

GAS TEMPERATURE DETERMINATION IN MICROWAVE DISCHARGES AT ATMOSPHERIC PRESSURE BY USING DIFFERENT OPTICAL EMISSION SPECTROSCOPY TECHNIQUES

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ABSTRACT

Non-thermal plasmas sustained at atmospheric pressure are considered as a very promising technology for different purposes, in which the knowledge of the gas temperature is an important issue. In this paper, the gas temperatures of different argon microwave (2.45 GHz) plasma torches were determined by using different Optical Emission Spectroscopy techniques. Thus, they were estimated through the analysis of N_2^+ (B-X) and OH (A-X) molecular spectra. On the other hand, a method based on the measurement of the van der Waals broadening of 588.99 nm Na I line was employed, and the temperatures obtained from it were compared to the rotational temperatures derived from N_2^+ (B-X) and OH (A-X) rotational bands. A reasonable good agreement was found between the values of temperatures obtained by using the 588.99 nm Na I line and those obtained from N_2^+ rotational band.

Keywords: Optical emission spectroscopy, Microwave plasmas, Atmospheric pressure, Gas temperature, Atomic spectral lines

INTRODUCTION

Nowadays non-thermal plasmas, i.e. those whose electron temperature is different from the corresponding to ions and neutrals (gas temperature), are considered as a very promising technology. Their non-equilibrium properties including low power consumption and the capacity to induce physical and chemical processes at relatively low gas temperatures, are responsible for the great attention that these plasmas have gained from an applied point of view [1-2]. In the last years, the interest in studying non-thermal plasmas sustained at atmospheric pressure has grown significantly. This pressure condition simplifies the handling of plasmas, avoiding the use of complicated vacuum systems. Selwyn et al. [2] claimed that, in addition to reduction in the capital cost of equipment and the elimination of constraints imposed by vacuum-compatibility, plasma processing at atmospheric pressure provides clear advantages over traditional vacuum-based plasma processing, offering improvements for generation of active chemical species, high chemical selectivity, minimal ion densities (resulting in low surface damage), and surface treatment methods unachievable by other means.

The gas temperature is a characteristic plasma parameter related to its capacity for degradation or heating. To know it in technological applications, such as those related to plasma surface treatments (thin film deposition, sterilization, surface functionalization...), plasma catalysis with the presence of a catalyst, or plasma treatment of liquids (water), could be crucial.

Optical Emission Spectroscopy (OES) techniques based on the analysis of molecular emission spectra are commonly used for gas temperature determination of plasmas at atmospheric pressure. The rotational temperature derived from them is considered as a good estimation of the kinetic temperature of the plasma heavy particles [3-4] due to the strong coupling between translational and rotational energy states under

these high pressure conditions. Emissions of molecular bands of the diatomic species OH, N₂, N₂⁺, CN, NH, NO, CH, C₂ and SiH, among others, have been traditionally employed with this purpose [5-12].

But, the use of molecular spectroscopy is not always easy for gas temperature determination. In this way, N₂, N₂⁺, CN emission bands are commonly overlapped in plasmas containing nitrogen [3], what often makes very difficult to get reliable values of the gas temperature. If these plasmas also contain some OH species, the OH band appears overlapped to N₂ band [13].

In argon/nitrogen plasmas, the rotational temperature obtained from the analysis of rovibrational transitions of the N₂ ($C^3\Pi_u \rightarrow B^3 \Pi_g$) second positive band, has a difficult interpretation because the very efficient quasi-resonant energy transfer from argon metastable atoms can populate the rotational levels of N₂ ($C^3\Pi_u$) state [14].

In plasmas in and in contact with liquids (such as plasma bubbles generated in water), the emission of the OH(A-X) band suffers from significant quenching because of the big concentrations of water vapor, and the rotational population distribution of OH(A) is an image of its own formation process, having a non-Boltzmann nature [15,16]. In this case, the rotational temperature of OH(A-X) is not a good estimate of the gas temperature.

Finally, in some plasmas under certain specific experimental conditions, none of the abovementioned diatomic species can be detected.

For all these reasons, alternative OES methods based on the measurement of the gas temperature from the van der Waals broadening of some argon atomic lines (425.9, 522.1, 549.6 and 603.2 nm Ar I) have been developed [17-20]. All these techniques are based on Ar I lines detection, and even sometimes on the additional detection of H_β (Balmer series hydrogen line) for electron density determination [21] (from its Stark

broadening contribution). But in plasmas containing nitrogen (Ar/N₂, He/N₂, Ar/He/N₂...) argon and hydrogen atomic lines are highly quenched [22-24], what limits the applicability of those techniques.

In the present work, the gas temperature of two different microwave plasma torches has been determined from the van der Waals broadening of the 588.99 nm atomic sodium line (sodium was present in these plasmas as an impurity coming from the quartz tube walls containing the discharge). This sodium line (one of the *sodium doublet lines*) is very intense and frequently emitted by plasmas in contact with quartz tubes. Unlike Ar I and H I lines, its emission rather than reduced is enhanced upon nitrogen introduction [25,26] (enhancement related to the resonant energy transfer from vibrational levels of N₂ ($X^1\Sigma_g^+$) state towards atomic sodium levels), making this alternative tool very useful for gas temperature determination in plasmas containing nitrogen (or air).

The values of the temperatures obtained using this method, have been compared with the rotational temperatures derived from the N₂⁺ and/or OH rotational bands, when possible, and conclusions about the use of these different thermometric species have been pointed out.

EXPERIMENTAL SETUP

Plasma generation

Figure 1 shows the experimental set-up used for the creation of the plasma. *Surfatron* and *surfaguide* devices [27] allowed to couple the energy coming from a microwave (2.45 GHz) generator (GMP 12kT/t SAIREM) to the support gas (argon with a purity of 99.99 %) within a quartz tube of 1.5-4 mm of inner and outer diameter, respectively. In the present work the microwave power was set at 130 W and 240 W levels for surfatron

and surfaguide respectively, and in both cases the length of the tube (2 and 3.3 cm from the coupling devices, respectively) was adjusted to achieve a plasma flame at its end. Radial contraction phenomenon was responsible for the progressive constriction observed at both the end of the pure argon plasma column and the subsequent plasma flame, and prevented the contact between the plasma and the tube walls.

