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Diagnostics of Argon Plasma Immersed into Water and Produced by a Non-Transferred ARC by Optical Emission Spectroscopy

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Abstract: Optical emission spectroscopy techniques based on evaluation of the plasma emission coefficients have been adopted for the measurements of plasma parameters of ARCs immersed into water and for determining potential active species and their distribution in the plasma. An electric ARC torch in argon has been considered working in non-transferred mode to produce the plasma. The resulting plasma jet is neither homogeneous nor stable one which makes it especially difficult for the OES measurements. So, the approach has been applied relying upon relative intensity of lines in the plasma total emission spectra and some general data on the plasma behaviour. The measurement results give a rather realistic picture of plasma parameters and spatial distributions of active species in the plasma jet with an admixture of water.

Key words: Spectroscopy techniques, plasma emission, species, ARC torch, OES, water

INTRODUCTION

It has been recently shown that thermal plasma of an ARC jet immersed into water spoiled by organics or by other waste aqueous solutions can be used for the wastewater decontamination (Violier *et al*., 2003). The process is based upon the plasma enhanced oxidation resulting in interaction of organics with active oxidants, atoms and radicals which are present in the plasma in large concentration (Violier *et al*., 2003). One needs data on properties of the water content plasmas to understand better main processes giving the positive decontamination result and to find optimal conditions and ways for the technology realisation. This research is devoted to an adaptation of Optical Emission Spectroscopy (OES) techniques for measurements of parameters of the ARC plasma with a water admixture and for determining potential active species and their distribution in the plasma. An electric ARC torch in argon has been considered working in non-transferred mode to produce the plasma. The resulting plasma jet is neither homogeneous nor stable one which makes it especially difficult for the OES measurements.

MATERIALS AND METHODS

The non-transferred dc ARC torch is mounted vertically in a vessel in such a way that a plasma flow from the torch nozzle is directed upward (Fig. 1a, b). Argon with an admixture of helium is used as the plasma forming gas. Water is injected through 8 holes of 0.5 mm diameter made in a cone wall at the nozzle exit. Several quartz windows mounted at the vessel side wall are used for the plasma optical observations. All metal units are cooled by a water flow. A generator supplying up to 400 A current at 300 V serves to feed the ARC.

The plasma emission spectra have been measured using a grating monochromator with a matrix detector (Fig. 2). The monochromator, Jobin-Yvon THR-1000 of a Czerny-Turner type has 1 m focal length, F/9 aperture and a holographic grating of 1200 grooves mm^{-1}. The detector (Hamamatsu C7041/S7031-1008) is mounted to the monochromator off-slit exit. The plasma jet is imaged onto the monochromator entrance slit. The observation direction coincides with the axis y. A system of mirrors and lenses forms the jet image with the axis z to be perpendicular to the slit edges.

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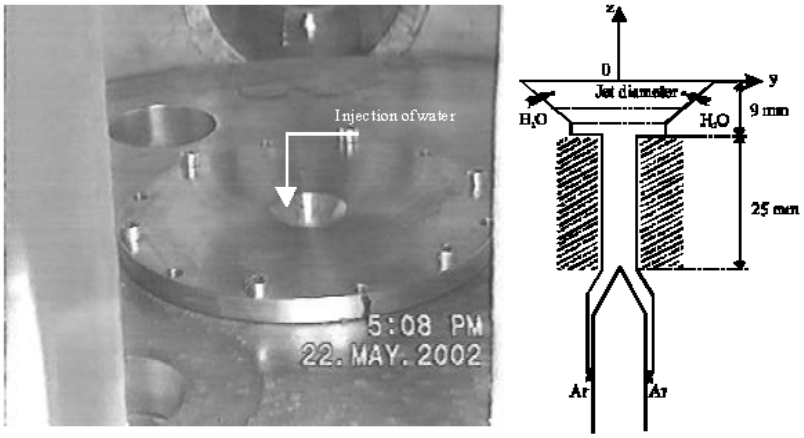

