Optical Emission Spectroscopy as a Diagnostic Tool for Characterization of Atmospheric Plasma Jets

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Abstract: A suitable technique for localized surface treatment of solid materials is an atmospheric pressure plasma jet (APPJ). The properties of the APPJ plasma often depend on small details like the concentration of gaseous impurities what influences the surface kinetics. The simplest and often most useful configuration of the APPJ is presented, characterized by optical emission spectroscopy (OES), and results are discussed in view of various papers. Furthermore, results of additional recent papers on the characterization of the APPJ by OES are presented as well. Because the APPJ is operating at atmospheric pressure, even the water vapor traces may significantly alter the type and concentration of reactive species. The APPJ sustained in noble gases represents a source of vacuum ultraviolet (VUV) radiation that is absorbed in the surface of the treated material, thus causing bond scission. The addition of minute amounts of reactive gases causes significant suppression of VUV radiation and the formation of reactive radicals. These radicals such as OH, O, N, NO, O$_3$, and alike interact chemically with the surface causing its functionalization. Huge gradients of these radicals have been reported, so the surface finish is limited to the area reached by the radicals. Particularly OH radicals significantly prevail in the OES spectra, even when using very pure noble gas. They may cause suppression of other spectral features. OH radicals are especially pronounced in Ar plasmas. Their density decreases exponentially with a distance from the APPJ orifice.

Keywords: atmospheric pressure plasma jet (APPJ); optical emission spectroscopy (OES); plasma-surface interactions; local surface modification; polymers; functionalization

1. Introduction

A standard method for tailoring surface properties is a brief treatment of a solid material by non-equilibrium gaseous plasma. Plasma sustained in molecular gases is rich in reactive chemical species that interact with surfaces of different materials, causing its modification. A variety of gaseous plasmas have been used for the treatment of different materials. Non-equilibrium plasmas are divided into low-pressure [1] and atmospheric-pressure plasmas [2]. Low-pressure plasmas are usually sustained in the range of pressures between about 1 and 1000 Pa. In-between 1000 and 100,000 Pa (1 bar), there is a black zone rarely tackled by researchers. Gaseous plasma can also be sustained at pressures well above 1 bar, but the practical applications are limited. Low-pressure plasmas often occupy large volumes, so any material is treated rather uniformly over the entire surface facing the plasma. The application of such low-pressure plasmas for modification of a specific area on the surface of products is, however, limited because of the complicated handling of the products that should enter a vacuum chamber. Treatment of numerous products in the continuous mode thus represents a technological challenge when low-pressure plasma is used for surface modification. This obstacle is the main reason for using atmospheric pressure plasmas which can be focused onto the desired surface area, especially when localized treatment is the goal. Atmospheric-pressure plasma jet (APPJ) enables, for example, polymer activation over an area of the order of the cross-section of
the visible plasma jet [3–5]. The APPJ is also very popular for medical applications such as wound treatment [6,7], cancer treatment [8,9], bacterial inactivation [10,11], and even for the deposition of thin films [12,13] and coatings [14,15]. In the latter case, the localized surface treatment may not be an advantage any more, especially if larger substrates need to be coated. This can be overcome by scanning the surface of the substrate material [16]. A review of recent applications of the APPJ was published by Penkov et al. [17].

Atmospheric-pressure plasmas are sustained either by a rather low-frequency alternative current (AC) discharges, or radiofrequency (RF), or even microwave (MW) discharges. Depending on the frequency of the power supply, the plasma may be continuous or in short pulses. When the frequency of the power supply is large enough so that the period is shorter than the typical life-time of gaseous plasma, the plasma is sustained in the continuous mode. The continuous mode often occurs at frequencies larger than MHz. Low-frequency discharges will typically create individual streamers of electrons, which will, in turn, cause the formation of a rather dense plasma with the life-time much shorter than the period of the voltage supply.

Numerous methods for atmospheric pressure plasma characterization have been invented [18–21]. Most are based on optical emission or absorption. As long as the discharge is in the continuous mode, methods will give the correct values of plasma parameters. In the case of pulsed plasmas, only a few methods will enable measuring plasma parameters in real-time. Most methods will just give values averaged over the acquisition time. Some methods have a high spatial resolution, while many others will average the signal over the probed volume. Most of the methods also require a deep understanding of the physical phenomena, so the interpretation of the measured signal is far from being trivial. This is a reason why they are not routinely used by researchers who work on the modification of materials’ surface properties by plasmas but are not specialists in plasma physics.

Because users of plasma techniques are often not familiar with physical processes in non-equilibrium gaseous plasmas, they are seeking an appropriate method that will give basic information about the properties of plasmas. Especially characterization of the APPJ plasmas [22,23] is of particular interest because they are simple to construct and do not require expensive, complicated instruments. APPJ plasmas may be of different configurations, but the simplest one is single-electrode APPJ. A review of APPJ devices can be found in [22,23]. Plasmas at atmospheric pressure are much more demanding for characterization than low-pressure plasmas because of the simple fact that large spatial or temporal gradients are typically present. Any improper interpretation of the measured signal will lead to a misunderstanding of the phenomena taking place on the surface of a sample during plasma treatment. To this end, the users are looking for a simple, cheap, and reliable technique for the characterization of atmospheric-pressure plasmas. One such technique is optical emission spectroscopy (OES), which can give information on the presence of various species in the discharge.

Let us briefly present this technique. Because plasma emits a light, the basic principle of OES is to collect and detect the emitted light photons. The gaseous atoms and molecules in plasma are excited to various levels upon plasma conditions. The excitation is often a consequence of an inelastic collision of a free electron with a molecule or atom. The electron energy has to be above the threshold. Many excited states are at the potential energy of approximately 10 eV, so much higher than the electron temperature. Therefore, only the electrons within the high-energy tail of the energy distribution function will be capable of exciting the radiative states. An alternative is a step-wise excitation: An electron first excites an atom or a molecule to a metastable state, and another electron causes excitation to the radiative level. Such two-step processes are effective as long as the excited metastable is not relaxed by any method (quenched). An alternative is a collision of at least one atom or molecule in a metastable state of high potential energy with another particle. The resultant molecule is of a short life-time and relaxes by radiation (excimer, exciplex molecules). A
three-body collision is often required in the latter case. Such collisions are likely to occur at atmospheric pressure because the three-body collision frequency is roughly 1 MHz at 1 bar. Whatever mechanism, the shelf-time of the radiative state is very short—of the order of nanoseconds. The extremely short shelf-time assures for relaxation of such states by radiation rather than any other method (such as quenching). Different atoms and molecules will radiate in a specific range of wavelengths that correspond to the potential energy difference between the upper and lower excited states. The lower state may or may not be the ground state. The relaxation of excited atoms is usually exhibited in separated lines. High-resolution spectrometers will also reveal the fine structure.

The two-atom molecules will radiate in bands. For a given electronic transition, there will be numerous vibrational transitions, and for a given vibrational, there will be rotational transitions. In some cases, the lower electronic state of a two-atom molecule is not stable but dissociates. In such cases, the molecule will relax by continuum radiation. More complex molecules will normally relax by radiating a continuum.

