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# Mass Spectrometry of Atmospheric Pressure Surface Wave Discharges

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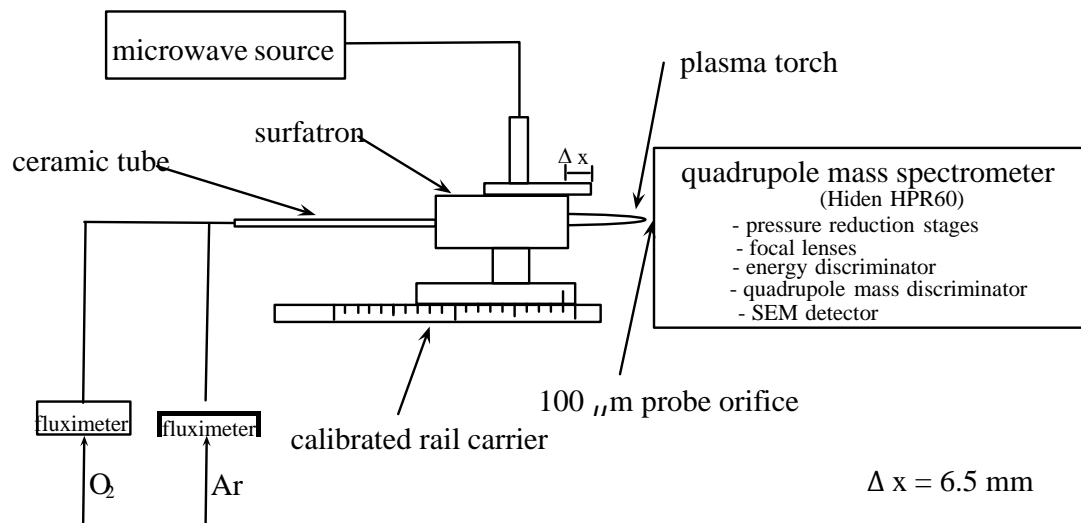
**Abstract.** By applying mass spectrometry techniques, we carried out measurements of ionic mass spectrum and their energy distribution in order to investigate an atmospheric argon discharge by using a surfatron surface-wave device. The mass and energy distribution measurements were performed with fixed flow rate (2.5 SLM) of pure argon gas (99,999%) and different Ar-O<sub>2</sub> gas mixture compositions (99-1, 98-2 and 97-3). The mass spectra and energy distributions were recorded for Ar<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup> and N<sub>2</sub><sup>+</sup>. The axial distribution profiles of ionic mass and their energy were obtained for different experimental conditions as a function of the plasma length. The results showed that the peak of the positive ion energy distributions shifted to higher energies and also that the distribution width increased as the distance between the sampling orifice and the launcher gap was increased. It was also found that under certain experimental conditions the ion flux of atomic species were higher than the ion flux of their diatomic counterpart. The motivation of this study was to obtain a better understanding of a surface wave discharge in atmospheric pressure that may play a key role on new second generation biofuel technologies.

## 1. Introduction

Atmospheric plasmas have found many applications in a wide range of fields such as materials processing [1] and biomedical [2]. There are some recent investigations showing that discharges at atmospheric pressure could also be used to process biomass [3, 4]. By applying mass spectrometry techniques [5, 6], we carried out measurements of the mass spectra and the ion energy distribution function of some representative positive species present in a surface wave discharge produced in Ar and Ar-O<sub>2</sub> mixtures. Since oxygen containing discharges is a possible candidate to be used in biomass treatment due to the presence of reactive oxygen species, knowing the effect of adding O<sub>2</sub> was also important.

The information concerning the ionic species is crucial for the understanding of degradation mechanisms of biomass by ionic impact dissociation in cold plasmas. Positive ions may play an important role on the process of cellulose dissociation and hydrolysis [7]. Moreover, these data can also be used to validate computational models describing the plasma chemistry.





