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# RADIAL STUDY OF ATOMIC AND IONIC ARGON SPECIES IN THE HELIUM-ARGON MICROWAVE PLASMA PRODUCED BY THE AXIAL INJECTION TORCH [1]

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In this work the radial distributions of the emission coefficient of some atomic and ionic argon lines in the thin helium plasma (∼1 mm diameter) produced by the axial injection torch are presented as a function of the supplied microwave power and the argon concentration. Radial distributions were obtained using an Abel inversion method on laterally resolved measurements of the plasma flame. Different radial behaviour was found for ionic and atomic argon levels.

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## 1 Introduction

The axial injection torch (TIA) produces a small (∼1 mm diameter and 10-20 mm long) and very stable microwave plasma. It can operate with atomic and molecular gases, including air, which makes it a very versatile plasma.

Due to the high ionization potential of He, the He plasma produced by the TIA is very useful as an excitation source for analytical chemistry [1]. It also makes the plasma an efficient device for destruction of dangerous compounds as Volatile Organic Compounds (VOCs) [2], an application that is improved when gas mixtures are considered. If a small amount of other gas different from helium is introduced in the discharge, the plasma properties can be altered. As a preliminary study of gas mixture plasmas created with the TIA, and in order to study the excitation mechanism of substances in the discharge, different amounts of Ar (0.05 – 0.5 %) were introduced in the plasma. This allowed the calculation of the relative population densities of ionic and atomic argon levels and, by means of the Abel inversion procedure, the study of their radial behaviour and its variation with the argon concentration in the plasma. The variation of these relative population densities with the supplied microwave power was also studied.

## 2 Experimental set-up

In order to obtain the radial distribution of the emission coefficient of a spectral line, line-of-sight integrated emission intensity values from different lateral positions of the discharge are required.

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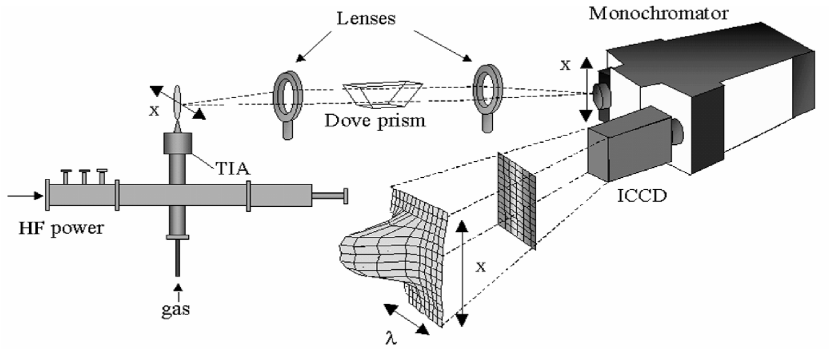


Fig. 1. Experimental set-up.

The experimental set-up used in this work allowed the obtainment of such values as described in Fig. 1. The image of the plasma was rotated $90^o$ by a Dove prism, and two achromatic lenses focussed it at the entrance slit of a 1-meter focal length monochromator. By that way, a line-of-sight integrated plasma slice at an axial position was selected. The resulting wavelength-dispersed image of such slice of the discharge falls on an intensified CCD camera placed at the monochromator exit window. The thus obtained bidimensional array of data provides an emission spectrum for each different lateral position of the discharge.

The behaviour of the gas mixture has been studied in this work by means of measuring some ionic and atomic argon lines in different plasma and mixture conditions, together with some atomic helium lines. The measurements were made at 1 mm above the nozzle tip, which is the maximum emission intensity axial position, with 6 l min$^{-1}$ He. The variation of the radial distribution of one atomic and one ionic Ar lines and one atomic He line with the supplied microwave power was studied for a 0.03 l min $^{-1}$ Ar flow-rate and microwave power values in the range 400-700 W. The difference in the radial distribution of the ionic and atomic argon lines was studied by measuring a number of ArI and ArII lines for a 0.03 l min $^{-1}$ Ar flow-rate and 600 W microwave power. In order to study the variation of the radial emission intensity of the mixture with the Ar concentration one ArI, one ArII and one HeI lines were measured for six Ar flow-rate values ranging from 0.03 to 0.3 l min $^{-1}$ , this is, from 0.05 to 0.5 % of the He flow-rate, with logarithmic spacing – i.e. 0.05x$10^{0.0}$, 0.05x$10^{0.2}$, …, 0.05x$10^{1.0}$.