In any case, the wavelengths indicate the upper and lower excited levels; therefore, the spectral features can be attributed to specific atoms or molecules. The radiation intensity depends on numerous factors, so optical emission spectroscopy is a qualitative technique. It may be semi-quantitative if a known concentration of another atom or molecule is added intentionally. The technique is often called actinometry or titration. Great care should be taken when interpreting the results of actinometry or titration [24].

Inexpensive spectrometers will cover a range of wavelengths between approximately 200 and 1200 nm, i.e., in the visible, near-infrared, and ultraviolet ranges. The spectral response is far from being constant, so calibration with a standard source is recommended at any attempt to use OES for plasma characterization. The standard spectrometers will therefore detect radiation arising in a range of photon energies between the upper and lower energy levels (1 and 6 eV). Most atomic transitions such as Ar, He, O, N, H, to the ground state are below 200 nm. These transitions are, therefore, invisible by standard spectrometers. The transitions to the ground state are normally much more extensive than to other states, so one misses most radiation when using standard spectrometers. This limitation should be taken into account at any attempt to interpret the plasma spectra acquired by OES. The VUV spectrometers (wavelength 100–200 nm) are increasingly popular in plasma science, but one should keep in mind that the radiation of photon energy above the dissociation energy of oxygen molecules (5.2 eV) is absorbed in air, what complicates the experimental setup. Still, knowing the above limitations, one can find OES a useful, simple, and inexpensive technique, so it is widely used for the basic characterization of atmospheric plasmas.

OES can also enable the determination of the gas temperature, electron density, and electron excitation temperature; however, this already requires more in-depth knowledge. The methods for deduction of these plasma properties are not trivial and are beyond the scope of this paper. Gas temperature is assumed to be similar to rotational temperature \( T_g \approx T_{rot} \). Gas temperature \( T_g \) is thus determined from the calculation of rotational temperature \( T_{rot} \) of diatomic molecules considering Boltzmann distribution of rotational states [13,25,26]. For the APPJ plasmas, \( \text{OH(A)} \) and \( \text{N}_2(\text{C}) \) excited states are usually used for the determination of the rotational states. However, the obtained \( T_{rot} \) may differ if calculated from \( \text{OH} \) or \( \text{N}_2 \), and it often leads to an overestimation of \( T_g \) [13].

The spatial resolution depends on the lenses mounted at the end of the optical fiber. Normally, the radiation is collected from a solid angle of few degrees. The acquisition time depends on the radiation intensity. Widely used inexpensive spectrometers will have an adjustable acquisition period between approximately 1 ms and several s. Obviously, simple spectrometers will be particularly useful for characterization of plasma in a continuous mode. When the plasma is in the form of streamers of shelf-time well below a ms, the OES will give values averaged over numerous streamers.

The present paper explains some basic properties of the OES technique and gives a review of published literature, which is summarized in Table 1 and further discussed in the main part (Sections 2 and 3). Moreover, additional details regarding the APPJ
configuration, flow rate, voltage, power, etc., are given in Table 1, making the comparison of various results easier. In the main part, some authors’ own experiments are presented and discussed in a view of the cited literature, which gives a more comprehensive insight in the phenomena likely to occur in APPJs.

Table 1. Summary of characterization of APPJ by OES.

| REF  | Gas Composition            | APPJ Configuration                                                                 | Findings by OES Diagnostics                                                                 |
|------|-----------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| [13] | Ar/TEOS (tetraethyl orthosilicate) | AlmaJET, single electrode corona jet, AC power supply, 12 kHz, 12 kV amplitude, power 11.5 W, Ar flow 2 slm, 17 ppm TEOS | Besides peaks characteristic for Ar plasma with the presence of water vapor, the addition of TEOS resulted in the appearance of additional excited species: CH, CN, and C₂ bands. T<sub>rot</sub> of OH(A), N₂(C), and CH(A) were determined using two different simulation software. T<sub>rot</sub> calculated from OH was much lower (410 K) than T<sub>rot</sub> calculated from N₂ (550 K) and CH (590 K). The length of the plasma jet was decreasing with increasing water content. At very high water content, the plasma was unstable. In pure Ar plasma, N₂ dominated in OES spectra measured 2 mm from the nozzle. With the addition of water vapor, N₂ diminished, and OH became dominant. T<sub>rot</sub> was determined, and it increased with water addition. Besides Ar, molecular N₂, atomic O and OH were observed in pure Ar plasma. The addition of CO₂ caused a decrease in emission lines and the disappearance of oxygen, whereas OH and N₂ were still observed. Additionally, the CO Angstrom band was observed in Ar/CO₂ mixture. OES was measured 15 mm from the ground electrode. OH and lines of Ar were found. T<sub>rot</sub> was determined, and it was increasing with the increase in the water content. The addition of water to Ar caused the decrease in all atomic line intensities. The emission of OH radicals was not linearly dependent on the water content, but it had a maximum at 350 ppm. The electron temperature was measured (0.4 eV). The plume temperature was also measured versus voltage and flow rate. Depending on the frequency and gas flow, it was in the range 25–40 °C. Ar, as well as atomic O, OH, and N₂ peaks, were found in Ar plasma. OH peak was much stronger than O line even if O₂ was added to Ar. The origin of water was the desorption of water molecules from the quartz discharge tube. Besides Ar lines, significant OH radiation was observed as well as N₂ lines and O-atom line. The increase in water content caused a decrease in all atomic lines. The addition of water also caused an increase in the gas temperature from 620 (pure Ar) to 1130 K (0.76% H₂O). OES profiles were measured along with the jet every 5 mm up to a distance of 35 mm. The OH concentration was maximal at the minimum addition of water to the feed gas (0.05%). |
| [27] | Ar + H₂O | 2.45 GHz MW plasma, 104 W, gas flow 1.7 slm, H₂O content = 0–1.9% | |
| [28] | Ar with/o CO₂ | DBD plasma jet, 71 kHz, 6 kV (peak-to-peak), 3 slm of pure Ar and 2.9/0.1 slm of Ar/CO₂ | |
| [29] | Ar + H₂O (up to 7600 ppm) | Second ring-shaped ground electrode, sinusoidal voltage frequency 71 kHz, 10–20 kV (peak-to-peak), power 12.88 W, gas flow 0.695–4.82 slm | |
| [30] | He or Ar (with/o addition of O₂) | Additional outer ground electrode, pulsed power supply (voltage up to 3 kV, 60 kHz), sinusoidal or RF power supply, Ar or He flow rate 1–8 L/min | |
| [31] | Ar with/o H₂O | Additional grounded outer electrode, 71 kHz, power 12.8 W, peak-to-peak voltage 12.2–17 kV, 0.7–4.8 slm with 0.05–0.76% of water | |
Table 1. Cont.

