Optical characterization of atmospheric pressure plasma excited by surface waves

L. Sudrie, L. Thérèse and Ph. Guillot

Laboratoire Diagnostics des Plasmas Hors Equilibre (DPHE), Université de Toulouse, INU Champollion, Albi, France

Abstract: In this work, characterization of surface wave discharges (SWD) in argon at atmospheric pressure was performed by intensified charge coupled device (ICCD) camera and optical emission spectroscopy (OES). The objective is to determine the spatial distribution of different species along the plasma jet and to estimate the electronic temperature.

Keywords: microwave induced plasma, ICCD, OES, electronic temperature calculation

1. Introduction

During the last decade increasing interest in cold atmospheric plasma jets (APPJ) has been reported. For example, APPJs are largely investigated in diverse fields such as decontamination and sterilization, nanomaterial synthesis, or analytical chemistry. This versatility in various application fields is provided by APPJs ability to propagate in ambient air and to allow the creation of enriched environments composed of ions, radicals and excited species. Many different APPJs exist, being the one studied in this work a microwave induced plasma, named Surfatron. As describe by Moisan in 1977 [1], the Surfatron was developed first for elemental analysis [2]. Moreover, soft ionization capabilities have been demonstrated [3] and recent studies reported the use of microwave induced plasmas excited by surface waves as soft ionization/desorption sources for Mass Spectrometry [4].

The surface wave plasma source (S-wave) used in this study is a commercial compact source (see Fig. 1) operating at atmospheric pressure. The plasma is generated in a dielectric quartz tube (4 mm internal diameter and 6 mm external diameter) by a solid-state microwave generator (200 W, 2.45 GHz). The microwave electric field propagates longitudinally at the dielectric/plasma interface. Radially, the microwave electric field is strongly attenuated (the skin depth is small). A plasma column is generated and sustained with varying lengths as a function of the operating microwave power, gas flow and gas nature. Two tuning adjustments are provided to match the impedance. In operation, nearly 0% of reflected power is attained using the integrated tuners.

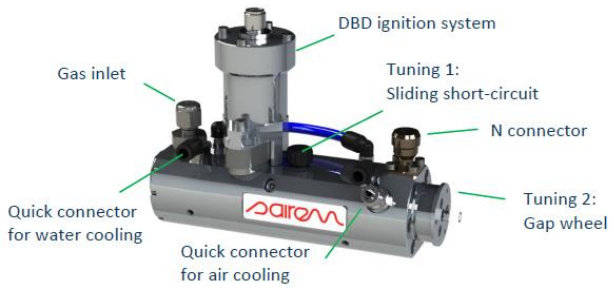

Fig. 1. Surfatron source from SAIREM [5].

The final aim of this work is to couple the microwave plasma source with a Time-Of-Flight Mass Spectrometer (TOF MS) for liquid sample analysis. There is, however, an important preliminary step that consists in the characterization of the source. In this sense, ICCD imaging and optical emission spectroscopy (OES) were performed for different gas flow rate and microwave power conditions in order to find the most stable plasma conditions, and to measure electronic temperature.

2. Experimental setup

The experimental setup is shown in Fig. 2. It is composed of:

- S-wave plasma source with a quartz tube 150 mm long, with its microwave generator, both designed by Sairem SAS.
- ICCD camera (Princeton instruments, PI-MAX, 1024 pixels × 1024 pixels) in combination with a UV objective (Nikkor zoom 80-400 mm f/4.5-5.6 ED) and several bandpass interference filters to observe the emission (argon Thorlabs FB 810-10, nitrogen Thorlabs FB 340-10),
- UV-visible spectrometer (Ocean optics HR2000+), wavelength response 200-1100 nm with 1 nm resolution. In order to obtain spatial resolution, two optical lenses with 300 and 100 mm focal distance and a diaphragm were used to eliminate non-parallel emission.

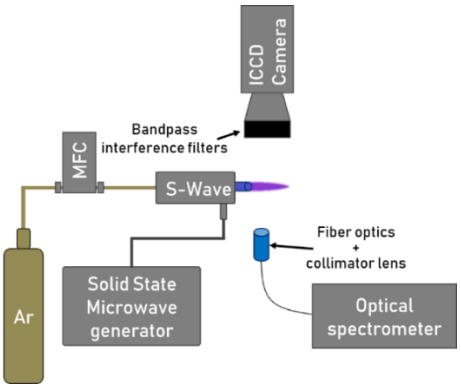

Fig. 2. Experimental setup diagram.

