

Excitation and analytical characteristics of an ethanol loaded U-shaped arc

MARIJA RAŠKOVIĆ¹, IVANKA HOLCLAJTNER-ANTUNOVIĆ^{1,#}, MIRJANA TRIPKOVIĆ² and DRAGAN MARKOVIĆ^{2,#}

¹Faculty of Physical Chemistry, University of Belgrade, P. O. Box 137, YU-11001 Belgrade and ²Institute of Physics, P. O. Box 57, 11001 Belgrade, Yugoslavia

(Received 26 June 2002)

Abstract: The effect of the ethanol load on the discharge and analytical parameters of an argon stabilised U-shaped DC arc has been recorded. Measurements of the radial distribution of the apparent temperatures and the electron number density of the DC plasma showed that ethanol addition causes a decrease in both plasma parameters. The changes in the plasma characteristics, as well as in transport and atomisation processes of the analyte cause a general change in the spectral line intensities, which depends on the physical characteristics of the analyte and the quantity of ethanol loaded into the plasma. Improved detection limits were obtained for V and Mn when a 10 % (v/v) water–ethanol solution was nebulized into the plasma.

Keywords: U-shaped DC arc, emission spectroscopy, ethanol addition, radial temperature distribution, electron number density distribution, equilibrium plasma composition, detection limits.

INTRODUCTION

At the present moment of enormous development in material science, organic compounds are frequently used as reactive components in various plasma chemical or technological applications. Organic compounds (especially solvents) are also used in the course of various analytical procedures and/or are present as constituents in the analyses of natural samples. Thus, these species reach the gas plasma (either a chemical reactor or analytical plasma source), taking part in different elementary processes. Therefore, the understanding of the influence of such components on the physical and analytical characteristics of a plasma is of essential importance in analytical atomic spectrometry, as well as in plasma chemistry and plasma processing. This effect has been investigated mainly in flames^{1–3} and inductively coupled plasmas^{4–13} and seldom in DC plasmas.¹⁴

The reference data considering this subject are generally controversial, mainly due to the incomplete understanding of the effect and to different experimental conditions.

The purpose of this work was to provide a detailed investigation of the influence of ethanol addition on the excitation and analytical characteristics of DC plasma. The paper

Serbian Chemical Society active member.

reports the results of an emission spectroscopic study of an ethanol loaded argon stabilised U-shaped DC arc with emphasise on the radial distributions of the apparent temperatures and of the electron number density. On the basis of plasma diagnostics, the main plasma processes relevant for analytical applications are discussed.

EXPERIMENTAL

An argon stabilised U-shaped DC arc with an aerosol supply was used as the excitation source. A modified version of the arc which provided better uniformity of the plasma along the observation path was applied. A detailed description of the arc device is given elsewhere.¹⁵

The employed U-shaped DC arc is mainly characterised by a well-defined, relatively long, horizontal, cylindrically shaped arc column. In order to investigate the influence of ethanol addition on the arc plasma characteristics, samples with and without ethanol were loaded to the plasma column. Aqueous solutions in the form of an aerosol were introduced with the argon flow, tangential to the central section of the arc column. The solutions were nebulized by the argon stream with a nebulizer connected with a double pass Scott-type spray chamber. Ethanol was chosen as being one of the most frequently used organic solvents.

A laboratory modified spectrograph PGS-2 equipped with a good quality grating and predisperser was used as a spectrometer. The analyte spectral lines were photoelectrically detected and recorded using a PC. The instrumentation and operation conditions are listed in Table I.

TABLE I. Instrumentation and operation conditions

Excitation source	Argon stabilized U-shaped DC arc
Spectrograph	PGS-2; Carl Zeiss; Jena
Grating	Bausch&Lamb; 600 grooves/mm; blaze angle 48.9°
Photomultiplier	R-106 (Hamamatsu)
AD conversion card	ED-300
Arc current	7.5 A
Nebulizer	Meinhard; TR-30-C1
Argon flow	2 dm ³ /min
Entrance slit/mm	0.06 for H _β and H _γ lines; 0.1 for other lines
Exit slit/mm	0.1

For the purpose of plasma diagnostics, the radial distributions of the temperature and electron number density, being the most significant fundamental plasma parameters, were determined. The horizontal part of the arc column was kept parallel with the optical axis of the monochromator, thus enabling end-on observation. The arc plasma column was vertically shifted by 0.5 mm steps and the radiation from the various sections of the cylindrically symmetric plasma column was focused on the entrance slit of the monochromator. In this way radiation emitted from a rather large volume of the arc column was measured in the end-on direction while the observation positions were located at different radial distances from the arc axis.

