Ionization of Elements in Medium Power Capacitively Coupled Argon Plasma Torch with Single and Double Ring Electrodes

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Abstract

A medium power, low Ar consumption capacitively coupled plasma torch (275 W, 0.4 L min^{-1}) with molybdenum tubular electrode and single or two ring electrodes in non-local thermodynamic equilibrium (LTE) was characterized with respect to its ability to achieve element ionization. Ionization degrees of Ca, Mg, Mn and Cd were determined from ionic-to-atomic emission ratio and ionization equilibrium according to Saha's equation. The ionization degrees resulted from the Saha equation were higher by 9 – 32% than those obtained from spectral lines intensity in LTE regime and closer to reality. A linear decrease of ionization with increase of ionization energy of elements was observed. Plasma torch with two ring electrodes provided higher ionization degrees (85 ± 7% Ca, 79 ± 7% Mn, 80 ± 7% Mg and 73 ± 8% Cd) than those in single ring arrangement (70 ± 6% Ca, 57 ± 7% Mn, 57 ± 8% Mg and 42 ± 9% Cd). The Ca ionization decreased linearly by up to 79 ± 4% and 53 ± 6% in plasma with two ring electrodes and single ring respectively in the presence of up to 400 μg mL^{-1} Na as interferent. The studied plasma was effective in element ionization and could be a potential ion source in mass spectrometry.

Keywords: Capacitively coupled plasma, local thermodynamic equilibrium, ionization degree, mass spectrometry, matrix effect

1. Introduction

Plasmas of low/medium power and low Ar or He consumption (< 300 W, < 1 L min^{-1}) such as radiofrequency capacitively coupled plasma (CCP) and microwave plasma are considered convenient sources for atomic spectrometry due to their advantages in terms of analytical versatility, reduced maintenance cost and miniaturization opportunity for on-site purpose.[1–7] Parallel-plate, annular and coaxial geometries of electrodes are used for coupling the radiofrequency power to the CCP torch.[1] The torch with two parallel-plate electrodes (200 W, 1 L min^{-1} Ar) proved to be an excellent tool in atomic absorption or atomic emission spectrometry[8,9] and possible ion source in elemental mass spectrometry.[10]

Furnace atomization plasma excitation spectrometry (FAPES) operated at 50–100 W and 0.2 L min^{-1} Ar or He

in the coaxial geometry of electrodes was originally developed as source for the multielemental analysis by atomic emission[11–14] and further investigated with respect to its capacity to generate ions for mass spectrometry.[15–17] Developments in the field of spectrometric techniques with plasma sources and their applications are periodically reviewed.[18–25]

In our laboratory it was developed a medium power and low Ar consumption CCP torch (275 W, 0.4 L min^{-1} Ar) in annular-coaxial geometry with one Mo tubular electrode and single or two ring electrodes for multielemental analysis by atomic emission[26–30] and atomic fluorescence spectrometry.[31–33] The sample was introduced as wet aerosol via pneumatic nebulization into the central zone of the discharge where the maximum dissipation of energy occurred ensuring optimal conditions for the atomization-excitation processes. Plasma was tolerant to re-

latively high concentration of easily ionizable elements as interferent. Another low power CCP microtorch (13.56 MHz, < 30 W and < 0.5 L min^{-1} Ar) equipped with a CCD microspectrometer was investigated in our laboratory for the simultaneous multielemental analysis of soil and river sediments[34] and mercury determination in non- and biodegradable materials after cold vapor generation.[35] The emission spectrum of elements in this plasma was simpler in comparison with that in inductively coupled plasma, with intense resonance lines, so that a non-expensive microspectrometer with FWHM of 1.5 nm was satisfactory for measurements.

The purpose of this study was the evaluation of the ionization degree of elements in the medium power argon CCP torch with single and two ring electrodes in order to estimate its usefulness in the atomic mass spectrometry technique. Since processes suffered by neutral and ionic species in atmospheric plasmas are governed by collision, it was necessary to check whether the local thermodynamic equilibrium (LTE) regime exists in plasma. The optical emission spectrometry was used for the characterization of plasma regime and ionization degree of Ca, Mg, Mn and Cd based on the atomic and ionic emission lines. Ionization degrees were correlated with ionization energy of elements, torch configuration and concentration of NaCl as matrix interferent. Remarks were formulated on the degree of ionization determined from the ion-atom lines intensity ratio and from the ionization equilibrium in agreement with the Saha's equation, respectively. The study is relevant for analytical practice as it provides supplemental knowledge on medium-power plasmas in respect with its capability to achieve element ionization and its possible use as ion source in mass spectrometry.