3. Results and discussion

a. ICCD imaging

Fig. 3 shown the spatial optical emission of plasma jets without filter at two different flow rates and microwave injected powers (1-2 l min^{-1} / 70-180 W). The plasma jets propagates inside the dielectric tube and extend outside to

the ambient air. The mark 0 cm corresponds to the end of the metallic part, 1 cm is the quartz tube end, and the mark 1.8 cm corresponds to the end of the most intensive plasma area for 1 l min^{-1}, 180 W.

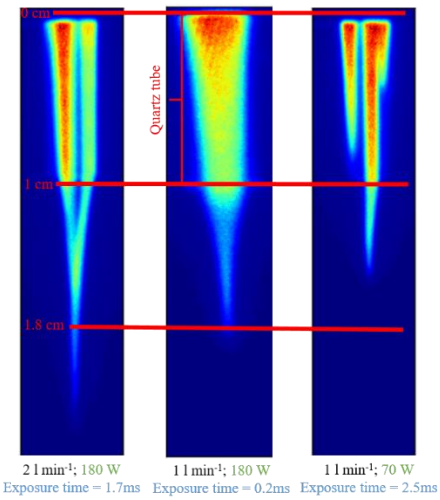

Fig. 3. ICCD pictures without filter; argon, 1-2 l min^{-1}, 70-180 W.

For the operating condition, 1 l min^{-1} and 180 W, the plasma jet generated is homogeneous. Decreasing the microwave power (180 to 70 W) for the same flow rate (1 l min^{-1}) or increasing the gas flow rate (1 to 2 l min^{-1}) for the same microwave power (180 W) has resulted in non-homogeneous plasma jets: it splits in different parts moving around the quartz tube. This can be explained as a contraction of the plasma, due to non-homogenous plasma heating and gas temperature gradient apparition[6]. It is a well-known phenomenon in plasma held by high frequency electromagnetic wave propagating along a surface wave-guide. According to an analytical point of view, a homogeneous plasma is strongly desired. As a result, the operating conditions (1 l min^{-1} 180 W) have been chosen as reference conditions.

Fig. 4 shows the spatial optical emission of plasma jets obtained using argon and nitrogen bandpass filters, respectively centered at 810 nm (Ar I 4s → 4p) and 335 nm (N_2 C → B). As expected, atomic emission (Ar I 810 nm) are mostly located in the quartz tube and molecular emission (N_2 335 nm) were shown to be maximum in the ambient air.

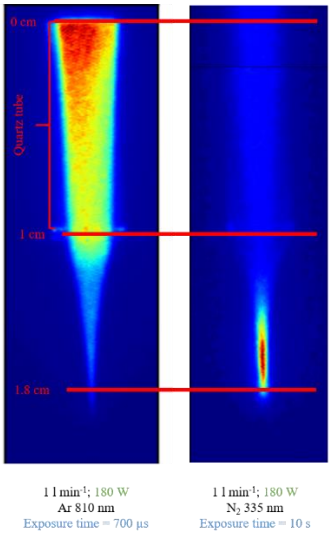

Fig. 4. ICCD pictures without filter; argon, 1-2 l min^{-1}, 70-180 W.

But the difference in exposure time show argon emission much stronger than nitrogen emission.

b. Optical emission spectroscopy

Spatially resolved optical emission spectroscopy along the plasma jet was performed.

The S-wave plasma source has been mounted on a manual 2D stage, allowing precise axial and radial displacement. Spectra have been recorded every 0.2 cm along the plasma jet. In Fig. 5 spectrum at 0.8 cm from the quartz tube exit, is shown. Emitting species from the gas and the ambient air have been identified in Table *1*.

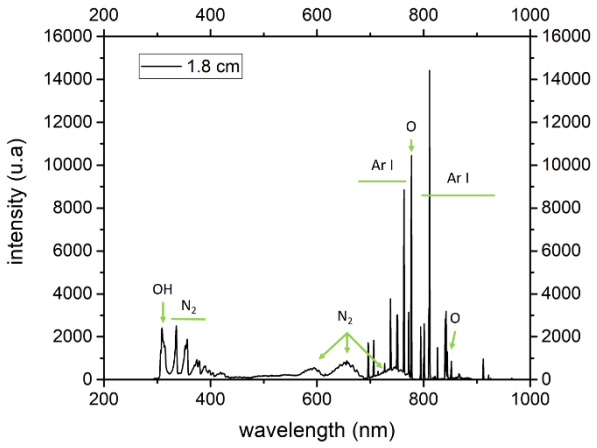

Fig. 5. Spectrum at 0.6 cm from the end of the quartz tube; 180 W, 1 l min^{-1}.