Fig. 1: (a) Non-transferred ARC torch photograph; b) non-transferred ARC torch diagram

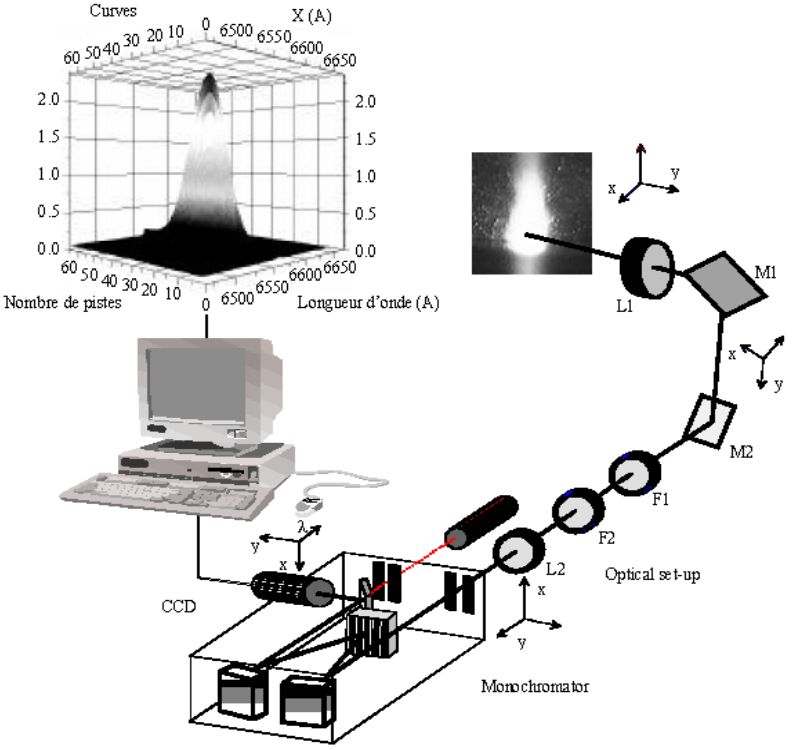

Fig. 2: Schematic diagram of the spectroscopic diagnostic set-up

In such a way, a cross-section distribution of the emission spectrum along the direction x perpendicular to z is recorded for the jet layer discriminated by the slit. The jet is moved vertically step-by-step along z-axis to obtain the distributions for different z positions. For each z position, a two-dimensional (space-spectrum) matrix of the jet emission intensity is measured. A mechanical comparator controls the jet positioning with a precision of 0.5 mm. The recording system spectral and space resolutions are estimated to be 0.06 and 0.1 mm, respectively. One can find details of the set-up elsewhere (Cerqueira *et al*., 2004; Zaag *et al*., 2005a, b).

OES measurement technique: Relative emission intensity has been chosen as a tool for OES measurements of the plasma parameters. Plasma temperature has been evaluated using an intensity ratio of two atomic argon spectral lines. Spectral lines of hydrogen and oxygen

atoms have been taken to find a concentration of the respective species in the plasma as compared to atomic argon by intensity ratios for corresponding atomic spectral lines. Common plasma diagnostics relying upon relative intensity suppose local measurements of the plasma emission coefficient which must be actually used instead of intensity, especially at non-homogeneous plasma cases.

According to the preliminary study, the jet under consideration is an inhomogeneous and unsteady plasma volume which generally has no axial symmetry. So, the emission coefficient cannot be measured with a reasonable precision using common Abel inversion. That is why the researchers have used the technique relying upon some approximations of the plasma volume spatial distribution and time behaviour (Ershov-Pavlov, 1999). According to the approach, plasma temperature distribution in the volume along the observation direction can be shown as follows:

$$T(y) = T_0[1 + (y/y_0)^{\alpha}]^{-1} \quad (1)$$

Where, α is a parameter accounting for a form of the temperature distribution, i.e., the plasma inhomogeneity rate. It makes possible to obtain for a spectral line in the plasma emission spectrum a rather simple relation between the emission coefficient of the plasma $\varepsilon(T_0)$ at the maximum temperature T_0 and the line total intensity I, recorded along y direction:

$$I = \frac{2y_0}{\alpha}\mu^{1/\alpha}\varepsilon(T_0)(1+\mu/\alpha)\Gamma(1/\alpha) \quad (2)$$

Where, $\mu = kT_0/E$, E is energy of the upper level of the optical transition giving the line under consideration; Γ is Gamma-function.

