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SPECTROSCOPIC STUDY OF ATMOSPHERIC PRESSURE ARGON/METHANE CAPACITIVELY COUPLED PLASMA

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ABSTRACT. The emission spectrum (200 – 1000 nm) and discharge characteristics of an atmospheric pressure Ar/CH_4 capacitively coupled plasma, 275 W, 27.12 MHz, 0.7 L min^{-1} Ar and 0-7.5 mL min^{-1} CH_4 as collision/reaction gas were studied. The emission spectrum of pure Ar plasma is dominated by molecular bands of OH and N_2 second positive system in UV as well as Ar I (4p→4s) lines in VIS range. The addition of CH_4 results in the appearance of the C_2 Swan band and quenching of OH, N_2 and Ar emission. Quenching is the consequence of the second-kind collisions of CH_4 molecule with Ar, N_2 excited species and chemical reaction with OH radical, respectively. Processes were confirmed by the decrease of the excitation temperature of Ar and electron number density when adding CH_4 in Ar plasma. The Ar/CH_4 plasma is of great interest for applications in atomic spectroscopy due to the possibility to remove spectral interferences by the collision/reaction gas method and the use of low resolution microspectrometers.

Keywords: *capacitively coupled plasma, molecular emission, collision/reaction gas, plasma diagnosis*

INTRODUCTION

Progress in the atomic emission spectrometry (AES) relied *inter alia* on new spectral sources to guarantee the analytical performances required in the multielemental determinations of high sensitivity. The development of spectral sources began with flame, continued with arc and spark, than inductively coupled plasma (ICP), while in recent years microplasmas on a chip have become an important field of innovation [**1**]. Currently, ICP-AES is a mature technique with excellent analytical capabilities for the rapid multielemental determination as it benefits from the advantages of CCD technology and dual-viewing. ICP-AES was standardized for the determination of elements in water and soil [**2,3**]. The shortcomings of ICP-AES associated to acquisition

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and maintenance high cost directed research towards the development of new plasma sources such as capacitively microwave plasma (CMP) [**4**], microwave induced plasma (MIP) [**5,6**], microwave plasma torch (MPT) [**7**] and radio-frequency capacitively coupled plasma (CCP) [**8,9**], less expensive and having several analytical performances similar to ICP. The advantages of the new plasma sources are related to the operation at atmospheric pressure, low consumption of Ar or He as support gas (< 1 L min^{-1}) and low operation power (< 300 W). This last feature enables the miniaturization to hand-held systems for in-situ analysis [**9**].

The results obtained in our laboratory have demonstrated that the atmospheric pressure CCP with tubular electrode operated at 275 W and below 1 L min^{-1} Ar is not only a relatively powerful excitation source in AES but also a promising atomization cell in atomic fluorescence spectrometry (AFS) [**10-13**]. The torch configuration favors the sample introduction right in the center of the plasma where most of the energy is dissipated. This ensures a better wet aerosol-plasma interaction and therefore the decrease of the matrix effects compared to MIP. Nevertheless, the emission spectrum is rich in molecular bands (OH, N_2) over a wide range (200-420 nm) because of the air diffusion in the Ar plasma. This raises problems of spectral interferences on analytes lines both in AES and AFS when using a low resolution microspectrometer. In a preliminary study it has been shown that the Ar/CH_4 plasma is suitable for Pb determination by AFS at 283.31 nm following circumventing spectral interferences by quenching of OH molecular emission [**13**].

Plasmas used for analytical purposes are usually developed in Ar and He, while those for thin film growth or surface treatment in mixtures of these gases with hydrocarbons (CH_4, C_2H_2) [**14**].

The aim of this work was the spectral characterization of an Ar/CH_4 plasma developed in the torch with tubular electrode and single ring electrode. The study presents the features of the background emission over the spectral range 200-1000 nm and physical and chemical processes in plasma responsible for quenching of OH and nitrogen molecular emission and argon lines. Results were corroborated with the electron number density (n_e) and excitation temperature (T_{ex}) of Ar lines. The study is of interest since the introducing CH_4 in the Ar plasma represents a simple method to remove spectral interference of the molecular emission on elements and allows the use of low-resolution microspectrometers in spectrochimical determinations.

