

## Figures of Merit and Fundamental Processes in the Analysis of Ca from Liquid Samples Using an r.f. CCP Torch with Tubular and Ring Electrodes

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A radiofrequency capacitively coupled Ar plasma, obtained with a molybdenum tubular electrode placed inside a quartz tube and one or two copper ring electrodes placed outside the tube, was used as spectral source for determination of atoms, ions and molecular radicals of calcium. A simultaneous spectrometer equipped with a photodiode array was used for detection of emission spectra. The atomization and ionization processes of Ca species were studied in the presence and absence of NaCl and H<sub>3</sub>PO<sub>4</sub> matrix, with both single ring and two rings electrode torches. The limits of detection are 250 ng mL<sup>-1</sup> for CaII 393 nm, 100 ng mL<sup>-1</sup> for CaI 423 nm, 230 and 100 ng mL<sup>-1</sup> for CaOH 555 nm and 622 nm. The recovery degree for certified plasma serum samples was 99.4 ± 4.4% and the RSD was between 3.8–4.9%. For 5 blood samples the RSD of Ca content is 2.9–4.4%.

*Key words:* atomic emission spectrometry; capacitively coupled plasma; Ca determination; blood analysis

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## INTRODUCTION

Radiofrequency (r.f.) generated plasmas, at atmospheric pressure, are the most commonly used spectral sources for analytical applications. Without any doubt, the most important is the inductively coupled plasma (ICP), which might be considered an ideal source with limits of detection about  $\text{ng mL}^{-1}$ .<sup>1</sup> Nevertheless, the ICP has some disadvantages, the most important being the great consumption of Ar for sustaining discharge, which can exceed  $20 \text{ L min}^{-1}$ . As a consequence, in the last 10 years, the low Ar consumption plasmas have reappeared in the field of analytical applications as alternative sources to ICP. One of these is the radiofrequency capacitively coupled plasma (r.f. CCP) sustained at low or medium power ( $< 600 \text{ W}$ ) and with support gas flow rates lower than  $1 \text{ L min}^{-1}$ . This plasma has similar characteristics to microwave induced plasma (MIP), and in some cases to ICP.<sup>2,3</sup> There are basically three different configurations for the arrangement of the electrodes for r.f. CCP: annular, parallel-plate and coaxial configurations.<sup>3</sup> Blades and co-workers have reported the use of a torch with parallel-plate electrodes, operated at  $30\text{--}600 \text{ W}$  in combination with an electrothermal vaporization system, for atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES).<sup>3,4</sup> The r.f. CCP torch with two annular electrodes distanced at  $10 \text{ cm}$ , around a water-cooled quartz tube was used by Egorova for the spectrochemical analysis of pneumatically or ultrasonically nebulized solutions.<sup>5</sup> This configuration was largely ignored by the analytical community until Platzter and co-workers described the application as an element-specific detector for gas chromatography.<sup>6</sup> The coaxial r.f. CCP developed in a graphite furnace, known as Furnace Atomization Plasma Emission Spectrometry (FAPES), was first described by Liang and Blade and by Sturgeon and co-workers.<sup>7,8</sup> The FAPES source can be used for simultaneous, multielemental determinations in microprobes.<sup>9</sup> However, the most promising application for miniature r.f. CCPs is that of the atomic emission spectrometric detector for gas chromatography (G.C. – r.f. CCP). This application was reported by Blades and co-workers and Gross and co-workers for detection of organo-metallic compounds and some nonmetals (F, Cl, Br, I, N, S, P) using ultraviolet and visible emission lines for metals and the near-infrared spectral region (NIR) for detection of nonmetals.<sup>10–13</sup> Due to the analytical success and the economic advantages of r.f. CCPs, some devices are offered as commercial products, for example the FAPES systems from Aurora Instruments Ltd. (Vancouver, Canada).

Cordos and co-workers have built a sequential atomic emission spectrometer equipped with an Ar r.f. CCP torch in tip-ring electrodes geometry operated at low power ( $85\text{--}275 \text{ W}$ ) and Ar flow rate lower than  $1 \text{ L min}^{-1}$ .<sup>14–20</sup> The limits of detection obtained with this device for a group of 19 elements in pneumatically nebulized solutions are in the range  $9\text{--}5700 \text{ ng mL}^{-1}$ .<sup>17</sup>

The present paper presents the emission spectra, detection limits, NaCl ionization interferences and  $\text{H}_3\text{PO}_4$  chemical interferences on molecular, atomic and ionic Ca species. The low power r.f. CCP torch has a tubular electrode and one or two ring electrodes. The measurements were made on molecular bands of CaOH, atomic and ionic lines of Ca, using a simultaneous spectrometer with photodiodes array (PDA). Finally, the processes of the analyte in plasma, as a function of torch configuration, are shown. The results were used for Ca determination from blood samples and certified plasma serum. The studies performed in this paper are an excellent contribution to the main figures of merit of plasma with one or two ring electrodes, obtained by the analysis of 20 elements from pneumatically nebulized liquid samples. Details on the torch construction and the main figures of merit were the subject of two recent papers.<sup>21,22</sup>