2. Experimental

2. 1. Stock Solutions and Reagents

Stock solutions of Ca, Cd, Mg, Mn and Na of 1000 μg mL^{-1} in 5% (v/v) HNO$_3$ purchased from Merck (Darmstadt, Germany) were used in this study. Monoelemental solutions of 10 μg mL^{-1} were prepared in order to estimate the ionization degree of elements. Solutions of 10 μg mL^{-1} Ca in the presence of 10–400 μg mL^{-1} Na were used to evaluate the influence of the easily ionizable element on the ionization degree of Ca. Argon (5.0 quality) from Linde Gas SRL Cluj-Napoca, Romania was used as plasma support gas.

2. 2. Instrumentation

Measurements were conducted by interfacing the CCP torch with a high resolution scanning monochromator elsewhere descibed.[26,27] The experimental set-up and operating conditions of the CCP-AES system are presented in Table 1, while the torch in Figure 1. The CCP torch

is based on a 27.12 MHz Ar plasma sustained at 275 W in a quartz tube (16 mm i.d., 10 cm length, 160 nm cut-off, H. Baumbach & Co Ltd., Ipswich Suffolk, UK) at the tip of a central water-cooled Mo tubular electrode (i.d. 3.5 mm) connected to the free-running RF generator. The quartz tube is surrounded by single or two grounded Cu ring electrodes. In the geometry with single ring this electrode was mounted 5 mm above the tip of the tubular one,

Table 1: Instrumentation and operating conditions of CCP-AES system (INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania)

| Equipment	Characteristics
Plasma power supply	RF generator, 275 W, free-running oscillator, 27.12 MHz
Plasma torch	Capacitively coupled with central Mo tubular electrode (i.d. 3.5 mm) connected to the RF generator and operated in two configurations with: (i) single ring electrode at 5 mm above the tubular electrode; (ii) two ring electrodes spaced at 60 mm. Ar flow rate as plasma support and aerosol carrier (0.4 L min^{-1}).
Sample introduction system	Concentric pneumatic nebulizer, peristaltic pump and Scott spray chamber. Aerosol intake into the plasma core through the tubular electrode (1 mL min^{-1}, 5% nebulization efficiency).
Optics	190–800 nm high-resolution scanning monochromator, 1 m Czerny-Turner mounting, 2400 groves mm^{-1}, grating blazed at 330 nm, 20 μm slits width, EMI 9781R photomultiplier tube.
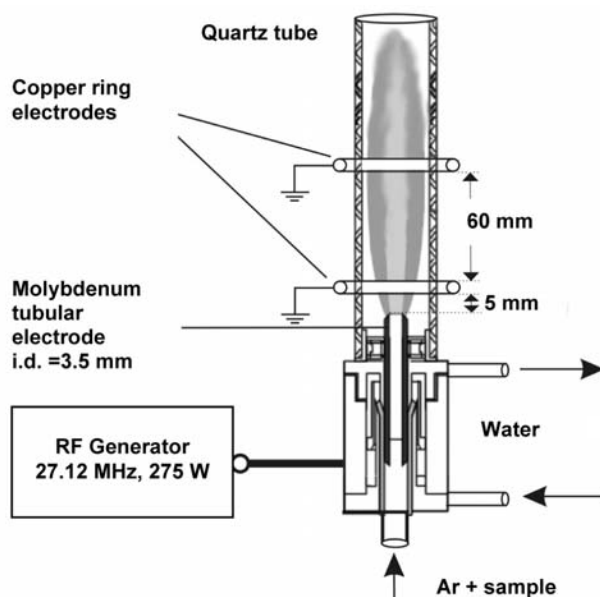
Figure 1: Schematic diagram of the CCP torch

while in the two rings arrangement the distance between them was 60 mm. For both arrangements it was obtained a stable plasma with good atomization and excitation capability of elements even in the presence of alkali and earth-alkali matrices.[28,30] The liquid sample was pneumatically introduced into plasma through the central tubular electrode using 0.4 L min^{-1} Ar support gas *via* a Meinhardt nebulizer and a Scott spray chamber.[26]

3. Results and Discussions

3. 1. Plasma Characterization

Atmospheric plasma sources are classified into LTE plasmas and non-LTE types. In Ar non-LTE plasma the following sequence of temperatures exists: $T_{Ar\ ion} > T_e > T_{ion} > T_{ex} > T_g \approx T_{rot}$, where $T_{Ar\ ion}$ – Ar ionization temperature; T_e – electron temperature; T_{ion} – analyte ionization temperature; T_{ex} – analyte excitation temperature; T_g – gas temperature; T_{rot} – rotational temperature.

