Spectroscopic study of atmospheric pressure 915 MHz microwave plasma at high argon flow rate

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Abstract In this paper results of optical emission spectroscopic (OES) study of atmospheric pressure microwave 915 MHz argon plasma are presented. The plasma was generated in microwave plasma source (MPS) cavity- resonant type. The aim of research was determination of electron excitation temperature $T_{\text{exc}}$, gas temperature $T_g$ and electron number density $n_e$. All experimental tests were performed with a gas flow rate of 100 and 200 l/min and absorbed microwave power $P_A$ from 0.25 to 0.9 kW. The emission spectra at the range of 300 - 600 nm were recorded. Boltzmann plot method for argon 5p - 4s and 5d – 4p transition lines allowed to determine $T_{\text{exc}}$ at level of 7000 K. Gas temperature was determined by comparing the measured and simulated spectra using LIFBASE program and by analyzing intensities of two groups of unresolved rotational lines of the OH band. Gas temperature ranged 600 - 800 K. The electron number density was determined using the method based on the Stark broadening of hydrogen Hβ line. The measured $n_e$ ranged $2 \times 10^{15} - 3.5 \times 10^{15}$ cm$^{-3}$, depending on the absorbed microwave power. The described MPS works very stable with various working gases at high flow rates, that makes it an attractive tool for different gas processing.

keywords: OES, electron excitation temperature, electron number density, gas temperature

1. Introduction
In plasma sources plasma is excited by applying high electric field to a gas. Tendero et al. give an overview of the numerous atmospheric pressure plasma sources which can be classified as DC, RF and microwave sources [1]. Atmospheric plasma sources are important tools for technological applications, e.g. the treatment of critical exhaust gases, plasma chemistry and activation and cleaning of materials [2-6]. Since there is no need for vacuum components, they are mostly easy to integrate in the process line.

The microwave plasma sources (MPSs) found applications in the processing of decomposition of gaseous pollutants like freon [7-11] and also production of hydrogen via methane conversion [12, 13].

Since thermal and electron reactions play an important role in the gas pollutants decomposition, the knowledge of the neutral gas temperature and electron number density in such plasmas is crucial for understanding the chemical kinetics of the gas decomposition process and its optimization.

In our previous spectroscopic investigations, the microwave plasma devices operated at 2.45 GHz and at low gas flow rates (0.5 - 2 l/min) were used [14-16]. The gas temperature and electron number density were about 4000 K and $10^{15}$ cm$^{-3}$, respectively.
In this paper, results of spectroscopic study of microwave plasma at high argon flow rates are presented. The plasma was generated in waveguide-supplied MPS cavity-resonant type operated at 915 MHz. At this frequency the skin effect is weaker, so electromagnetic wave more deeply penetrates the plasma. It can be helpful in the gas processings.

The use of high gas flow rate in the presented device is expected to be of low cost and effective, and thus promising for applications in the treatment of gases. Moreover, the high gas flow rate cools device and protects the electrodes from erosion.

2. Theory
In this paper optical emission spectroscopic (OES) was used for diagnostics of 915 MHz microwave argon plasma. Plasma parameters were determined using the method based on the measurements of intensity and spectral line broadening.

2.1. Electron excitation temperature
Electron excitation temperature is a parameter describing a population of excited atomic levels. The excitation temperature may be determined from argon emission lines intensities. Atmospheric pressure microwave plasma are generally in partial local thermodynamic equilibrium (PLTE) [17, 18].

This suggests to use a Boltzmann plot method to determine the \( T_{\text{exc}} \). Thus an observed light intensity \( I_{nm} \) of radiative transition between levels \( n \) and \( m \) may be given by [17-18]:

\[
I_{nm} = A_{nm} \frac{h c \lambda_{nm}}{\lambda_{nm}} \frac{g_n \exp(-E_n/kT_{\text{exc}})}{Z} N
\]

where: \( A_{nm} \) is the Einstein coefficient for transition \( n \rightarrow m \), \( h \) is the Planck constant, \( c \) is the light speed constant, \( \lambda_{nm} \) is wavelength for transition \( n \rightarrow m \), \( g_n \) is the statistical weight of the upper level \( n \), \( Z \) is the canonical partition function, \( N \) is the population of the ground state level, \( E_n \) is the energy of the upper level \( n \) and \( k \) is the Boltzmann constant.