| REF  | Gas Composition | APPJ Configuration | Findings by OES Diagnostics |
|------|-----------------|--------------------|----------------------------|
| [32] | Ar, He (with/o addition of CH$_4$ or C$_2$H$_2$) | Coaxial configuration with the inner and outer electrode, 13.56 MHz, rms voltage 200–250 V, rms current 0.4–0.6 A, 3 slm of Ar/He and 160 sccm Ar(He)/CH$_4$ | The collimating lens was positioned 140 mm from the end of the jet. The special construction of APPJ allowed the insertion of Ar(He)/CH$_4$ gas by a capillary tube into the main Ar/He flow, which prevents the mixing of the surrounding gas. In pure Ar plasma, the Ar and OH emission dominated. Additionally, in the Ar/CH$_4$ mixture, CH and C$\text{}_2$ bands were observed. In Ar/CH$_4$, CH was more dominant than C$\text{}_2$; whereas, in Ar/C$_2$H$_2$, C$\text{}_2$ band was more intense. Opposite to other authors, no N$_2$ emission was detected by OES because of special construction that prevented the mixing of the surrounding air. Electron density ($8 \times 10^{20}$ m$^{-3}$) and gas temperature (<400 K) were also measured from the fine structure of the rotational bands of OH. OES was measured at various axial positions along with the plasma jet up to 12 mm (sampled every 2 mm). A maximum in the intensity of Ar lines was at 4 mm from the exit. The intensity of N$_2$ lines was increasing along with the jet because of the mixing of the surrounding gas. Significant OH emission was also detected. They found that APPJ is a source of UV-B (309 nm) and UV-A radiation (350, 380 nm), whereas no UV-C was detected in the range 250–280 nm. Irradiance in the UV range was determined to be 5 mW/cm$^2$ at the maximum power and the lowest axial distance. It can be concluded that several seconds of exposure of skin does not exceed the allowed exposure limit of 3 mJ/cm$^2$. |
| [33] | Ar kINPen, DC supply, 3–6 W, Ar flow 5 slm | AC power supply, 18 kV, 15 kHz, He flow 20 L/min, H$_2$O flow 3 mL/min | An increase in OH was observed when water droplets were added to He APPJ. For Ar plasma, OH and N$_2$ species were dominant. For He plasma, N$_2^+$ and O were observed. Emission profiles were measured versus a distance from the tube exit. Production of OH and O radicals was investigated. The production of OH and O was increasing with increasing Ar content in the gas mixture and with the applied voltage, but decreasing with increasing air flow. |
| [34] | He + H$_2$O | DBD type APPJ, AC power supply, 5 kV, 50 kHz, He flow: 2–4 slm, Ar flow: 1–3.5 slm 2% H$_2$O in Ar/Air mixture, Ar flow 3 lpm, air flow: 3–15 lpm, voltage 4–7 kV, 250 Hz square wave power source | NO, OH, N$_2$ molecular, atomic N, He and O, and O$_2^+$ species observed. Gas temperature was found to be ~310 K, and the electron excitation temperature was ~5420 K. OES was also used to investigate the generation of various species when the plasma jet was impinging onto the liquid. Besides He lines, also OH, O, N$_2$, and N$_2^+$ species were detected. Rotational and vibrational temperatures from OH radical were determined in the active and afterglow region. Gas temperature slightly increased when O$_2$ was added or when moved from active to afterglow region. In the active plasma region, it was 310 and 340 K for He or He/O$_2$, respectively. Whereas $T_{\text{vib}}$ was 2200 or 2500 K, respectively. |
| [35] | Ar or He | DBD plasma jet, pulsed DC power supply, 10 kHz, duty cycle 20%, peak-to-peak voltage 2–3.2 kV, min. power 5 W, He flow 2.5–5.5 slm | |
| [36] | Air/Ar/H$_2$O | DBD-type APPJ, AC power supply, 60 kHz, peak to peak voltage 6–14 kV, 18 W, gas flow 3 slm, 0.1–0.5% of O$_2$ | |
| [37] | He | | |
| [38] | He + O$_2$ | | |
Table 1. Cont.

| REF  | Gas Composition | APPJ Configuration | Findings by OES Diagnostics |
|------|-----------------|--------------------|----------------------------|
| [39] | He              | DBD type APPJ, square wave AC supply, peak-to-peak voltage 6 kV, flow rate: 2–7 L/min | The spatial distribution of radicals along the plasma plume was investigated versus the applied voltage and gas flow rate. Various He emission lines, O, OH, N\(_2\) and N\(_2^+\) were observed. A strong decrease in emission intensity of He, O, and OH with a distance from the APPJ exit was observed. Opposite, N\(_2\) and N\(_2^+\) reached a maximum at a distance of 5 mm from the exit and then gradually decreased. |
| [40] | He/O\(_2\)      | Powered hollow electrode, 2–10 kV\(_{pp}\), 18 kHz, up to 0.33% O\(_2\) addition, flow 3 slm | The radiation intensity of RN and ROS radicals was strongly dependent on the O\(_2\) concentration. For ROS radicals, different behavior of the emission intensity versus the O\(_2\) concentration was observed than for RN radicals. |
| [41] | Ar              | kINPen, 1.4 MHz, gas flow: 5–15 slm | Production of NO radicals versus air admixture was investigated. The NO emission had a maximum at 0.1–0.2% of air admixture in Ar. The influence of the MW power and gas flow rate on the emission intensity of plasma radicals was investigated. A strong dependence of emission intensities on the power was observed. |
| [42] | Ar, He, Ar + He | MW power 5–70 W, gas flow 100–1000 sccm | OES measurements in UV and VUV for the various admixture of O\(_2\) from 0 to 0.6%. The following species were observed in the range 100–350 nm: O, O\(_2\), NO, and OH. |
| [43] | He/O\(_2\)      | Micro-APPJ, 13.56 MHz, up to 0.6% O\(_2\) admixture | C, CN, CH, and C\(_2\) species were observed in ethanol plasma. An increase in ethanol content in Ar caused a decrease in Ar lines and an increase in the relative amount of C\(_2\). No significant dependence of the intensity ratio of excited species with the increase in RF power. |
| [44] | Ar/C\(_2\)H\(_5\)OH | 33 MHz RF power source, various powers | |

2. OES Characterization of the Reactive Species along the APPJ Plasma Jet

APPJs have nowadays become very important in many applications, especially for localized treatment of polymers and for various biomedical applications. Therefore, the knowledge on the generation of excited species and the control of their intensities during the treatment of materials with the APPJ is important. OES is a method that enables the real-time monitoring of the reactive plasma species during the operation of the APPJ.