Deviation from LTE in the plasma under study was estimated using three criteria: (i) relationship between T_e and T_g; (ii) deviation from the linearity of the Bolzmann plot of atomic lines and (iii) electron number density (n_e). The T_g was considered as T_{rot} of OH radicals resulted from the negative slope of the Bolzmann plot using lines from the R branch of molecular band 308.90 nm ($A^2\Sigma^+$, $\nu = 0$ → $X^2\Pi$, $\nu = 0$).[27] In accord with the observation of Alder et al.[36] we expected that the temperature derived from the ionic lines intensity could reasonably estimate T_e. Thus, T_e was obtained as the average value of excitation temperatures of Ca, Mg and Mn ionic species using in each case the two-line method and spectroscopic data in Table 2.[37]

Table 2: Spectroscopic data for ionic lines[37]

Line	λ (nm)	E_{ex} (eV)	gA 10^8 (s^{-1})
Ca II	393.367	3.152	5.88
Ca II	501.997	9.980	1.4
Mg II	279.553	4.434	10.72
Mg II	384.821	12.084	0.118
Mn II	259.373	4.778	18
Mn II	407.924	5.225	1.5

E_{ex} – excitation energy

Several authors have shown that there is no unique excitation temperature for a thermometric species in plasma where LTE does not prevail.[36,38] Thus, any deviation from the linearity of the Bolzmann plot can be interpreted as an indicator of departure from LTE state and shows an overpopulation of various energy levels of elements. According to this observation, the deviation from the linearity was checked for Ar I and Fe I lines. In the spectrum of our plasma only Ar I lines corresponding to 4p → 4s transition (690–950 nm) with excitation energies up to

13.5 eV were observed, while lines related to 5p → 4s transition (415–430 nm) with excitation energies above 14 eV were not identified. It was also observed a noticeable brake in slope of the Bolzmann plot for Fe I lines with excitation energy below and higher than 5 eV, respectively.

Electron number density in plasma estimated previously from Ca ionic-to-atomic intensities ratio[27] and Boumans and de Boer equation[39] was compared to the value corresponding to LTE criterion proposed by Griem.[40] Under this criterion, in a LTE plasma n_e must fulfils the condition:

$$n_e(cm^{-3}) \geq 9.2 \times 10^{17} \left(\frac{k_B T_e}{E_{H^+}}\right)^{1/2} \left(\frac{E_2 - E_1}{E_{H^+}}\right)^3 \qquad (1)$$

where: k_B – Boltzmann constant; T_e – electron temperature (K); E_2–E_1 – energy difference between the ground state and the first excited level for Ar (11.548 eV); E_{H^+} – ionization energy of the hydrogen atom (13.597 eV).

Table 3 presents the characteristics of Ar plasma developed in the torch with single and two ring electrodes geometry. Uncertainties of T_{rot} and T_{ex} resulted from the standard deviation of the Bolzmann slope, while that of T_e from the standard deviation of successive measurements of intensity in the two-line method. According to data in Table 3 plasma generated in both torch configurations clearly presents deviation from the LTE regime since $T_e > T_{ex} > T_{rot}$, there is no unique excitation temperature for a thermometric species and the electron number density is lower than that required by the Griem criterion. The features of our plasma are in reasonable agreement to those reported by Sturgeon et al.[38] for the capacitively coupled plasma in FAPES source, which also shows deviation from the LTE regime. For this source it was reported a deviation from the Bolzmann linearity of Fe I and a higher T_{ex} for lines with excitation energy in the range of 5.5–7 eV than for those with excitation energy below 5 eV, respectively.