## EXPERIMENTAL

### *Reagents*

The Ca stock solution ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolution of 2.497 g  $\text{CaCO}_3$  in 20 mL of  $\text{HNO}_3$  1:4, followed by dilution to 1 L with distilled water. Single element working standards in the range  $1\text{--}100 \mu\text{g mL}^{-1}$  were obtained by diluting the stock solution with distilled water. To study the NaCl ionization interferences and  $\text{H}_3\text{PO}_4$  chemical interferences on Ca,  $5 \mu\text{g mL}^{-1}$  Ca with  $0\text{--}500 \mu\text{g mL}^{-1}$  Na or  $0\text{--}1\%$   $\text{H}_3\text{PO}_4$  solutions were prepared.

### *Blood Sampling and Certified Standard Materials*

Three certified plasma serum samples were used for accuracy determinations (*ROCHE Control Serum N, Lot / Ch. - B P1531B*, from ROCHE DIAG. SIST. MS Division of Hoffmann - La Roche Ltd, Basel, Switzerland; *NobiCon I Kontrollserum, Lot / Ch. - B 210067* and *NobiCon II Kontrollserum, Lot / Ch. - B 210117*, from NO-BIS Labordiagnostica GmbH, Endingen, Germany). As application 5 blood samples were analyzed. The standard addition method was used for determination of Ca content from blood samples or certified plasma serums. After coagulation, the blood samples were centrifuged for 5 minutes at  $3000 \text{ rot min}^{-1}$ . An aliquot of 1 mL blood serum or certified plasma serum was diluted to 25 mL with distilled water. In order to avoid the matrix effect of Na and  $\text{H}_3\text{PO}_4$  in the blood samples on Ca determination, the standard addition method was used. Thus, 1 mL of distilled water, 1 mL of 5, 10, 20  $\mu\text{g mL}^{-1}$  Ca were added to four aliquots of 4 mL blood serum or certified plasma serum.

### *Instrumentation*

A schematic diagram of the coaxial r.f. CCP torch with tubular electrode and outer ring electrodes is provided in Figure 1.

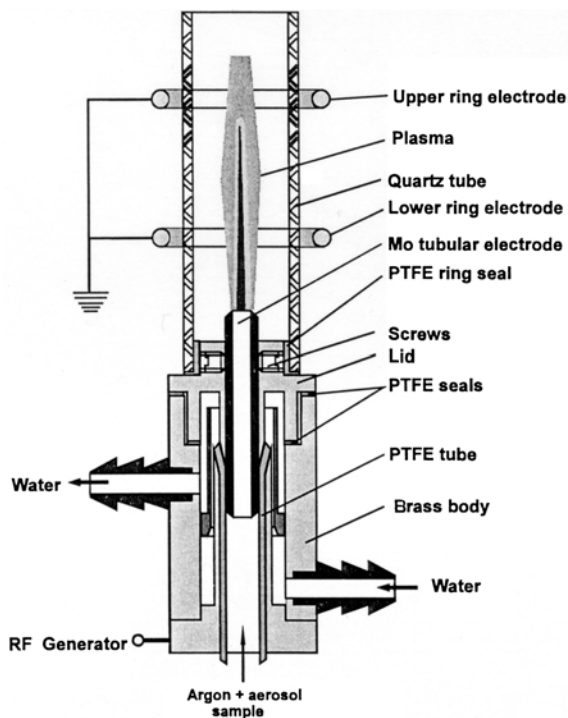


Figure 1. Coaxial r.f. CCP torch with a central Mo tubular electrode and outer ring electrodes.

The torch has a water-cooled Mo tubular electrode fixed in a body of brass. The tubular electrode is connected to the oscillating circuit of the radiofrequency generator. The quartz tube (i.d = 15 mm) is surrounded by ring electrodes (ring diameter 25 mm) connected to the ground. The Ar plasma is generated in two configurations: single ring electrode torch (SRT) when the torch has only the lower ring electrode at 5 mm above the tubular electrode, and two ring electrodes torch (TRT) when an upper electrode is added at 60 mm above the first. The plasma generated with both torches has a central channel that allows introduction of the aerosol sample into the core of the plasma. The operating conditions for both torches are: r.f. power 275 W, 27.12 MHz and high purity Ar as plasma support gas (Azo-Mures, Tg.-Mures, Romania), Ar flow rate  $0.4 \text{ L min}^{-1}$ . Liquid samples were nebulized using a concentric nebulizer via a 4-roller peristaltic pump. The mixture aerosol-support gas was introduced into the core of the plasma through the tubular electrode. The emission signal was detected using a PDA spectrometer manufactured by the Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania. Data processing was done by a software (Research Institute for Analytical Instrumentation Cluj-Napoca, Romania) using a PC 486 DX-4.