Lower level configuration of all visible argon emission lines between 670 nm and 1000 nm is $3p^5 4s$, which is divided in four energetic states: 11.54 eV, 11.62 eV, 11.72 eV, and 11.82 eV. The two energy levels 11.54 and

11.72 eV correspond to metastable states. Only radiative states were used for temperature calculations.

Table 1. Identification emission lines from Fig. 5.

Wavelength (nm)	Species	Level energy $E_u \rightarrow E_i$ (eV)	Lower level type
308.9	OH	A → X	
337.13	N_2	C → B	
340-780	N_2		
696.54	Ar I	13.32 → 11.54	Metastable
706.72	Ar I	13.30 → 11.54	Metastable
714.70	Ar I	13.28 → 11.54	Metastable
727.29	Ar I	13.32 → 11.62	Radiative
738.39	Ar I	13.30 → 11.62	Radiative
750.38	Ar I	13.47 → 11.82	Radiative
751.46	Ar I	13.27 → 11.62	Radiative
763.51	Ar I	13.17 → 11.54	Metastable
772.42	Ar I	13.32 → 11.72	Metastable
776.59	O I		
794.81	Ar I	13.28 → 11.72	Metastable
801.47	Ar I	13.09 → 11.54	Metastable
810.36	Ar I	13.15 → 11.62	Radiative
811.53	Ar I	13.07 → 11.54	Metastable
826.45	Ar I	13.32 → 11.82	Radiative
840.82	Ar I	13.30 → 11.82	Radiative
842.46	Ar I	13.09 → 11.62	Radiative
844.63	O I		
852.14	Ar I	13.28 → 11.82	Radiative
912.29	Ar I	12.90 → 11.54	Metastable

As it was shown in the ICCD camera images, molecular emissions were maximum in the ambient air. Similar behavior is observed in Fig. 6. Before 1.5 cm, molecular emission is nearly inexistent, compare to argon emission. Oxygen and nitrogen emission lines peak around 1.8 cm.

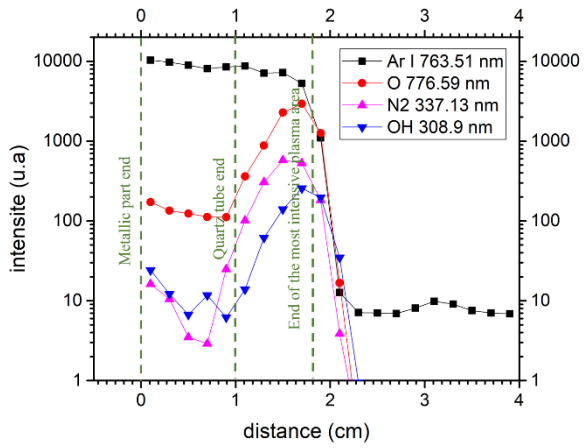

Fig. 6. Line emission intensity along the plasma after 0.8 cm from the quartz tube; 180 W, 1 l min^{-1}.

c. Excitation and electronic temperature

The plasma studied in this work is far away from local thermodynamic equilibrium. Spectroscopic methods were used to estimate the excitation temperature and the electron temperature with argon optical emission lines intensities recorded along the plasma jet direction. Available isolated and intense lines were used, but unfortunately with upper level energy quite close.

The electronic temperature (T_e) was calculated without any assumption on local thermodynamic equilibrium, using the two temperatures line-to-continuum intensity ratio method from Sola [7]:

$$\frac{I_1}{I_{continuum}} = \frac{A}{T_e}\left[exp\left(\frac{B}{T_e}\right) exp\left(-\frac{C}{T_{exc}}\right)\right]\left(\xi - 0.7exp\left(-\frac{D}{T_e}\right)\right)^{-1} \quad (1)$$

$$A = \lambda C_r \frac{A_{ij} g_i}{U}\ nm.K$$

$$B = \frac{E_{ioni} - \Delta E_{ioni}}{k_B}\ K$$

$$C = \frac{E_i}{k_B}\ K$$

$$D = \frac{hc}{\lambda_{ij} k_B}\ K$$

ξ is the free-bound continuum correction factor, U is the partition function of ion, $C_r = \frac{h^4 \varepsilon^{3/2} c^3}{256 \times \pi^3 e^6 k_B}$, E_{ioni} is the argon ionization energy, ΔE_{ioni} is the lowering of the ionization potential, h is the Planck's constant, c the celerity, all value were taken from [7].