**Figure 1.** Experimental setup scheme.

## 2. Experimental Setup

A surfatron surface-wave launcher was connected to a 2.45 GHz Sairem power supply. The gas flowed continuously through a ceramic tube placed inside the surfatron cavity at a flow rate fixed at 2.5 SLM. The flow rate of each component of the mixture was controlled by a MKS flow meter. Measurements were carried out with Ar gas with purity of 99.999% and also with different Ar-O<sub>2</sub> mixtures (99:1, 98:2 and 97:3) flowing at a fixed rate of 2.5 SLM. Measurements were performed with applied power of 100 W at atmospheric pressure and room temperature.

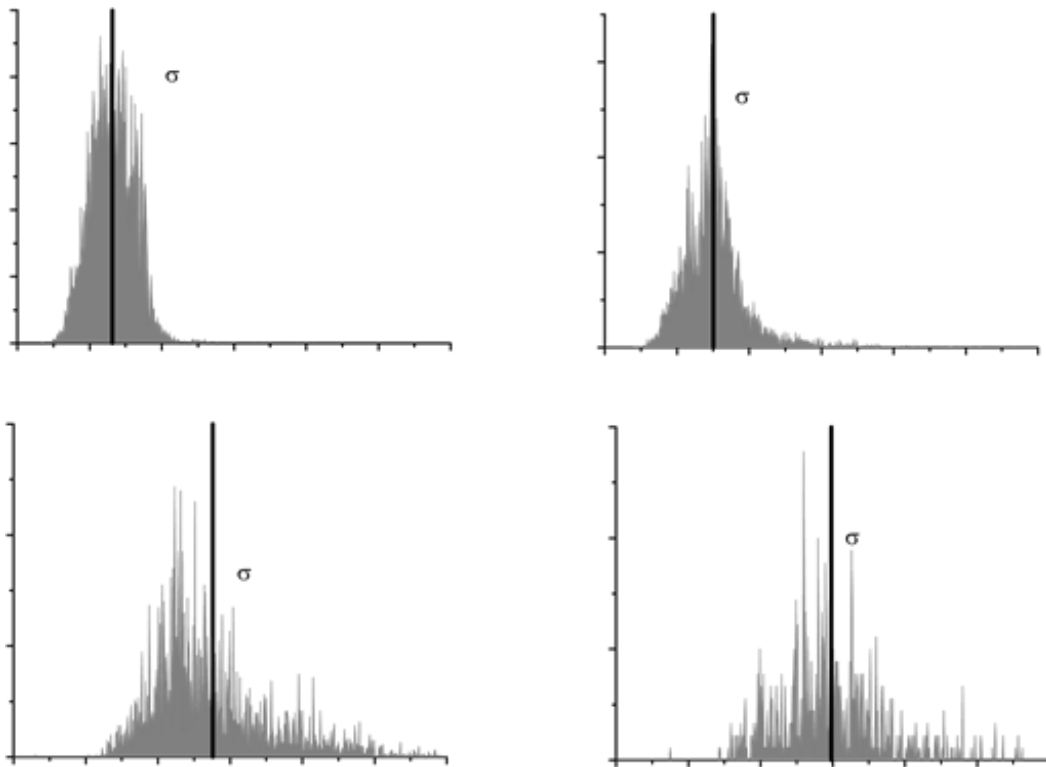
The energy distributions were measured by a Hiden EQP mass/energy quadrupole analyzer HPR60. The surface-wave launcher was mounted on an optical rail carrier, which provided displacements in parallel and perpendicular directions on the spectrometer probe plane. The plasma column was aligned to the sampling orifice by adjusting the surfatron position. The diameter of the sampling orifice was equal to 100 μm. The origin of the axial measurements was located at the position where the surfatron was closest to the sampling orifice. That position was 6.5 mm distant from the launcher gap as shown in figure 1. The measurements were performed in 1 mm step along the plasma and the distribution profiles of the ion energy distribution were obtained. A simplified scheme of the experimental setup is showed in figure 1.