3. 2. Ionization Degree of Elements vs. Ionization Energy

Ionization degrees were determined for Ca, Mg, Mn and Cd with first ionization energies between 6–9 eV. Measurements were recorded at viewing heights of 20–24 mm and 16–20 mm corresponding to maximum ionic emission in plasma torch with single or two ring electrodes, respectively. Elements were selected based on the following reasons: intense ionic and atomic emission lines in spectrum; close dissociation energies of oxides for similar atomization degree; atomic and ionic lines with comparable excitation energies for similar behavior to temperature variation in plasma; spectral lines of the element close enough to each other to avoid correction of emission signal with respect to detector response curve and grating efficiency; freedom from self-absorption. Previous reports on CCP with single and double ring electro-

des revealed the presence of emission lines of atoms and single charged species of Ca, Mg, Mn and Zn.[26]

Table 3: Characteristics of Ar plasma torch with single and two ring electrodes

Parameter	CCP with single ring electrode	CCP with two ring electrodes
T_{rot} OH (K)[a]	2450 ± 50	2670 ± 50
T_{ex} Ar I 4p→4s (K)[b]	4200 ± 230	4980 ± 540
T_{ex} Fe I (<5 eV) (K)[b]	3200 ± 250	3325 ± 280
T_{ex} Fe I (>5 eV) (K)[b]	4850 ± 210	7535 ± 300
T_e (K)[c]	6920 ± 500	8200 ± 700
n_e in our plasma (cm^{-3})[d]	10^{13}	$4.5\ 10^{14}$
n_e Griem criterion (cm^{-3})[e]	$>1.2\ 10^{17}$	$> 1.3\ 10^{17}$

[a] from Bolzmann plot of the OH molecular band 308.90 nm (A $^2\Sigma^+$, v = 0 → X ^{2} Π, v' = 0),[27]   [b] from Bolzmann plot of Ar I and Fe I lines using spectroscopic data from,[34]   [c] from the two-line method (Table 2),   [d] from the Boumans and de Boer equation[39] for the intensity ratio Ca II 393.367 nm/Ca I 422.673 nm,   [e] from the Griem equation[40]

Once established the plasma deviation from LTE regime, the ionization degree of each element was calculated based on: (i) ratio of number density of ionic and atomic species determined from the relative intensities of ionic and atomic lines and (ii) number density of ionic and atomic species in accord with the ionization equilibrium described by the Saha's equation. Only single charged ions of elements were considered in this study. The results were used to find the average ionization degree (α) and the corresponding uncertainty.

The ionization degree obtained from the ratio of ionic-to-atomic emission intensity according to ref.[10,17] was computed using both T_g and T_{ex} of atomic species.

$$\frac{\alpha}{1-\alpha} = \left(\frac{I\lambda B(T)}{gA}\right)_{ion} \times \left(\frac{gA}{I\lambda B(T)}\right)_{atom} \times e^{((E_{ex})_{ion} - (E_{ex})_{atom})/k_B T} \quad (2)$$

where: I – intensity of the spectral line at λ; B(T) – electronic partition function of neutral and single ionized species dependent on temperature; gA – transition strength (s^{-1}); $(E_{ex})_{atom}$ and $(E_{ex})_{ion}$ – excitation energies of atomic and ionic lines used in measurement; k_B – Boltzmann constant; T – temperature as T_g and T_{ex}.

The ionization degree calculated using the Saha's equation is:

$$\frac{\alpha}{1-\alpha} = \frac{4.83\times10^{15}}{n_e} T_{ion}^{3/2} \frac{B(T)_{ion}}{B(T)_{atom}} \times 10^{-5040\times E_{ion}/T_{ion}} \quad (3)$$

where: n_e – electron number density in plasma (cm^{-3}); T_{ion} – ionization temperature (K) of the element; E_{ion} – ionization energy.

The electronic partition functions of atoms and ions of elements for both plasma configurations were calcula-

ted using the equation of de Galan et al.[41] for T_g (Table 3), T_{ex} and T_{ion} of atomic species (Table 7). The excitation temperatures of atomic species were estimated from the Bolzmann plots:

$$\log\left(\frac{I\lambda}{gA}\right) = f(E_{ex}) \quad (4)$$

where: I – corrected net peak intensity considering the convolution of the grating and detector efficiency in conjunction with the wavelength; gA – transition strength; E_{ex} – excitation energy of the upper level of the transition.

