4.34	1.14	1.10
Mg II	279.553	–	4.43	1.28	1.28
MgO	500.730	–	–	1.61	1.37
Zn I	334.502	9.39	7.78	1.58	1.61

Considering the emission distributions of all the plasma components from the arc, it can be concluded that the hot narrow plasma core is characterized by emission of atomic components with high ionisation potentials (Ar, H, C, Pt, Zn), ionic components and a continuum. The easily ionised atoms (Al, Ca and Mg), as well as molecules (CaO and MgO) and radicals (CN, OH) emit radiation from the colder periphery of the plasma.

The presence of ethanol does not change the shape of the lateral distribution of the spectral lines. Thus, the position of the maximum of the radiation intensity is

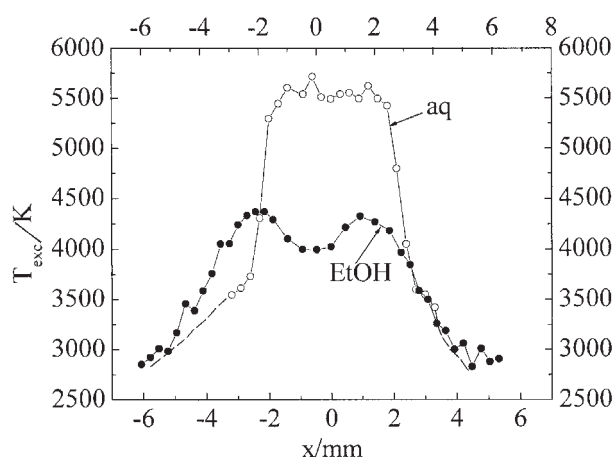


Fig. 6. Lateral distribution of  $T_{exc}$  in the arc plasma, measured from the ratio of the emission intensities of Fe I 373.713 nm and Fe I 373.486 nm.

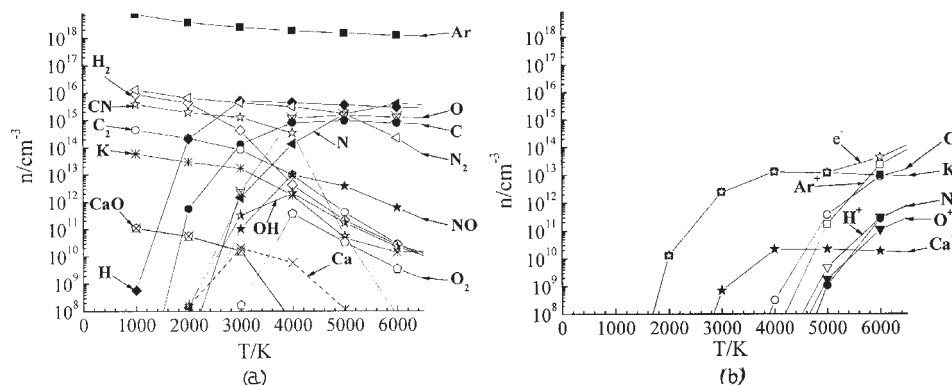


Fig. 7. Equilibrium plasma composition of plasma loaded with ethanol (a) neutral and (b) charged particles.

practically the same regardless of whether the plasma is loaded with an aqueous or with an ethanol–aqueous solution. However, the introduction of ethanol vapor extends in some extent the plasma excitation zone, which is evident from all the distributions. This was also confirmed by the lateral distribution of the excitation temperature (Fig. 6). It was found previously that the introduction of ethanol decreases the average plasma temperature by about 10%.<sup>8,9</sup> The lateral distribution of the excitation temperature shows that the ethanol load in the plasma causes a broadening of the plasma excitation zone and a lowering of the average temperature of the plasma column. The obtained results are in agreement with literature data.<sup>12–14</sup> As the formation of  $\text{C}_2$  and CN, molecular components in the arc plasma spectra were noticed when an aerosol with organic solvent was nebulized, it can be assumed that part of the supplied energy is used for the dissociation of these components and that this process can cause the lowering of the plasma temperature. The specific shape of the plasma excitation temperature in the presence of ethanol can be explained on the basis of a complex plasma composition which changes the energy transport in the plasma. The lower plasma temperature provokes the reduced ionisation and lower electron number density ( $n_e$ ) in the presence of ethanol.<sup>8,9</sup>

In another study, the influence of the addition of ethanol to the aqueous solution on the composition of the equilibrium plasma was investigated. The obtained results showed that the addition of ethanol changes the relative ratio of both the main and trace components. The theoretically calculated number densities of the main and trace neutral (a) and charged components (b) are presented in Fig. 7, for a water–ethanol mixture. The atomic H and C constituents are increased the most in the presence of ethanol, when the main components are considered. The increased quantity of C in the plasma causes higher number densities of carbon species such as C,  $\text{C}^+$ , CN and  $\text{C}_2$ . The ionisation of C, besides Ar, is the main source of electrons in the high temperature zone in the presence of ethanol (Fig. 7b). In the plasma periphery (below 4000 K), electrons originate from the ionisation of K, al-

though the concentration of this component is less by approximately two orders of magnitude than the concentration of the other components.

Previous studies showed that relatively small ethanol concentrations cause significant increases in the spectral line intensities due to a higher nebulization efficiency.<sup>8,9</sup> Therefore, besides the changed excitation and ionisation conditions in a plasma loaded with ethanol, the altered nebulization, atomization and transport processes should also be taken into consideration. The altered nebulization and transport processes cause a higher concentration of the analyte in a plasma with added ethanol. This can explain the enhancement of the emissions of all the plasma constituents, both the main and trace components. However, the different influence of added ethanol on the radiation of the atomic and ionic components of the same element indicates that besides changes in the transport processes, the changes in other conditions in the plasma should also be taken into consideration.

#### CONCLUSION

The addition of ethanol to an arc plasma does not change the shape of experimentally determined lateral distributions of the intensity of a spectral line emission of various trace and main components. However, this addition causes an enhancement of the emission of all the species but to different extents. The different influence of an ethanol plasma load on the radiation of atomic and ionic components of the same element indicates that, besides changes in the transport processes previously noticed, changes in other plasma conditions should also be taken into consideration.

The experimentally measured decrease in the excitation temperature in the presence of ethanol can explain the increase in the number densities of atomic and molecular components (equilibrium plasma composition). However, the number density of the ionic components of the same analyte should be decreased under these conditions. The consequence of the changes in the lateral distributions of the plasma parameters, especially in  $n_e$ , as well as changes in the plasma volume, is a changed radial electric field and radial transport of particles in the plasma.<sup>15</sup> The slower transport in a radial direction in the presence of ethanol causes a prolonged residence time of charged plasma species and enhanced emitted radiation.

#### IZVOD

##### UTICAJ ETANOLA NA LATERALNU RASPODELU ZRAČENJA I SASTAV PLAZME U VERTIKALNOM ARGONOM STABILIZOVANOM LUKU

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Plazma argonom stabilizovanog vertikalnog jednosmernog luka na atmosferskom pritisku koristi se kao spektrohemijski izvor. Eksperimentalno su određene lateralne raspodele intenziteta emisije nekoliko elemenata prisutnih u tragu (Zn, Pt, Cd, Mg, Ca i Al) u vodenim i etanol-vodenim rastvorima. Ove raspodele su dovedene u vezu sa izraženim ravnotežnim sastavom luke i plazme i



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