## 3. Ion Energy Distribution Function ( IEDF )

When the mass spectrometer is used to measure the positive ion mass spectra the energy of the particles that will be admitted into the quadrupole stage must be selected. In order to find this optimal energy, the ion energy distribution function (IEDF) must be measured at a fixed mass. Figure 2 shows the IEDF of the species whose atomic mass to charge ratio were equal to 40 au/e. In this case, these species were the ions Ar<sup>+</sup>. This IEDF was measured when the power applied to the plasma source was 100W and a 99:1 Ar-O<sub>2</sub> mixture was used.

The mean energy of the distribution is nearly constant if the distance is lower than 3 mm, but it changes when the distance is higher or equal to 4 mm. Because of that, there is no fixed energy that could simultaneously yield the maximum count rate in all cases. Therefore the total positive ion flux will be better estimated as the IEDF summation,

$$Y_{\alpha}^a = \sum_i F(\varepsilon_i) \quad (1)$$



**Figure 2.** IEDF of the ionic species whose atomic mass to charge ratio were equal to 40 au/e. In this case, these species are the ions  $\text{Ar}^+$ . This IEDF was measured when the power applied to the plasma source was 100W and a 99:1 Ar- $\text{O}_2$  mixture was used. The IEDF mean energy  $hE_i$  and standard deviation  $\sigma$  values are also shown. The thick vertical line indicates the mean energy position.

where  $Y_\alpha^a$  is the total count rate of specie  $\alpha$  and  $F_\alpha(\varepsilon_i)$  is the count rate of specie  $\alpha$  at energy interval  $\varepsilon_i + \Delta\varepsilon$ . The relative ion flux  $Y_\alpha^r$  of specie  $\alpha$  was calculated as the ratio between  $Y_\alpha^a$  and the sum of all total fluxes,

$$Y_\alpha^r = \frac{Y_\alpha^a}{\sum_\beta Y_\beta^a} \quad (2)$$

Bruggeman *et al* [6] also reported high mean energies in the IEDF measured in a plasma at atmospheric pressure using the same mass spectrometer and a sampling orifice of 100  $\mu\text{m}$ . They claimed that the IEDF mean energy decreased to values comparable to the thermal energy when a 20  $\mu\text{m}$  sampling orifice was used instead. Indeed, if the plasma sheath length was approximately equal to the diameter of the sampling orifice, the positive ions experienced a nearly collisionless electrode fall. That could also explain the high mean energies of the IEDF we measured. We will assume that in spite of this effect there were no significant changes in the relative abundance of different species.

#### 4. Mass Measurements of Positive Ions

Figures 3 to 6 show the count rates and relative ion fluxes of  $\text{Ar}^+$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  as a function of distance. The argon (Ar) and oxygen ( $\text{O}_2$ ) gas flow rates were controlled in order to obtain relative concentrations of 99:1, 98:2 and 97:3 in the Ar- $\text{O}_2$  mixture. The total flow rate was kept constant at 2.5 SLM.

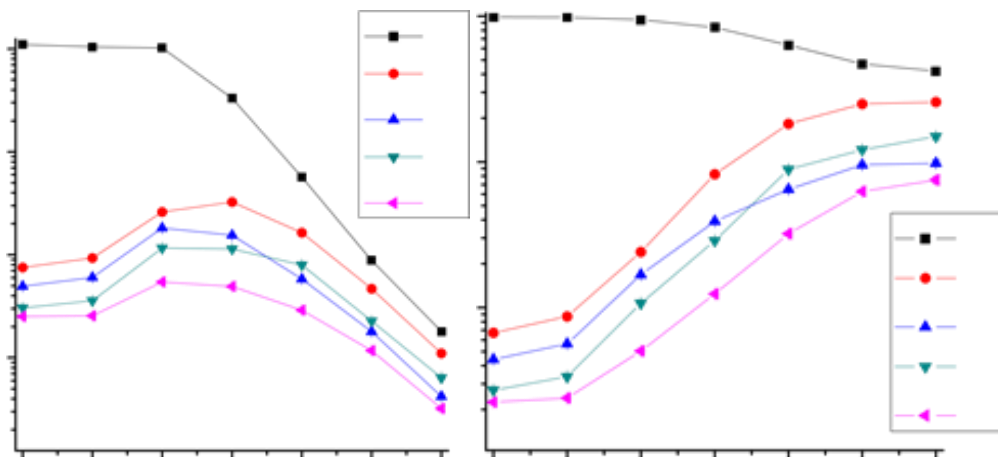
The result of the measurement in which the discharge was produced in pure Ar is shown in figure 3. Near the gap, at  $x = 0$  mm, the relative ion flux of  $\text{Ar}^+$  was much larger than the ion flux of other