For unsteady plasmas using the approach it was shown (Ershov-Pavlov and Stepanov, 2001), T_0 fluctuations around its mean value $\bar{T}_0$ can be chosen to present plasma instability supposing y_0 and α to be constant, as far as namely T_0 influences spectral line intensity more effectively.

The following expressions have been found by Ershov-Pavlov and Stepanov (2001) for the mean intensity values of a spectral line at sinusoidal and sawtooth fluctuation modes, respectively:

$$\langle I_{Sn}\rangle \approx C\sqrt{\frac{2}{\pi}}y_0\frac{\Gamma(1/\alpha)}{\alpha}\frac{1}{\sqrt{\sigma}}\frac{1}{\bar{T}_0}\mu^{1/\alpha+1/2}\left(1+\frac{\mu}{\alpha}\right)\exp\left(-\frac{E}{kT_m}\right) \quad (3a)$$

$$\langle I_{Sw}\rangle \approx Cy_0\frac{\Gamma(1/\alpha)}{\alpha}\frac{1}{\sigma}\frac{1}{\bar{T}_0}\mu^{1/\alpha+1}\left(1+\frac{\mu}{\alpha}\right)\exp\left(-\frac{E}{kT_m}\right) \quad (3b)$$

Where, $T_m = \bar{T}_0(1+\sigma)$ is the highest value of the maximum temperature T_0 in the temperature distribution along y during the observation time.

Finally, from the Eq. 2 and 3 the following expression can be found for the plasma temperature evaluation by relative intensity of two spectral lines (1, 2) (Ershov-Pavlov and Stepanov, 2001):

$$kT_m \approx (E_1 - E_2)\left[\ln(C_1/C_2) - \ln(I_1/I_2) - \Omega\ln(E_1/E_2)\right]^{-1} \quad (4)$$

Where, $T_m = \bar{T}_0(1+\sigma)$ is the highest value of the maximum temperature T_0 in the temperature spatial distribution along the line of sight and during the observation time, $\sigma = \Delta T/\bar{T}_0$ is the fluctuation amplitude, $C_{1,2} = (Ag/\lambda)_{1,2}$ is a common parameter combination for the lines due to transitions from the respective energy levels, $E_{1,2}$. In the temperature region under consideration the parameter $\mu << 1$ and the ratio $(1+\alpha/\mu)_1/(1+\alpha/\mu)_2 \approx 1$ is taken when obtaining Eq. 4. The parameter $\Omega = 1/\alpha$ for stationary plasmas ($T_m = T_0$) $\Omega = 1/\alpha+1/2$ and $\Omega = 1/\alpha+1$ for plasmas with sinusoidal and sawtooth temperature fluctuations, respectively. Note, when the plasmas are homogeneous ($\alpha = \infty$) and stationary ones, $\Omega = 0$ and Eq. 4 gives a common Boltzmann equation for the plasma temperature measurements by relative intensity of spectral lines (Richter, 1968).

Here the researchers have used the Eq. 4 for plasma temperature measurements. They have supposed the plasma components are distributed homogeneously (their partial pressure is constant along the observation line and during the measurements time).