## 3 Calculation of the radial distributions

The Abel inversion relates the radial distribution of the emission coefficient of a spectral line, $\varepsilon(r)$, with the line-of-sight integrated intensity distribution, $I(x)$:

$$\varepsilon(r) = -\frac{1}{\pi}\int_{r}^{R} \frac{I'(x)}{\sqrt{x^2 - r^2}}\mathrm{d}x, \tag{1}$$

where $R$ is the plasma radius and $I'(x)$ is the first derivative of $I(x)$ respect to $x$. The Hankel-Fourier method for Abel inversion of discrete sets of data, presented in a previous paper [3], was used in this work, as it has been found to provide more accurate radial distributions for sets of lateral intensity data than other methods present in the literature.

The emission radial distributions of the ArI, ArII and HeI lines were obtained after performing Abel inversion on the lateral distributions of intensity of each line. The error of these results equals that of the Abel inversion method, which increases towards the plasma centre. This error has been calculated previously [3], and yielded a relative error for the results of less than 8% for the range of radial positions shown in the results.

## 4 Results and discussion

### 4.1 Variation of the radial emission coefficient with the supplied power

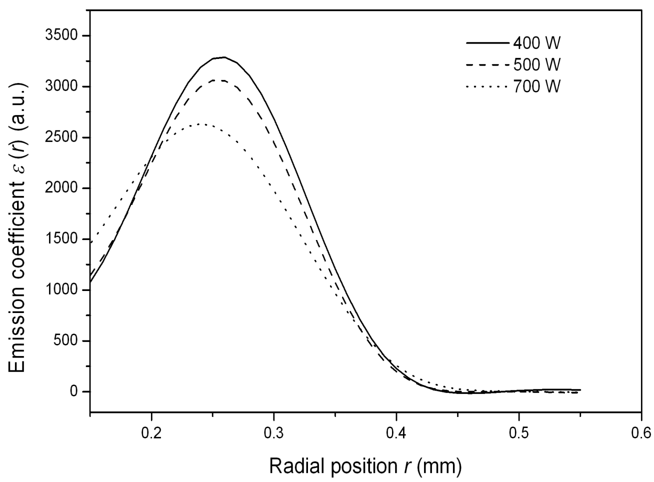


Fig. 2. Variation of the radial emission coefficient of the 696.5 nm atomic Ar lines with the supplied microwave power for 6 l min$^{-1}$ He flow and 0.03 l min$^{-1}$ Ar flow.

The results of the variation of the radial distribution of some emission lines of the gas mixture species ArI, ArII and HeI are presented in Figs. 2, 3, and 4. Fig. 2 shows the variation of the radial distribution of the 696.5 nm atomic argon line, which is directly related to the population density of the upper atomic level of the transition. According to these results, the population density of the Ar atomic level has a decreasing behaviour when the supplied HF power is increased. The opposite behaviour is shown by the 506.2 nm ionic argon line, as can be seen in Fig. 3; the population density of the corresponding ionic level increases with the microwave power, mainly in the central plasma zone. As to the 447.2 nm HeI line in Fig. 4, its intensity also increases with the supplied microwave power, with the maximum of the radial distributions situated at around 0.3 mm from the plasma axis.

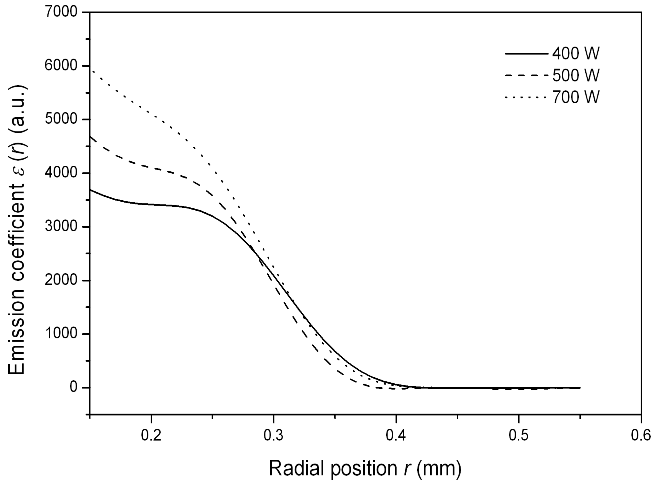


Fig. 3. Variation of the radial emission coefficient of the 506.2 nm ionic Ar line with the supplied microwave power for 6 l $\min^{-1}$ He flow and 0.03 l $\min^{-1}$ Ar flow.