species as expected, since this plasma region has lower concentrations of species coming from the surrounding air. As the distance increases, the relative relevance of  $O^+$ ,  $O_2^+$ ,  $N^+$  and  $N_2^+$  increased, since these ions were originated by species from air diffusing into the discharge and whose concentration must increase as a function of distance. On the other hand, the absolute count rate of all species decreased after a given distance because the plasma degree of ionization and temperature decrease with distance. The absolute count rates of  $O^+$ ,  $O_2^+$ ,  $N^+$  and  $N_2^+$  exhibited a maximum value due to the effect of air species diffusing into the plasma.

Another interesting feature of this discharge was that the ratio between the molecular ion and the respective atomic ion decreased as a function of distance. This may be explained by the fact that at the region near the gap heavy species and electrons are hotter, producing high rates of thermal and electron impact dissociation. Since the gas and electron temperature decreases with distance, ion-electron and ion-ion recombination rate of atomic species become much higher than dissociation rates.

When the oxygen ( $O_2$ ) gas was added to argon, the relative ion flux of  $O_2^+$  and  $O^+$  at point zero were higher than the relative ion flux of  $N_2^+$  and  $N^+$ , as expected. In all cases in which a Ar- $O_2$  mixture was used, the concentration of the atomic ions was often higher than the concentration of the respective molecular ions at points near the gap. At a given point more distant from the gap, however, this relation necessarily changed.

This could also be explained by the fact that at the region near the gap heavy species and electrons are hotter. Nevertheless, only a detailed study of the electron and reaction kinetics

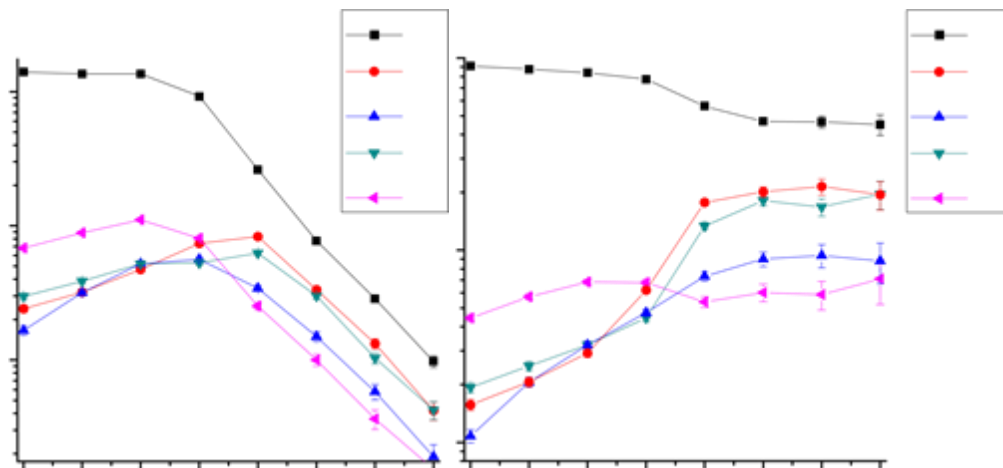


**Figure 3.** On the left, absolute count rate of  $Ar^+$ ,  $O^+$ ,  $O_2^+$ ,  $N^+$  and  $N_2^+$  as a function of distance. On the right, relative ion flux of  $Ar^+$ ,  $O^+$ ,  $O_2^+$ ,  $N^+$  and  $N_2^+$  as a function of distance. Measurements were carried out with applied power of 100W and pure Ar (99,999%).