Spectroscopic data used to compute T_{ex} of atomic species of Ca, Mg, Mn and Cd are presented in Table 4. The ionization temperatures resulted from the ratio of ionic-to-atomic emission lines using Boumans and de Boer equation[39] based on data in Tables 5 and 6. Values of T_{ex} and T_{ion} of elements are presented in Table 7.

Table 4: Spectroscopic data for atomic lines used to calculate excitation temperatures of atomic species of Ca, Mg, Mn and Cd[37]

Element	λ (nm)	E_{ex} (eV)	gA 10^8 (s^{-1})
Ca	445.589	4.680	1
	504.162	5.167	0.99
	518.885	5.321	2
	526.556	4.876	1.3
Mg	285.213	4.346	14.7
	383.829	5.946	2.02
	517.268	5.108	1.01
	518.360	5.108	1.68
Mn	279.827	4.429	22
	403.307	3.073	0.99
	403.875	6.832	0.38
	405.554	5.198	3.45
Cd	228.812	5.417	16
	361.051	7.379	9.1
	479.911	6.383	1.2
	508.582	6.383	1.7

Table 5: Spectroscopic data for lines used to calculate ionization temperature and ionization degree of elements[37]

Line	λ (nm)	E_{ex} (eV)	E_{ion} (eV)	gA 10^8 (s^{-1})	$E_{ox, disoc}$ (eV)
Ca I	422.673	2.932	6.11	6.54	5.0
Ca II	393.367	3.152	–	5.88	–
Mn I	279.482	4.435	7.42	30	4.0
Mn II	259.373	4.778	–	18	–
Mg I	285.213	4.346	7.64	14.7	4.4
Mg II	279.553	4.434	–	10.72	–
Cd I	228.812	5.417	8.99	16	3.8
Cd II	214.441	5.780	–	11	–

E_{ex} – excitation energy; E_{ion} – ionization energy; $E_{ox, disoc}$ – dissociation energy of oxides

Table 6: Ratio of ionic-to-atomic emission used to calculate the ionization temperature and ionization degree of Ca, Mg, Mn and Cd

Element	Ionic/atomic line (nm)	CCP with single ring electrode		CCP with two ring electrodes	
		Intensity ratio	Observation height (mm)	Intensity ratio	Observation height (mm)
Ca	393.367/422.673	0.40	24	1.0	16
Mg	279.553/285.213	0.30	22	1.0	16
Mn	259.373/279.482	0.16	20	0.50	16
Cd	214.441/228.812	0.06	24	0.40	18

Table 7: Excitation temperature (T_{ex}) and ionization temperature (T_{ion}) of atomic species of Ca, Mg, Mn and Cd

Element	CCP with single ring electrode		CCP with two ring electrodes	
	T_{ex} (K)[a]	T_{ion} (K)[b]	T_{ex} (K)[a]	T_{ion} (K)[b]
Ca	3290 ± 230	3900 ± 150	4210 ± 250	5300 ± 90
Mg	3670 ± 120	4690 ± 80	4550 ± 210	6200 ± 160
Mn	3550 ± 185	4690 ± 100	4250 ± 300	6380 ± 180
Cd	3460 ± 120	5290 ± 120	4190 ± 200	6950 ± 180

[a] from the negative slope of Bolzmann plot, while uncertainty from the standard deviation of slope; correlation coefficient between 0.963–0.995,   [b] from Boumans and de Boer equation; uncertainty resulted from 5 successive measurements of emission intensity

The relationship between the average ionization degree of elements and their first ionization energy is presented in Fig. 2. Error bars correspond to relative standard deviation (%) of ionization degree found from the ratio of ionic-to-atomic emission and Saha's equation.
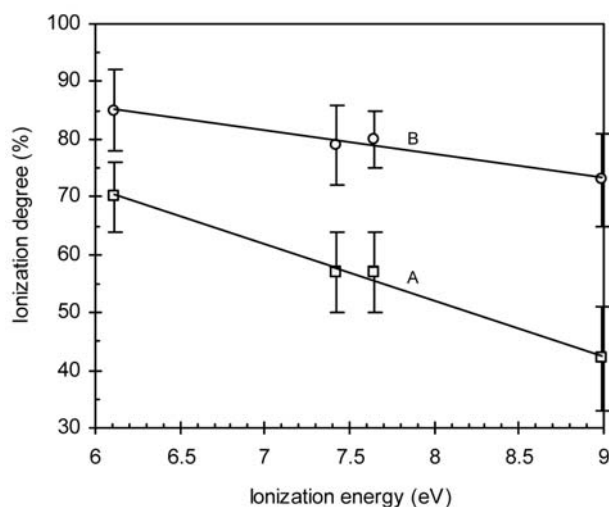