Due to the spatial inhomogeneity of the radiation emitted from the plasma, different thermometric species had to be applied.¹⁶ The excitation temperature was determined from Boltzmann plots of titanium ionic lines in the plasma region from 2 to 4 mm from the arc axis. Titanium was added to the solution at a concentration of 1.25 mg/ml. The most intensive lines of the set were previously tested by self-absorption.

At distances further from the arc axis ($r > 4$ mm), in the plasma periphery, the temperature was evaluated from the rotational lines of the OH A²Σ⁺ – X²Π band spectra. The physical parameters of the spectral lines used for temperature determinations are specified in Tables II and III.

The electron number density was evaluated from the Stark broadening of the hydrogen H_β and H_γ lines by applying the theory of Vidal *et al.*¹⁷ The spectral line profiles were scanned at different radial distances from the arc axis thus enabling the determination of the radial distribution of the electron number density.

Besides plasma diagnostics, specific regard was paid in the experimental to the effect that ethanol plasma load had on the analytical performances in U-shaped arc plasma-atomic emission spectrometry (AES). Therefore, the spectral line intensities of various trace elements were measured. The influence of ethanol addition on the radial distribution of the spectral lines was investigated.

TABLE II. Physical parameters of the Ti ionic lines selected for the determination of the temperature

λ/nm	$E_{\text{exc}}/\text{cm}^{-1}$	$\log gf$
324.199	30837	-0.12
323.904	30959	-0.02
323.228	39927	-0.25
322.940	40075	-0.45
322.919	30959	-0.57
322.861	39677	-0.20
322.284	31114	-0.49

TABLE III. Physical parameters of the rotational lines of the OH band selected for determination of the temperature

λ/nm	$E_{\text{exc}}/\text{cm}^{-1}$	gA
307.703	32778.49	8.9
307.437	32947.05	12.8
307.303	36902.90	57.2
307.114	36393.24	53.2
306.968	35911.59	49.1
306.918	33630.38	24.8
306.928	33949.67	28.8

The enhancement factor (the ratio of the net spectral line intensity in the presence and in the absence of ethanol) of atomic and ionic lines of elements with different ionisation energies was measured too.

All the solutions contained 0.5 % (w/v) of KCl, known as a spectrochemical buffer. The optimal conditions for stable arc burning and maximum signal to background ratio was achieved with 10 % (v/v) of ethanol in the solutions.

THEORETICAL

Calculation of equilibrium plasma composition

One of the important features for the complete understanding of the elementary processes and the definition of the state of a gas plasma is the concentration of various species of such a complex system. Numerous chemical components are present in various plasma zones as a result of chemical reactions. The knowledge of their yield is of great importance for the development and improvement of new technological processes.

The method of minimising the Gibbs free energy function, together with the mass action law and the charge conservation principle was applied¹⁸ for the calculation of the equilibrium plasma composition of the plasma burning in argon as the plasma gas both with and without the addition of ethanol.

It was supposed that the plasma is a monophasic system with a constant ratio of the main and added components in the stationary state, at a pressure of 1 bar and in the temperature range corresponding to the experimentally found values. The calculations were performed taking into account the most probable collision processes.

RESULTS AND DISCUSSION

Radial distribution of temperature

The radial distributions of temperature, determined for the horizontal argon arc plasma column are presented in Fig. 1a. The results are given for the arc burning with and without ethanol and with 0.25 % of KCl. The experimental measurements show that the addition of ethanol causes a decrease in the excitation temperature in the plasma region from 2 to 6 mm from the arc axis. It was not possible to measure the temperature in the plasma core from the radiation densities of the applied thermometric species. Namely, the main feature of this plasma is a spatially inhomogeneous emission primarily caused by the demixing effect.¹⁹ The shape and maximum position of the radial radiation density distribution depend dominantly on the ionisation energy of the elements. The non-easily ionised elements are excited in the centre of the plasma core while the easily ionised elements are excited at distances further from the arc axis.