More details about the instrumentation and operating conditions are given in Table I. A diagram of the experimental set-up is provided in Figure 2.

TABLE I  
Instrumentation and operating conditions

Equipment	Characteristics
Plasma power supply	Plasma r.f. generator, free-running oscillator, 27.12 MHz, 275 W (Research Institute for Analytical Instrumentation Cluj-Napoca Romania)
Plasma torch	Capacitively coupled in coaxial configuration with central Mo tubular electrode (i.d. = 3.5 mm; o.d. = 5 mm) operated with a single ring electrode – SRT (a) or two ring electrodes – TRT (b). Tubular electrode is connected to the r.f. generator and the ring electrodes with 25 mm diameter are connected to the ground. For SRT, the distance between tubular electrode and ring electrode is 5 mm, and for TRT the distance between ring electrodes is 60 mm (Research Institute for Analytical Instrumentation Cluj-Napoca Romania). Plasma support gas: high purity Ar (Azo Mures, Targu-Mures, Romania), flow rate 0.4 L min <sup>-1</sup> .
Sample introduction system	Concentric pneumatic nebulizer, equipped with 4 rollers peristaltic pump (Research Institute for Analytical Instrumentation Cluj-Napoca Romania). Desolvation: 120 cm <sup>3</sup> glass chamber Aerosol intake into the core of the plasma through the tubular electrode (1 mL min <sup>-1</sup> , 5% nebulization efficiency)
Optics	Simultaneous spectrometer equipped with (PDA), Paschen-Runge mount, spectral range 200–900 nm, 95 mm focal length, 133 grooves mm <sup>-1</sup> grating blazed at 330 nm, bandpass 8 nm, wavelength calibration with a dydim filter (Research Institute for Analytical Instrumentation Cluj-Napoca Romania). PDA detector type S3904-512Q MOS linear image sensor, number of photodiodes 512; sensitive area 25 x 2500 µm (Hamamatsu, Japan). Analytical wavelengths: CaII 393 nm, CaI 423 nm, CaOH 555 nm and CaOH 622 nm
Data acquisition and processing	Computer model PC486 DX-4, laboratory constructed interface, data acquisition in-house software (without automatically background correction)

## RESULTS AND DISCUSSION

### *Emission Spectra*

The PDA spectrometer can cover, in two steps, the spectral range from 200 nm to 900 nm. Figure 3 shows the emission spectrum of Ar r.f. CCP for this spectral range.

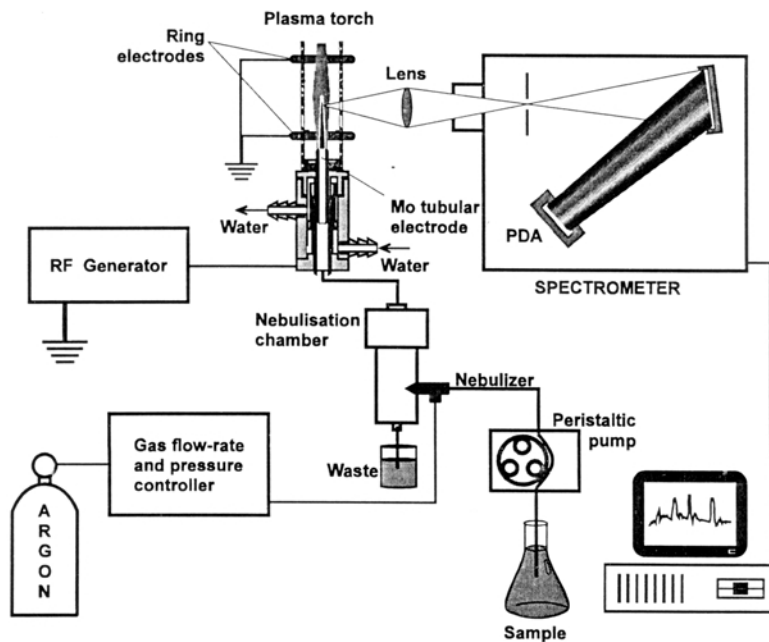


Figure 2. Block diagram of the experimental set-up.

Prominent features of the emission spectrum are the OH bands 280–317 nm,  $N_2$  bands 330 nm and Ar lines in the range 640–820 nm. The emission spectra of Ca species for the single ring-electrode torch, and the two ring electrodes torch out-distanced at 60 mm are shown in Figure 4.