From the plot \( \ln(I_{nm} \lambda_{nm} / g_n A_{nm}) \) versus the energy \( E_n \), we can estimate the excitation temperature from the slope of the best line that fits the experimental points [17-18].

2.2. Gas temperature
Gas temperature in microwave plasma is close to the rotational temperature \( T_{\text{rot}} \) of the OH radicals [19-21]. The OH \( (A^2 \Sigma \rightarrow X^2 \Sigma) \) transition is one of most intense systems emitted by low temperature plasmas containing even a small amount of H\(_2\)O. This band is widely used for gas temperature estimations.

The rotational temperature can be obtained by fitting the entire band in LIFBASE [22] program or more simply from the relative intensities of groups of unresolved rotational lines corresponding \( G_0, G_1 \) and \( G_{\text{ref}} \) branches of the OH \( (A^2 \Sigma \rightarrow X^2 \Sigma) \) band. These branches form distinct peaks at about 306.4 nm, 306.8 and 309.1 nm, respectively. This OH band has been studied thoroughly by Ch. de Izarra [21]. In order to avoid the difficulties encountered in experimental measurements of group line intensities it has been decided to only consider the maximum amplitude of the groups of lines \( G_0 \) and \( G_1 \). His research has shown that the intensity of \( G_0 \) and \( G_1 \) strongly depends on the rotational temperature. A more detailed analysis of the groups \( G_0 \) and \( G_1 \) shows that the wavelength of their maximum amplitude varies as a function of the \( T_{\text{rot}} \). It is obvious that this amplitudes are dependent on the instrumental broadening \( \Delta \lambda_{\text{I}} \) that must be precisely determined. Izarra publication contains a set of relations \( G_0/G_{\text{ref}} \) and \( G_1/G_{\text{ref}} \) as a function of the gas temperatures varying from 600 – 9000 K, in 200 K steps, and for \( \Delta \lambda_{\text{I}} \) varying from 0.02 – 0.98 nm, in 0.02 nm steps. The similar method was used by Jasinski et al. in [14].

2.3. Electron number density
In plasmas with the electron number densities greater than \( \sim 5 \times 10^{13} \text{ cm}^{-3} \), spatially and temporally resolved \( n_e \) can be determined using the OES of the line shape of the Balmer transition (4-2) of atomic hydrogen at 486.13 nm (H\(_\text{β} \) line) [15, 18, 23-26].

The lineshape of the H\(_\text{β} \) emission is determined by Lorentzian (Stark, van der Waals, resonance, natural) and Gaussian (Doppler, instrumental) broadening mechanisms that result
in a Voigt profile. The convolution of the Gaussian and Lorentzian components results in a Voigt profile. The relation between Gaussian, Lorentzian and the resulted Voigt full-widths at half-maximum (FWHM) profiles is given by \[18, 26\]:

\[
\begin{align*}
\Delta \lambda_V &= \frac{\Delta \lambda_L}{2} + \sqrt{\frac{\Delta \lambda_G^2}{4} + \Delta \lambda_G^2} \\
\Delta \lambda_G &= \Delta \lambda_D + \Delta \lambda_I \\
\Delta \lambda_L &= \Delta \lambda_W + \Delta \lambda_S + \Delta \lambda_N + \Delta \lambda_R
\end{align*}
\]  

where the subscripts represent: V - Voigt , L - Lorentzian, G - Gaussian, D - Doppler, I - instrumental, W - Van der Waals, S - Stark, N - natural, R - resonance. Resonance and natural broadenings are usually negligible due to very low FWHM values in comparison to the Stark, the Doppler, van der Waals and instrumental broadenings \[18, 26\].

The random motion of the atoms in the plasma causes the Doppler broadening of the spectral lines. The FWHM of the Doppler profile is \[24, 26\]:

\[
\Delta \lambda_D = 7.17 \times 10^{-7} \lambda_0 \sqrt{\frac{T_g}{m}} \quad [\text{nm}]
\]  

where \(T_g\) is the gas temperature in Kelvin, \(m\) is the atomic mass in a.m.u. and \(\lambda_0\) is the wavelength.