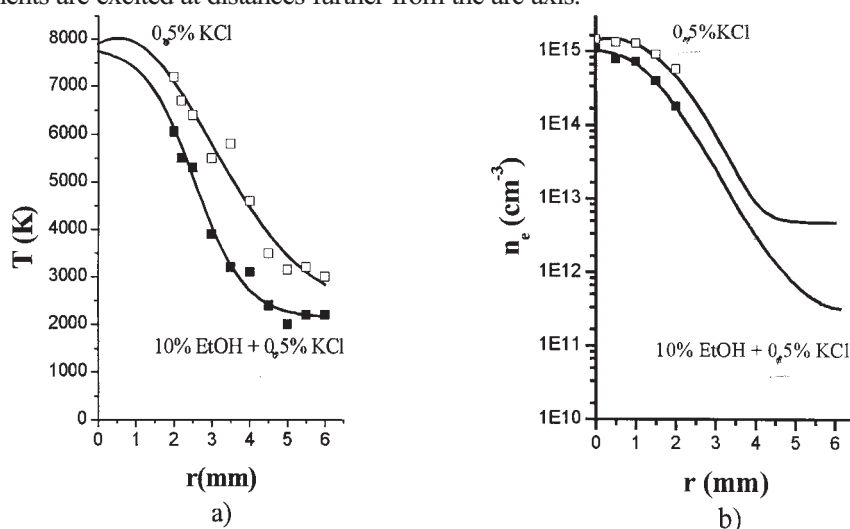


Fig. 1. Radial distributions of a) temperature and b) electron number density of the arc burning without and with ethanol.

Therefore, the temperature in the region 2 mm from the arc axis is estimated from theoretical calculations of the equilibrium plasma composition. The equilibrium number densities of various species in dependence on the temperature are presented in Fig. 2. Thus, the temperature distribution in the plasma core corresponding to the electron number densities measured from the Stark broadening are taken from theoretical calculations. These values are presented in Fig. 1a. It is evident that the decrease in temperature obtained in the plasma core is on average lower than in the plasma periphery.

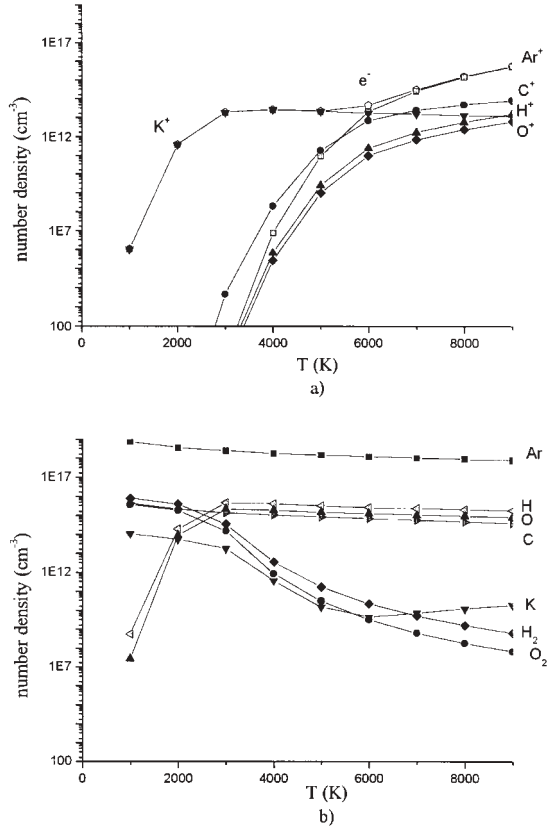


Fig. 2. Equilibrium plasma composition of a) ionic and b) atomic species in the plasma with 10 % of ethanol.