RESULTS AND DISCUSSIONS

Study of background emission spectrum of Ar/CH_4 plasma

The main features of the emission of plasma developed in pure Ar and Ar/CH_4 mixture are shown in Table 1, while the background spectra in Figure 1.

Table 1. Main features of emission spectra of Ar and Ar/CH_4 plasmas

Species	System	Transition	Excitation energy (eV)
OH	282.90 nm (0,1) 308.90 nm (0,0)	$A^2\Sigma^+ \rightarrow X^2\Pi$	4.05
N_2 second positive system	337.13 nm (0,0) 357.69 nm (0,1) 380.49 nm (0,2)	$C^3\Pi_u \rightarrow B^3\Sigma_g$	11.05
C_2 Swan band	438.3 nm (0,2) 473.7 nm (0,1) 516.5 nm (0,0) 563.6 nm (1,0) 619.1 nm (2,0) 685.0 nm (3,0)	$D^3\Pi_g \rightarrow A^3\Pi_u$	2.40
Ar I	690-950 nm	4p→4s	12.90-13.50

The emission spectrum of the pure Ar plasma consists of OH bands, N_2 second positive system (SPS) and Ar I lines (690-950 nm) corresponding to 4p→4s transitions (E_{ex} up to 13.5 eV). Argon I lines related to 5p→4s transitions (415-430 nm) (E_{ex} above 14 eV) are much less intense, indicating low electron temperature values and a lower excitation capability. Results were similar to those reported by Yanguas-Gil et al. [**14**], who stated that the 5p→4s Ar I transitions were almost negligible in an Ar/CH_4 microplasma jet. Other emissions are those of atomic nitrogen (402.456 nm) and atomic oxygen (477.291 nm and 477.375 nm) with excitation energies similar to Ar I 4p→4s lines.

The OH radicals develop from H_2O molecules that dissociate following collisions with oxygen atoms resulted from O_2 traces diffused into plasma:

$$O + H_2O \rightarrow OH + OH \tag{1}$$

The molecular emission of OH radicals is the result of their excitation by collisions with electrons [**13**].

The emission of the N_2 SPS is principally due to second-kind collisions with metastable argon atoms [**15-17**]. Argon has 2 metastable energy levels for the 4s states ($^2P^0_{3/2}$ -11.55 eV; $^2P^0_{1/2}$ – 11.72 eV). The $C^3\Pi_u$ state of N_2 is similar in energy to Ar 4s metastable levels and therefore an energy transfer is possible [**18**]. The relatively strong band of N_2 SPS $C^3\Pi_u \rightarrow B^3\Sigma_g$ observed in our Ar plasma is the direct result of this energy transfer between a metastable Ar atom and a ground state N_2 molecule.