Figure 2: Average ionization degree of elements vs. ionization energy in CCP with single ring electrode (A), α = 124.51 – 9.506xE_{ion} (r = 0.991) and two ring electrodes (B), α = 110.51–4.180xE_{ion} (r = 0.950). E_{ion} – ionization energy. Error bars correspond to relative standard deviation (%).

As shown in Fig. 2 the ionization degree decreased linearly with the ionization energy of elements. Plasma in two ring electrodes configuration achieved an ionization degree up to two times higher than plasma with single ring electrode as indicated by the slopes of the curves. Thus ionization degrees were 85 ± 7% Ca (6.11 eV), 79 ± 7% Mn (7.42 eV), 80 ± 7% Mg (7.64 eV) and 73 ± 8% Cd (8.99 eV) in two ring electrodes plasma and decreased to 70 ± 6% Ca, 57 ± 7% Mn, 57 ± 8% Mg and 42 ± 9% Cd in plasma with single ring electrode. Results are consistent with a higher increase of ionic emission for plasma operated in two ring electrodes configuration. The increase of ionic emission was inversely proportional with ionization energy of elements, namely 2.5 times for Ca, 3.1 for Mn, 3.3 for Mg and 6.7 for Cd, respectively.

Ionization degrees in single ring electrode plasma computed using the Saha's equation and T_{ion} of elements were higher by 13% for Ca, 9% for Mg, 13% for Mn and 14% for Cd that those resulted from the ion-atom emission intensity ratio at T_g and T_{ex}. As for the two ring electrodes plasma, the ionization degrees were higher by 12% for Ca, 24% for Mg, 18% for Mn and 32% for Cd. Differences are greater as the ionization energy of element and T_{ion} increase, or plasma departure from LTE is more pronounced. One can say that ionization degrees given by Saha's equation are closer to reality since in calculating the ion-atom ratio all species are taken into consideration regardless the excitation state. Moreover, the ionization process is governed by the electronic density in plasma and occurs by collision at a temperature higher than T_g. In other words, ionization degrees resulted from the ratio of ionic-to-atomic emission lines assuming LTE in plasma are only indicative.

Ionization degrees of Mg and Cd in our plasma were comparable with those reported in other plasma sources with similar operating conditions and showing departure from LTE. Thus, Rahman and Baldes[10] reported ionization degree of 83% for Mg and 48 % for Cd in CCP with two parallel-plate electrodes operated at 200 W and 1 L min^{-1} Ar flow rate. Lu et al.[17] found ionization degrees of 40–90% for Cd, Cr, Fe and Zn in the FAPES source at power levels up to 100 W. In the same time the ionization degree of Cd in the single ring electrode plasma was close to 49%, value reported in microwave induced plasma,[42] while in the two rings configuration it was higher.

3. 3. Effect of NaCl Matrix Concentration on Ionization Degree of Calcium

The influence of NaCl matrix up to the concentration of 400 μg mL^{-1} Na on Ca ionization degree is depicted in Figure 3. The same methodology as above was used to evaluate the ionization degree of Ca at optimum observation height (Table 6). As shown in Figure 3, the NaCl matrix diminished the ionization capability of plasma in both configurations, although in different extent. The de-