TABLE IV. Excitation temperatures with absolute errors of determination

Radial distance/mm	3		5	
Aqueous solution	$T_{\text{exc}} = 5790 \text{ K}$	$\Delta T = 70 \text{ K}$	$T_{\text{exc}} = 3450 \text{ K}$	$\Delta T = 90 \text{ K}$
Aq.-ethanol mixt.; 10 % (v/v)	$T_{\text{exc}} = 4090 \text{ K}$	$\Delta T = 90 \text{ K}$	$T_{\text{exc}} = 2280 \text{ K}$	$\Delta T = 120 \text{ K}$

It should be added that although the optimal conditions for arc burning were attained with an aqueous solution containing 10 % (v/v) of ethanol, the stability of the arc burning was higher without ethanol. The error of the slope of the Boltzmann plot is higher in the temperature determinations of the arc burning in the presence of ethanol than without ethanol, for both thermometric species. This is illustrated in Table IV, for two different arc radial positions.

Radial distribution of the electron number density

Under the employed experimental conditions and by application of the Stark broadening method, the electron number densities could be determined only in plasma core region, up to 2.5 mm from the arc axis and the obtained results are presented in Fig. 1b. In the plasma periphery, the electron number density was estimated on the basis of the equilib-

rium plasma composition and experimental measurements of the temperature, considering LTE concept prevails in the U-shaped arc plasma.¹⁶ The decrease in temperature causes a decrease in the electron number density, this effect being more pronounced in the plasma periphery when $r > 4$ mm.

The equilibrium plasma compositions as a function of temperature with ethanol addition are presented in Fig. 2 for ionic a) and atomic b) components. The addition of ethanol slightly changes the relative ratio of the main components, *i.e.*, Ar, H, O and C. Considering the neutral species, it can be concluded that in the high temperature region the main component (besides Ar) is atomic hydrogen while in the plasma periphery it is molecular hydrogen. Due to the high thermal conductivity of hydrogen (compared to Ar), the increase in the number density of hydrogen may decrease the plasma temperature. If ionic species are considered, it can be concluded that in the high temperature region the main source of electrons is ionisation of Ar (plasma gas). In the plasma periphery ($T < 5500$ K), the electrons come from the ionisation of K (spectrochemical buffer). In this region the lowering of the electron number density is more pronounced with decreasing temperature.

Influence of ethanol load on spectral line intensities

The addition of 10 % of ethanol into the investigated solution caused the enhancement of the emitted intensities of the spectral lines. The scanned emitted spectra of titanium, in

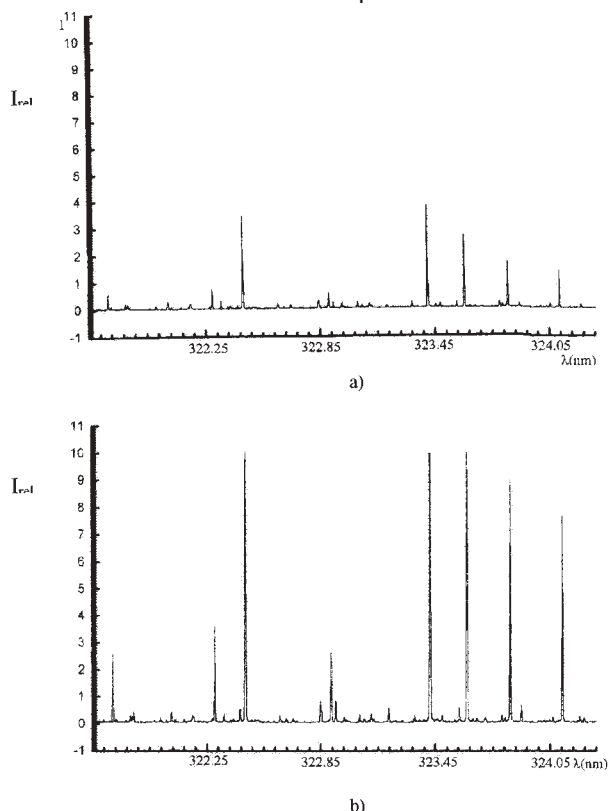


Fig. 3. Recorded tracing of the titanium spectra in the region from 320 to 324 nm of the U-shaped arc burning in: a) aqueous and b) aqueous with ethanol addition solutions.

spectral region from 320 to 324 nm, is presented, as an illustration, in Fig. 3a without and b with ethanol addition. Both spectra were recorded at a radial distance of 3 mm from the arc axis, under the same experimental conditions. The enhancement of the emitted radiation densities depends not only on the amount of added ethanol but also on the physical parameters of the element analyzed and on the radial distance from the arc axis. Such a complex dependence is a consequence of the numerous elementary processes that take place during ethanol loading.