An external concentric tube (of 6-8 mm inner and outer diameter, respectively) was employed to allow helium gas (with a purity of 99.99 %) to flow around the discharge tube and the plasma torch, so avoiding uncontrolled contact of the flame with the surrounding air. When pure helium was used, the radial contraction was reduced, and an expanded plasma torch getting the walls of the tubes was achieved [25,28].

Different amounts of nitrogen (with a purity of 99.99 %) were introduced through different ways into the plasma torch generated using the surfaguide device: axially together with the argon main gas (nitrogen flow rate of 8 sccm), axially with the helium cooling gas (nitrogen flow rate of 10 sccm) and laterally at the end (6.5 cm from the coupling device) of the expanded flame (50 and 100 sccm) [28]. In surfatron experiences, nitrogen at 25 and 65 sccm flow rate levels was added to the plasma through the helium flow and at 8 sccm level together argon central channel. In this way, torches of different sizes were obtained, some of them provoking erosion of the external tube wall in some point, and so emitting light corresponding to 588.99 nm Na I line from this plasma-wall contact zone. A characteristic orange emission coming from such small points was observed (*orange spots*).

Optical Emission Spectroscopy

Figure 1 includes a scheme of the optical detection assembly and data acquisition system to process spectroscopic measurements. Light emission from the plasma was

analyzed by using a spectrometer of 1 m focal length equipped with a 1200 grooves/mm holographic grating and a photomultiplier as a detector. The spectra were recorded with a spectral resolution (measured through the instrumental broadening) of 0.055 nm. The light was side-on collected at the plasma oranges spots by using an optical fiber.

Spectra recorded allowed to identify the different species existing in the corresponding plasma region and to estimate its gas temperature from both (i) the van der Waals broadening of Na I lines and, (2) the rotational temperature deduced from the analysis of N_2^+ (first negative system) and/or OH(A-X) molecular bands.

The axial origin of the OES measurements was located at the beginning of the plasma (y-axis) (see Fig. 2). The *expanded flame* started at the end of the central quartz tube ($y = 3.3$ cm position for surfaguide experiments and $y = 2.0$ cm for surfatron ones), just where the previous *plasma column* ended.

VAN DER WAALS BROADENING OF 588.99 NM SODIUM ATOMIC EMISSION LINE AND GAS TEMPERATURE DETERMINATION

The profile of the spectral lines emitted by plasmas generated at pressures higher than 100 Torr can be fitted to a Voigt function resulting from the convolution of a Gaussian function with a Lorentzian function [29]. Under such pressure conditions, the whole line broadening is mainly governed by collisional processes perturbing emitters (atoms and molecules). The Lorentzian part of the spectral profiles is due to both the *Stark effect*, and the *van der Waals effect*. On the other hand, the Gaussian part includes the *Doppler broadening* and the *instrumental broadening*.

Under the experimental conditions of the plasmas studied and for the 588.99 nm Na I line considered in the present work, other effects with potential influence on their profiles could be considered as negligible. So, self-absorption effect was neglected

because the light analyzed was picked up from a very small plasma region (orange points). Also, the resonance broadening contribution did not affect to 588.99 nm line corresponding to a transition to the ground state [30]. Finally, both Zeeman [31] and fine structure effects [32] on the profiles can be neglected in the case of lines emitted by SWDs at atmospheric pressure [17,24].

Dimitrijevic et al. [33] have calculated the Stark broadening for this line under a broad range of experimental conditions and, for the values of electron densities and temperatures corresponding to the present experiments ($n_e \approx 7 \cdot 10^{13} \text{ cm}^{-3}$, $T_e \approx 5000 \text{ K}$ [28]), it can be neglected ($\sim 0.00020 \text{ nm}$). Thus, the Lorentzian *full width at half maximum* ($\Delta\lambda_L$) of 588.99 nm Na I line can be considered as a measure of its van der Waals broadening ($\Delta\lambda_{Waals}$).

Applying the Lindholm-Foley theory (see e.g. [34]), it is found that $\Delta\lambda_{Waals}$ is determined by the following expression [35]:

$$\Delta\lambda_{Waals} = 8.18 \times 10^{-26} \lambda^2 \left(\alpha < \bar{R}^2 > \right)^{2/5} \left(\frac{T_{gas}}{\mu} \right)^{3/10} N \quad (1)$$

where α is the atomic polarizability of the neutral perturber (equal to $16.54 \times 10^{-25} \text{ cm}^3$ for argon and $2 \times 10^{-25} \text{ cm}^3$ for helium), λ is the wavelength in nm, T_{gas} is the gas temperature in K, μ the reduced mass emitter-perturbing, $N \text{ (cm}^{-3}\text{)}$ is the number density of particles (argon and helium atoms, and nitrogen molecules) in the ground state and $< \bar{R}^2 > = < \bar{R}_U^2 > - < \bar{R}_L^2 >$ is the difference of the square radius of the emitting atom in the upper and lower levels.

Plasmas studied in the present work were generated using different proportions of argon, helium and nitrogen. For these cases, expression (2) can be written as follows

$$\Delta\lambda_{Waalts} = 8.18 \times 10^{-26} \lambda^2 \left(\langle \bar{R}^2 \rangle \right)^{2/5} \left(T_g \right)^{3/10} \sum_{i=Ar,He,N_2} (\alpha_i)^{2/5} \left(\frac{1}{\mu_{Na-i}} \right)^{3/10} N_i \quad (2)$$

The density of atoms (N_{Ar} and N_{He}) and nitrogen molecules (N_{N_2}) can be substituted by the ideal gas equation taking into account the volume fraction (χ_{Ar} for argon, χ_{He} for helium and χ_{N_2} for nitrogen) of the constituting gases.