It allowed replacing the ratio of the plasma emission coefficients with the relevant ratio of the directly measured intensity of spectral lines at the evaluation the components relative density N_a^1/N_a^2:

$$\frac{N_a^1}{N_a^2} = \frac{I_{ki}^1}{I_{ki}^2}\left(\frac{E_k^1}{E_k^2}\right)^{\Omega}\left(\frac{\lambda_{ki}g_f}{A_{ki}g_k}\right)_1 \times \left(\frac{\lambda_{ki}g_f}{A_{ki}g_k}\right)_2^{-1}\exp\left(\frac{E_k^1 - E_k^2}{kT}\right) \quad (5)$$

Where, partition functions of the atoms are replaced with the statistical weights g_f of their ground levels. The atom density relative ratio evaluated using Eq. 5 is strongly influenced by the exponent and spectral lines with closer upper energy levels $\Delta E_k \to 0$ have to be taken to minimise the influence. In such a way the ratio dependence on temperature can be practically eliminated.

OH spectrum simulation: Emission of OH radicals has been also used to learn the species distribution in the plasma. The band spectrum has been simulated due to transitions between $A^2\Sigma^+$ and $X^2\Pi_i$ electronic states. The resulting vibrational 0-0 band has a head at 306.1 nm and is degraded to the spectrum red side. The transition principal parameters, as well as the calculation algorithm have been taken from (Dieke and Crosswhite, 1962).

RESULTS AND DISCUSSION

Distributions of the plasma parameters across the ARC jet have been measured with a step of 0.25 mm at different distances z. The measurements have been made at 250 A ARC current, at 30 and 4 NL min^{-1} flows of argon and helium, respectively and at 0.1, 0.5 and 1 L h^{-1} of water introduction.

The value z = 0 has been chosen at the cone base which corresponds to the distance of 9 mm from the torch nozzle.

Parameters of all lines chosen for the measurements have been taken from the NIST tables (Zaag *et al*., 2005c). Two Ar I lines at λ = 714.7 and 720.7 nm have been used for the plasma temperature evaluation. According to preliminary observation data, sawtooth fluctuations and $\alpha = 2$ ($\Omega = 3/2$) have been taken at the plasma temperature and relative composition evaluation. The researchers estimated the uncertainty in the temperature values to be within 15%. For the studied region of 9-17 mm from the torch nozzle, temperature changes in 7000-10000 K interval. Some temperature measurement results are shown in Fig. 3a-c, where the distributions are shown for three water contents. The researchers can notice a non-symmetry of the jet. There are probably preferential points of collision of the ARC in the nozzle. Generally, the temperature distributions change not much with water quantity but a tendency is observed for a temperature decrease at smaller water input.

Relative content of hydrogen and oxygen have been measured using H_α and O I λ = 777.2 nm lines, respectively and Ar I λ = 696.5 nm line as a reference one.

The hydrogen density measurement results are shown in Fig. 4a-c for three water contents. According to the observations, atomic hydrogen density does not depend much on water quantity introduced and slightly increases with the distance from the nozzle: it changes between 10^{16} and 1.5 10^{17} atoms cm^{-3}. So, hydrogen density is about ten times lower than argon one. In fact, absolute H, O density values have been evaluated from the plasma composition calculated supposing the plasma consists of argon only. The approximation relies upon generally small admixture quantity. The researchers can