pressive effect of NaCl on the ionization degree of Ca in plasma generated in two ring electrodes torch was two times lower than in that with single ring electrode as demonstrated by the slopes of the curves in Fig. 3. This means that plasma in two ring electrodes configuration is less altered by high concentration of easily ionization matrix. The ionization degree of Ca decreased almost linearly with Na concentration up to 400 μg mL^{-1} from 70 ± 6% to 53 ± 6% (r=0.995) and 85 ± 7% to 79 ± 4% (r = 0.969) in plasma with single ring and double ring electrodes, respectively. The linear decrease of Ca ionization as the Na concentration increased was caused by the shift in ionization equilibrium toward neutral species and partial consumption of plasma energy for vaporization, atomization and excitation of matrix components. Results agreed with previous observations on the depressive effect of NaCl matrix on Ca atomic and ionic emission and the increasing one on molecular emission of CaOH 554 and 622 nm in both electrode geometries of CCP torch.[27] The decrease of Ca ionization degree was similar to that observed by Rahman and Blades[10] for Mg in the presence of Na in CCP with two parallel-plate electrodes.
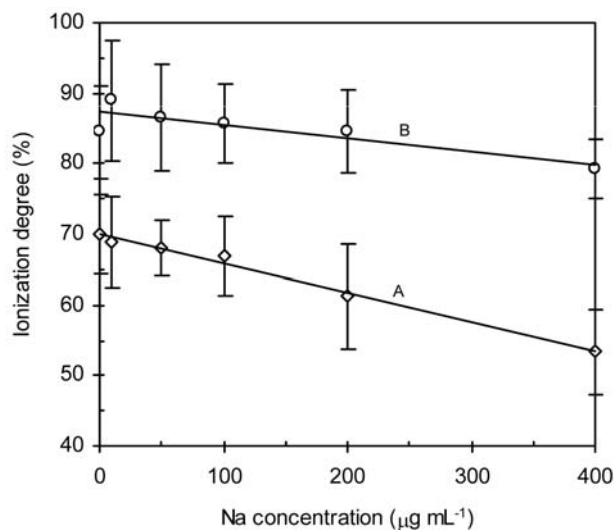

Figure 3: Effect of Na concentration on Ca ionization degree in single ring electrode plasma (A), and double ring electrode plasma (B). Error bars correspond to relative standard deviation (%).

4. Conclusions

It was demonstrated that a capacitively coupled Ar plasma torch with single or two ring electrodes operated at 275 W was capable to achieve element ionization. Our plasma showed deviation from the LTE regime and the ionization degree resulted from the Saha's equation at T$_{ion}$ was closer to reality and higher by 9–32% than that calculated using ionic-to-atomic intensity ratio at LTE. For both geometries of the torch the ionization degree decrea-

sed linearly with the increase of the ionization energy of elements. Plasma torch with two ring electrodes accomplished an ionization degree up to two times higher than that operated with single ring. The presence of easily ionizable elements such as Na caused a linear decrease of Ca ionization degree as a result of shift in ionization equilibrium towards neutral species. The suppression of ionization induced by the NaCl matrix was more evident in plasma torch with single ring electrode. The investigated CCP torch is attractive because of low Ar consumption and could be a valuable ion source for mass spectrometry. However the ionization degree is only one parameter for assessing the capability of plasma for mass spectrometry as the study of di- and polyatomic interferences is equally important.

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Povzetek

Okarakterizirali smo kapacitivno sklopljeno Ar plazmo srednje jakosti z majhno porabo Ar (275 W, 0,4 L min^{-1}), z molibdenovo cevno elektrodo ter enojnimi ali dvojnimi obročnimi elektrodami pri odstopanju od lokalnega termodinamskega ravnotežja (LTE). Opazovana karakteristika je bila zmožnost ionizacije elementov. Stopnjo ionizacije Ca, Mg, Mn in Cd smo določili iz emisijskega razmerja ioni-atomi in ionizacijskega ravnotežja po Sahovi enačbi. Stopnje ionizacije po Sahovi enačbi so bile za 9–32 % višje od stopenj, določenih iz intenzitet spektralnih črt v LTE režimu, ter bliže realnemu stanju. Opazili smo linearno zniževanje ionizacije glede na zviševanje ionizacijske energije elementov. V plazmi z dvema obročnima elektrodama so bile stopnje ionizacije višje (85 ± 7 % Ca, 79 ± 7 % Mn, 80 ± 7 % Mg in 73 ± 8 % Cd) kot pri plazmi z enojnim obročem (70 ± 6 % Ca, 57 ± 7 % Mn, 57 ± 8 % Mg in 42 ± 9 % Cd). Ionizacija Ca se je linearno zniževala do 79 ± 4 % pri dvojni in do 53 ± 6 % pri enojni obročni elektrodi v prisotnosti do 400 μg mL^{-1} Na kot interference. Proučevana plazma je učinkovito ionizirala elemente in bi lahko bila potencialni ionski izvor za masno spektrometrijo.