Preliminary results in atmospheric pressure Ar-He microwave sustained discharges

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This is a preliminary study previous to the use of an Ar–He microwave (2.45 GHz) sustained discharge at atmospheric pressure as a source for sample excitation for chemical analysis by optical emission spectroscopy. First results obtained for an atmospheric pressure, surface wave sustained Ar–He plasma column are revised and special attention is paid to linear absorbed power density, column length, radial contraction and atomic line intensity, all of them being the most influential parameters for the further application of those discharges to chemical analysis. In addition some important aspects on discharge cooling that may alter the behaviour and measures of the discharge are highlighted.

1. Introduction.

Gas mixtures nowadays are a usual feature in most of the technological applications of plasmas such as chemical analysis, steel nitriding, volatile organic compounds (VOCs) abatement or plasma display panels. The first of the applications named above has been widely developed in the last decades, especially for inductively coupled plasmas (ICP) and glow discharges (GD).

Several studies have been made on the use of surface wave discharges for chemical analysis, almost always related to single gas discharges. As a previous step to its use for chemical analysis, a short study has been performed concerning the most influential features related to the excitation capabilities of an Ar–He SWD.

2. Experimental Setup and Procedure.

The setup corresponding to this paper is composed of a SAIREM 12KT/T microwave generator able to supply 2000 W in continuous mode equipped with a water cooled circulator to avoid power reflection damage. Microwave power is coupled to the discharge with a surfaguide [1].

The discharge is contained in quartz tubes of 2 and 3 mm inner and 3 and 4 mm outer radii, respectively, surrounded by a 8.5 mm (radius) cooling column filled with a dielectric liquid (1–Tetradecene) or air alternatively to avoid quartz tube erosion. In our experiments the plasma column is extended to both sides of the wave launcher, a direct and an inverse column appearing.

High purity Ar and He (99.99%) is introduced into the discharge by gas flow controllers (Bronkhorst Hightech) of different maximum flow limits (0.25 and 5 slm/min). Different Ar and He fluxes were used to achieve different proportions of gases in the discharge, keeping the same total flux.

An optical fibre is used to drive the light emitted from the discharge to a 1 m Jobin Yvon–Horiba Czerny–Turner type monochromator previously calibrated and equipped with a 2400 grooves/mm holographic grating, a Hammamatsu R928P photomultiplier and a Symphony CCD-1024x256-OPEN-STE CCD camera.

Two different sets of experiments were carried out. In the first one inner and outer dielectric liquid cooled quartz tube radii were 2 and 3 respectively and measures where taken at z = 4.5 cm from the end of the column. The second set was performed with a 3 and 4 inner and outer radii quartz tube dielectric liquid and air cooled alternatively. In this second set measures were taken at z = 1.5 cm from the end of the column.

In each measure, spectrums from OH radical (306 – 312 nm) were taken, as well as those of some Ar I lines. Line H_β from Balmer series was also taken for electron density diagnosis. No atomic lines from He or ionic lines from Ar were detected under the experimental conditions presented in this paper.

3. Results and Discussion.

3.1 Radial contraction.

When dealing with high enough pressure discharges radial contraction is one of the main problems to overcome in some applications since it reduces the contact volume of the samples to be analyzed, abated or modified.

Main mechanisms and causes of radial contraction and filamentation in SWDs have been studied elsewhere [2] and a strong influence of the inner tube radius and gas thermal conductivity (κ), which is directly related to the existence of high gas temperature (T_{gas}) gradient, has been found.

	He	Ar
κ(300 K)	20.6	1.17
κ(2000 K)	82-103	6.45

Table 1. He and Ar thermal conductivity (in 10^{-2} W/mK) for different gas temperatures

Given that Ar has a lower thermal conductivity than He (*Table 1*), it shows higher contraction under the same experimental conditions. But when the He proportion is increased in the mixture, thermal conductivity rises [3] and T_{gas} gradients decrease. The macroscopical result of this variation is that filamentation disappears leaving a single plasma column that fills the whole tube's cross section when helium proportion is increased, as can be seen in *Figure 1*.

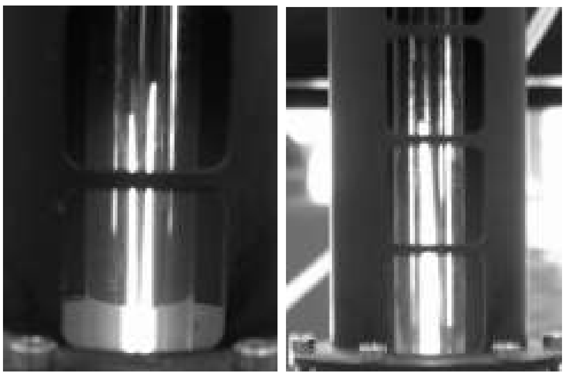

Figure 1. Reverse columns of an Ar/He discharge in a 3 mm outer, 2 mm inner radii quartz tube for [He] = 0% (left) and [He] = 20% (right).