The excitation temperature (T_{exc}) had been evaluated by the line ratio method [8]:

$$\frac{I_1}{I_2} = \frac{\nu_1 \times g_{i,1} \times A_{i,1}}{\nu_2 \times g_{i,2} \times A_{i,2}} exp\left(-\frac{E_{i,1} - E_{i,2}}{k_B \times T_{exc}}\right) \quad (2)$$

$I_{1/2}$ is the relative emission intensity, ν is the wavelength in Hz, $A_{i,\,1/2}$ is the Einstein coefficient in s^{-1}, g the statistic weight, k_B the Boltzmann constant, E the energy level, ν the transition frequency. Index i corresponds to the upper level, 1 corresponds to a transition line, and 2 corresponds to the other one.

For T_e calculation, continuum intensities were taken at the feet of each line presented in Table 2, and calculation were done for each one. The mean value is presented in Fig. 7.

Table 2. Argon wavelengths used for calculations.

λ (nm)	A ×10^8 (s^{-1})	E_i (eV)	g
738.39	0.085	13.30	5.0
750.38	0.45	13.47	1.0

T_e and T_{exc} were calculated using the lines presented in Table *2*. The results are presented in Fig. 7. At the tube exit, T_e and T_{exc} were similar, but at the beginning of the molecular area (1.4 cm), T_e becomes higher. At the end of this area T_e and T_{exc} maximize, while lower temperature was expected. Before 1.8 cm T_e mean value is 6747 K, after is 8125 K, it's in a good agreement with value found in the literature [7].

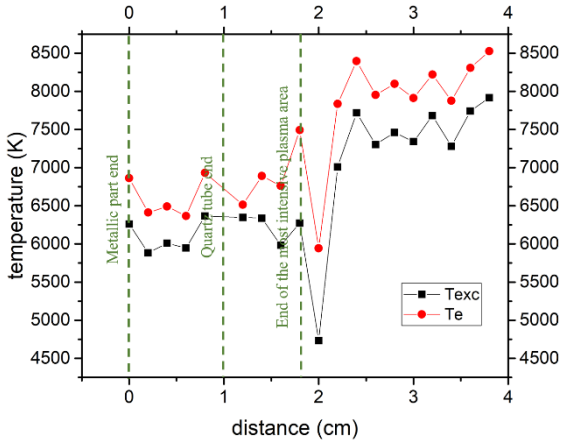

Fig. 7. T_e and T_{exc} as a function of the distance; 180 W, 1 l min^{-1}.

4. Conclusion

Optical diagnostics were performed to allow a better understanding of the plasma along it axis. Plasma length and homogeneity depend on gas flow and power. In order to calculate the electronic temperature, a homogenous plasma is first obtained by optimizing the conditions (Ar flow rate and applied power). Lower temperature was obtained in the first part of the plasma (before 0.8 cm). In aim to complete those diagnostics rotational temperature will be calculated.

This characterization has shown stable plasma behavior without perturbation. The final goal is to couple the S-wave with a mass spectrometer for liquid sample analysis. In this sense, a comparison of the plasma in presence and absence of the sample will be perform that will help to optimize the way to introduce it.

5. Acknowledgements

This research work was supported by the Occitanie region, France.

The authors would like to express acknowledgement to SAIREM SAS for the material and technical support.

6. References

[1] M. Moisan, United States Patent, 4049940 (1977).
[2] J. Hubert, Spectrochimica Acta Part B: Atomic Spectroscopy, **34**, 1 (1979).
[3] E. Poussel, Analytical Chemistry, **60**, 9 (1988).
[4] X. Zhan, Analytical Chemistry, **85**, 9 (2013).
[5] Sairem (2018).
[6] Y. Kabouzi, Journal of Applied Physics, **91**, 3 (2002).
[7] A. Sola, Journal of Physics D: Applied Physics, **28**, 6 (1995).
[8] R. K. Marcus, Glow Discharge Plasmas in Analytical Spectroscopy, (2003).