EXCITATION MECHANISM OF ATOMIC AND IONIC SPECIES IN THE ARGON CAPACITIVELY COUPLED PLASMA IN ANNULAR-COAXIAL GEOMETRY WITH SINGLE AND TWO RING ELECTRODES

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The plasma-chemical model based on the interpretation of the atomic-to-ionic line intensity ratios of several elements (Ca, Mg, Mn and Cd) was applied to explain the atomic and ionic excitation species in a medium power Ar capacitively coupled plasma source. Plasma was generated in annular-coaxial geometry with Mo tubular electrode and single or two ring electrodes. The emission of 22 elements has the characteristic pattern of the arc spectrum with atomic resonance lines much more intense than ionic lines as the excitation of species occurs mostly by electron collisions. In the geometry with double ring electrodes it was observed a higher increase of the ionic emission attributable to the excitation through Penning transfer following collision with metastable Ar atoms. The selection of the emission lines of elements in the medium power capacitively coupled plasma should take into consideration both excitation energy and that necessary for the analyte oxides dissociation.

$$Me^0 + e^- \rightarrow Me^* + e_s^-$$
$$Me^0 + Ar^m \rightarrow Me^{+*} + Ar + e_s^-$$
$$Me^0 + Ar^+ \rightarrow Me^{+*} + Ar + \Delta E$$
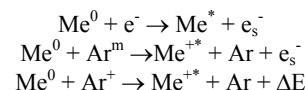
INTRODUCTION

The excitation mechanisms and matrix interference in radiofrequency inductively coupled plasma (ICP) still remain of interest as they allow the understanding of the fundamental processes occurring in the plasma. Often, the improvement of sensitivity, precision and detection limits results from an empirical approach for the optimization of analytical performances disregarding the fundamental processes of plasma. Obviously, a substantial performance enhancement of plasma as analytical source is not achievable without an in-depth knowledge and understanding of the atomization, excitation and ionization processes occurring in the discharge. Besides fundamental research in the field of pure Ar plasma or containing limited molecular gases, the interest was directed toward the generation of pure molecular gases plasma (air, nitrogen and oxygen).[1,2] The development of these sources has become a routine and the use of computer simulation models resulted in the improvement of vaporization, atomization, excitation and ionization processes in plasma.[3-5] Besides ICP, radiofrequency capacitively coupled plasmas (CCPs) of low/ medium power and low Ar consumption (< 300 W, < 1 l min^{-1}) are considered convenient sources for atomic spectrometry due to their advantages in terms of analytical versatility and reduced

maintenance cost.[6-8] Parallel-plate, annular and coaxial geometries of electrodes are used for coupling the radiofrequency power to the CCP torch.[6]

This paper is an attempt to elucidate the excitation mechanism of atomic and ionic species in an Ar radiofrequency capacitively coupled plasma of medium power (275 W) in annular-coaxial geometry with a Mo tubular electrode and single or double ring Cu electrodes. The torch construction, its main characteristics and several analytical applications in atomic emission and fluorescence spectrometry have been already presented.[9-15] The advantage of the annular-coaxial geometry with Mo tubular electrode and ring electrodes is to facilitate the sample introduction into the central zone of the discharge where the dissipation of energy occurred ensuring optimal conditions for the atomization/excitation processes. This plasma is tolerant to relatively high concentration of easily ionizable elements as interferent.[15] The excitation mechanism of species is explained based on the plasma-chemical model using the atomic-to-ionic line intensity ratios for several elements (Ca, Cd, Mg and Mn) exhibiting intense emission lines in this source. The characteristics of the emission spectrum are correlated with the dissociation energy of the oxides of elements under study, ionization energy of neutral atoms and excitation energy of atomic and ionic species. A selection rule of the analytical lines for 22 elements in CCP is presented in comparison with ICP and Goldwasser and Mermet energy level diagram, in which elements are grouped according to periodicity of properties.[16]

RESULTS

### Emission line measurements in CCP and comparison of line intensities

Emission intensity of the atomic resonance lines and ionic lines of Ca, Mg, Mn and Cd in CCP with annular-coaxial geometry with single or double ring electrodes were measured at identical photomultiplier voltage. After correction according to the photomultiplier response curve, emission intensities were normalized by assessing the most intense line of an element the value of 100%. The obtained results along with the spectrochemical characteristics of elements are presented in Table 1.