Van der Waals broadening results from the interaction of an excited atom with neutral ground state atom of another species and is an important broadening mechanism in high-pressure plasmas. The FWHM of the van der Waals profile is \[24\]:

\[
\Delta \lambda_W = 6.48 \times 10^{-22} \frac{P}{kT_g^{0.7}} \quad [\text{nm}]
\]  

where \(P\) is the pressure. One can see that the van der Waals broadening is a gas temperature dependence: if temperature is higher, the broadening is lower.

Perturbation in the wave function on the excited states of hydrogen by the electric field induced by the charged particles of the plasma causes the Stark broadening of the spectral lines. The \(\Delta \lambda_S\) can be calculated using the theory GKS \[27\], where Stark broadening is estimated in a quasi-static approximation using the classic Holtsmark field. The more recent Gig-Card theory is suitable to be used to determine the electron density in atmospheric pressure microwave discharges and give best results that correlates \(\Delta \lambda_S\) and \(n_e\) \[23-26, 28\]. This theory incorporates the ion dynamics to evaluate the Stark broadening of lines spontaneously emitted by the plasma.

3. Experiments

The experimental setup consisted of: microwave generator (915 MHz), isolator, rectangular waveguide (WR 975) as a feeding line, directional coupler, power meters, MPS cavity-resonant type with movable plunger, gas supply and flow control system (see figures 1, 2). To measure the plasma spectrum we used the spectrograph (DK-480 CVI with 1200 and 3600 grooves/mm) equipped with CCD sensitivity calibrated camera (SBIG ST-6 750*242). A PC computer was used to control the spectrograph and acquire the data.

In the resonant cavity two opposite electrodes were placed coaxially in the cavity axis. A gas to be treated at atmospheric pressure flows into the cavity through a gas inlet forming swirl flow round electrodes and then passes between them, so that a microwave plasma is initiated between the two electrodes. One of the electrodes has an axial hole to provide an outlet from the resonant cavity for the plasma and operating gas (based on patent rights \[29, 30\]). The absorbed microwave power \(P_A\) by the discharge was calculated as \(P_I - P_R\), where \(P_I\) and \(P_R\) are the incident and reflected microwave powers, respectively. The incident and reflected microwave powers \(P_I\) and \(P_R\) were directly measured using directional coupler equipped with bolometric heads and HP power meters.

Window in the wall of the generator allows for observation of the microwave discharge. To measure the spectra, the light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length – 75 mm) onto double diaphragm with pinholes of a 1 mm diameter
at the entrance slit of the spectrometer (see figure 3). The width of the spectrometer entrance slit was 50 µm (20 mm height). The double diaphragm were placed to collimate the light. Photos of microwave argon plasmas at different values of absorbed microwave power are shown in figure 4. The figure shows, that the light intensity increases with increasing the value of absorbed microwave power.

![Figure 1. Diagram of the experimental setup.](image1)

![Figure 2. Photo of the experimental setup.](image2)

![Figure 3. The experimental setup used for the spectroscopic investigation.](image3)
4 Results and discussion

In this section we present OES measurements of electron excitation, gas temperature and electron number density. Spectra were recorded and then corrected according to the wavelength sensitivity of CCD camera. The wavelength sensitivity of CCD camera was determined using a tungsten halogen calibration lamp. Using a Hg-Ne low-pressure calibration lamp ($\lambda = 365.02$ nm, 435.84 nm and 546.07 nm, Hg I) we measured that the Gaussian instrumental line profile FWHM was about 0.134 nm and 0.06 nm for 1200 and 3600 grooves/mm grating, respectively. Typically, spectra were measured with 1200 grooves/mm grating. Only for OH ($A^{2}Σ \rightarrow X^{2}Σ$) rotational band measurements the 3600 grooves/mm grating was used. All experimental tests were performed with the argon flow rate of 100 and 200 l/min.