Of course, the inner radius of the discharge tube is also related to this behaviour as explained above. While the helium proportion required to avoid filamentation in both direct and inverse columns in a 2 mm inner radius tube is 20%, it increases to 40% in a 3 mm inner radius tube.

3.2 Linear power density.

It is well known that in a SWD, power propagates as a wave through the discharge tube decreasing the wave's power as it moves farther from the launcher so that, the higher the wave's power, the longer the discharge.

In our experiments, helium was progressively added to a pure argon discharge keeping the length of the direct column constant. While generating an air cooled discharge, it was not possible to sustain the discharge for Helium concentrations over 30% due to inefficient cooling. On the other hand, while generating a liquid cooled discharge, He concentrations ranged up to 60%.

In capillary discharges, one of the macroscopic parameters allowing us to understand the amount of energy needed to sustain the discharge is linear power density (L), which is the absorbed power (P_{abs}) divided by the column length (l), taken as the sum of both direct and inverse column lengths. *Figure 2* shows linear power density for the different conditions considered in this paper.

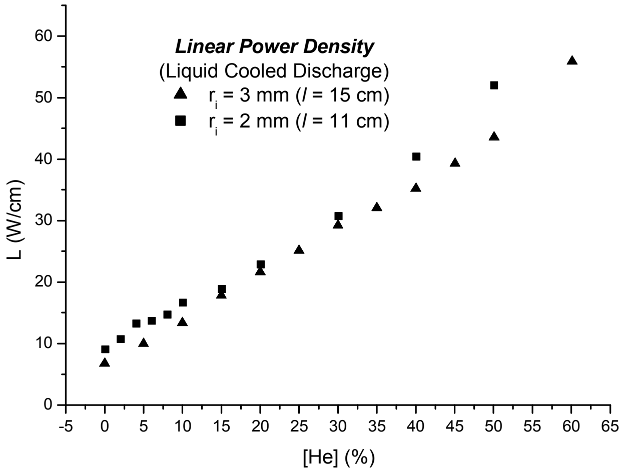

Figure 2. Linear power density (L) dependence on He concentration for a given geometric conditions (discharge length and tube radius)

It can be seen that there exist an almost linear dependence for L on He concentration, showing that, when He is introduced into the discharge, more energy is needed to keep the same column length for a given discharge tube radius.

This probably happens because the ionization potential of He (24.73 eV) is much higher than that of Ar (15.80 eV).

3.3 Electron density.

In SWDs, the end of the column is determined by a critical value in the electronic density and, on the other hand, electrons are known to control discharge kinetics, so it is important to be aware of the variations this parameter undergoes.

Electron density was evaluated from the Stark broadening of the Balmer series H_β (486.13 nm) line using KGS theory [4] and the GC model [5], obtaining similar results from both calculations. As expected in SWDs, electron density decreases

(*Figure 3*) as we approach the end of the column (lower *z* values).

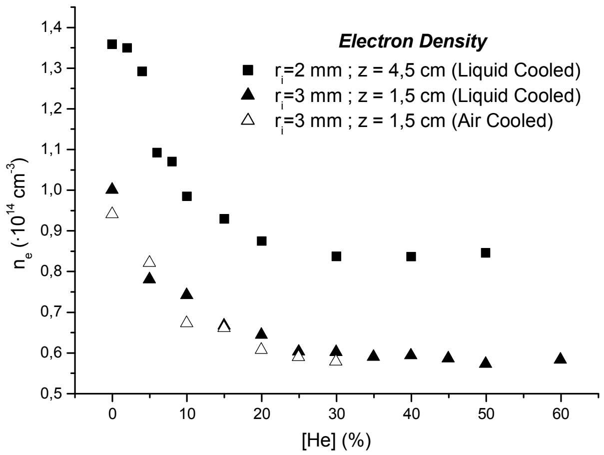

Figure 3. Electron density for the different experimental conditions measured from the H_β Balmer series Stark broadening.

The introduction of He in the discharge even in small amounts implies a quick decrease in electron density as can be seen in *Figure 3*. Once again, this behaviour could be expected knowing that the ionization potential of He is much higher than that of Ar. Nevertheless surpassing a certain He concentration (30 %), electron density seems to stabilize.

3.4 Atomic line emission intensity.

Line intensity is related to the population density of the upper level of a given transition and so it is important to know the deviations occurring when Helium is added to the discharge since this can provide some insights into plasma kinetics.

Up to a He concentration of 20%, all intensities decrease monotonically, as can be seen in *Figure 4*. In this figure, relative intensity is calculated taking into account the dilution factor as in [6]. For He concentrations over 20% in discharge line intensities, and so populations, behaviour depends on the upper level of the transition.