DISCUSSION

Data in Table 1 show that for both geometries of plasma operation the atomic emission lines are much more intense than the ionic lines. After the correction of the atomic emission intensity according to the photomultiplier response curve their ratio was CaI:MgI:MnI:CdI = 1:1.4:1.5:2.2. The examination of data in relation with the energy necessary for oxide dissociation ($E_{ox,dissoc}$) and atomic excitation energy reveals an obvious increase of the atomic emission with the decrease of E_{dissoc} and, strangely, with the increase of E_{ex}. The conclusion is that the process limiting emission intensity in the plasma with single ring electrode geometry is the analyte atomization ($MeO \rightarrow Me + O$) rather than the excitation itself. The atomization efficiency in plasma is mostly depended on the gas temperature considered as the rotational temperature of the OH radical and much less on collision with electrons or other particles in plasma. These phenomena are consistent with the relatively low plasma temperature (2450±50 K), similar with an air-acetylene flame or electric arc.[14] The presence of atomic lines with E_{ex} up to 5.4 eV in the spectrum means that the excitation in the plasma discharge with this geometry occurs mostly by atom-electron collisions (Eq. 1)

$$Me^0 + e^- \rightarrow Me^* + e_s^- \qquad (1)$$
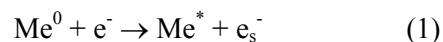
In the geometry with single ring electrode the ratio of the ionic lines was found to be CaII:MgII:MnII:CdII 1:1.3:4.3:2.5, demonstrating a relatively efficient excitation of ionic lines for elements with E_{ion} below 9 eV, or the sum of E_{ion} and E_{ex} below 15 eV. The presence of ionic lines in the plasma spectrum highlights the possibility of excitation *via* Penning mechanism by collision with argon metastable (Ar^*) atoms (12 eV) or charge transfer from Ar^+ ions (15.86 eV).

$$Me^0 + Ar^m \rightarrow Me^{+*} + Ar + e_s^- \qquad (2)$$

$$Me^0 + Ar^+ \rightarrow Me^{+*} + Ar + \Delta E \qquad (3)$$
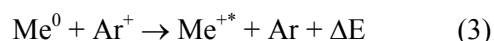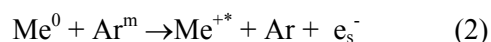
However, ionic lines are much less intense than those of neutral atoms and suggests that excitation concerns mostly atoms by electron collisions, while ionization and excitation by Ar^* or charge transfer from Ar^+ are less common.

Table 1

Atomic and ionic lines intensities in CCP in annular-coaxial geometry with Mo tubular electrode and single or double ring electrodes

Line	λ (nm)	$E_{ox, dissoc}$ (eV)	E_{ex} (eV)	E_{ion} (eV)	Emission intensity	
					CCP with single ring electrode	CCP with double ring electrodes
Ca I	422.673	5.0	2.93		22	100
Ca II	393.367		3.15	6.11	6	60
Mg I	285.213	4.4	4.34		30	71
Mg II	279.553		4.43	7.64	8	33
Mn I	403.075	4.0	3.08		32	83
Mn II	257.610		4.81	7.42	26	76
Cd I	228.802	3.8	5.41		48	67
Cd II	214.441		5.78	8.99	15	19

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

For the plasma with two ring electrodes the ratio of the atomic lines was found to be CaI:MgI:MnI:CdI 1.5:1.1:1.2:1 showing the highest increase of the emission intensity for elements forming refractory oxides. This is the result of the enhancement of atomization efficiency of elements following the increase of the gas temperature to 2670±50 K.[14] The increase of the atomization degree with the introduction of the second ring electrode in the discharge arrangement was obvious, since the highest enhancement of the emission signal (4.5 times) was registered for Ca with the lowest E_{ex} of atomic line and highest $E_{ox,dissoc}$. At the opposite side was Cd, with the highest E_{ex} of atomic line and lowest $E_{ox,dissoc}$, for which the atomic emission increase was below twice. The same behavior was found for the ionic lines, for which the increase was 3-10 times compared to the plasma geometry with single ring electrode. The greater enhancement of ionic than atomic emission is due to the fact that plasma in double ring arrangement is more energetic and Penning excitation and charge transfer processes became more efficient. Thus, the more efficient excitation of species by electron collision in the two ring electrodes plasma is in agreement with the increase of the excitation temperature of atomic lines (T_{ex}) from 3200-4850 K in the single ring electrode plasma to 3325-7535 K in that with two ring electrodes. In the same time, this behavior correlates with the increase of the electrons energy as their temperature (T_e) raises from 6920 K to 8200 K, while the electron number density increases from 10^{13} cm^{-3} to 4.5 10^{14} cm^{-3} in plasma with two ring electrodes.[14] Stronger both atomic and ionic emission indicates an increase of collisions per unit volume and time (C(v)) that is a function of the velocity of particles or their kinetic energy.[17]

$$C(\upsilon) = Nn_e \int_0^\infty v\sigma(v)f(v)dv \qquad (4)$$

where: N – total number of atoms (ions) of the analyte, n_e – electron number density in plasma, $\sigma(v)$ – electron-atom (ion) collision cross section, $f(v)$ – electron velocity distribution.

Eq. 4 shows that atomic and ionic lines, for a constant number of the corresponding species, could be enhanced by increasing the electron number density or their energy, respectively. It was previously reported that the ionization efficiency of neutral species increased in the CCP with two ring electrodes to 70-85% from 40-70% in that with single ring consistent with the increase of ionic species and hence of ionic emission.[14] The ionization degree was found to be inversely proportional with E_{ion} of elements and reflected in the relative intensities of ionic lines.