In order to investigate the influence of the quantity of ethanol loaded to the plasma on the emitted radiations, the relative spectral line intensity of V I 437.9 nm was measured in the presence of ethanol in concentrations up to 40 % (v/v) and the results are presented in Fig. 4. It is obvious that the addition of ethanol causes an enhancement of the spectral line intensity. If the concentration of ethanol in water is increased above a certain limit (above 40 %), the plasma is unstable and is extinguished.

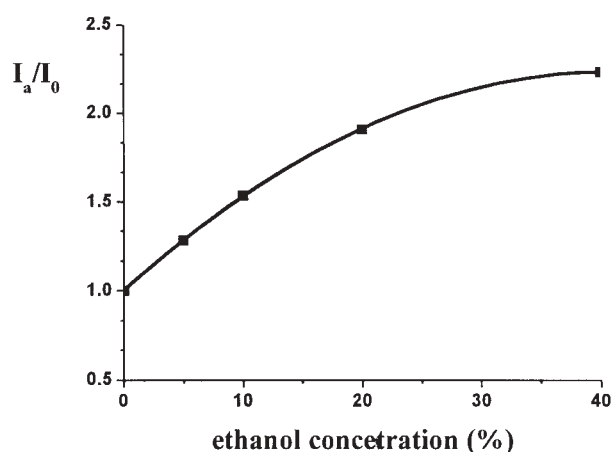


Fig. 4. Influence of the ethanol concentration on the enhancement factor of the V I 437.9 nm line.

The dependence of the enhancement effect of ethanol addition on the physical parameters of the analysed element was investigated by the determination of the enhancement factors of both the atomic and ionic lines of elements with different ionisation energies. The observed results are given in Table V for the atomic and ionic lines of trace elements such as V, Ti, Mn, Fe and Be and of H and Ar which are present in the plasma in higher concentrations. It can be concluded that the enhancement factors for both atomic and ionic lines of similar excitation energies (3.2 – 4.8 eV) of trace elements are approximately constant, ranging from 1.6 to 2.2. The radii of the emission maximum are generally further from the arc axis when the first ionisation energy of the element is lower. The maximum of the enhancement factor is not always at the same radial position as the maximum of the spectral line without addition of ethanol. In the case of elements with higher ionisation energies, *i.e.*, H and Ar present in higher concentration in the plasma, there is slight enhancement for H and decrease for Ar when ethanol is added to the plasma.

TABLE V. The enhancement factors of the spectral line intensities due to the presence of ethanol in the analysed solutions

Element	E_{ion}/eV	Type of line	λ/nm	E_{exc}/eV	r_{max}/mm	Enhancement
V	6.74	I	296.28	4.28	3.5	2.1
		II	294.46	4.58	2.5	1.85
Ti	6.82	I	365.35	3.44	2.5	1.58
		II	323.9	4.91	2.0	1.87
Mn	7.43	I	280.11	4.43	1.5	1.69
		II	260.57	4.75	1.0	1.99
Fe	7.87	I	302.58	4.21	2.5	2.18
		II	261.19	4.79	2.0	1.88
Be	9.39	I	234.86	5.28	1.0	1.7
H	13.59	I	434.05	13.84	0	1.1
Ar	15.75	I	433.35	14.68	0	0.7

The specific effect of ethanol addition was observed in the case of the OH radical. The enhancement factors of the OH band head are presented in Table VI for different radial distances from the arc axis. The intensity of the head of the OH band is increased in the presence of ethanol in the peripheral arc zones. This low temperature zone is obviously convenient for OH band excitation, especially in the presence of ethanol.