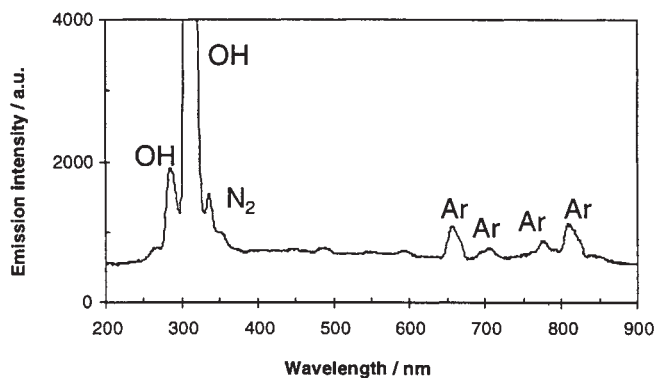


Figure 3. Background spectrum of the Ar rf CCP torch.

In these spectra, emission of the ionic line (Ca II 393 nm), atomic line (Ca I 423 nm) and emission of the CaOH molecular bands at 555 nm and 622 nm can be observed. In the case of the two ring electrodes torch, the intensities of all emission lines and bands are increasing, the greatest increa-

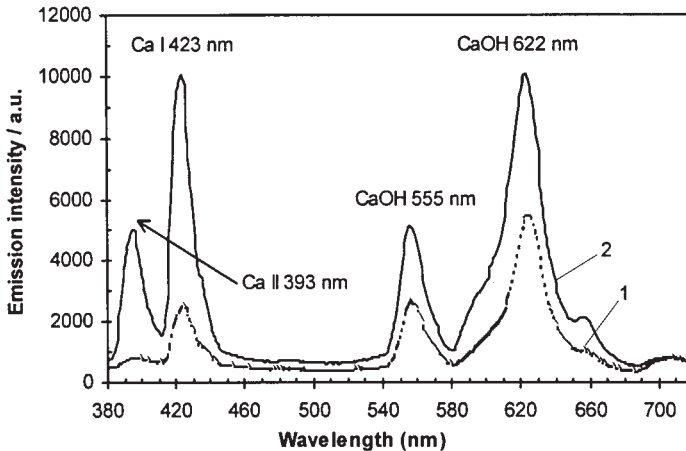


Figure 4. Ca emission spectra in Ar r.f. CCP torch: 1 — single ring electrode; 2 — two ring electrodes.

se being for ionic and atomic lines. Also, in the case of the single ring electrode torch, the relative intensities of emission increase in the order:  $\text{CaII} < \text{CaI} \leq \text{CaOH}$ , while in the presence of two ring electrodes the order is:  $\text{CaII} \leq \text{CaOH} \leq \text{CaI}$ .

#### *Observation Height*

The relative intensities of CaII 393 nm, CaI 423 nm, CaOH 555 nm and 622 nm as a function of torch configuration and observation height measured above the tubular electrode are presented in Figure 5. All the following measurements were made at the observation height at which the emitted signal is maximum. These heights are given in Table II.

As shown in Figure 5 and Table II, the optimum observation heights decrease if the plasma is operated in the two ring electrodes torch, as compared to the single ring electrode torch. Also, in both coupling geometries, the observation heights decrease from Ca II line to CaOH bands, and they are in a good agreement with the necessary energy for the atomization, ionization and excitation processes in the plasma.

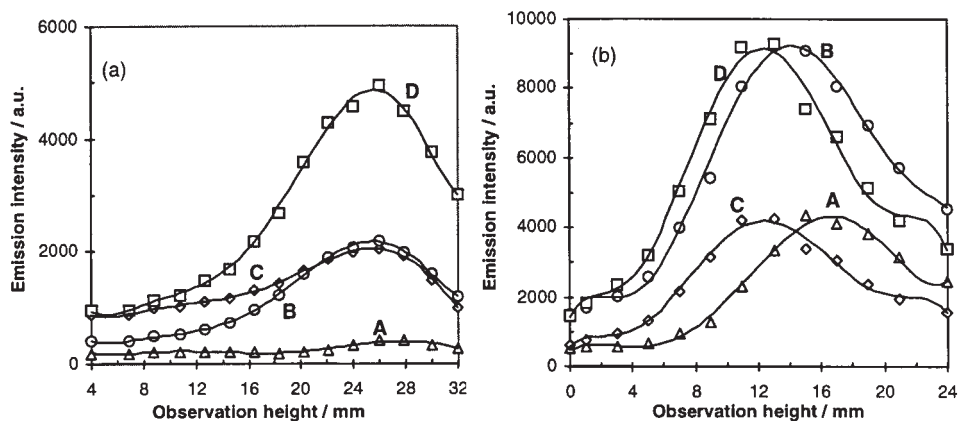


Figure 5. Emission intensities of CaII 393 nm (A), CaI 423 nm (B), CaOH 555 nm (C) and CaOH 622 nm (D) as a function of observation height for the single ring electrode torch (a) and the two ring electrodes torch (b).