4.1. Electron excitation temperature measurements

The electron excitation temperature can be determined using the Boltzmann-plot method from the selected argon $4p-4s$ and $5p-4s$ transition lines (figure 5). The list of selected argon lines with spectroscopic parameters: $g_n$, $A_{nm}$, $\lambda_{nm}$ and $E_n$ are shown in table 1. Electron excitation temperature can be estimated from the best linear fit of plot $\ln(I_{nm}/g_nA_{nm})$ versus the energy $E_n$ [17-18] (figure 6a). Figure 6b shows electron excitation temperature as a function of absorbed microwave power. Obtained $T_{exc}$ at level 7000 K is independent of absorbed microwave power and flow rate.

Figure 5. Emission spectrum of argon plasma with selected argon $4p-4s$ and $5p-4s$ transition lines for Boltzmann-plot method. Absorbed microwave power - 0.4 kW, flow rate - 200 l/min.
### Table 1. Spectroscopic parameters of argon lines for Boltzmann plot method [31].

| λ [nm] | Radiative transition | $A_{\text{rad}} \times 10^7$ [s$^{-1}$] | $g_n$ | $E_n$ [cm$^{-1}$] |
|--------|----------------------|--------------------------------------|------|-----------------|
| 394.9  | 4s - 5p              | 0.0333                               | 3    | 118459          |
| 404.44 | 4s - 5p              | 0.0455                               | 2    | 118469          |
| 415.86 | 4s - 5p              | 0.1400                               | 5    | 117183          |
| 420.06 | 4s - 5p              | 0.0967                               | 7    | 116942          |
| 425.93 | 4s - 5p              | 0.3980                               | 1    | 118870          |
| 427.75 | 4s - 5p              | 0.0797                               | 3    | 117151          |
| 430.01 | 4s - 5p              | 0.0377                               | 5    | 116999          |
| 434.51 | 4s - 5p              | 0.0297                               | 3    | 118407          |
| 451.07 | 4s - 5p              | 0.1180                               | 1    | 117562          |
| 518.77 | 4s - 5d              | 0.1308                               | 5    | 123372          |
| 555.87 | 4s - 5d              | 0.1420                               | 5    | 122086          |
| 560.67 | 4s - 5d              | 0.0333                               | 3    | 121932          |
| 573.95 | 4s - 5d              | 0.0455                               | 2    | 123505          |
| 603.21 | 4s - 5d              | 0.1400                               | 5    | 122036          |

**Figure 6.** a) Boltzmann plot for argon $4p$–$4s$ and $5p$–$4s$ transition lines ($P_d = 0.4$ kW, $Q = 200$ l/min), b) Electron excitation temperature as a function of absorbed microwave power $P_d$ for two values of argon flow rate 100 and 200 l/min.

#### 4.2. Gas temperature measurements

To determine rotational temperature the emission spectra at the range of 305.5 - 309.5 nm were recorded (figure 7). The OH radical emissions are results of water vapor naturally present as impurity in the gas, so the intensity of the ($A^2 \Sigma \rightarrow X^2 \Sigma$) rotational band was very low. According to this in measurements the width of the entrance slit of the spectrograph was set at 100 µm. Due to the low light intensity, the double diaphragm (at the entrance slit) was not used.

After having the experimental spectrum of OH, a simulation of this band was carried out using LIFBASE program. The simulated OH ($A^2 \Sigma \rightarrow X^2 \Sigma$) band was fitted to the experimental one by variation of the rotational temperature. Figure 7 shows the comparison of the both spectra: experimental and simulated fitted to the experimental one. Figure 8 presents obtained $T_{rot}$ as a function of absorbed microwave power. The temperature slowly increases with increasing absorbed microwave power and with decreasing the working gas flow rate (figure 8). The second way to determine $T_{rot}$ was maximum amplitude relations $G_0/G_{ref}$, $G_1/G_{ref}$ from the measured spectrums.
4.3. Electron number density measurements

To obtain a detectable intensity of H\(_\beta\) emission spectral line a small addition of H\(_2\) (0.5\%) was introduced to argon flow. Assuming that the gas temperature in discharge is constants (absence dependence of the absorbed microwave power, figure 8) and is at the level of 700 K for Q = 100 l/min and 650 K for Q = 200 l/min, respectively. For this values, dependence (3) allows to estimate the value of the Doppler broadening for the H\(_\beta\) line. From equation (2) the FWHM of Gaussian profile can be determine. The FWHM values of the Gaussian profile of H\(_\beta\) line is given in table 2. The parameters presented in table 2 are independent of the absorbed microwave power.

| Q [l/min] | \(\Delta\lambda_1[/nm]\) | \(\Delta\lambda_2[/nm]\) | \(\Delta\lambda_G[/nm]\) |
|-----------|----------------|----------------|----------------|
| 100       | 0.134          | 0.009          | 0.134          |
| 200       |                |                |                |
Figure 9 shows an example of Hβ spectral line profile measured in microwave argon plasma and the Voigt profile fitted to the experimental points.