Here we report an example of the OES measurement along the plasma jet of one of the most commonly used and simple configurations of the APPJ (Figure 1). It is a single electrode APPJ having only one electrode. Alternatively, an additional electrode can be placed outside the dielectric tube, but in many practical cases, this is not necessary. A glowing plasma is stretching from the tip of the metallic electrode (a copper wire) mounted coaxially into the dielectric tube (made of Pyrex glass). The luminosity of gaseous plasma is the largest at the electrode tip and decreases with increasing distance. More details of this APPJ can be found in [3]. The discharge tube was made from Pyrex. The length of the discharge tube was 15 cm, and the inner diameters was 3 mm. A copper wire electrode was mounted inside the tube. A diameter of the copper electrode was 0.3 mm and the length of the electrode was the same as the length of the dielectric tube, i.e., 15 cm. The length of luminous plasma depends on the type of gas flown through the dielectric tube, the gas flow, and the properties of the power supply. In our case, a visible part of the plasma jet extended up to 3 cm from the exit of the discharge tube. The plasma jet shown in Figure 1 was fed with Ar gas with a purity of 5.0. The flow rate was adjusted to 1 slm. The powered copper electrode that was mounted inside the Pyrex dielectric tube was connected to an AC
power supply. The voltage of the power supply used in this study was 7 kV (peak-to-peak), whereas the excitation (sinusoidal) frequency was 25 kHz. The power was estimated to a few Watts. The electrical field is the highest at the tip of the electrode. The high enough electric field causes the formation of electron streamers. Therefore, our plasma was in the form of streamers rather than continuous plasma. The electron streamers may also appear along the electrode, but they are much weaker because of the lower electric field. The configuration of streamers, as shown in Figure 2, is typical for the case when the plasma device is in ambient air. If the device is placed in a container filled with a noble gas, the intense streamers will not be observed only along the axis but will also propagate radially.

Figure 1. A photo of the atmospheric-pressure plasma jet. The substrate is a wooden plate at a floating potential.

Figure 2. Schematic presentation of the axial plasma jet characterization by moving the optical fiber.

OES was applied for basic plasma characterization of the glowing plasma as shown in Figure 2. The radiation was acquired through an optical fiber, which was mounted on a movable holder. An appropriate lens was placed on the tip of the optical fiber to enable space-resolved measurements. The spectrum acquisition time depends on the luminosity of the plasma jet and the properties of the spectrometer, but the typical value was 10 ms. The time resolution of the simple spectrometer was therefore good enough to perform a
gradual characterization with a reasonable vertical resolution by moving the optical fiber vertically along the jet, as shown in Figure 2.

A typical OES spectrum of Ar plasma acquired close to the electrode tip of the APPJ device (i.e., 2 mm from the exit) is shown in Figure 3 (lower curve). Moreover, the OES spectra acquired 10 and 25 mm from the electrode tip are shown in Figure 3 as well. Figure 3 reveals transitions of neutral Ar atoms that correspond to the relaxation of highly excited states to the metastable state. The transitions are in the red part of the spectrum. There are also transitions to the ground state, but they appear in the far UV range, which cannot be probed with the simple optical spectrometer. Interesting enough, Ar lines are not the only spectral features in plasma 2 mm from the exit of the dielectric tube. The most intensive feature appears at the bandhead of approximately 309 nm, and it corresponds to the transition of the OH radicals from the electronically excited to the ground state. Furthermore, there is a band of lines in the near UV range that corresponds to the transition of highly excited neutral nitrogen molecules in $C^3Π_u$ state to $N_2$ molecules in $B^3Π_g$ state. This transition is called 2nd positive system. Details on the most common transitions of various atoms and molecules likely to occur in the APPJ are very well presented in the paper of Golda et al. [45]. Spectral features as observed in Figure 3 in the spectrum acquired close to the APPJ exit also persist in the spectra recorded at longer distances from the exit of the discharge tube; however, their intensity is significantly lower, and also their ratio strongly depends on the distance from the dielectric tube. The axial distribution of the major spectral features versus the distance is shown in Figure 4.

![Figure 3. The OES spectra recorded at various distances from the exit of the discharge tube. The spectra were normalized to Ar line at 764 nm.](image)

Park et al. [30] used a device similar to what is shown in Figure 1 but powered it with a DC pulsed discharge. In such discharges, the streamers, as shown in Figure 2, shrink to bullets of a spatially confined dense plasma, which propagate away from the powered electrode at a velocity of the order of $10^4$ m s$^{-1}$. The visible appearance of gaseous plasma is not much different from the one shown in Figure 1, but the electrical properties are completely different. Despite the difference, the optical spectra acquired by Park et al. are similar to those in Figure 3. In the optical spectra acquired by Park et al., the OH line at 309 nm was dominant, and the $N_2$ band in the near UV range was clearly visible, too (Figure 5). They also provided images of the discharges taken with the fast camera to show
the evolution of the plasma bullets. The optical spectra taken in such cases obviously give values averaged over numerous such localized plasma bullets.

Figure 4. The axial distribution of the major OES spectral features versus the distance from the exit of the discharge tube.

Figure 5. Emission spectra of: (a) Ar pulsed 2 kV plasma, and (b) He pulsed 2 kV plasma showing the presence of a significant amount of OH and N$_2$ species. Reprinted with permission from [30] (Park et al.). Copyright 2021 American Institute of Physics.

Additionally, also Sarani et al. [28] and Seo et al. [35] observed similar spectra as shown in Figure 3 for the dielectric-barrier discharge (DBD) type APPJ feed with pure Ar as well as Weltman et al. [33]. Sarani et al. [28] used the APPJ very similar to the device shown in Figure 1. Intensive OH radiation was observed even in pure Ar, and suppressed by the intentional addition of other gases. They provided possible channels for the formation of hydroxyl radicals. The OH radical can be generated by a collision of the water molecule and an electron (electron-impact dissociation), or a metastable Ar atom, or by the reaction of an excited oxygen atom with a water molecule, which was found the dominant mechanism by Sarani et al. Their arguments were based on the papers of Herron et al. [46] and Kim et al. [47]. In addition, Roy et al. [36] used OES to investigate the production of OH and O radicals in air/Ar/H$_2$O plasma and found that Ar plays a significant role in their production. The production of OH and O radicals was increasing with increasing Ar content.

As already explained before, the appearance of OH and N$_2$ spectral features in Figure 3 is not because of the inadequate purity of Ar gas, but rather because of the interaction of gaseous plasma with the neighboring atmosphere. As shown schematically in Figure 2,
the electron streamers are formed stochastically in the APPJ, which is powered with an AC discharge at a typical frequency of 10 kHz. The streamers propagate along the axis of the Ar jet. They will not propagate in air because of the numerous channels for the loss of electrons’ kinetic energy. Still, some streamers reach the edge of the Ar gas jet, where diffusion of air from the surrounding atmosphere occurs. Furthermore, the streamers inside the Ar jet cause formation of Ar metastables with a large radiation life-time. The metastables are therefore quenched rather than relaxed by the radiation. The quenching is unlikely to occur in pure Ar, but very probable at a collision between an Ar metastable and a gaseous molecule. The Ar metastables diffuse within the jet and may finally reach the edge of the pure Ar jet, where they transfer their potential energy to air molecules. The optical spectrometer will collect any radiation arising from a certain solid angle, as determined by the lenses (Figure 2). That is why the nitrogen emission lines appear in the spectrum collected close to the electrode (Figure 3). The relative intensity of nitrogen emission depends on the kinetics of gas mixing and on the plasma excitation of gaseous species. Figure 5 shows a maximum in the nitrogen emission along the axis. A maximum is usually a consequence of two opposite effects. In this particular case, the diffusion of nitrogen inside the plasma jet increases with increasing distance from the electrode. From this point of view, the N₂ emission should increase with increasing distance from the electrode. On the other hand, the absolute luminosity of gaseous plasma decreases with increasing distance. The combination of these two opposite effects causes the maximum in nitrogen radiation, as revealed in Figure 5. Figure 6 shows the intensities of nitrogen and OH radicals radiation normalized to the main Ar line at 764 nm. Now we observe that the relative intensity of nitrogen radiation keeps increasing with increasing distance and remains large even at the distance of 25 mm where the absolute intensity is poor. The effect is explained by the mixing of the gases. A maximum in N₂ emission versus a distance was also observed by Chauvet et al. [39]; however, they observed a maximum at a somehow shorter distance at approximately 5 mm.