$$N_2 + Ar^* \rightarrow N_2^* + Ar \tag{2}$$

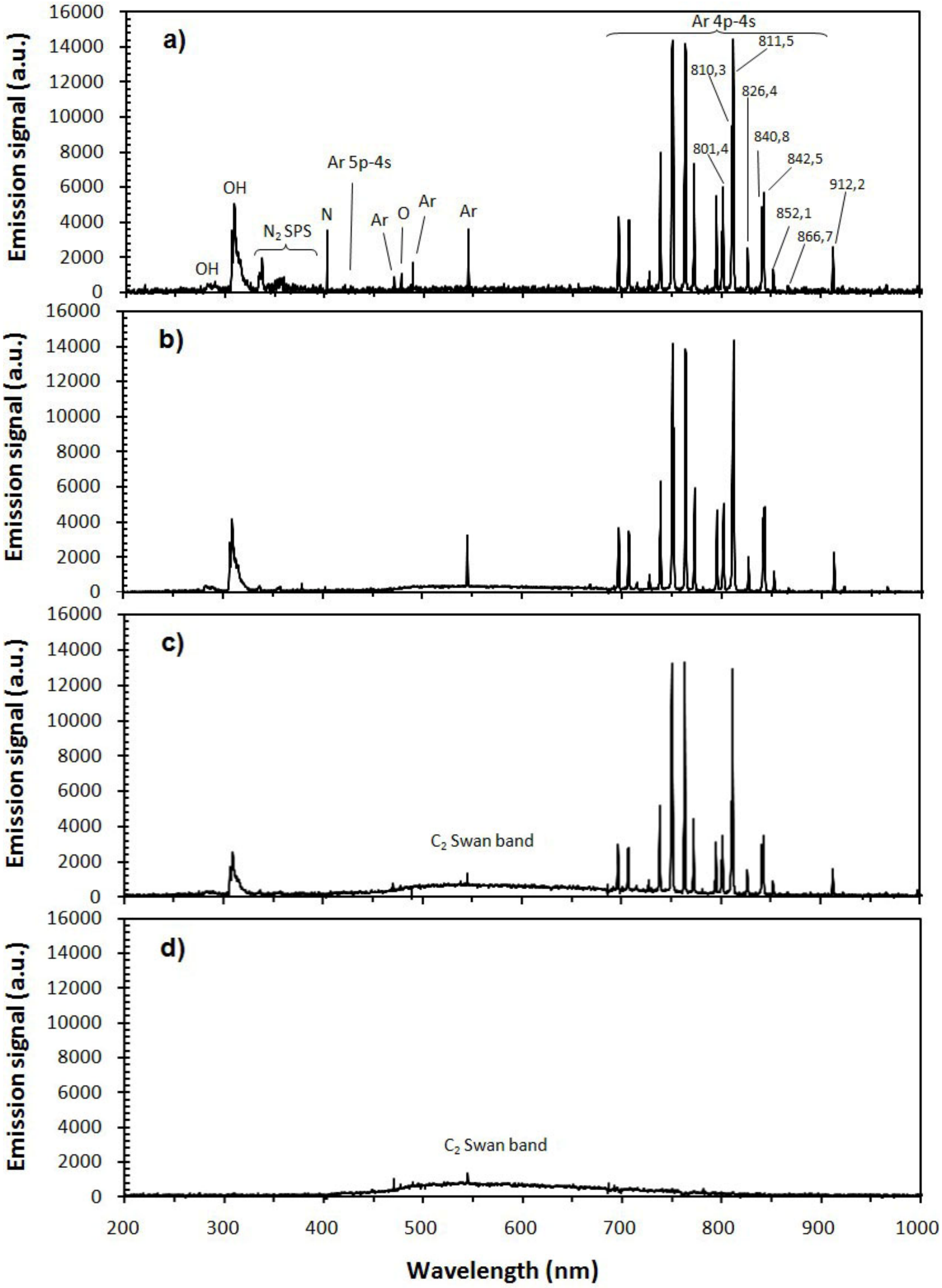

Figure 1. Background emission spectra of Ar and Ar/CH_4 plasmas. Experimental conditions: 275 W; 70 mm observation height; 0.7 L min^{-1} Ar; CH_4 flow rate (mL min^{-1}): (a) 0; (b) 2.5; (c) 5; (d) 7.5.

The emission spectra in Fig. 1 shows that the CH_4 content in the Ar plasma controls the emission intensity of OH, N_2 SPS and Ar I. The quenching of OH emission is the result of its photochemical reaction with CH_4 due to the radical affinity toward a hydrogen atom.

$$OH + CH_4 \rightarrow CH_3 + H_2O \tag{3}$$

The mechanism of this reaction is discussed in [**19-22**].