TABLE II

The optimum observation heights for ionic (II), atomic (I) lines and molecular emissions of Ca

Analytical wavelength	Optimum observation height / mm	
	Single ring electrode torch	Two ring electrodes torch
CaII 393 nm	28	16
CaI 423 nm	25	14
CaOH 555 nm and 622 nm	25	12

### Analytical Performances

The statistics for calibration curves in the concentration range of 1–100  $\mu\text{g mL}^{-1}$  (number of points  $n = 9$ ) for atomic and ionic lines and Ca OH bands (for both torches) are presented in Table III. Determinations were made in optimum operation conditions (power 275 W and 0.4 L  $\text{min}^{-1}$  Ar flow) and at the optimum observation height for each species.

It can be observed that the slopes of all calibration curves increase in the case of the two ring electrodes configuration. An explanation of this fact can be the increase of the r.f. power density in the plasma when two ring electrodes are used, which determine a powerful interaction of samples with the plasma and implicitly an increase of atomization and ionization degree



TABLE III

Statistics of the calibration curves in the range 1–100  $\mu\text{g mL}^{-1}$  Ca ( $n = 9$ )

Analytical wavelength	Torch configuration	Equation curve $y = x_b + mc$	Standard deviation of the intercept $\sigma_{x_b}$	Standard deviation of the slope $\sigma_m$	Correlation coefficient
Ca II 393 nm	SRT	$y = 428 + 8 c$	13.6	0.3	0.993
	TRT	$y = 684 + 87 c$	57.2	1.2	0.999
CaI 423 nm	SRT	$y = 427 + 41 c$	41.7	0.9	0.997
	TRT	$y = 650 + 186 c$	121.7	2.5	0.999
CaOH 555 nm	SRT	$y = 418 + 44 c$	21.0	0.4	0.999
	TRT	$y = 659 + 85 c$	77.4	1.6	0.997
CaOH 622 nm	SRT	$y = 423 + 99 c$	51.3	1.0	0.999
	TRT	$y = 653 + 188 c$	235	4.7	0.996

$y$  = gross signal;  $x_b$  = background signal;  $m$  = slope of the calibration curves;  $c$  = Ca concentration; SRT-single ring electrode torch; TRT-two ring electrodes torch

of the analyte. The slope increases: 10 times for CaII, 4.5 for CaI and 2 for CaOH, respectively. The linearity of atomic and ionic Ca calibration curves is better (higher values for the correlation coefficient) for the two ring electrodes torch, while the linearity for CaOH decreases in this configuration (smaller values for the correlation coefficient). This relative ratio of correlation coefficients indicates a thermal instability of CaOH species compared to atomic and ionic species when the power density in the plasma increases.

In Table IV, the limits of detection (LODs) are presented for each analytical species. The LOD was calculated using the  $3\sigma$  criteria and according to the methodology from references.<sup>23,24</sup>

$$\text{LOD} = 0.03 \cdot \text{RSDB} \cdot \text{BEC} \text{ (ng mL}^{-1}\text{)}$$

where: RSDB – relative standard deviation of background (10 successive measurements)

BEC – background equivalent concentration calculated from the calibration curves equation.  $\text{BEC} = x_b / m$

$x_b$  – background signal;  $m$  – slope of the calibration curves

As shown in Table IV, the limits of detection decrease for the single ring electrode torch in the following order: 1600  $\text{ng mL}^{-1}$  for Ca II > 310  $\text{ng mL}^{-1}$  for Ca I > 290 or 130  $\text{ng mL}^{-1}$  for CaOH molecular bands. Since the limit of detection is the lowest for CaOH 622 nm (130  $\text{ng mL}^{-1}$ ), this band is recommended for the spectrochemical analysis of Ca. In the presence of two ring

TABLE IV

Background equivalent concentration (BEC) and limits of detection (LOD) for CaII, CaI and CaOH as a function of torch configuration

Analytical wavelength	Torch configuration	BEC <sup>(a)</sup> (ng mL <sup>-1</sup> )	LOD <sup>(b)</sup> (ng mL <sup>-1</sup> )	Improvement LOD TRT / SRT
Ca II 393 nm	SRT	53500	1600	–
	TRT	7860	250	6.4
CaI 423 nm	SRT	10420	310	–
	TRT	3490	100	3.1
CaOH 555 nm	SRT	9500	290	–
	TRT	7750	230	1.3
CaOH 622 nm	SRT	4270	130	–
	TRT	3470	100	1.3