Figure 6. The intensities of nitrogen (337 nm) and OH normalized to the main Ar line at 764 nm.

Such a maximum as observed for nitrogen species in Figure 5 is not observed for OH radiation. For OH radicals, we observe intensive radiation in the first few mm from the exit of the discharge tube and then rather fast decay. Water vapor abounds in air in any laboratory. The saturated water vapor pressure at room temperature (25 °C) is about 3.2 kPa. This value corresponds to 100% humidity. The air humidity in the lab is never that high, but it is rarely below 10%, so the partial pressure of water vapor is still several tenths of kPa. The water vapor from ambient air cannot explain the completely different behavior of the OH as compared to N₂. A more feasible explanation is the presence of water vapor within the dielectric tube. Unlike nitrogen, which is quickly removed from the dielectric tube by passing Ar at a rather large flow rate, water molecules stick to surfaces of solid materials, where they form a layer that is only slowly desorbed at room temperature. The consequence of this water film is the appearance of strong OH radiation even at the
electrode tip. The OH radiation depends on the amount of water released from the surfaces, which in turn depends on the amount of water absorbed. Upon continuous flushing of the dielectric tube with Ar, the water concentration decreases with time but remains significant for hours. Figure 7 represents the evolution of Ar and OH lines for one and a half hours [48]. As the discharge is turned on, the OH signal is larger than the Ar line. Within the first minutes, the Ar line increases, and the OH remains fairly intact. After prolonged treatment, the Ar line finally reaches a constant value, but OH keeps decreasing. This important fact should be taken into account at any attempt to explain the plasma-surface interaction upon activation of a polymer product by the APPJ sustained in a noble gas. We should be aware that any APPJ sustained in pure Ar at ambient conditions is therefore rich in OH radicals.

Figure 7. Stability and time evolution of Ar and OH lines after ignition of the APPJ [48].

Similar results were observed by other authors too. Seo et al. [35] used Ar of purity 99.999% for sustaining the APPJ at the frequency of 50 kHz and reported optical spectra similar to those in Figure 3. They employed a somehow more sophisticated discharge configuration with an additional grounded ring mounted on the other side of the dielectric tube but observed practically identical behavior of the OH signal as in Figures 5 and 6 when using Ar feed gas. In contrary, the peak of the nitrogen radiation was not so obvious as in Figure 5, but the relative intensity was almost identical to the behavior, as shown in Figure 6. Here we should also mention, that Seo et al. found a dominant OH emission only in the case of Ar plasma, whereas in the case of He plasma, OH emission was only minor. Because of a very high OH radical concentration in Ar plasma, they obtained a much better improvement of surface hydrophilicity of polydimethylsiloxane when treated with Ar gas than with He.

Figures 5 and 6 are also in agreement with the reports by Srivastava et al., who found that the decay length of OH radicals was much shorter than the length of the visible plasma jet [27]. As shown in Figure 5, the intensity of OH radiation remains roughly constant for the first few mm and then decreases rapidly. In Figures 5 and 6, the OH signal becomes marginal for lengths more than approximately 15 mm, although the radiation from nitrogen bands persists much longer. One can assume that the OH radicals are lost along the jet, but it should be stressed that optical emission spectroscopy is a qualitative technique, and it does not reveal the concentration of radicals in the ground state. A comparison with similar configurations, where absolute techniques were used, is recommended. Srivastava et al. [27] performed a complete characterization of the APPJ sustained in pure Ar with a small admixture of water vapor. They measured the absolute density of OH radicals by a reliable technique (cavity ring-down spectroscopy) and found the OH density as large as $3 \times 10^{22}$ m$^{-3}$ for high purity Ar. The OH density increased up to approximately $5 \times 10^{22}$ m$^{-3}$ for the admixture of approximately 1 vol.% of water. Therefore, an important conclusion is that a common APPJ, as shown in Figure 1, always contains a large number of OH radicals, which typically arise from the desorption of water.
molecules from the dielectric tube or even connecting tubes. Srivastava et al. also employed optical absorption spectroscopy to measure the variation of the OH density along the axis of the APPJ and found a rather exponential decay with a characteristic length of a few mm, as shown in Figure 8 [27]. The decay length depended on the concentration of water vapor in Ar. The decay was the fastest at the maximal concentration of OH radicals, i.e., at the water admixture of approximately 1%. Srivastava et al. also provided explanations for the loss of OH radicals, which included recombination reactions, three-body collision quenching, and reactions of OH with H, O, or even NH radicals. They found the most extensive loss by the reaction $H + OH \rightarrow H_2O$ with a coefficient of approximately $2 \times 10^{-16}$ m$^3$ s$^{-1}$ [27].

Figure 8. Decay length of the density of OH radicals in Ar plasma with various H$_2$O contents from 0 to 1.5%. Reprinted with permission from [27] (Srivastava et al.). Copyright 2021 American Institute of Physics.

The results reported above clearly show that a relative gas humidity of the atmosphere may significantly alter the density of reactive species what may lead to unrepeatable results of the APPJ treatment. APPJs are usually feed by a noble gas (Ar or He), because in this case, the gaseous plasma expands rather far from the powered electrode, whereas in the case of molecular gases, the plasma plume is much shorter. Any APPJ sustained in pure noble gas at ambient conditions is thus rich in OH radicals. In fact, there is hardly any report in the literature on OES characterization of the APPJ without a significant signal arising from OH radicals. Some authors used high purity Ar and carefully pre-treated the APPJ devices, but none reported the OH-free optical spectrum [27–33]. Many authors also intentionally added a small admixture of water vapor to the feed gas to investigate the kinetics of the OH formation and its concentration profile [27–29,31,34].