The quenching of the N_2 SPS is the result of the second-kind collision with CH_4 molecule and decrease of the population of Ar metastable atoms in the Ar/CH_4 plasma. Following this collision the N_2 molecule from $C^3\Pi_u$ goes to the ground state $A^3\Pi_u$ that remains unchanged in the presence of CH_4 [**23**]:

$$N_2^* + CH_4 \rightarrow N_2 + CH_4^* \rightarrow N_2 + CH_3 + H \tag{4}$$

The quenching of the Ar I emission in the visible spectral range is attributed to an energy transfer from Ar I excited state to the CH_4 molecule, which is dissociated according to the process:

$$Ar^* + nCH_4 \rightarrow Ar + nCH_4^* \rightarrow Ar + CH + CH_2 + CH_3 + H \tag{5}$$

This process is in agreement with a previous report in the literature [**24**]. For an addition of 7.5 mL min^{-1} CH_4 to 0.7 L min^{-1} Ar it occurred a complete quenching of OH and nitrogen molecular emission in UV and an almost complete one of Ar I 4p→4s in the visible range.

Interestingly, there is no evidence of the CN molecular emission ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$; E_{ex} = 3.19 eV; 359.04 nm (0,1) and 388.34 nm (0,0)) in the spectrum of Ar/CH_4 plasma, which demonstrates that the chemical reaction between N_2 and methane is insignificant in the quenching of nitrogen molecular emission:

$$N_2^* + CH_3 \rightarrow N + HCN + H_2 \tag{6}$$

The lack of the CN emission was reported in other atmospheric pressure Ar/CH_4 microplasmas [**14**].

Another feature of the Ar/CH_4 plasma spectrum is the absence of the molecular emission corresponding to CH (CH 314.3 nm system $C^2\Sigma^+ \rightarrow X^2\Pi$; CH 390 nm system $B^2\Sigma^+ \rightarrow X^2\Pi$; CH 430 nm system $A^2D \rightarrow X^2\Pi$) and CH_2 (360-390 nm) as well as the presence of the intense C_2 Swan band ($D^3\Pi_g \rightarrow A^3\Pi_u$; 409-690 nm). Our finding is in agreement with that of Yanguas-Jil et al. [**14**] who reported the decrease of the CH/C_2 emissions ratio in the Ar/CH_4 plasma when increasing the CH_4 addition.

The approach of quenching the molecular emission by CH_4 addition in Ar plasma is superior to that based on oxygen-sheated plasma studied by Jin et al. [**7**] in Ar MPT. Whereas the method using CH_4 as reaction/collision gas ensures quenching of both OH and N_2 SPS molecular emission, the approach using oxygen accomplishes only the removal of nitrogen emission signal, while that of OH increases.

Discharge parameters

Electron number density and excitation temperature of the Ar atoms were determined from the Ar emission spectrum. Spectroscopic data are summarized in Table 2 [**25**].

Table 2. Spectroscopic data for Ar I lines (4p→4s) [25]

□ (nm)	E_{ex} (eV)	gA 10^8 (s^{-1})
801.478	13.09	0.464
810.369	13.15	0.750
811.531	13.07	2.32
826.452	13.32	0.459
840.821	13.29	1.12
842.465	13.09	1.08
852.144	13.28	0.417
866.794	13.15	0.0729
912.297	12.90	0.567

Plasma diagnostics by optical emission spectrometry is a passive technique easy to implement but assumes that plasma is in local thermal equilibrium (LTE). In accord with the observation of Alder et al. [**17**] that electron temperature (T_e) is close to T_{ex} of species with high excitation energy, we considered that T_e could correspond to T_{ex} for Ar I (4p→4s). The gas temperature (T_g), n_e and T_e characterize the capability of atomization and excitation of a plasma source. Low T_g and high T_e recommend plasma as excitation source in atomic emission. The excitation temperature of Ar I (4p→4s) was estimated from the Bolzmann plot considering the convolution of the grating and detector efficiencies in conjunction with the wavelength. The excitation temperature of Ar I (4p→4s) *vs.* viewing height in the absence of CH_4 and with addition of 2.5 and 5 mL min^{-1} CH_4 in 0.7 L min^{-1} Ar is presented in Figure 2. The variation of electron number density under the same conditions is shown in Figure 3.