Figure 9. Measured Hβ line profile and the Voigt function fitted to the experimental points for argon plasma. Absorbed microwave power $P_A$ - 0.4 kW, flow rate - 200 l/min.

The fitting was made using the Voigt function with a Gaussian line width of 0.134 nm (table 2) in Origin software. Deconvolution the Voigt profile return value of the FWHM Lorentzian profile (Stark and van der Waals). The van der Waals broadening can be calculated from equation 4. Obtained $\Delta \lambda_W$ at the level of 0.051 nm for 650 K and 0.046 nm for 700 K, respectively. The difference between the measured FWHM of Lorentzian profile and calculated the van der Waals broadening gives the Stark broadening (2).

The electron number density calculated from Gig-Card and GKS theory is shown in figure 10. Obtained electron number density $n_e$ ranged $2 \times 10^{15} - 3.5 \times 10^{15}$ cm$^{-3}$ depending on the absorbed microwave power and flow rate. Generally, Gig-Card theory always gives lower values of the electron number density than GKS theory.

Figure 10 Electron density as a function of absorbed microwave power for two values of argon flow rate: a) 100 l/min, b) 200 l/min.
5. Conclusions

Spectroscopic study of microwave 915 MHz argon plasma at atmospheric pressure and high flow rate was presented in this work. The study concerns to determine electron excitation, gas temperature and electron number density. The results showed that:

- Electron excitation temperature obtained at level 7000 K is independent of absorbed microwave power and argon flow rate,
- The rotational temperatures of OH radical ranged from 600 up to 800 K, depending on absorbed microwave power and argon flow rate,
- Electron number density was from $2 \times 10^{15} \text{ cm}^{-3}$ to $3.5 \times 10^{15} \text{ cm}^{-3}$, depending on the operating parameters (absorbed microwave power, argon flow rate) and theory that was used (GKS or Gig-Card theory).

The investigated microwave plasma source cavity-resonant type works very stable with various working gases. The parameters (flow rate, absorbed microwave power) can be changed in wide range that makes MPS an attractive tool for different gas processing at high flow rates.