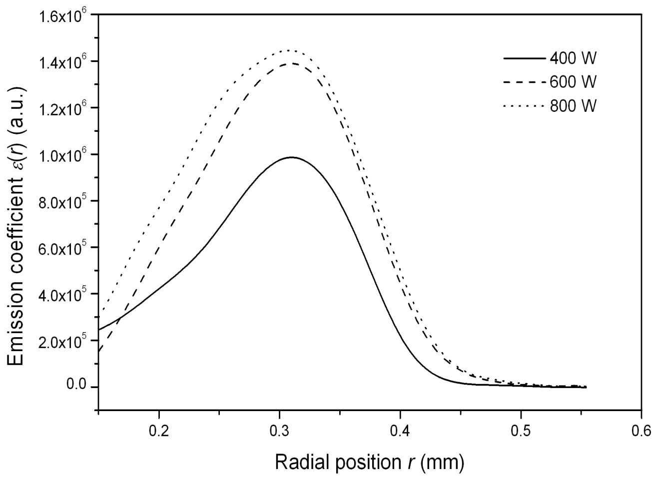


Fig. 4. Variation of the radial emission coefficient of the 447.2 nm atomic He line with the supplied microwave power for 6 l $\min^{-1}$ He flow and 0.03 l $\min^{-1}$ Ar flow.

The increment of the HeI line emission with the power was to be expected: a higher supply of microwave power will increase the population of the HeI excited states, as has been already measured by our group [1]. As to the argon lines, a possible explanation of the difference in their behaviour with the power is that an increment of the power will cause a higher ionization rate in the plasma [1], hence increasing the ionic states population on account of the atomic states population.

Attending to the radial behaviour, the atomic and ionic Ar lines also show important differences. While the ArI line emission coefficient in Fig. 2 has a radial distribution similar to that of the atomic helium, peaking at $\sim$0.25 mm radial position from the center and decreasing from there towards the plasma axis, the ArII line in Fig. 3 peaks near the plasma centre, decreasing towards the plasma edge. The plasma zone with higher population of the helium excited levels, which in our plasma is at $\sim$0.3 mm radial position, can fairly be supposed to be the plasma zone with a higher excitation capability [4], where the population density of both ArI and ArII sould be higher. The atomic argon radial distribution agrees with this, but the ionic argon does not. An explanation of the radial behaviour of the ArII could be the decreasement of the population of the ionic argon levels that is caused by the interaction of ArII with atoms and molecules that enter the plasma coming from the surrounding air, which has already been reported for other He-Ar mixture plasmas [5]. This interactions would then displace the position of the maximum of the ionic argon lines radial distributions to positions closer to the plasma center, as can be seen in the obtained results shown in Figs. 2, 6, and 9. One of those interactions is the charge transfer mechanism between ArII and $N_2$, which has been measured by our group inside the plasma. This mechanism is known to be quasi-resonant and one of the main ion destruction channels in an argon plasma [6]. However, the complete study of the destruction mechanisms of the argon ions in the plasma edge is beyond the aim of this work, and will be the subject of future studies.

### 4.2 Variation of the radial emission coefficient with the percentage of argon in the helium-argon plasma

The results of these measurements are shown in Figs. 5, 6, and 7, where the variation of an atomic Ar line, an ionic Ar line and an atomic He line respectively can be seen. It is clear from the results that these three different species have a different behaviour with the change in the Ar percentage: both the HeI and the ArII emission intensities substantially decrease when the Ar percentage is increased, while the atomic argon line emission intensity grows with the introduction of argon in the discharge.

In order to understand this behaviour, the fact that the excitation energy of argon is much lower than that of the helium has to be taken into account: the introduction of argon in the discharge will then cause a depopulation of the helium excited levels while the microwave power supplied to the plasma is redirected to the excitation of argon. With the depopulation of the He excited levels there will be fewer helium atoms in the metastable levels, and, being the main excitation channel of the argon ion levels the energy transfer with the metastable levels of helium [7], the ArII excited levels population will decrease with the argon concentration.

As to the radial behaviour of the emission intensity, it can be seen in Figs. 5, 6, and 7 that it does not change with the introduction of argon in the plasma, being the same as described in Section 4.1.