The excitation temperature of Ar I in pure Ar plasma is in the range 1210 – 1950 K and decreases to 780 – 1460 K and 580 – 1365 K when adding 2.5 and 5 mL min^{-1} CH_4 respectively. The error in the determination of T_{ex} evaluated from the standard deviation of the slope of the Bolzmann plot was in the range 5 – 15 %. The decrease of T_{ex} for Ar I confirms quenching of Ar emission caused by second-kind collisions between argon excited atoms and CH_4 molecules. The decline of the population of 4s Ar metastable atoms involved in the excitation of nitrogen SPS when adding CH_4 proves the decrease of the nitrogen molecular emission.

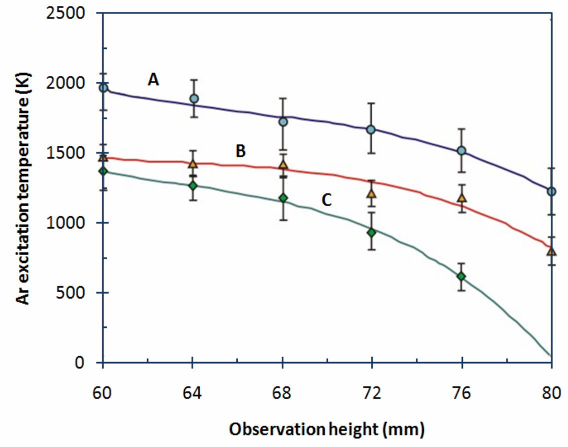

Figure 2. Dependence of the excitation temperature of Ar I (4p→4s) on the viewing height in plasma operated at 275 W and 0.7 L min^{-1} Ar. CH_4 flow rate (mL min^{-1}): A - 0; B - 2.5; C - 5. Error bars correspond to uncertainty in temperature determination

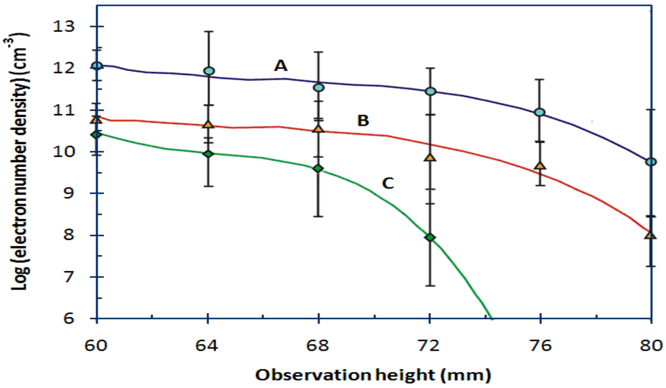

Figure 3. Electron number density *vs*. viewing height in plasma operated at 275 W and 0.7 L min^{-1} Ar. CH_4 flow rate (mL min^{-1}): A - 0; B - 2.5; C - 5. Error bars correspond to uncertainty in temperature determination

The value of n_e was calculated from the Saha's equation considering the statistical weights for electrons and ions (g_e=2 and g_i=6) and T_e equal to T_{ex} of Ar atoms.

$$\ln\left(\frac{hc}{I}\frac{gA}{\lambda}\right) = 51.72 - 2\ln n_e + \frac{3}{2}\ln T - \frac{E_i - E_{ex}}{kT} \tag{7}$$

where: E_i – ionization energy of Ar (15.86 eV)
E_{ex} – excitation energy of Ar I lines

Thus, $\ln\left(\frac{hc}{I}\frac{gA}{\lambda}\right)$ was plotted *vs.* $\frac{E_i - E_{ex}}{k}$ (Fig.3) and n_e was calculated from the intercept.

The value of n_e in the plasma tail (60 – 80 mm) of pure Ar is in the range 6.34×10^{9} – 1.37×10^{12} cm^{-3}, lower than in the inferior zone of the discharge (0 – 32 mm), of 4.35×10^{12} – 2.37×10^{13} cm^{-3} [**26**]. This parameter decreases at 1.21×10^{8} – 7.70×10^{10} cm^{-3} and 1.06×10^{8} – 3.79×10^{10} cm^{-3} when adding 2.5 and 5 mL min^{-1} CH_4, respectively. The error in n_e determination was in the range 5 – 15 %.