For those transitions whose upper level is a low energy one (4p) (e.g.: Ar I 696.5 nm), intensity undergoes little or no variation up to 60% He concentration. This is the same behaviour seen for electron density in *Figure 3*.

A small increase is detected for lines belonging to higher energy upper states (5p, 4d 6s) (e.g.: Ar I 430.0 nm) over the previously mentioned He concentration; and finally, for those transitions whose upper level is closer to the ionization degree (5d, 7d, 6d) (e.g.: 522.1), relative intensity increase is more significant.

This is related, as depicted above, to electron density, showing that n_e controls discharge kinetics [7]. Deviations occurring in higher level relative densities are the same as those presented in [6] and may be related, as mentioned there, to reactions with metastable He_2 molecules, whose energy is high enough to excite the higher atomic Ar levels from ground level.

Since more energy is absorbed by the discharge and taking into account that, in microwave discharges, electrons are the main responsible party for absorbing electromagnetic field energy and distributing it among the rest of the plasma particles, it could be thought that the bulk of the electron energy distribution function is displaced to higher energies, facilitating excitation of Ar atoms from the metastable levels to those close to the ionization limit.

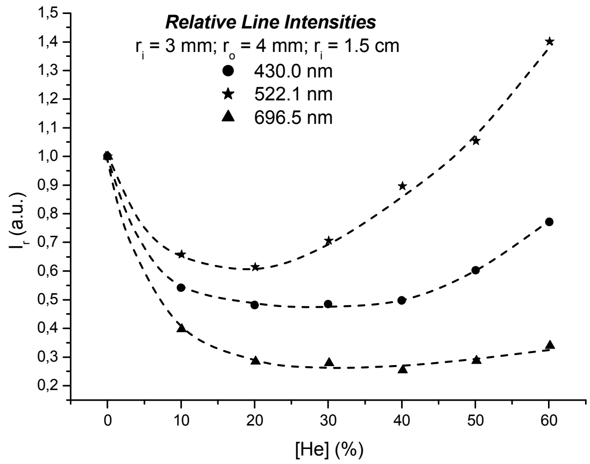

Figure 4. Some Ar I line's relative intensity calculated taking into account the dilution factor.

3.5 1–Tetradecene and air optical, electric and thermal performance.

Some troubles may arise from the use of cooling to avoid discharge tube degradation. First of all, it is important to ensure that thermic properties of the coolant are such that heat is efficiently evacuated.

Another potential problem is microwave power absorption by the coolant. If microwave absorption by the coolant is too high, this may result in a higher power demand to sustain a column with the same characteristics.

Finally, optical performance is also important when optical diagnosis of the discharge is to be carried out. Absorption of some lines or bands is a usual feature and may disable some diagnostic techniques or modify the results.

In the case of air and 1–Tetradecene, while the first one is easy to implement, its thermic properties are generally poorer compared to those of a liquid coolant, particularly 1–Tetradecene, and so no discharge with He concentration over 30% could be sustained without endangering the tube.

On the other hand, tetradecene's main trouble is that, under the same geometrical conditions (launcher gap, tubes radii, column length…) it clearly partially absorbs the microwave energy yielded to the discharge and so, more energy is needed to sustain a similar column (up to 20% more) (*Figure 5*).

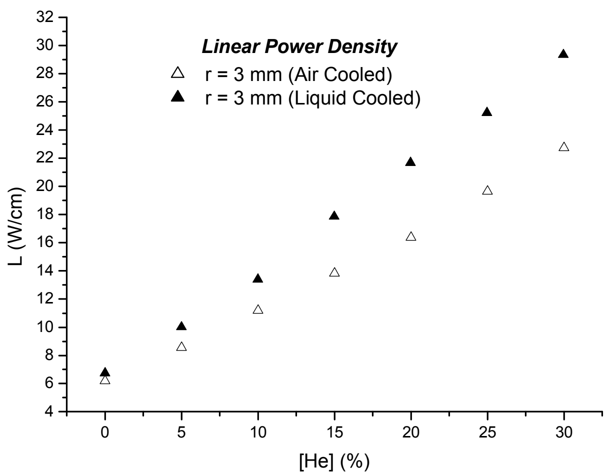

Figure 5. Linear Power Density dependence on He concentration for two different cooling fluids (air and 1–tetradecene)

Finally, while the testing of air cooling shows it does not alter optical measurements, 1–Tetradecene absorbs light for wavelengths under 350 nm (ultraviolet) and makes gas temperature diagnosis from OH rotational band impossible. On the other hand, absorption by the coolant of the OH band will require the use of a different technique to measure the gas temperature. Nonetheless, no noticeable absorption was detected in the visible region of the spectrum, allowing the Ar I to be correctly detect.

Problems dealing with high absorption may be circumvented by using a thinner coolant film, exposing less volume to microwaves. Another option that will solve both problems consists of looking for a low loss dielectric liquid with at least similar thermic characteristics that show no absorption in the near ultraviolet spectrum.

4. References.

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