Selection rule of the analytical lines in CCP compared to ICP

Assuming that excitation in CCP occurs by electron collision rather than Penning reactions there were estimated the most intense analytical lines for 22 elements (Li, Na, K, Cu, Ag, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Al, Pb, Bi, V, Cr. Mn, Fe, Co, Ni, Eu) in comparison to ICP and Goldwasser and Mermet diagram.[16] According to this, in ICP the elements in the I, V and VI main groups and secondary II group of the periodic table give more intense atomic lines, while the elements in the II main group, III and IV both main and secondary groups, and V and VI secondary groups exhibit more intense ionic lines. Unlike ICP, in CCP having lower energy regardless of the configuration

with one or two ring electrodes, all the 22 elements under study produced a more intense atomic emission. The most intense lines in CCP were the atomic resonance ones with E_{ex} below 7 eV. In both CCP configurations, the earth-alkaline elements, i.e. Ca, exhibits, besides the atomic line, a quite intense molecular emission (CaOH radical, 554; 622 nm), which can also be selected for analysis.[15] Thus, emission spectra in CCP and ICP sources are quite different. While in ICP the spectrum is similar to that given in spark with more intense ionic lines, the spectrum in CCP is rather comparable to that in arc exhibiting resonance lines and few intense molecular bands. These arise from the substantial difference between the two plasma sources in terms of operation power, power density, discharge gas temperature, electron number density and energy of species, with more beneficial characteristics for ICP.[3] It can be assumed that the differences are mainly determined by the lower gas temperature in CCP and thus a poorer atomization, particularly in the case of elements forming refractory oxides (Mg, Ca, Ba, Al, etc.). Thus, in the selection of the analytical lines in CCP one can take into consideration, besides E_{ex}, the dissociation energy of oxides.

EXPERIMENTAL

Instrumentation

The instrumentation used in this study was previously described.[9,14,15] The capacitively coupled plasma torch (275 W, 27.12 MHz) consists of a quartz tube of 16 mm i.d and 20 cm length with a Mo tubular electrode (i.d. 3.5 mm, o.d. 5 mm) connected to the radiofrequency generator and surrounded by a single or two grounded Cu ring electrodes. Thus, plasma was operated in annular-coaxial geometries with: (a) single ring electrode at 5 mm above the Mo tubular electrode and (b) two ring electrodes spaced at 60 mm. An argon flow of 0.4 l min⁻¹ at atmospheric pressure was used in both cases as plasma support gas and sample carrier as aerosol. Emission spectra were recorded using a sequential spectrometer (200-800 nm) in Czerny-Turner mounting (1 m focal length) equipped with a R1414 photomultiplier (Hamamatsu). The experimental set-up was assembled at the Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania. The scheme of the spectrometer with capacitively coupled plasma source was already given.[9,14,15]

Reagents

Monoelemental solutions in the range 10-100 µg ml⁻¹ Ca, Cd, Cu, Mg and Mn were prepared starting from the corresponding 1000 µg ml⁻¹ stock solutions (Merck, Darmsdadt, Germany). All solutions were stabilized in 2% (v/v) HNO_3. Argon 5.0 (Gas SRL, Cluj-Napoca, Romania) was used as plasma support gas.

The plasma-chemical model

One of the models used to explore the rf plasma discharge is the plasma-chemical one, which is based on the interactions occurring between plasma and sample. Besides data regarding the physical characterization of the plasma, such as closeness or departure from the local thermodynamic equilibrium (LTE), this model provides information on mechanisms generating atoms and ions, and their excitation process.[3] In the same time, the model tries to elucidate the occurrence of interelement interference and the matrix influence on plasma physical characteristics (excitation, ionization, rotational and vibrational temperatures, electron number density, etc.). The plasma-chemical model involves the interpretation of the atomic-to-ionic line intensity ratios of certain lines emitted by the elements introduced into plasma. The model was already used to perform a physical characterization of CCP with single and double ring electrode and to investigate the non-spectral interference of the easily ionizable elements on the emission of molecular, atomic and ionic species of the analyte.[15] It was concluded that, in both geometries, plasma exhibited a departure from LTE state and the non-spectral interferences were found to be dependent on electrodes configuration in the torch, nature of the analyte and interfering species.

CONCLUSIONS

The plasma-chemical model based on the evaluation of the atomic-to-ionic line intensity ratios showed that in the CCP in annular-coaxial geometry with single or two ring electrodes excitation occurred mostly by electron collision. This plasma spectrum with atomic emission lines, especially those of resonance, much more intense than the ionic lines, was found to be similar to that of an arc source. The spectrum differs from that in ICP showing intense ionic lines, which is a characteristic of spark spectra. In the annular-coaxial geometry of CCP with two ring electrodes there was an enhancement of both atomic and ionic emission in agreement with the plasma characteristics. A higher increase was observed for the ionic emission as a result of excitation and ionization by collision with metastable Ar atoms in Penning reactions.

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