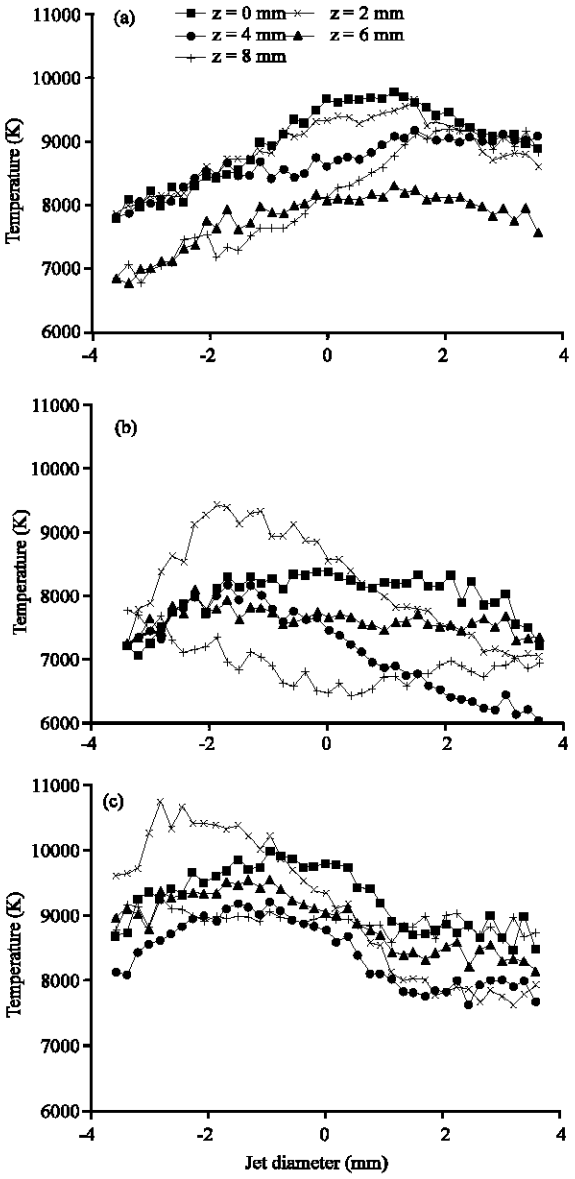

Fig. 3: Temperature distribution in the plasma jet at (a) 0.1 L h^{-1} (b) 0.5 L h^{-1} (c) 1 L h^{-1} of water introduction

notice that the hydrogen density distributions present dissymmetries similar to those that observe on the distributions of temperatures.

Atomic oxygen density changes between 10^{16} and 4 10^{16} cm^{-3}. It is about two times lower than that of hydrogen which corresponds to the admixture stoechiometry. It also increases with *z* which can be due to further water evaporation down along the plasma jet. Examples of oxygen density measurement results are shown in Fig. 5a-c for three water contents.