For 588.99 nm Na I line the reduced mass, μ , of the emitter-perturbing pair (Na-Ar), (Na-He) and (Na-N₂) can be considered as being approximately equal to 14.6, 1.84 and 12.63 a.m.u. respectively, and $\langle \bar{R}^2 \rangle = 20.415$. So, the expression for $\Delta\lambda_{Waalts}$ can be written as

$$\Delta\lambda_{Waalts} = \chi_{Ar} \frac{0.96}{T_g^{0.7}} + \chi_{He} \frac{0.77}{T_g^{0.7}} + \chi_{N_2} \frac{1.03}{T_g^{0.7}} (nm) \quad (3)$$

RESULTS AND DISCUSSION

Figure 3 shows a typical spectrum emitted by the expanded flame when no amount of nitrogen was added (only very little amounts of it coming from some air impurities in argon and helium bottles). This is a relatively clean spectrum where no relevant interferences appear. On the contrary, Figs. 4 and 5 correspond to plasma flames in which some proportions of nitrogen were introduced. When nitrogen was added to plasma flame, all argon and hydrogen lines emitted were highly quenched, being the dominant features in the spectra due to species containing nitrogen (NH, CN, N₂, N₂⁺). These effects were especially intense when nitrogen was introduced together the argon

gas through the central channel, case in which only the most intense Ar I and H I lines could be detected (Fig. 5).

In the spectra emitted at plasma points eroding the tube wall (orange spots), intense Na I lines at 588.59 and 589.59 nm could be observed too (Figs. 3, 4 and 5). These lines correspond to resonant transitions from $3p$ states of Na I system (of very low excitation energy, 2.1 eV) towards ground state. As already explained, the emission of that lines, provided the contact between plasma flame and external tube wall kept high enough, rather than reduced was enhanced upon nitrogen introduction [25]. That fact would confer to the alternative method employed in the present work an advantage for the gas temperature determination against those based on the Ar I lines, N_2^+ or OH rotational bands detection.

Figure 6 shows a typical profile of the 588.99 nm Na I line, corresponding in this case to the $y = 3.3$ cm position of the expanded flame generated using the surfatron coupling device and under the experimental conditions specified in the figure. Its fit to a Voigt type profile obtained using the peak fitting module of Microcal Origin (Microsoft ®) has been also plotted. The deconvolution process included in that code (based on the Levenberg-Marquardt algorithm for minimum squares) allowed discriminating the Lorentzian and Gaussian parts of the whole profile. Figure 7 shows that only a Voigt profile can adjust the whole line profile, because the shape of the wings can only be reproduced if a Lorentzian contribution is considered.

Taking into account that the Stark effect contribution to Lorentzian broadening was negligible for this line, its van der Waals broadening was determined (0.00580 ± 0.00017 nm, for this particular case). Thereafter, the value of gas temperature at this plasma position was obtained using Eq. 3 relating the theoretical van der Waals broadening for the 588.99 nm Na I line to this plasma parameter ($T_{gas} = 1290 \pm 60$ K).

For this case, a good enough OH rovibrational spectrum was also detected. The corresponding rotational temperature was deduced through comparisons between this experimental spectrum and its theoretical simulation one. For this purpose, LIFBASE code developed by Luque and Crosley [36] was employed.

On the contrary, the N_2^+ rotational spectrum recorded at this plasma position was very small and noisy and it could not be employed for T_{gas} determination. Indeed, at this plasma region very far from the coupling device, there was a very small amount of argon ions and, as a consequence, of N_2^+ species [25].

The same procedure was followed with the rest of the cases studied, just rewriting eq. 3 for each specific set of volume fractions corresponding to every case. Tables I and II resume the values of van der Waals broadenings measured at different positions of the torches generated (with surfaguide and surfatron, respectively) and the corresponding gas temperatures obtained from it and N_2^+ and/or OH rotational bands simulations, when possible.

From these results, it was observed that in those cases in which N_2^+ could be detected acceptably, there was a very good agreement between the values of T_{gas} using 588.99 nm Na I line and the rotational temperatures $T_{rot}(N_2^+)$ derived from N_2^+ rotational band. Only in two cases studied (marked with an asterisk in Table I) there was no agreement, and they corresponded to measurements from points nearest the inner tube end (beginning of the expanded flame), where likely the mixture argon/helium was not yet well accomplished, and so the calculation of the volume fraction for every gas was not estimated correctly.

For both cases, a second determination of the gas temperature was performed as if a very poor mixture of the helium to the argon/nitrogen central gas had taken place. When doing so, values of T_{gas} according to $T_{rot}(N_2^+)$ were obtained.

On the contrary, there was not a single case in which T_{rot} (OH) agreed to either the values of T_{gas} measured from Na I line or T_{rot} (N_2^+). In all the cases studied, the rotational temperature of OH (A-X) band much overestimated the gas temperature.

These results seem to indicate that OH (A) does not behave as a good thermometric species under the experimental conditions of the microwave plasmas studied in the present work. As commented previously, the use of this species for gas temperature determination has been often questioned [13,15,37,38,39,40]. Bruggeman et al. in [13], pointed out that in plasmas containing argon, a vibrational energy transfer could influence the rotational population distribution of OH(A) states, what can explain its non-Boltzmann nature. On the other hand, Matejka et al. in [38], and Annusová et al. in [39] have shown that OH(A) species cannot be employed as molecular pyrometer for a RF argon/water discharge at atmospheric pressure because their rotational population distribution is influenced by the energy transfer from the argon metastable atoms. Finally, Workmann et al. in [40] have found that in ICPs (Inductively Coupled Plasmas), the rotational temperatures of OH band also lead to temperatures larger than the ones derived from N_2^+ , suggesting that N_2^+ may provide a number of advantages over OH radical as a thermometric probe species in the determination of plasma rotational temperature.