TABLE VI. Enhancement factor of the band head 306.357 nm of the OH radical

r/mm	0.5	1.5	2.5	3.5	4.5	5.0
Enhancement	0.90	0.89	0.89	1.0	1.29	1.55

It can be concluded that the explanation of spectral line intensity enhancement caused by ethanol addition in thermal plasma is not simple. Its explanation requires the simultaneous consideration of the processes of sample transport, nebulization, evaporation, atomisation, excitation and ionisation.

Namely, on the one hand, the addition of ethanol causes changes in the plasma parameters, *i.e.*, decrease in temperature and in electron number density. This is convenient for the excitation of some analytes. On the other hand, the addition of ethanol also changes factors which determine the introduction of the aerosol into the plasma and transport processes in the plasma. Our measurements (which are in accordance with literature data^{5-7,14}) show that due to the higher viscosity of a 10 % (v/v) ethanol–water mixture than that of water, the sample is introduced more slowly into the plasma.¹⁴ However, as the surface tension of the ethanol–water solution is lower and evaporation is higher than in the case of water, the efficiency of nebulization of the ethanol–water solution is enhanced by about 20 %. The difference in the physical parameters of the solution also causes a difference in the distribution of the aerosol drop size.⁶ Therefore, in spite of the lower uptake rate of the solution on addition of ethanol, the atomisation is enhanced and analyte concentration in the plasma is generally higher in the presence of ethanol.

Influence of ethanol load on the analytical parameters of V and Mn

The observed enhancement effect of ethanol addition on the spectral line intensities was applied for the quantitative determination of trace elements in solutions containing ethanol. Calibration graphs for the V I 437.9 nm and Mn I 403.1 nm lines with and without ethanol addition are presented in Fig. 5a and b.

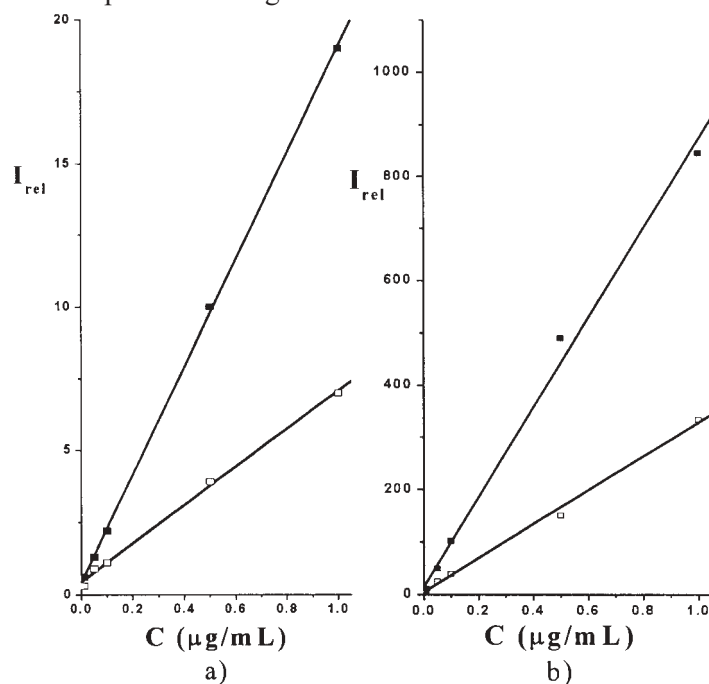


Fig. 5. Calibration lines for a) V I 437.9 nm and b) Mn I 403.1 nm : (□) aqueous solutions, (■) solutions with 10 % of ethanol.

TABLE VII. Relative standard deviations and detection limits of the V I 437.9 nm and Mn I 403.1 nm spectral lines without and with the addition of 10 % (v/v) of ethanol

Element	V I		Mn I	
	0.5 % KCl	0.5 % KCl + 10 % EtOH	0.5 % KCl	0.5 % KCl + 10 % EtOH
RSD/%	0.2	0.3	0.8	0.9
DL/(µg/mL)	2.0×10^{-2}	1.0×10^{-2}	1.5×10^{-3}	1.0×10^{-3}

It can be concluded that addition of ethanol results in a higher slope of the analytical graphs, *i.e.*, causes an increase in the sensitivity of the determination of both elements. The relative standard deviations (*RSD*) of the background emission and the detection limits (*DL*) with and without ethanol are presented in Table VII. Although the *RSD* of the background is higher in the presence of the ethanol–water mixture, the detection limit is improved with ethanol addition. This fact can be practically applied for the analytical determination of trace elements.