<sup>a</sup> –  $BEC = x_b / m$  ( $x_b$  – background signal;  $m$  – slope of the calibration curves)

<sup>b</sup> – LOD limit of detection estimated according to  $3\sigma$  criteria

electrodes, an improvement of all the LODs can be observed. They are 6.4 times smaller for Ca II, 3.1 times for Ca I and 1.3 times for CaOH bands. The presence of the upper ring electrode also modified the order of the limits of detection (250 ng mL<sup>-1</sup> for CaII > 230 or 100 ng mL<sup>-1</sup> for CaOH ≥ 100 ng mL<sup>-1</sup> for CaI) as compared with that obtained for the single ring electrode torch. Thus, the limits of detection decrease to 100 ng mL<sup>-1</sup> for Ca I line and CaOH 622 nm band, which are recommended for the spectrochemical analysis in this configuration. In both coupling geometries the order is determined mainly by the intensity of the signal and less by the stability or the background of the plasma.

#### *Ionization Interferences and Chemical Interferences*

Figure 6 shows the ionization interferences of 0–500 µg mL<sup>-1</sup> Na as NaCl on Ca emission.

The matrix effect was expressed as the ratio of emission signals in the presence and absence of the matrix. The matrix effects are complex and depend both on the matrix concentration or Ca species nature as well as on torch geometry. For SRT (curves 1), the NaCl matrix effects are enhanced for all Ca species when Na concentration is lower than 150 µg mL<sup>-1</sup>. This is explained by increases of the electron number density in plasma and increases of excitation degree for each species. At a higher matrix concentration, the effect remains constant for CaOH (C1 and D1) but becomes depressive

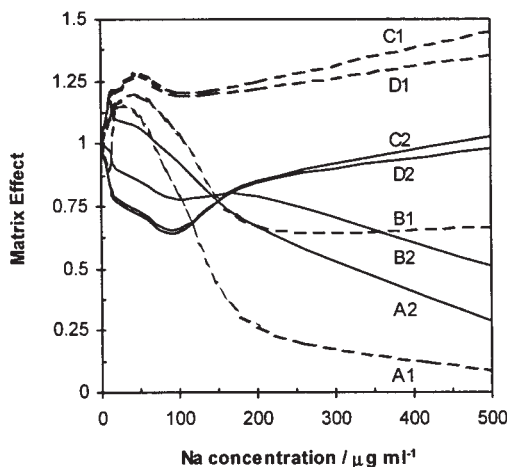


Figure 6. Ionization interferences of Na as NaCl on Ca species as a function of torch geometry.

1 – single ring electrode torch (SRT); 2 – two ring electrodes torch (TRT).  
 A – CaII 393 nm; B – CaI 423 nm; C – CaOH 555 nm; D – CaOH 622 nm.

for atomic (B1) and ionic (A1) species. The effect is a thermic one due to the plasma cooling at an overload with the matrix. In comparison, for TRT (curves 2), the effects are depressive for all species, being slowly enhanced in the very diluted matrix of NaCl (lower than  $10 \mu\text{g mL}^{-1}$  Na). Also, both enhanced and depressive effects for all species are smaller for TRT. Otherwise, the NaCl matrix influences less the emission signal of TRT. The fact that the matrix effects are smaller in TRT, especially in concentrated solutions, shows that the thermic effect of the matrix, which cools the plasma, is less significant and the plasma accepts a more concentrated matrix. In both torches, the intensity of matrix effects from the depressive to enhanced can be ordered: CaII > CaI > CaOH. Only in the TRT case, the effects are in the order CaOH > CaI > CaII for a lower concentration than  $150 \mu\text{g mL}^{-1}$  Na, whereafter the order is changed, probably due to plasma cooling at more concentrated matrix. In the same torch configurations (TRT), the matrix effect is not dependent on the nature of the Ca species if the matrix concentration is  $150 \mu\text{g mL}^{-1}$  Na. What is important to mention for both torches is the appearance of a buffering effect for concentrations up to  $200 \mu\text{g mL}^{-1}$  Na. Also, for both torches, a pair dependence of matrix effect (CaI with CaII) *versus* CaOH is observed.

Figure 7 shows the chemical interferences of  $\text{H}_3\text{PO}_4$  (0–1%) on Ca emission.

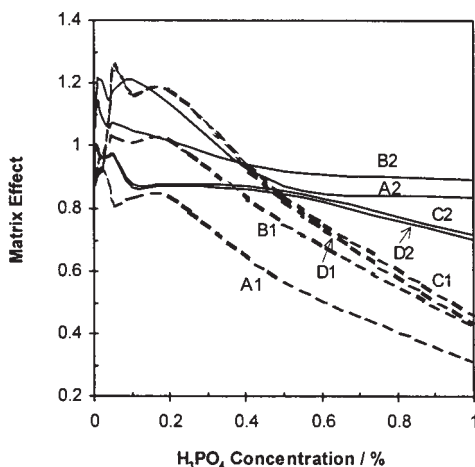


Figure 7. Chemical interferences of  $\text{H}_3\text{PO}_4$  on Ca species.