For each specific torch studied, the lowest values of T_{gas} were measured at the farthest plasma position from coupling device ($y = 7.3$ cm), where electron temperature and density had their smallest values too [28]. Also, high values of T_{gas} were measured when big (enough) amounts of nitrogen were added, as it was expected, due to the introduction of molecules into an argon plasma provoke important changes in its microscopic kinetics due to the fact that the energy transfer from electrons to heavy particles (very poor in argon pure plasmas as a consequence of the big mass difference

between electron and argon atoms or ions) does improve thanks to electron induced vibrational excitation of molecular species.

Table II also includes points corresponding to the plasma column region where the Na I line could not be detected. Thus, it could be verified that the gas temperature estimated for the expanded flame was actually lower than those corresponding to the plasma column as it was expected [28], and so our results were consistent.

CONCLUSIONS

In this work, the gas temperatures of two argon microwave (2.45 GHz) plasma torches were determined by using different Optical Emission Spectroscopy techniques.

In first instance, a method based on the measurement of the van der Waals broadening of the 588.99 nm Na I line was employed. The method is applicable to plasmas containing some sodium impurities. This is the case of the microwave expanded plasma torches generated at the end of an argon column when an appropriate ambience of helium is created around it. As the plasma expanded to the walls of a quartz external tube containing sodium impurities, the contact of the plasma-walls provoked some plasma etching and the presence of sodium atoms in the discharge. Unlike in other methods using the van der Waals broadening of argon lines, the presence of nitrogen in the discharge rather than inconvenient enhanced the emission of 588.99 nm Na I line, making this method very helpful for these cases in which no other thermometric species can be employed for the gas temperature determination.

In the cases analyzed in which both Na I line and N_2^+ band could be adequately registered, a reasonable good agreement has been found between the values of T_{gas} obtained using the van der Waals broadening of the 588.99 nm Na I line and the rotational temperatures obtained from N_2^+ rotational band.

On the contrary, rotational temperatures obtained from OH(A-X) rotational band were much higher, likely overestimating the gas temperature. Thus, for the microwave surface wave sustained discharges studied in the present work, the use of OH(A) as thermometric species should be reconsidered.

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REFERENCES

- [1] J. Park, I. Henins, H.W. Hermann and G.S. Selwyn, Gas breakdown in an atmospheric pressure radio-frequency capacitive plasma source, *J. Appl. Phys.* 89 (2001) 15-19.
- [2] G.S. Selwyn, H.W. Hermann, J. Park, and I. Henins, Materials processing using an atmospheric pressure RF-generated plasma source, *Contrib. Plasma Phys.* 6 (2001) 610-619.
- [3] H. Nassar, S. Pellerin, K. Mussiol, O. Martinie, N. Pellerin, J.M. Cormier, N₂(+)/N₂ ratio and temperature measurements based on the first negative N₂(+) and second positive N₂ overlapped molecular emission spectra *J. Phys. D: Appl. Phys.* 37 (2004) 1904-1916.
- [4] N. Britun, M. Gaillard, A. Ricard, Y.M. Kim, K.S. Kim, H.G. Han, Determination of the vibrational, rotational and electron temperatures in N₂ and Ar-N₂ rf discharge, *J. Phys. D: Appl. Phys.* 40 1022 (2007).
- [5] X.M. Zhu, W.C. Chen, Y.K. Pu, Gas temperature, electron density and electron temperature measurement in a microwave excited microplasma, *J. Phys. D: Appl. Phys.* 41 (2008) 105212 (6pp).
- [6] Q. Wang, I. Koleva, V.M. Donnelly, D.J. Economou, Spatially resolved diagnostics of an atmospheric pressure direct current helium microplasma, *J. Phys. D: Appl. Phys.* 38 (2005) 1690-1697.
- [7] M.H. Abdallah and J.M. Mermet, The Behavior of Nitrogen Excited in an Inductively Coupled Argon Plasma, *J. Quant. Spectrosc. Radiat. Transfer.* 19 (1978) 83-91.
- [8] C.O. Laux, T.G. Spence, C.H. Kruger, R.N. Zare, Optical diagnostics of atmospheric pressure air plasmas, *Plasma Sources Sci. Technol.* 12 (2003) 125-138.

- [9] U. Fantz, Emission spectroscopy of molecular low pressure plasmas, *Contrib. Plasma Phys.* 44 (5-6), 508-515 (2004).
- [10] M. Mora, M.C. García, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, Transformation of light paraffins in a microwave-induced plasma-based reactor at reduced pressure, *Int. J. Hydrogen Energy* 35 (2010) 4111-4122.
- [11] F. Iza and J.A. Hopwood, Rotational, vibrational, and excitation temperatures of a microwave-frequency microplasma, *IEEE Trans. Plasma Sci.* 32 (2) (2004) 498-504.
- [12] G. Lombardi, F. Benedic, F. Mohasseb, K. Hassouni, A. Gicquel, Determination of gas temperature and C-2 absolute density in Ar/H-2/CH4 microwave discharges used for nanocrystalline diamond deposition from the C-2 Mulliken system, *Plasma Sources Sci. Technol.* 13 (2004) 375-386.
- [13] P. Bruggeman, D.C. Schram, M.G. Kong, C. Leys, Is the Rotational Temperature of OH(A-X) for Discharges in and in Contact with Liquids a Good Diagnostic for Determining the Gas Temperature?, *Plasma Process. Polym.* 6 (2009), 751-762.
- [14] J. Henriques, E. Tatarova and C.M. Ferreira, Microwave N-2-Ar plasma torch. I. Modeling, *J. Appl. Phys.* 109, (2011) 023301.
- [15] P. Bruggeman, D.C. Schram, M.A. González, R. Rego, M.G. Kong, C. Leys, Characterization of a direct dc-excited discharge in water by optical emission spectroscopy, *Plasma Sources Sci. Technol.* 18 (2009) 025017 (13 pp)
- [16] P. Bruggeman, T. Verreycken, M.A. González, J.L. Walsh, M.G. Kong, C. Leys, D.C. Schram, Optical emission spectroscopy as a diagnostic for plasmas in liquids: opportunities and pitfalls, *J. Phys. D: Appl. Phys.* 43 (2010) 124005 (8pp).
- [17] M. Christova, E. Castaños-Martínez, M.D. Calzada, Y. Kabouzi, J.M. Luque, M. Moisan, Electron density and gas temperature from line broadening in an argon surface-

wave-sustained discharge at atmospheric pressure, *Appl. Spectrosc.* 58 (2004) 1032-1037.