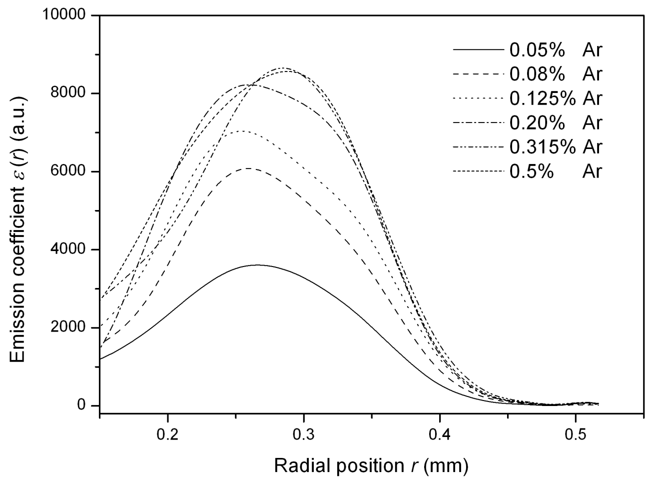


Fig. 5. Variation of the radial emission coefficient of the 696.5 nm atomic Ar line with the percentage of argon introduced in the plasma for 6 l $\mathrm{min}^{-1}$ He flow and 600 W supplied power.

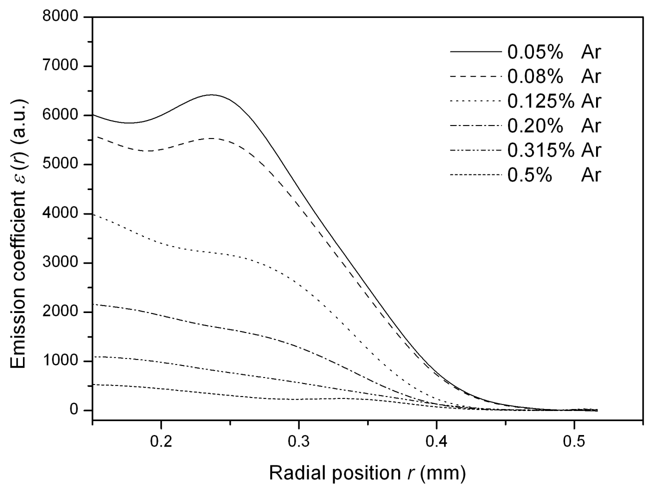


Fig. 6. Variation of the radial emission coefficient of the 506.2 nm ionic Ar line with the percentage of argon introduced in the plasma for 6 l $\mathrm{min}^{-1}$ He flow and 600 W supplied power.

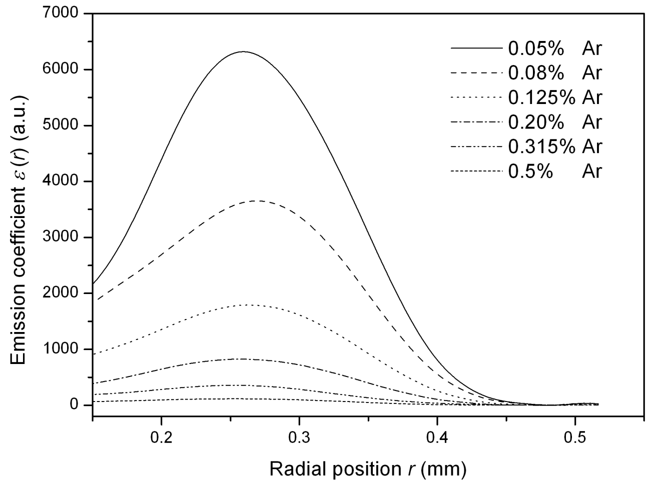


Fig. 7. Variation of the radial emission coefficient of the 587.6 nm atomic He line with the percentage of argon introduced in the plasma for 6 l min$^{-1}$ He flow and 600 W supplied power.

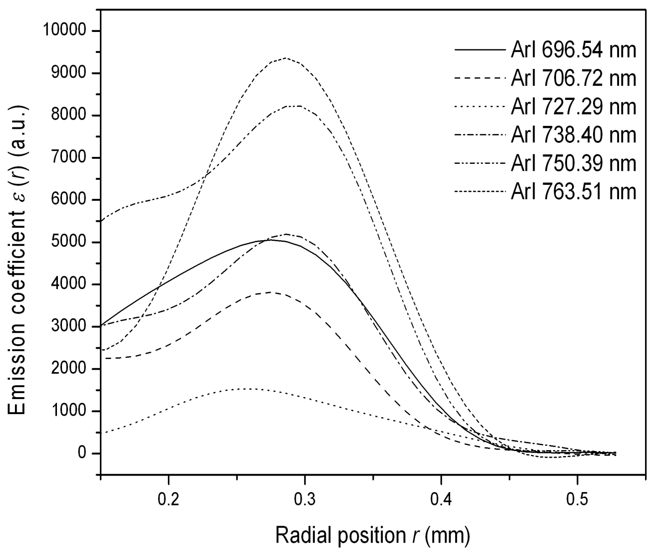


Fig. 8. Radial distribution of the emission coefficient of different atomic argon lines.