1 - single ring electrode torch (SRT); 2 - two rings electrodes torch (TRT).  
 A - CaII 393 nm; B - CaI 423 nm; C - CaOH 555 nm; D - CaOH 622 nm.

The matrix effect of  $\text{H}_3\text{PO}_4$  was determined both by the chemical processes of refractory compounds formed between  $\text{Ca-PO}_4^{3-}$  in solution and by processes suffered in plasma.

For SRT (curves 1), the  $\text{H}_3\text{PO}_4$  presence determines a depressive effect due to refractory compounds that can hardly decompose in plasma. It is in diluted solution of  $\text{H}_3\text{PO}_4$  (lower than 0.25%) that an increase of the signal for CaOH can be observed. The depressive matrix effect can be ordered:  $\text{CaII} > \text{CaI} > \text{CaOH}$ , which supports the affirmation that the depressive effect is due especially to the losses of analyte as a consequence of the refractory compound forming in the solution. In TRT (curves 2), the depressive effect of  $\text{H}_3\text{PO}_4$  is more diminished, which indicates the decomposition of refractory compounds in plasma. In this configuration, the smallest matrix effect is in the case of the atomic line.

#### *The Fundamental Processes for Ca*

One of the purposes of this paper was to study the fundamental processes suffered by the analyte in this particular type of plasma. Therefore, a correction for the spectral response of the PDA had to be done. These corrections were made according to the spectral response curve, given by the manufacturer (Hamamatsu Ltd., Japan). The relative ratio of the intensities  $\text{Ca II} : \text{Ca I} : \text{CaOH 555 nm} : \text{CaOH 622 nm}$  in the plasma obtained with

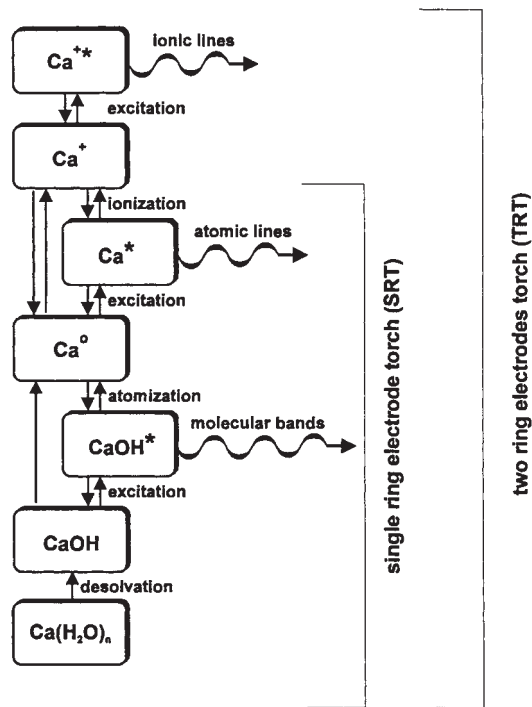


Figure 8. Fundamental processes for Ca in coaxial r.f.CCP with tubular and single or two ring electrodes configuration:  $^{\circ}$  atomic ground state (fundamental level); \* atomic and ionic excited state; + ionic state.

SRT is 0.2 : 0.7 : 0.5 : 1. This ratio becomes favorable for ionic and atomic species in the two ring electrodes torch configuration (Ca II : Ca I : CaOH 555 nm : CaOH 622 nm = 1 : 1.7 : 0.5 : 1). These results can be easily explained by the increase of the coupling power efficiency in the center of the discharge for the capacitively coupled torch with annular electrodes and a stronger interaction of the plasma with the samples due to higher temperature. Therefore, the upper ring electrode has an important influence on the atomization, ionization and excitation mechanism for Ca in the studied plasma. The fundamental processes for the Ca species versus coupling geometry are presented in Figure 8.