References

[1] Tendero C Tixier C Tristant P Desmaison J and Leprince P 2006 Atmospheric pressure plasmas: a review Spectrochim. Acta B 61 2-30
[2] Leins M Alberts L Kaiser M Walker M Schulz A Schumacher U and Stroth U 2009 Development and characterisation of a microwave-heated atmospheric plasma torch Plasma Process. Polym. 6 227-232
[3] Baeva M Pott A and Uhlenbusch J 2002 Modelling of NOx removal by a pulsed microwave discharge Plasma Sources Sci. Technol. 11 135–141
[4] Uhm H S Hong Y C and Shin D H 2006 A microwave plasma torch and its applications Plasma Sources Sci. Technol. 15 26-34
[5] Mizeraczyk J Jasinski M and Zakrzewski Z 2005 Hazardous gas treatment using atmospheric pressure microwave discharges Plasma Phys. Control. Fusion 47 589-602
[6] Kabouzi Y Moisan M Rostaing J C Trassy C Guerin D Keroack D and Zakrzewski Z 2003 Abatement of perfluorinated compounds using microwave plasmas at atmospheric pressure J. Appl. Phys. 93 9483- 9497
[7] Jasinski M Mizeraczyk J Zakrzewski Z Ohkubo T and Chang J 2002 CFC-11 destruction by microwave tower generated atmospheric-pressure nitrogen discharge J. Phys. D: Appl. Phys. 35 2274–2280
[8] Jasinski M Mizeraczyk J and Zakrzewski Z 2004 Microwave torch plasmas for decomposition of gaseous pollutants J. Adv. Oxid. Technol. 40 51-58
[9] Jasinski M Mizeraczyk J Zakrzewski Z and Chang J 2002 Decomposition of C2F6 in atmospheric-pressure nitrogen microwave torch discharge Czech. J. Phys. D 52 743-749
[10] Jasinski M Mizeraczyk J and Zakrzewski Z 2002 Decomposition of freons in atmospheric-pressure air using coaxial-line-based low-power microwave torch plasma Journal of High Temperature Material Processes 6 317-320
[11] Jasinski M Dors M and Mizeraczyk J 2009 Destruction of freon HFC-134a using a nozzleless microwave plasma source Plasma Chem. Plasma Process. 29 363-372
[12] Jasinski M Dors M and Mizeraczyk J 2009 Przegląd Elektrotechniczny 85 121-123
[13] Jasinski M Dors M and Mizeraczyk J 2009 Eur. Phys. J. D 54 179-183
[14] Jasinski M Mizeraczyk J and Zakrzewski Z 2002 Measurements of neutral gas temperature in microwave torch plasmas at atmospheric pressure Czech. J. of Phys. D 52 421-426
[15] Jasinski M Mizeraczyk J and Zakrzewski 2006 Spectroscopic measurements of electron density in atmospheric-pressure surface wave sustained discharge in argon Czech. J. of Phys. D 56 787-794
[16] Czylkowski D Jasinski M and Mizeraczyk J 2006 Argon and neon plasma columns in continuous surface wave microwave discharge at atmospheric pressure Czech. J. of Phys. B 56 684-689
[17] Griem H R 1964 Plasma Spectroscopy (New York, McGraw-Hill)
[18] Sismanoglu B N Grigorov K G Santos R A Caetano R Rezende M V O Hoyer Y D and Ribas V W 2010 Spectroscopic diagnostics and electric field measurements in the near-cathode region of an atmospheric pressure microplasma jet *Euro. Phys. J. D* **60** 505-16

[19] Moon S and Choe W 2003 A comparative study of rotational temperatures using diatomic OH, O2 and N2+ molecular spectra emitted from atmospheric plasmas *Spectrochim. Acta Part B* **58** 249-257

[20] Kopecki J Kiesler D Leins M Schulz A Walker M Kaiser M Muegge H and Stroth U 2010 Investigations of a high volume atmospheric plasma torch at 915 MHz *Surface & Coatings Technology* **205** 342-346

[21] Izarra Ch 2000 UV OH spectrum used as a molecular pyrometer *J. Phys. D: Appl. Phys.* **33** 1697-1704

[22] Luque J and Crosley D R 1999 LIFBASE: Database and spectral simulation program (Version 1.5) *SRI International Report* MP 99-009

[23] Hrycak B Jasinski and M Mizera czyk J 2010 Spectroscopic investigations of microwave microplasmas in various gases at atmospheric pressure, *Euro. Phys. J. D* **60** 610 - 619

[24] Lazzaroni C Chabert P Rousseau A and Sadeghi N 2010 Sheath and electron density dynamics in normal and self-pulsing regime of a micro hallow cathode discharge in argon gas *Euro. Phys. J. D* **60** 555-563

[25] Jasinski M Mizera czyk J and Zakrzewski Z 2004 in *Proceedings of the XVth Int. Conf. on Gas Discharges and their Applications*, Toulouse

[26] Sismanoglu B N Grigorov K G Caetano R Rezende M V O and Hoyer Y D 2010 Spectroscopic measurements and electrical diagnostic of microhollow cathode discharges in argon flow at atmospheric pressure *Euro. Phys. J. D* **60** 505-516

[27] Griem H R 1974 Spectral line broadening by plasmas *Academic Press New York* 316

[28] Gigosos M A and Cardenosos V 1996 *J. Phys. B: AT. Mol. Opt. Phys.* **29** 4795

[29] Gillespie R F Hall S I and Raybonde D and Winterbottom F 2000 Plasma gas processing U.S. patent no. US 5418430

[30] Bayliss K H 1995 Plasma generator with field-enhancing electrodes U.S. patent no. US 5418430

[31] http://physics.nist.gov/PhysRefData