Water vapor was added to the APPJ intentionally by Ilik et al. [34]. They used He as a carrier gas. The flow rate was as large as 20 slm. They managed to spray water droplets into the APPJ and studied the evolution of optical spectra. The discharge was powered with a sinusoidal AC supply operating at 18 kV and 15 kHz. The spectra were averaged over a rather long jet, but were similar to the one presented in Figure 3 except that a weak He line was observed instead of Ar lines. The authors demonstrated that the addition of water droplets did not influence the spectra much. In particular, the relative intensity of nitrogen prevailed at all experimental conditions. The water spraying only caused suppression of all spectral features, thus indicating the negative effect on the electron density or temperature.

The influence of water vapor on the electrical and spectral properties of the APPJ was further investigated by Nikiforov et al. [29]. They used a device similar to that presented in Figure 1, except that the electrode was deep inside the dielectric tube, and a grounded electrode was also applied. They provided precious information about the electrical behavior of an AC discharge because they measured both the voltage and current, as well as the Lissajous curves, which give information on the exact power of the discharge. The
intensive electron streamers, as shown schematically in Figure 2, are clearly presented in the paper by Nikiforov et al. The measurements allowed for estimation of the real discharge power absorbed by gaseous plasma versus the adjustable voltage of the AC power supply, which operated at the frequency of 70 kHz. At a given voltage, the maximum power was absorbed by plasma at the lowest concentration of the water vapor. The maximum emission arising from OH radicals was found at a water vapor concentration of 350 ppm. Although the content of H₂O was varied in a broad range up to several 1000 ppm, the maximum effect of polymer sample surface modification was observed at the water admixture in the range between 200 and 500 ppm. Based on this observation, Nikiforov et al. concluded that the yield of OH radicals was the highest at such a low water admixture.

Weltmann et al. elaborated the evolution of optical spectra along the APPJ operating in the semi-continuous mode [33]. They used an RF supply operating at a frequency of 1.1 MHz. They observed gradual decay of the OH and N₂ spectral features with the distance from the powered electrode. The OH radiation reached the peak value 2 mm away from the electrode, while nitrogen about 10 mm. The observations are, therefore, similar to those presented in Figures 3, 5 and 6. They also managed to measure the axial and radial temperature profiles using a glass fiber temperature probe. As expected, the highest gas temperature was observed where the luminosity was the highest, but the plasma tip temperature at the axis was about 48 °C. Rather strong radial gradients were observed, and the gas remained at room temperature a few mm from the visible plasma jet. These results indicate that the rotational temperatures, as reported by the above-cited authors, may not be representative for the estimation of the neutral gas kinetic temperature.

Production of OH radicals in the bullet-like APPJ was recently elaborated also by Gott and Xu [49]. The APPJ was sustained in He gas of purity 99.9999% with a pulsed discharge powered with a 10 kV supply. The voltage rise-time of 60 ns only assured for almost perfectly-shaped bullets propagating from a tungsten electrode which was placed into a quartz glass tube, similar to Figure 1. The emission from OH radicals was much larger inside than outside the tube, confirming that the water vapor originated from the walls inside the discharge tube. The authors explained the extensive radiation from OH radicals by electron-impact dissociation and subsequent excitation rather than the influence of He metastables.

The formation of the bullet-like discharge was further elaborated by Cordaro et al. [50]. They performed a detailed characterization of a plasma jet useful for blood coagulation. Plasma was sustained in He or Ne using a low-frequency discharge, which provided current pulses of a duration of approximately 1 µs. No additional gas was added intentionally, but the OES spectra revealed nitrogen bands even within the dielectric tube despite the rather large gas flow of 2 slm. At a distance of 5 mm from the exhaust, the spectral features corresponding to N₂ and O transitions prevailed over the radiation from He atoms. Unfortunately, the spectrometer used by Cordaro et al. [50] did not allow for measuring the OH line at 309 nm to compare the intensities like in Figure 3. In another paper, the same group reported the thermal effects caused by the treatment of biological matter with such an APPJ [51]. They found experiments with biological materials unfeasible because of the unknown thermal properties, so they used metallic samples and found significant differences for grounded or floating objects. The heating rate depended on the distance from the electrode, indicating the loss of the discharge power along the APPJ.

Chauvet et al. [39] performed an investigation of the spatial distribution of excited and ionized species along the bullet-like APPJ sustained in He at different flow rates. The emission of H, O, and OH strongly decreased with the distance from the APPJ exit, whereas N₂⁺ and N₂* reached a maximum at few mm from the tube exit.

Gerling et al. [40] investigated the production of reactive oxygen species (ROS) such as OH and O and reactive nitrogen species (RN) such as N₂ and N₂⁺ in He plasma with various oxygen admixtures up to 0.33%. They found a strong dependence of ROS and RN species versus O₂ admixture. The different behavior of the emission intensity of ROS and RN radicals versus O₂ concentration was observed. In the case of RN radicals, N₂⁺
emission exhibited a maximum at 0.05%, whereas \( \text{N}_2 \) at 0.1% of \( \text{O}_2 \) addition. For ROS radicals, the emission intensity of \( \text{O} \) was first increasing with the \( \text{O}_2 \) addition and reached a saturation when 0.15% of \( \text{O}_2 \) was added to He. For OH radicals, the opposite behavior was observed. After the initial saturation, it decreased if the addition of \( \text{O}_2 \) was more than 0.1%. Similar work was also performed by Pipa et al. [41]. The authors investigated the production of NO versus air admixture in Ar plasma and found a maximum in the NO emission intensity at 0.1–0.2% of the air in Ar.

Jia et al. [42] used OES to investigate the influence of microwave power and gas flow on the emission intensity of specific species (Figure 9). The authors used the APPJ created in Ar, He, or Ar + He mixture. The intensity of the emission was monotonously increasing with power. The increase was explained by the increase in the electron density and electron temperature. The variation of the emission intensity with the flow was less dramatic. After a slight initial increase, it slightly decreased at higher flow rates.

![Figure 9. Influence of: (a) microwave power and (b) gas flow rate on the emission intensities of Ar spectral features. Reprinted with permission from [42] (Jia et al.). Copyright 2021 American Institute of Physics.](image)

A simple optical spectrometer usually operates in the spectral range between approximately 200 and 1000 nm. The optical transitions in this range occur from the excited to the ground level only for the case of OH radicals and any metallic impurities, but most other transitions arise from the relaxation from one (higher) to another (lower) excited state. For example, atomic Ar lines shown in Figure 3 appear at transitions to the level at the excitation energy as high as about 12 eV. Apart from these transitions, there are also transitions that appear to the ground state. These transitions are in the far UV range of the spectrum, below the detection limit of a simple spectrometer, which is usually approximately 200 nm [45]. Such short wavelength radiation is quickly absorbed in the air, as well as in the optical fiber and even lenses, so special types of spectrometers should be used to detect transitions of many gaseous species to the ground state. Among such transitions, there is H-atom Lyman series with the predominant line at 121 nm (transition from the first excited state to the ground state), O-atom transitions with the predominant line at 130 nm, Ar-atom transitions with the most intensive line at 107 nm, and N-atom transition at 149 nm. These transitions may be dominant in the spectra of atmospheric-pressure plasma jets.