[18] M. Christova, V. Gagov, I. Koleva, Analysis of the profiles of the argon 696.5 nm spectral line excited in non-stationary wave-guided discharges, *Spectrochim. Acta B* 55 (2000) 815-822.

[19] C. Yubero, M.S. Dimitrijevic, M.C. García, M.D. Calzada, Using the van der Waals broadening of the spectral atomic lines to measure the gas temperature of an argon microwave plasma at atmospheric pressure, *Spectrochim. Acta B* 62 (2007) 169-176.

[20] J. Muñoz, M.S. Dimitrijevic, C. Yubero, M.D. Calzada, Using the van der Waals broadening of spectral atomic lines to measure the gas temperature of an argon-helium microwave plasma at atmospheric pressure, *Spectrochim. Acta B* 64 (2009) 167-172.

[21] M.A. Gigosos and V. Cardeñoso, New plasma diagnosis tables of hydrogen Stark broadening including ion dynamics, *J. Phys. B: At. Mol. Opt. Phys.* 29 (1996) 4795-4838.

[22] K. Wagatsuma and K. Hirokawa, Quenching mechanisms in argon-nitrogen or neon-nitrogen glow-discharge plasmas, *Anal. Chem.* 61 (1989) 326-329.

[23] Q.S. Yu and H.K. Yasuda, An optical emission study on expanding low-temperature cascade arc plasmas, *Plasma Chem. Plasma Process.* 18 (4) (1998) 461-485.

[24] M.C. Garcia, C. Yubero, M.D. Calzada, M.P. Martínez-Jiménez, Spectroscopic characterization of two different microwave (2.45 GHz) induced argon plasmas at atmospheric pressure, *Appl. Spectrosc.* 59 (4) (2005) 519-528.

- [25] M. C. García, M. Varo and P. Martínez, Excitation of Species in an Expanded Argon Microwave Plasma at Atmospheric Pressure, *Plasma Chem. Plasma Process.* 30 (2010) 241-255.
- [26] A. Ricard, T. Czerwicz, T. Belmonte, S. Bockel and H. Michel, Detection by emission spectroscopy of active species in plasma-surface processes, *Thin Solid Films* 341 (1-2) (1999) 1-8.
- [27] M. Moisan, J. Pelletier, *Microwave Excited Plasmas. Plasma Technology*, Chap. 3, Elsevier, Amsterdam, 1992.
- [28] M.C. García, M. Varo, P. Martínez, Spectroscopic Study of an Expanded Argon Microwave (2.45 GHz) Plasma at Atmospheric Pressure in a Helium Environment, *Appl. Spectroscopy* 63 (2009) 822-829.
- [29] J. M. Luque, M.D. Calzada and M. Sáez, Experimental research into the influence of ion dynamics when measuring the electron density from the Stark broadening of the H-alpha and H-beta lines, *J. Phys. B: At. Mol. Opt. Phys.* 36 (2003) 1573-1584.
- [30] N. Konjević, Plasma broadening and shifting of non-hydrogenic spectral lines; Present status and applications, *Phys. Rep.* 316 (1999) 339-401.
- [31] S. Günter and A. Könies, Diagnostics of dense plasmas from the profile of hydrogen spectral lines in the presence of a magnetic field, *J. Quant. Spectrosc. Radiat. Transfer* 62 (1998) 425-431.
- [32] W. Olchawa, R. Olchawa, B. Grabowski, Stark broadening of hydrogen spectral lines with fine structure effects, *European Physical Journal D* 28 (2004) 119-124.
- [33] M. S. Dimitrijevic and S. Sahal-Bréchet, Stark broadening of neutral sodium lines, *J. Quant. Spectrosc. Radiat. Transfer* 34 (1985) 149-161.

- [34] M. Findeisen, T. Grycuk, A. Brielski, J. Szudy, On the role of Maxwellian averaging in the interpretation of pressure broadening and shift of spectral lines, *J. Phys. B.: At. Mol. Phys.* 20 (1987) 5997-6003.
- [35] W.R. Hindmarsh, A.D. Petford, G. Smith, Lectures at the Winter College on Atoms, Molecules and Lasers, Trieste, IAEA, Vienna, 1973, p. 133.
- [36] J. Luque and D.R. Crosley, "LIFBASE: Database and Spectral Simulation (version 1.5)", SRI International Report MP 99-009 (1999).
- [37] A. Ricard, L. St-Onge, H. Malvos, A. Gicquel, J. Hubert, M. Moisan, Microwave-excited plasma torch-2 complementary configurations, *J. Phys. III* 5 (1995) 1269-1285.
- [38] M. Matejka, S. Ocadlik, J. Jasik, V. Martisovits, P. Veis, Study of the OH(A)-OH(X) emission in Ar + H₂O RF discharges, 16th ESCAMPIG and 5th International Conference on Reactive Plasmas, Conference Proceedings, 2 (2002) 277-278.
- [39] A. Annusova, J. Kristof, P. Veis, C. Foissac, P. Supiot, WDS'12 Proceedings of Contributed Papers, Part II, (2012) 99-104.
- [40] J. M. Workman, P.A. Fleitz, H.B. Fannin, J.A. Caruso, C.J. Seliskar, A Comparative Study of Rotational Temperatures in a Microwave Plasma: OH Radical Versus N₂⁺, *Appl. Spectrosc.* 42 (1988), 96-100.