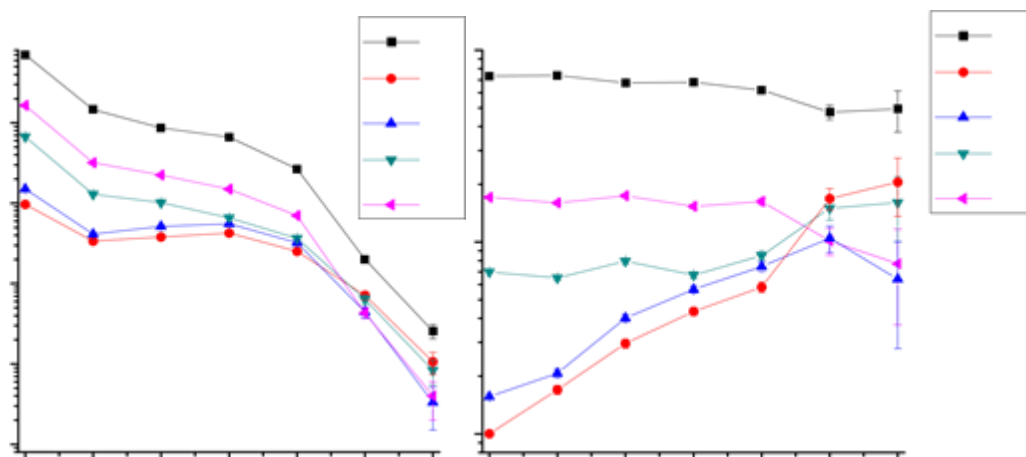
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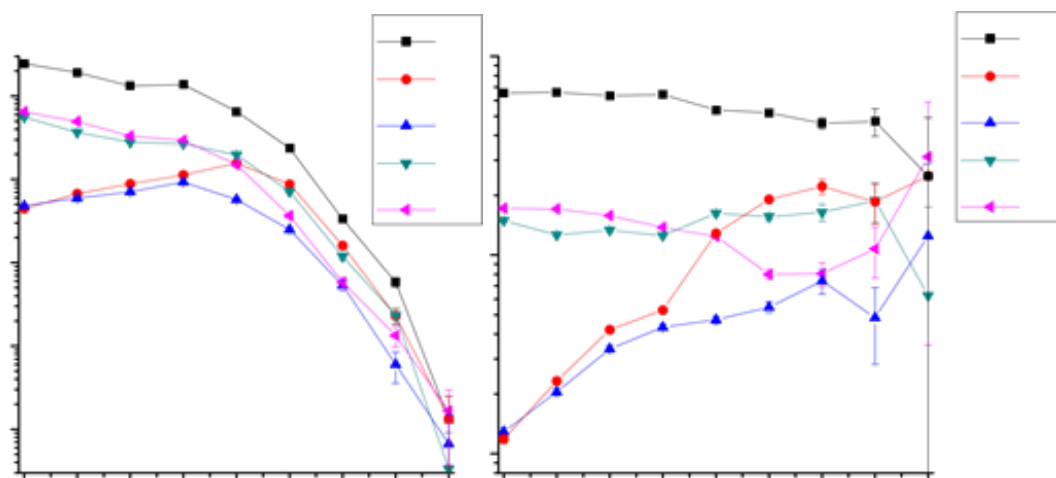
**Figure 4.** On the left, absolute count rate of Ar<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup> and N<sub>2</sub><sup>+</sup> as a function of distance. On the right, relative ion flux of Ar<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup> and N<sub>2</sub><sup>+</sup> as a function of distance. Measurements were carried out with applied power of 100 W and a Ar-O<sub>2</sub> (99:1) mixture.