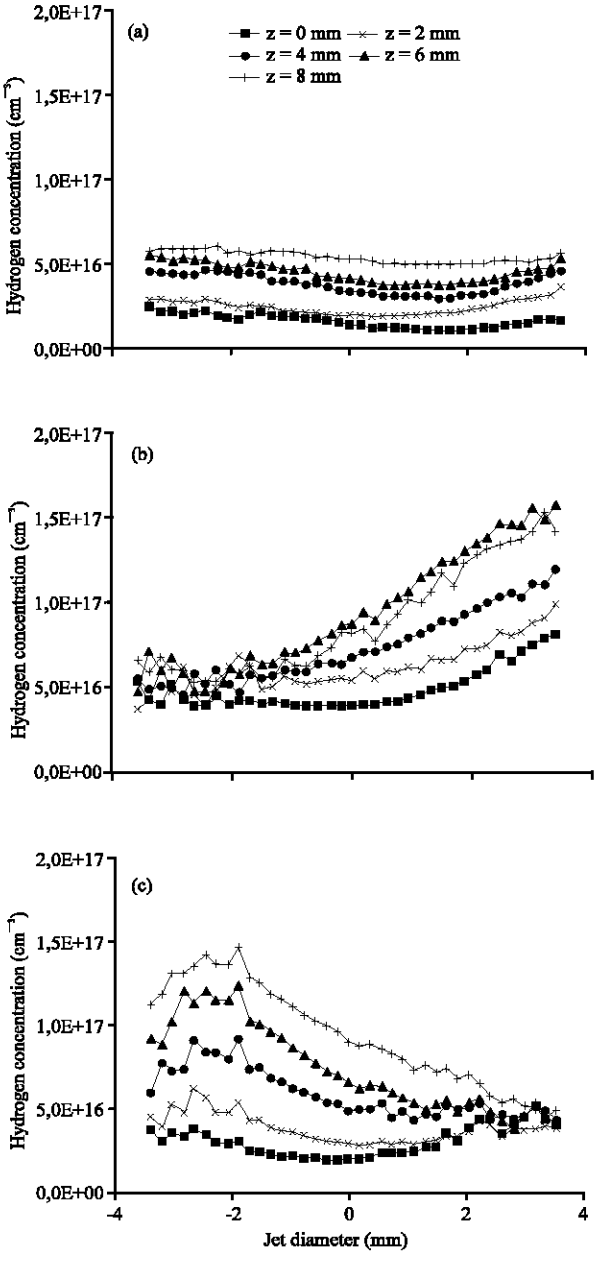

Fig. 4: Htdrogen density distribution in the plasma jet at (a) 0.1 L h^{-1} (b) 0.5 L h^{-1} (c) 1 L h^{-1} of water introduction

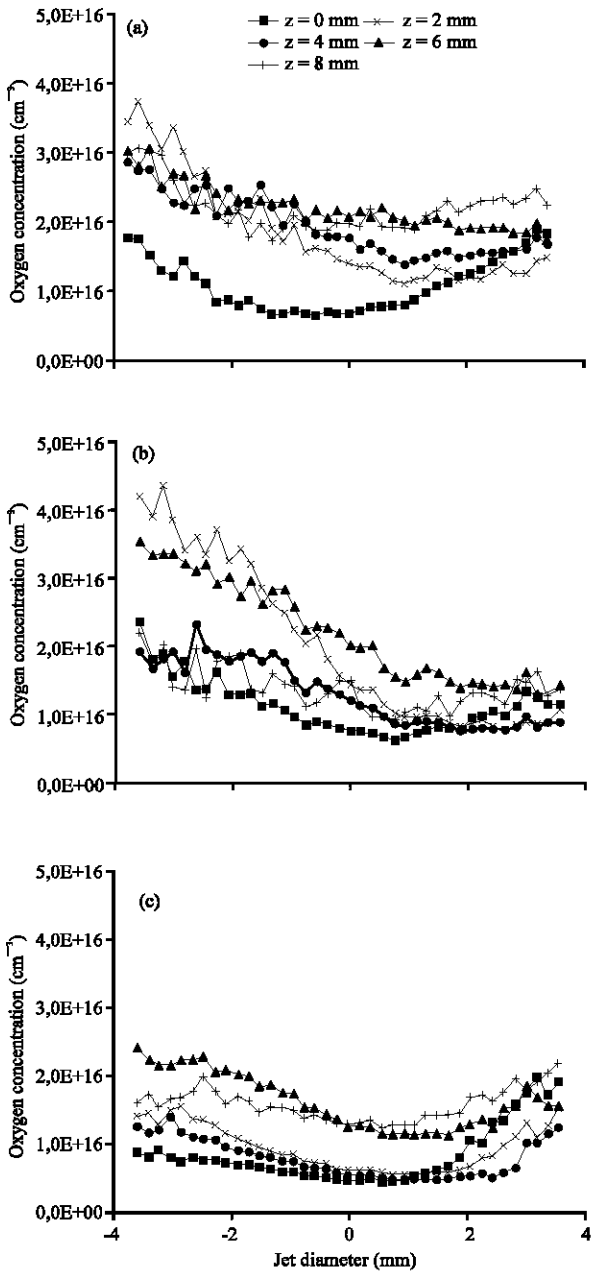

Fig. 5: Oxygen density distribution in the plasma jet at (a) 0.1 L h^{-1} (b) 0.5 L h^{-1} (c) 1 L h^{-1} of water introduction

In the jet emission, molecular OH spectra have been also observed which are due to water dissociation (Cerqueira *et al*., 2004).