The decline of n_e in the presence of CH_4 in the Ar plasma suggests a sharp decrease of the ionization degree of the support gas. The gas temperature of Ar plasma was in the range 2330 - 2550 K [**26**]. The relatively high gas temperature and low electron temperature and n_e in the plasma tail are benefit for a good atomization of sample but provide low excitation capabilities, what is suitable as atoms cell in AFS [**11-13**].

CONCLUSIONS

The spectral characterization of an Ar/CH_4 plasma operated at low power and gas consumption was carried out. The emission spectrum of the pure Ar plasma was dominated by the OH, N_2 SPS band and Ar I lines $4p\rightarrow4s$ transitions. Addition of CH_4 in Ar plasma resulted in quenching of the molecular emission and Ar I lines following chemical reactions with OH and second-kind collisions with nitrogen molecules and Ar atoms. In the Ar/CH_4 plasma molecular emission of CH_x (x=1, 2) is missing, while the C_2 Swan band is relative intense. The role of CH_4 in quenching of emission subsequent second-kind collisions was evidenced by the decrease of Ar I excitation temperature and electron number density. The low background spectrum and low excitation capability of the Ar/CH_4 plasma recommend it as an attractive atomization source in atomic spectrometry using low resolution microspectrometers.

EXPERIMENTAL SECTION

Instrumentation

The discharge was characterized by optical emission spectrometry using spectrum ranging from 200 – 1000 nm recorded with the low resolution HR4000 microspectrometer from Ocean Optics with FWHM of 1.5 nm. Detailed about the measurement settings are given in Table 3, while the experimental set-up in Figure 4. Under standard conditions, plasma was generated at a flow rate of 0.7 L min^{-1} Ar (5.0 quality). In the approach with CH_4 (4.5 quality) as collision/reaction gas, plasma was developed in a mixture using the same Ar flow rate as above and CH_4 in the range of 2.5-7.5 mL min^{-1}.

Table 1. Characteristics and operating conditions for the experimental system CCP torch-microspectrometer

Power supply	Free running generator, 275 W, 27.12 MHz (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania)
Plasma torch	Capacitively coupled with Mo tubular electrode (i.d. 3.5 mm) connected to the generator and grounded ring electrode of Cu spaced at 5 mm; 16 mm i.d. quartz tube, 10 cm length, GFC 17 model CH_4 mass flow meter (Aalborg Instr. and Controls, USA).
Sample introduction system	Meinhardt nebulizer equipped with impactor spray chamber (Perkin Elmer, Norwalk, USA) without desolvation, 5% nebulization efficiency; aerosol intake into the plasma *via* the tubular electrode.
Optics	HR4000 Microspectrometer Ocean Optics (200-1100 nm), 1200 grooves mm^{-1}, Toshiba TCD1304AP CCD array, 3636 pixels, focal length 101.6 mm, FWHM 1.5 nm, collimating system-74 UV, fibre optic QP 600 μm, 25 cm length (Ocean Optics, Dunedin, USA).
Data acquisition	Spectra Suite Soft (Ocean Optics); average of 10 successive measurements for 5 s integration time

Throughout the experiment a flow rate of 1 mL min^{-1} water with 5% nebulization efficiency was introduced into plasma. The emission signal was collected through the quartz tube with a collimating lens placed in the radial direction related to the plasma by means of the fibre optic of the microspectrometer. Measurements were performed in plasma tail at viewing heights greater than 60 mm above the tubular electrode, the zone considered as optimum for fluorescence measurements [**13**].

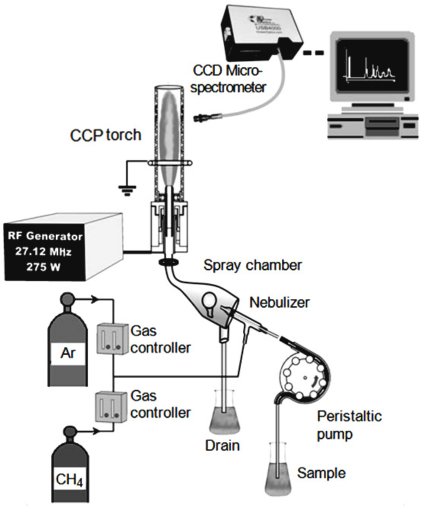

Figure 4. Experimental set-up of the capacitively coupled plasma torch and HR4000 Ocean Optics microspectrometer.