**Figure 5.** On the left, absolute count rate of Ar<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup> and N<sub>2</sub><sup>+</sup> as a function of distance. On the right, relative ion flux of Ar<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup> and N<sub>2</sub><sup>+</sup> as a function of distance. Measurements were carried out with applied power of 100 W and a Ar-O<sub>2</sub> (98:2) mixture.

supplemented with experimental information about electron and gas temperature could explain why most of the molecular positive species were dissociated into its atomic counterpart.

The relative ion fluxes of atomic ions were higher near the gap in all cases, but this effect was more pronounced when gas mixtures 98:2 were used. In the case of the mixture 97:3 and the pair N<sub>2</sub><sup>+</sup> and N<sup>+</sup> this was certainly true only at the distance  $x = 0$  mm. For the pair O<sub>2</sub><sup>+</sup> and O<sup>+</sup> the atomic ion flux was higher only if the distance was lower or equal to  $x = 3$  mm. On the other hand, when the gas mixture 98:2 was used the N<sup>+</sup> flux was higher from the origin to  $x = 3$  mm and the O<sup>+</sup> flux was higher from the origin to  $x = 4$  mm. Taking into account the fact that O<sub>2</sub> causes electron attachment, it is expected a drop on electron density as O<sub>2</sub> concentration increases, causing a temperature drop.



**Figure 6.** On the left, absolute count rate of  $\text{Ar}^+$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  as a function of distance. On the right, relative ion flux of  $\text{Ar}^+$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  as a function of distance. Measurements were carried out with applied power of 100 W and a Ar- $\text{O}_2$  (97:3) mixture.

This explains why dissociation decreases if  $\text{O}_2$  concentration is higher than a threshold value. In order to satisfactorily explain why the mixture 98:2 produced higher dissociation, the electron and the reaction kinetics must be studied. Experimental information about electron and gas temperature would also be useful.

## 5. Conclusions

The axial distribution profiles of ionic showed that the addition of a small percentage of oxygen ( $\text{O}_2$ ) in the gas mixture changed the relative abundance of oxygen ionic species in the plasma torch. In the region of the plasma column near the launcher gap, not only the oxygen species were dominant in comparison with nitrogen species, but also atomic species were dominant in comparison with their diatomic counterpart. Nevertheless, in the plasma region near the end of the plasma column, diffusion effects always lead to an increase of the concentration of nitrogen species relative to oxygen species. Diffusion effects also explains why the ion flux of nitrogen species first increase before decreasing due to recombination at regions near the end of the plasma column. It was also observed that as the axial coordinate increased, the relative flux of the atomic ions decreased in comparison with the relative flux of their diatomic molecule counterpart, showing that dissociation rates of molecules decreased, probably due to plasma cooling and decreased plasma density.

## References

- [1] Benedikt J, F F, Yanguas-Gil A and von Keudell A 2006 *Appl. Phys. Lett.* **89** 251504
- [2] Stoffels E, Flikweert A J, Stoffels W W and Kroesen G M W 2002 *Plasma Sources Sci. Technol.* **11** 383
- [3] Wang C X and Qiu Y P 2007 *Surf. Coat. Technol.* **201** 6273
- [4] Souza-Corrêa J A, Pimenta M T B, Rocha G J M, Gomez E O, Squina F M, Curvelo A A S and Amorim J
- [5] 2010 *Plasmas for environmental issues* (Sofia: St. Kliment Ochridsky University) p 68
- [6] Malovi'c G, Pua'c N, Lazovi'c S and Petrovi'c Z 2010 *Plasma Sources Sci. Technology* **19** 034014
- [7] Bruggeman P, Iza F, Lauwers D and Gonzalvo Y A 2010 *Plasma Sources Sci. Technol.* **43** 012003 (6 pp)
- [8] Song C L, Zhang Z T, Chen W Y and Liu C 2009 *IEEE Transactions on Plasma Science* **37** 1817–1824