*Application. Determination of Ca from Certified Plasma Serums and Blood Samples*

Measurements were made at the atomic line Ca I 423 nm in TRT configuration because this line is very intense and slightly influenced by chemi-

TABLE V  
Results obtained for Ca determination in certified plasma serums  
(5 successive measurements)

Certificate sample	Certificate concentration / mg L <sup>-1</sup> ( $\mu \pm s_d$ )	Found concentration / mg L <sup>-1</sup> ( $\bar{c} \pm s_d$ )	$t_{\text{calculated}}$	$t_{\text{tabulated}}$ ( $\nu = 4$ ; 95%)
Roche Control Serum N	90.4±4.4	91.2±4.2	0.426	2.776
NobiCon I Control Serum	86.8±8.0	86.1±3.3	0.474	2.776
NobiCon II Control Serum	134.9±13.4	132.2±6.5	0.928	2.776

$$t_{\text{calculated}} = \frac{(\bar{c} - \mu)}{s} \sqrt{n}$$

$n$  – number of successive measurements

$\nu$  – number of freedom ( $\nu = n-1$ )

TABLE VI  
Results obtained for Ca determination in blood samples (5 successive measurements)

Sample	S1	S2	S3	S4	S5
Ca concentration * (mg L <sup>-1</sup> ) average $\pm s_d$	85.2±3.2	100.4±4.4	97.8±2.9	91.6±3.4	105.1±4.2

$s_d$  – standard deviation

\* – normal serum level of Ca: 90–110 mg L<sup>-1</sup>

cal interferences. The analytical results obtained for three certified plasma serums, with statistical calculus<sup>25</sup> ( $t$ -test), are presented in Table V.

For all certified serum samples  $t_{\text{calculated}} < t_{\text{tabulated}}$ , thus there are no significant differences between the mean concentration obtained by r.f. CCP-AES and these certificates. The grade of recovery of Ca in the three certificate plasma serum samples is  $99.4 \pm 4.4\%$ , while the percentage relative standard deviations (RSDs) for five successive measurements are: 4.6%, 3.8%, 4.9%, respectively. The RSDs are similar or better than those for certificate serum samples, analyzed by four methods (flame atomic emission spectrometry – FAES, flame atomic absorption spectrometry – FAAS, molecular absorption spectrophotometry and potentiometry) with high differences between RSDs.

In Table VI, the results obtained for 5 blood samples are presented.

It results from Table VI that the concentrations of Ca determined from blood samples are precise. If standard deviation is reported up to the concentration average, an RSD between 2.9–4.4% is obtained.

## CONCLUSIONS

It has been shown that a coaxial Ar r.f. CCP torch with a central tubular electrode and a single ring electrode or two ring electrodes could be a valuable spectral source for determination of Ca by emission spectrometry. In both coupling geometries, the existence of the analyte (Ca) in plasma, as ions, atoms and molecular species, was ascertained. If the plasma is operated in a torch with a single ring electrode, the weight of molecular species is higher, as compared to atomic and ionic species. In the presence of two ring electrodes, the atomization and ionization of Ca increase and the weight of molecular species decreases. Also, the ionization interferences and the chemical interference are smaller in the case of TRT configuration. On the other hand, it can be concluded that the upper ring electrode determines an increase of r.f. power density in the plasma, having an important role in atomization, excitation and ionization processes. As a consequence, the optimum wavelength with the lowest limit of detection is CaOH 622 nm, if the plasma is operated with a single ring electrode. In the case of plasma with two ring electrodes, the wavelengths recommended for Ca analysis are Ca I 423 nm or CaOH 622 nm. Using a simultaneous spectrometer equipped with a PDA detector, the optimum wavelengths for the spectrochemical analysis can be selected more easily. Plasma can be used in a clinical laboratory for the analysis of biological samples.

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## SAŽETAK

### **Analiza kalcija u tekućim uzorcima uporabom radiofrekvencijske, kapacitivno spregnute plazme (r.f. CCP) cilindričnim i prstenastim elektrodama: Temeljni procesi i prednosti postupka.**

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Kapacitivno spregnuta argonska plazma u radiofrekvencijskom području (složena od molibdenske cilindrične elektrode u kvarcnoj cijevi na čiju su vanjsku stranu pričvršćene dvije bakrene prstenaste elektrode) upotrebljena je kao spektralni izvor za analizu atoma, iona i molekulnih radikala kalcija. Spektrometar opremljen nizom fotodioda upotrijebljen je za detekciju emisijskih spektara. Atomizacijski i ionizacijski procesi u vrstama što sadrže kalcij proučavani su u prisutnosti i odsutnosti NaCl i H<sub>3</sub>PO<sub>4</sub> matrica, s jednom ili dvjema prstenastim elektrodama. Detekcijski pragovi iznose: 250 ng mL<sup>-1</sup> (CaII, 393 nm), 100 ng mL<sup>-1</sup> (CaI, 423 nm), 230 ng mL<sup>-1</sup> (CaOH, 555 nm), 100 ng mL<sup>-1</sup> (CaOH, 622 nm). Stupanj pouzdanosti analize za standardne uzorke seruma jest 99,4 ± 4,4% (s relativnim odstupanjem od 3,8–4,9%, te od 2,9–4,4% za relativno standardno odstupanje kalcija u pet uzoraka).