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REFERENCES

1. J.A.C. Broekaert, *Applied Spectroscopy*, **2008**, *62*, 227A.
2. ISO 11885: 2007, Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES).
3. ISO 22036 Soil quality - Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP - AES).
4. A.E. Croslyn, B.W. Smith, J.D. Winefordner, *Critical Review Analytical Chemistry,* **1997**, *27*, 199.
5. D.L. Haas, J.A. Caruso, *Analytical Chemistry*, **1984**, *56*, 2014.
6. K. Jankowski, *Journal of Analytical Atomic Spectrometry*, **1999**, *14*, 1419.
7. Q. Jin, W. Yang, F. Liang, H. Zhang, A. Yu, Y. Cao, J. Zhou, B. Xu, *Journal of Analytical Atomic Spectrometry*, **1998**, *13*, 377.
8. M.W. Blades, *Spectrochimica Acta*, **1994**, *49B*, 47.
9. T. Frentiu, D. Petreus, M. Senila, A.I. Mihaltan, E. Darvasi, M. Ponta, E. Plaian, E.A. Cordos, *Microchemical Journal*, **2011**, *97*, 188.
10. E.A. Cordos, T. Frentiu, A.M. Rusu, S.D. Anghel, A. Fodor, M. Ponta, *Talanta,* **1999**, *48*, 827.
11. T. Frentiu, E. Darvasi, M. Senila, M. Ponta, E. Cordos, *Talanta,* 2008, **76**, 1170.
12. T. Frentiu, M. Ponta, M. Senila, A.I. Mihaltan, E. Darvasi, M. Frentiu, E. Cordos, *Journal of Analytical Atomic Spectrometry*, **2010**, *25*, 739.
13. T. Frentiu, M. Ponta, A.I. Mihaltan, E. Darvasi, M. Frentiu, E. Cordos, *Spectrochimica Acta*, **2010**, *65B*, 565.
14. A. Yanguas-Gil, K. Focke, J. Benedikt, A. von Keudell, *Journal of Applied Physics*, **2007**, *101*, 103307.
15. D.W. Setser, D.H. Stedman, J.A. Coxon, *Journal of Chemical Physics,* **1970***, 53*, 1004.
16. N. Bibinov, A. Fateev, K. Wiesemann, *Journal of Physics. D: Applied Physics,* **2001***, 34*, 1819.
17. J.F. Alder, R.M. Bombelka, G.F. Kirkbright, *Spectrochimica Acta*, **1980**, *35B*, 163.
18. W.K. McGregor, Proc. V Bienn. Gas Dynamics Symp., Evanson 1963, Chapter 8. Northwestern University Press (**1963**).
19. J.R. Dunlop, F.P. Tully, *Journal of Physical Chemistry*, **1993**, *97*, 11148.
20. F.P. Tully, A.R. Ravishankara, *Journal of Physical Chemistry*, **1980**, *4*, 3126.
21. J.G. Calvert, R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.J. Wallington, G. Yarwood, “The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons”, Oxford University Press, UK, **2002**.
22. T. Gierczak, R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, A.R. Ravishankara, *Journal of Physical Chemistry.* A **1997,** *101*, 3125.
23. M. Shimozuma, H. Tagashira, *Journal of Physics. D: Applied Physics*, **1981**, *14*, 1783.
24. A. Gicquel, M. Chenevier, Kh. Hassouni, A. Tserepi, M. Dubus, *Journal of Applied Physics*, **1998**, *83*, 7504.
25. NIST Atomic Spectra Database Lines Form http://physics.nist.gov/PhysRefData/ASD/lines_form.html (accessed November 2010)
26. T. Frentiu, M. Ponta, E. Darvasi, M. Frentiu, E. Cordos, *Acta Chimica Slovenica*, **2010**, *57*, 173.