FIGURE CAPTIONS

Figure 1. Block diagram of the experimental setup used.

Figure 2. Details of the *plasma column, expanded flame* and zone of introduction of external gases.

Figure 3. Spectrum emitted by the argon/helium expanded flame when no amount of nitrogen was added.

Figure 4. (a) Spectrum emitted by the expanded flame when nitrogen was added together helium cooling gas; **(b)** and **(c)** Details of this spectrum showing overlapping between bands.

Figure 5. Spectrum emitted by the expanded flame when nitrogen was added together argon main gas.

Figure 6. Typical profile of the 588.99 nm Na I line and its fit to a Voigt type profile.

Figure 7. Fitting of the 588.99 nm Na I line measured experimentally to pure Gaussian and Voigt type profiles.

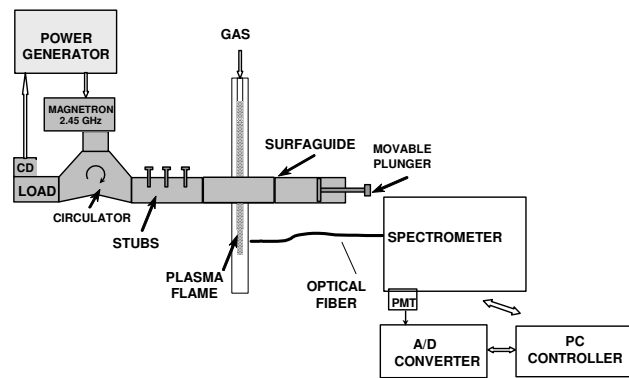


Figure 1. Yubero et al.

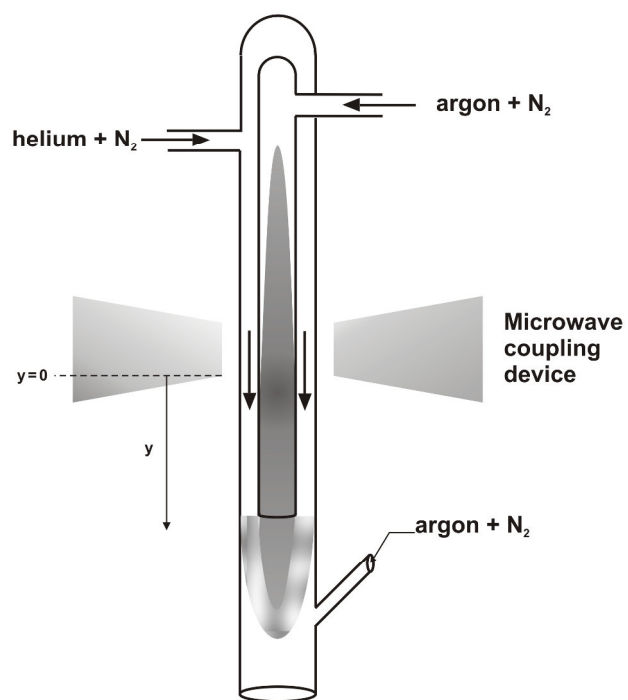


Figure 2. Yubero et al.

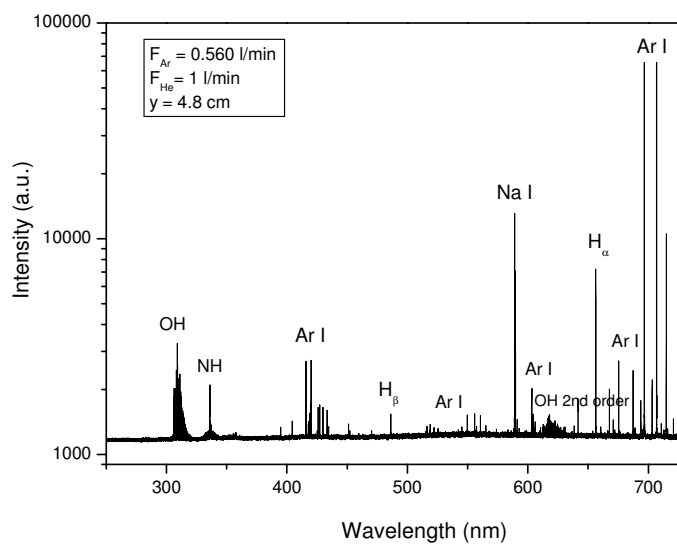


Figure 3. Yubero et al.