Schulz-von der Gathen et al. [52] measured OES of He discharge with various oxygen admixtures in UV and VUV regions. For low or zero oxygen admixture, NO and OH emissions were very strong. In addition, the atomic oxygen line was dominant at low oxygen admixture (0.06%).

An excellent comparison of radiation intensity in the far and near UV range was provided by Golda et al. [45]. They measured the spectra of the APPJ sustained by a sinusoidal RF voltage at the frequency of 13.56 MHz. The VUV spectrometer was mounted onto a special aerodynamic window and placed in a high-vacuum chamber. For He
discharge, they found the intensity of OH at about 282 nm marginal as compared to radiation in the range between 60 and 100 nm. A similar result was also observed for Ar, except for this case, the major far UV radiation occurred between 110 and 130 nm. The OH peak at 282 nm is a consequence of the radiative transition from the first vibrational excited state of the OH (A) electronic state to the ground state. This transition is normally 10-times less intense than the major transition at 309 nm, but the latter could not be probed by the spectrometer used by Golda. In any case, the major radiation from the pure argon APPJ aroused from Ar continuum. Even small impurities of water vapor in the monochromator caused decreasing of this radiation to half of the original value. The absorption cross-section for H$_2$O molecules was also provided by Golda et al. and may be as high as $10^{-17}$ cm$^2$.

For He plasma, the intensive radiation within 60 and 100 nm was suppressed even by a very small addition of a reactive gas. For example, the addition of 0.01% O$_2$ caused suppression of the He radiation by a factor of two. Unfortunately, no data for water vapor were provided by Golda et al. Based on the discussion above, it is possible to conclude that a simple plasma jet operating in the configuration of Figure 1, may be a source of radiation in the far UV range, but this cannot be probed with the simple spectrometer. The experimental configuration with a VUV spectrometer, as adopted by Golda et al., is highly recommended, but difficult to realize.

According to this literature review and our results, we can conclude that OH radicals are the most important reactive species in the APPJ. As OES is a qualitative technique, it enables investigation of the relative variation of the density of plasma species along the axis. However, for quantitative determination of the densities, other techniques must be applied. The OH density profile along the plasma jet is usually measured by laser-induced fluorescence (LIF) [53–56] or two-photon absorption LIF (TALIF) [57–59]. Other methods, such as cavity ringdown spectroscopy (CRDS) [27,60–62] and absorption spectroscopy [57,63] can be used as well. Schröter et al. measured the concentration of the OH radicals in the humidified He discharge sustained in an RF driven APPJ by using vacuum ultra-violet high-resolution Fourier-transform absorption spectroscopy and ultra-violet broad-band absorption spectroscopy [57]. They found an extensive dissociation of H$_2$O molecules upon plasma conditions. The density of OH radicals was approximately $3 \times 10^{20}$ m$^{-3}$. Such a large density expanded several cm along the discharge channel. An order of magnitude lower OH density was observed by Fuh et al. [62] in a pulsed He discharge with CRDS method. Whereas Yonemori et al. [56] obtained even lower densities of approximately $1 \times 10^{18}$ m$^{-3}$ with LIF. In another paper, Yonemori et al. [55] measured the OH density in the humidified He pulsed discharge. The H$_2$O content in He gas was varied between 0 and 800 ppm. A maximum in the OH density peaking at $6 \times 10^{18}$ m$^{-3}$ was found at the H$_2$O content of 200 ppm. Additionally, Srivastava et al. measured the variation of the OH density along the axis of the APPJ [27,60] by using CRDS method. Srivastava et al. [60] measured the OH density in Ar, Ar/N$_2$, and Ar/O$_2$ APPJ discharge at various powers and flow rates. The OH density was decreasing along the jet. The OH density also strongly depended on the power and it was increasing with the increasing power. For Ar plasma, the OH density ranged from $1.3 \times 10^{18}$ to $1.1 \times 10^{22}$ m$^{-3}$, depending on particular conditions. For Ar/N$_2$ it was in the range between $4.1 \times 10^{19}$ to $3.9 \times 10^{21}$ m$^{-3}$, whereas for Ar/O$_2$ it was between $7.0 \times 10^{18}$ to $4.6 \times 10^{22}$ m$^{-3}$ [60].

3. Examples of Using OES for Gas Temperature and Electron Density Measurements

The temperatures can be deduced from the optical spectra only when high-resolution spectrometers are used. Furthermore, more knowledge is needed and application of the simulation software. That is why the rotational and vibrational temperatures are rarely reported. Therefore, the spectra shown in Figure 3 will not reveal the temperatures because of the insufficient resolution of the spectrometer. A user of APPJ should, however, beware when concluding about the temperatures involved within the plasma jet. The temperature may differ depending on which emission line (OH(A) or N$_2$(C)) is used for its
calculation [13]. Furthermore, the temperatures reported in the literature may significantly differ, although similar jets and plasma parameters were used.

Nikiforov et al. measured rather high-resolution OES spectra to deduce the rotational ($T_{\text{rot}}$) and vibrational ($T_{\text{vib}}$) temperatures of OH radicals [29]. For “pure” Ar, the temperatures were found independent from the distance from the electrode at the values of $T_{\text{rot}} = 450$ K, and $T_{\text{vib}} = 1500$ K. An addition of 500 ppm of water vapor did not have a significant effect on the temperatures away from the electrode, but near the electrode, the vibrational temperature was approximately 2000 K. When 7600 ppm of H$_2$O was added, $T_{\text{rot}}$ increased to approximately 800 K rather far from the electrode, where $T_{\text{vib}}$ was almost 5000 K. The values were even larger next to the electrode.

High $T_{\text{rot}}$ and $T_{\text{vib}}$ temperatures were also reported by Srivastava et al. for the case of the APPJ sustained with a microwave (MW) discharge (i.e., in the continuous mode) [27]. In almost pure Ar, $T_{\text{rot}}$, and $T_{\text{vib}}$ temperatures were practically equal at approximately 900 K. The addition of 1 vol.% H$_2$O caused an increase in both temperatures to approximately 1100 K. The huge discrepancy between the results of Srivastava et al. [27] and Nikiforov et al. [29] may be explained by different discharges. While Srivastava et al. used a continuous plasma, Nikiforov et al. selected pulsed discharge with electron streamers, as shown schematically in Figure 2. Obviously, the pulsed plasmas created by rather low-frequency discharges cause overpopulation of highly vibrational excited states, whereas continuous plasmas cause almost equal $T_{\text{rot}}$ and $T_{\text{vib}}$. In any case, the temperatures are large, in many cases well above the softening or melting point of polymers. Such hot OH radicals interact abruptly with polymer surfaces, causing functionalization and chemical etching at prolonged treatment times. These effects should be taken into account at any attempt to activate a polymer surface by atmospheric pressure plasmas.