### 4.3 Radial behaviour of different ionic and atomic argon lines

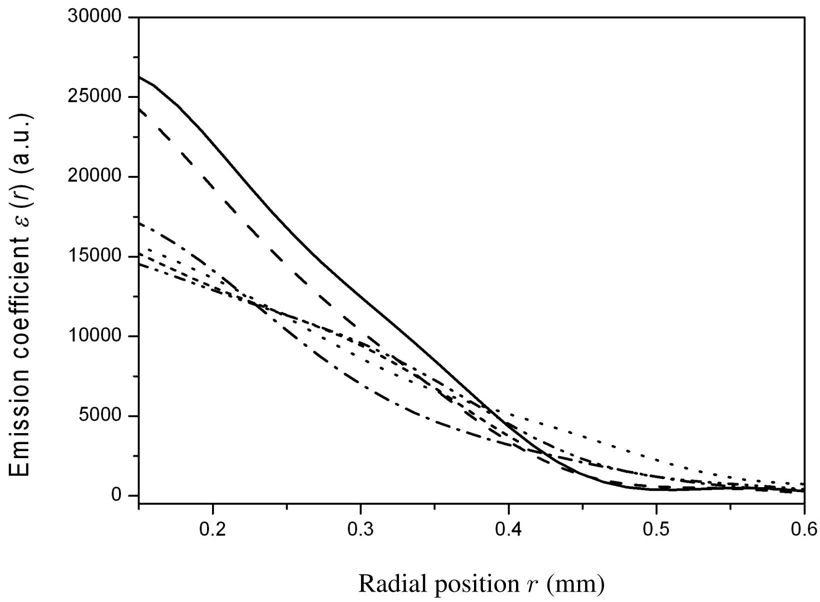


Fig. 9. Radial distribution of the emission coefficient of different ionic argon lines.

In order to test if the measured radial behaviour of the argon ionic and atomic levels is the same for all or only applies to the results obtained for the two measured lines, a number of ionic and atomic argon lines were measured and Abel-inverted. The results are shown in Figs. 8 and 9, were the radial distributions of the emission coefficient of 6 atomic and 12 ionic argon lines respectively are plotted in arbitrary intensity units. These two figures support the explanation for the shape of the radial distribution of the argon lines given in Section 4.1.

Some properties of the measured lines are presented in Table 1, from where it can be seen that all the measured ionic argon lines, which were the lines intense enough to be measured in our plasma, are caused by transitions from states with similar energy. In fact, the electron configuration of the upper level of the transition is the same for all the ionic lines: $3s^2\ 3p^4\ (\,^3\mathrm{P})4p$. With the atomic argon lines happens the same: they are all produced by transitions from states with the same electron configuration, $3s^2\ 3p^5\ (\,^2\mathrm{P}_{1/2})4p$ in this case. The energy of all but two of the Ar II upper levels is close and below the He first metastable level energy (19.82 eV). Those two levels are between the first and second He metastable levels. This points to the energy transfer between He metastable levels and Ar II as the main Ar II population mechanism. The population mechanism in the case of the Ar I levels is probably the resonant energy transfer between argon atoms and $He_2$ metastable molecules, which have a estimated energy in the range 13.3-17.4 eV [7].

Tab. 1. Main parameters of the ionic and atomic argon lines measured.

| **Argon specie** | **Wavelength (nm)** | **$A_{kl}$ ($10^8$ s$^{-1}$)** | **$E_k$ (eV)** |
|---|---|---|---|
| Ar II | 434.8064 | 1.171 | 19.49454 |
| | 442.6001 | 0.817 | 19.54901 |
| | 457.9349 | 0.800 | 19.97254 |
| | 465.7901 | 0.892 | 19.80109 |
| | 473.5905 | 0.580 | 19.26109 |
| | 480.6020 | 0.780 | 19.22290 |
| | 484.7809 | 0.849 | 19.30535 |
| | 493.3209 | 0.144 | 19.26109 |
| | 500.9334 | 0.151 | 19.22290 |
| | 506.2037 | 0.223 | 19.26109 |
| | 514.5308 | 0.106 | 19.54901 |
| | 664.3697 | 0.147 | 19.49454 |
| Ar I | 696.5430 | 0.0639 | 13.32786 |
| | 706.7217 | 0.0380 | 13.30223 |
| | 727.2935 | 0.0183 | 13.32786 |
| | 738.3980 | 0.0847 | 13.30223 |
| | 750.3868 | 0.445 | 13.47989 |
| | 763.5105 | 0.245 | 13.17178 |

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