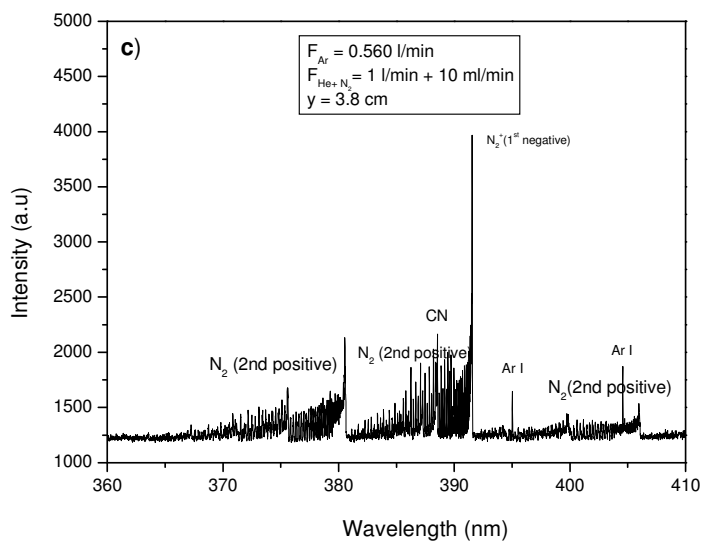
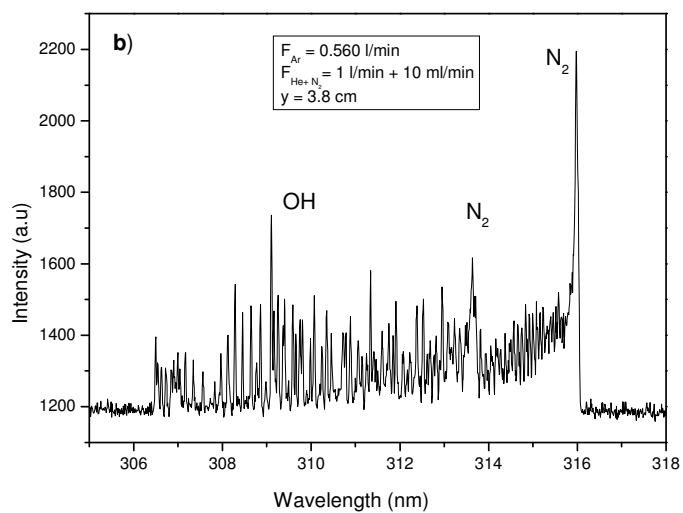
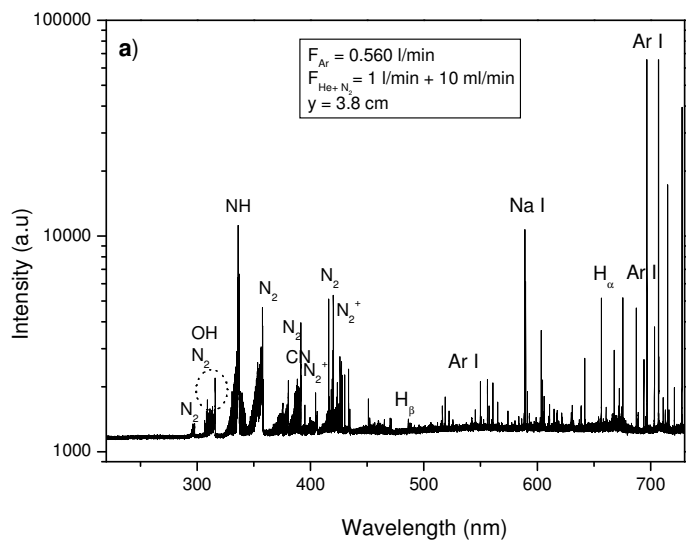


Figure 4. Yubero et al.

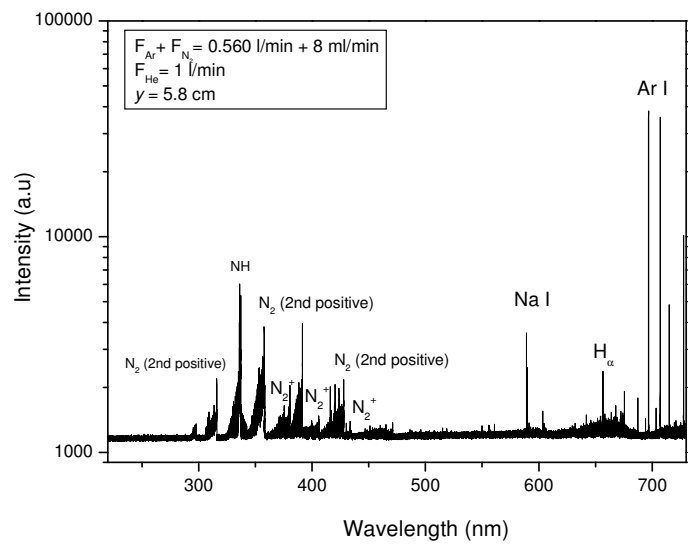


Figure 5. Yubero et al.

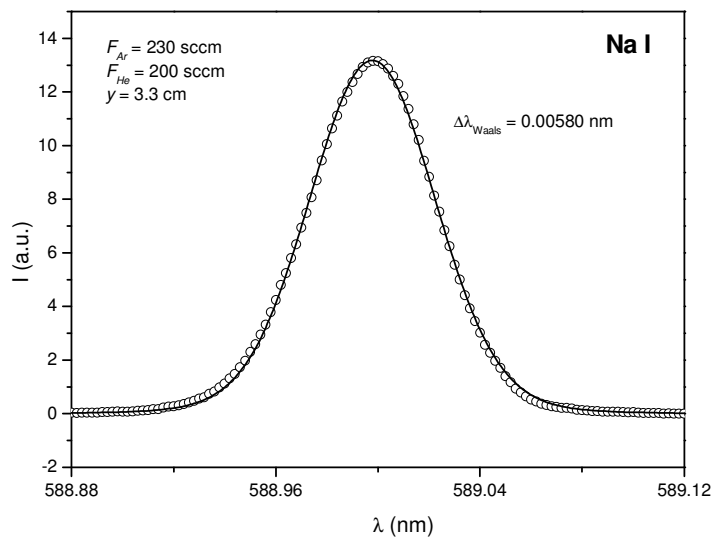


Figure 6. Yubero et al.

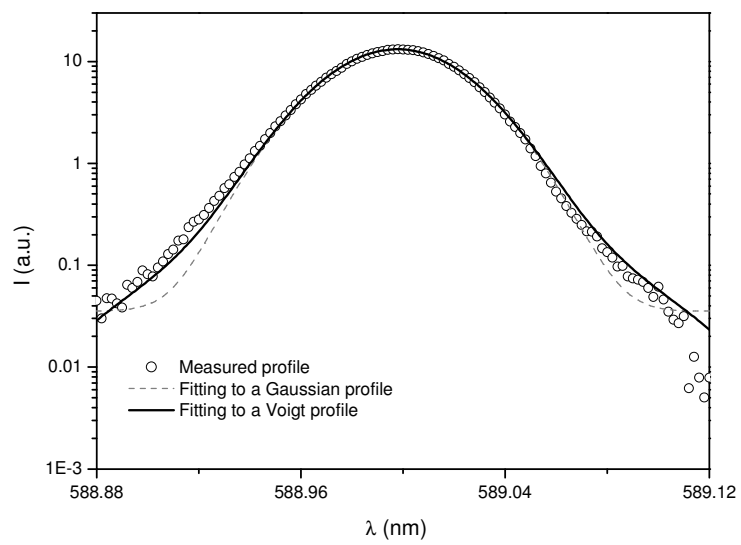


Figure 7. Yubero et al.