Figure 6 shown OH band spectrum at 310 nm due to transition $A^2\Sigma^+$-$X^2\Pi_i$, recorded at the jet axis and z = 25 mm with 0.5 L h^{-1} water admixture. Also in the figure the simulation result for the spectrum is shown supposing the jet plasma to be homogeneous at 6000 K. One can see rather fair general coincidence of the spectra relative intensity. It means a homogeneous OH distribution in the jet which is also confirmed by OH emission profiles across the jet. Also plasma temperature in these jet regions is evidently around 6000 K.

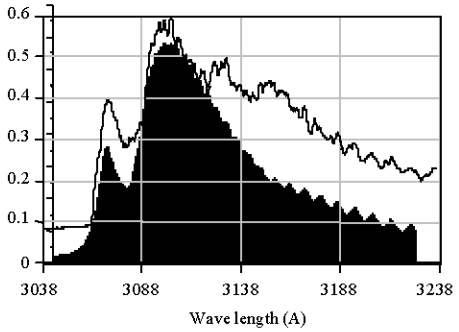

Fig. 6: OH band due to transition $A^2\Sigma^+ - X^2\Pi_i$, recorded at the jet axis and z = 25 mm with 0.5 L h^{-1} water admixture (white) and simulated for T = 6000 K (black)

CONCLUSION

OES techniques have been adopted for the measurements of plasma parameters of ARCs immersed into water spoiled by waste aqueous solution for the water decontamination. Such plasmas are extremely unstable and inhomogeneous, so instead of common OES techniques based on evaluation of the plasma emission coefficients which here do not give reliable results a modified approach has been applied relying upon relative intensity of lines in the plasma total emission spectra and some general data on the plasma behaviour.

The approach has been tested at diagnostics of argon-water plasma produced by a non-transferred ARC. Distributions of the plasma parameters across the ARC jet have been measured with a step of 0.25 mm at different distances z. The measurements have been made at 250 A ARC current, at 30 and 4 NL min^{-1} flows of argon and helium, respectively and at 0.1, 0.5 and 1 L h^{-1} of water introduction. Also, relative content of hydrogen and oxygen have been measured using H_α and O I λ = 777.2 nm lines, respectively and Ar I λ = 696.5 nm line as a reference one. Absolute H, O density values have been evaluated from the plasma composition calculated supposing the plasma consists of argon only.

Emission of OH radicals has been also used to learn the species distribution in the plasma. The band spectrum has been simulated due to transitions between $A^2\Sigma^+$ and $X^2\Pi_i$ electronic states. The resulting vibrational 0-0 band has a head at 306.1 nm was found degrading to the spectrum red side. According to the observation, hydrogen density is about ten times lower, than argon one. It does not depend much on water quantity introduced and slightly increases with the distance from the nozzle. Atomic oxygen density is about two times lower, than that of hydrogen, which corresponds to the admixture stoechiometry. It also increases with z which can be due to further water evaporation down along the plasma jet. Generally, the apparatus and the measurement techniques applied give a rather realistic picture of a spatial distribution of active species, such as H, O and OH, in the water content plasma jet. The results can be applied for a study and/or control of plasmas with much higher water content, e.g., at plasma technology processes of water decontamination.

NOMENCLATURE

- A = Probability of optical transition (s^{-1})
- C = Constant, dimensionless
- $C_{1,2}$ = Combination of parameters for spectral lines 1, 2 under consideration (s^{-1} nm^{-1})
- E = Energy of upper level (J)
- $g_i g_k$ = Statistical weights of atomic ground and upper energy levels, respectively, dimensionless
- I = Intensity of a spectral line (W cm^{-2} sr^{-1})
- k = Boltzmann constant (J K^{-1})
- N_a = Atomic density (cm^{-3})
- T = Temperature (K)
- T_0 = Maximum value in a temperature distribution along the observation direction (K)
- $\bar{T}_0$ = Mean value of the temperature T_0 during the observation time (K)
- T_m = Highest value of the maximum temperature T_0 during the observation time (K)
- y = Direction of observation, dimensionless
- y_0 = Effective dimension of the volume (m)
- z = Distance from the torch nozzle (m)

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