ИЗВОД

ЭКСТИТАЦИОНЕ И АНАЛИТИЧКЕ КАРАКТЕРИСТИКЕ ЈЕДНОСМЕРНОГ ЛУКА
U-ОБЛИКА У ПРИСУСТВУ ЕТАНОЛАМАРИЈА РАШКОВИЋ¹, ИВАНКА ХОЛЦЛАЈТНЕР-АНТУЊОВИЋ¹, МИРЈАНА ТРИПКОВИЋ² И ДРАГАН
МАРКОВИЋ²¹Факултет за физичку хемију, Универзитет у Београду, б. бр. 137, 11001 Београд и ²Институт за физику, б. бр. 57,
11001 Београд

Испитиван је утицај етанола на карактеристике пражњења и аналитичке параметре аргонском стабиланом једносмерном луку U-облика. Мерења радијалних расподела температура и бројчане густине електрона лучне плазме су показала да додаток етанола доводи до снижења оба поменуто параметра. Промене у карактеристикама плазме као и у транспортним и процесима атомизације, генерално мењају интензитете спектралних линија. Ове промене зависе од физичких карактеристика аналита и количине уведеног етанола у плазму. Запажени ефекат је искоришћен за побољшање аналитичких карактеристика испитиваног лука. Добијене су ниже границе детекције за V и Mn када се у плазму распршује водени раствор етанола концентрације 10 % (v/v).

(Примљено 26. јуна 2002)

REFERENCES

1. E. Pungor, M. Mahr, *Talanta* **10** (1963) 537
2. I. Kojima, C. Iada, *J. Anal. Atom. Spectrom.* **2** (1987) 463
3. M. Todorović, I. Holclajtner-Antunović, V. Milićević, R. Mihajlović, *J. Serb. Chem. Soc.* **65** (2000) 315
4. S. Greenfield, D. H. McGeachin, B. P. Smith, *Anal. Chim. Acta* **84** (1976) 67
5. M. Todorović, S. Vidović, Z. Ilić, *J. Anal. Atom. Spectrom.* **8** (1993) 1113
6. R. I. McCrindle, C. J. Rademeyer, *J. Anal. Atom. Spectrom.* **9** (1994) 1087
7. R. I. McCrindle, C. J. Rademeyer, *J. Anal. Atom. Spectrom.* **10** (1995) 399
8. S. Ražić, M. Todorović, I. Holclajtner-Antunović, Z. Ilić, *Fresenius J. Anal. Chem.* **355** (1996) 274
9. D. G. Weir, M. W. Blades, *J. Anal. Atom. Spectrom.* **9** (1994) 1311
10. D. G. Weir, M. W. Blades, *J. Anal. Atom. Spectrom.* **9** (1994) 1323
11. D. G. Weir, M. W. Blades, *J. Anal. Atom. Spectrom.* **11** (1996) 43
12. D. G. Weir, M. W. Blades, *Spectrochim. Acta* **49B** (1994) 1231
13. B. Huang, J. Yang, A. Pei, X. Zeng, P. W. J. M. Boumans, *Spectrochim. Acta* **46B** (1991) 407
14. I. Holclajtner-Antunović, S. Ražić, M. Todorović, M. Stoilković, *ACH-Models in Chemistry* **136** (1999) 83
15. M. Pavlović, N. Pavlović, M. Marinković, *Spectrochim. Acta* **46B** (1991) 1487
16. G. Malović, M. Tripković, I. Holclajtner-Antunović, *Contrib. Plasma Phys.* **34** (1994) 773
17. C. R. Vidal, J. Cooper, E. W. Smith, *Astrophys. J. Suppl. Ser.* **25** (1973) 37
18. W. B. White, S. M. Johnson, G. B. Dantzig, *J. Chem. Phys.* **28** (1958) 751
19. M. Pavlović, M. Marinković, *Spectrochim. Acta* **53B** (1998) 81.