Table I. Values of temperatures obtained from van der Waals broadening and N_2^+ and OH rotational bands at different positions of the torches generated with surfaguide.

<i>Flow rates (sccm)</i>	$\Delta\lambda_{\text{waals}}$ (nm)	T_{gas} (Na I) (K)	T_{rot} (N_2^+) (K) (LIFBASE)	T_{rot} (OH) (K) (LIFBASE)
<i>Plasma position (cm)</i>				
$F_{Ar} = 560$ $F_{He} + F_{N_2} = 1000 + 0$ $y = 4.8$	0.0056 ± 0.0003	1290 ± 110	-	1700
$F_{Ar} = 560$ $F_{He} + F_{N_2} = 1000 + 0$ $y = 5.8$	0.0054 ± 0.0004	1350 ± 160	-	1700
$F_{Ar} = 560$ $F_{He} + F_{N_2} = 1000 + 10$ $y = 4.8$	0.0058 ± 0.0008	1200 ± 300	1300	1600
$F_{Ar} + F_{N_2} = 840 + 0$ $F_{He} = 1500$ $y = 5.8$	0.0066 ± 0.0005	1010 ± 130	-	1500
$F_{Ar} + F_{N_2} = 840 + 0$ $F_{He} = 1000$ $y = 5.8$	0.0051 ± 0.0003	1510 ± 140	1400	1800
$F_{Ar} + F_{N_2} = 560 + 0$ $F_{He} = 1500$ $y = 4.8$	0.0063 ± 0.0009	1100 ± 300	-	1500
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 0$ $y = 3.3$	0.0053 ± 0.0005	1700 ± 300	1800	2100
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 0$ $y = 1.8$ (<i>plasma column</i>)	-	-	2500	-
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 1000$ $y = 3.8$	0.0049 ± 0.0005	$1600 \pm 300^*$ ($\chi_{He} = 0.64$) 1900 ± 400 ($\chi_{He} = 0$)	2100	overlapped
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 1500$ $y = 3.8$	0.0048 ± 0.0005	$1500 \pm 300^*$ ($\chi_{He} = 0.73$) 1900 ± 400 ($\chi_{He} = 0$)	2000	overlapped
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 1000$ $y = 2.8$ (<i>plasma column</i>)	-	-	2300	overlapped
$F_{Ar} + F_{N_2} = 560 + 8$ $F_{He} = 1000$ $y = 1.8$ (<i>plasma column</i>)	-	-	2500	overlapped
$F_{Ar} = 560$ $F_{He} = 340$ $y = 6.8$	0.0068 ± 0.0006	1060 ± 150	(very noisy)	1600
$F_{Ar} = 560$ $F_{He} = 340$	0.0077 ± 0.0004	880 ± 80	(very noisy)	1500

F_{N_2} (laterally) = 50				
$y = 6.8$				
$F_{Ar} = 560$	$0.0074 \pm$	1000 ± 200	1200	1500
$F_{He} = 340$	0.0009		(very noisy)	
$F_{Ar} + F_{N_2}$ (lat) = 200 + 100				
$y = 6.8$				
$F_{Ar} = 560$	$0.0064 \pm$	1190 ± 180	-	1600
$F_{He} = 340$	0.0006			
$F_{Ar} + F_{N_2}$ (lat) = 100 + 100				
$y = 7.3$				
$F_{Ar} = 560$	$0.0060 \pm$	1300 ± 300	-	1800
$F_{He} = 340$	0.0005			
$F_{Ar} + F_{N_2}$ (lat) = 100 + 100				
$y = 6.3$				
$F_{Ar} = 560$	$0.0070 \pm$	1030 ± 150	-	1500
$F_{He} = 340$	0.0006			
$F_{Ar} + F_{N_2}$ (lat) = 100 + 50				
$y = 6.8$				
$F_{Ar} = 560$	$0.0065 \pm$	1160 ± 210	1300	1600
$F_{He} = 340$	0.0007			
$F_{Ar} + F_{N_2}$ (lat) = 100 + 50				
$y = 6.3$				

Table II. Values of temperatures obtained from van der Waals broadening and N_2^+ and OH rotational bands at different positions of the torches generated with surfatron.

<i>Flow rates (sccm)</i>	$\Delta\lambda_{Waals}$ (nm)	T_{gas} (Na I) (K)	T_{gas} (N_2^+) (K) (LIFBASE)	T_{gas} (OH) (K) (LIFBASE)
<i>Plasma position</i> (cm)				
$F_{Ar} = 340$ $F_{He} = 200$ $y = 3.3$	0.00590 ± 0.00013	1200 ± 100	-	1800
$F_{Ar} = 300$ $F_{He} = 200$ $y = 3.3$	0.0057 ± 0.0006	1350 ± 240	-	1800
$F_{Ar} = 230$ $F_{He} = 0$ $y = 3.3$	0.0079 ± 0.0003	960 ± 60	-	-
$F_{Ar} = 230$ $F_{He} = 200$ $y = 3.3$	0.00580 ± 0.00017	1290 ± 60	-	1900
$F_{Ar} = 230$ $F_{He} + F_{N_2} = 200 + 25$ $y = 3.3$	0.0060 ± 0.00022	1260 ± 70	-	1800
$F_{Ar} = 230$ $F_{He} + F_{N_2} = 200 + 65$ $y = 3.3$	0.0073 ± 0.0003	960 ± 60	-	1300
$F_{Ar} + F_{N_2} = 230 + 8$ $F_{He} = 0$ $y = 3.3$	0.0043 ± 0.0003	2330 ± 260	2300	2200