Opposite to Srivastava [27] and Nikiforov [29], Sahu et al. [37] reported a very low $T_{\text{rot}}$ of only approximately 330 K. Such low $T_{\text{rot}}$ was also determined by Thiyagarajan et al. [38] for DBD-type APPJ in He plasma with small O$_2$ admixture. Plasma was characterized in the active plasma region and in the afterglow region. It was found that gas and vibrational temperatures increased when O$_2$ was added. The temperature was also slightly higher in the afterglow region compared to the active plasma region. Gas temperature was found to be 310 and 340 K for He and He/O$_2$, respectively, whereas $T_{\text{vib}}$ was 2200 and 2500 K, respectively. Sahu et al. [37] determined rotational temperature using N$_2$ line at 337 nm, whereas Thiyagarajan et al. [38] used OH. As will be shown later, the calculated temperature may differ depending on the radical used for calculation.

Sarani et al. [31] also performed a detailed characterization of pulsed discharges using the same equipment as Nikiforov et al. [29]. They used pulsed discharges of a duration of approximately a microsecond. They managed to estimate the electron density inside such a plasma streamer to approximately $10^{19}$ m$^{-3}$. The rotational and vibrational temperatures, as calculated from the high-resolution OES spectrum of the OH radical, were found dependent on the population of the excited states. A strong overpopulation of highly excited rotational states was observed, so the rotational temperature is not defined for such discharges. Such a rather unexpected population of excited states was explained by the quenching of excited OH radicals which, according to Sarani et al., depended on the excitation level.

High electron densities were also reported for the APPJ similar to the one in Figure 2 sustained in Ar with an admixture of organic gas, in particular, tetraethyl orthosilicate (TEOS) [13]. The electron density peaked at approximately $10^{23}$ m$^{-3}$ in a short time during the evolution of streamers. This value is much larger than what was reported by other authors. For example, Sarani et al. [31] reported four orders of magnitude lower electron density. As already explained, the discharges sustained by rather low-frequency AC power supplies cause the formation of numerous streamers of short duration where the peak electron density is difficult to measure. One should beware of averaging results over the time scale much longer than a streamer duration. The intensity of spectral features followed the evolution of the electron density. The OH band at 309 nm prevailed despite the fact that no water vapor was added to the gas mixture intentionally. The peak power
absorbed by plasma enabled extensive radicalization of the organic precursors, and even C₂ dimers were detected in the optical spectrum. Barletta et al. [13] also determined rotational temperature calculated from CH, N₂, or OH radicals. This was the first time that CH radical was used for the estimation of \( T_g \). Despite the rather large average power of 11.5 W, the rotational temperature was between approximately 410 K, if calculated from OH, and 550 and 590 K if calculated from N₂ and CH radicals, respectively. The authors showed that taking CH radical leads to an overestimation of \( T_g \). Taking into account the results reported by previously cited authors, it is clear that the deduction of the gas temperatures involved in APPJs may not be straightforward. The APPJ device used by Barletta et al. [13] was also applied for the deposition of thin-films from Ar/TEOS, where knowing \( T_g \) is one of the key parameters needed to have control over the deposition process.

An RF discharge operated at 13.56 MHz at rather high power was also used for sustaining a micro-plasma jet by Yanguas-Gil et al. [32]. As mentioned earlier, such plasmas operate in continuous mode. The authors found the electron density close to \( 10^{21} \text{ m}^{-3} \), although the neutral gas temperature was below 400 K. They used a coaxial configuration, and the plasma plume expanded a few mm from the tip of the powered electrode. They managed to assure negligible diffusion of air into the plasma plume, so the optical spectra consisted only of Ar lines and OH band. A small addition of N₂ into the gas caused significant radiation of the N₂ second positive band and suppression of OH radiation, similar to what is observed in Figure 3.

4. Some Examples of Using OES in Practical Applications of APPJs

In the introduction, some possible applications of the APPJ were mentioned to outline its increasing importance. Although the aim of this paper was to give some examples of using OES for basic characterization of the APPJ plasma, we here further report some examples of using OES in combination with practical applications of the APPJ. For example, Cheng et al. [64] used OES for characterization of the APPJ for wound healing. The authors found that relative intensities of reactive species increased 2–3 times when the plasma jet was in contact with the epidermis. The authors concluded that the epidermis reacted as a floating electrode, causing a locally enhanced electric field at the interface. Additionally, Jacofsky et al. [65] used OES to characterize the APPJ used for wound healing. OES was used to find the most optimal parameters in terms of the flow rate, the distance of the APPJ from the surface, and gas composition. No differences in active species generation were found when the metallic or organic substrate were used. The authors conclude that the secondary electron emission plays a small role in the chemistry induced in the jet. Lin et al. [66] used OES to investigate the correlation between the intensity of OH radicals in the APPJ with various O₂ addition to Ar feed gas and inactivation of bacteria. With the help of OES the authors concluded that the trace amount of O₂ addition into working gas enhanced the OH radicals formation what also speeded up the killing of bacteria and endospore. Another example reported the application of OES in the case when the APPJ was used for the deposition of thin films from styrene and methyl methacrylate precursors [67]. OES was used to investigate the degree of monomer dissociation versus the power and a carrier gas flow rate. In addition, Zhao et al. [68] used OES to characterize the APPJ for deposition of Cu thin films on a polymer, where a Cu wire inserted inside the discharge tube acted as the evaporation source. Enhancement in the Cu film deposition rate and increased purity was obtained by H₂ gas addition to Ar feed gas. Furthermore, increased rotational temperature was observed when adding H₂. The authors concluded that atomic hydrogen produced by the plasma plays an important role in heating the gas to promote the evaporation of Cu atoms. The last example is the application of OES in combination with the APPJ for polymer surface modification. Kehrer et al. [69] used OES to investigate the influence of water admixture (OH radicals) on the functionalization of polymer surfaces. The authors found that the influence of water admixture on polymer surface modification strongly depends on the type of the carrier gas.
5. Summary

An atmospheric pressure plasma jet is useful for localized surface treatment of various materials, as well as tissues. Therefore, knowing the interactions of both radiation and chemically reactive plasma species with the surface is important. Characterization of the APPJ is recommended before any application to control surface reactions and reproducibility of the results. The simplest technique is optical emission spectroscopy (OES). This technique enables space-resolved determination of the radiative species in the APPJ. Usually, OES is mostly used to identify species and monitor reaction products when the plasma interacts with the surface being treated. However, the application of OES to measure the gas temperature is rising, although it requires more in-depth knowledge and the use of computer models. Spectrometers are available with different spectral resolution. Spatial and temporal resolution of the spectrometers are continuously increasing with technological development. Recently, Weiss et al. [70] performed spatially resolved OES using integrating (Ulbrecht) sphere for the first time. This ensured many diffusive reflections of the light in the spherical cavity thus enabling uniform and spatial resolved OES. When comparing to the regular use of OES, similar emission and distribution of excited species was detected, however, species in the visible and near infrared (VIS/NIR) region and especially those in UV region were detected with 4–5 times higher intensity. Nevertheless, because plasma is a rich source of VUV photons, the major drawback of OES is still inability to measure in the VUV range, where more expensive VUV spectrometers are needed.

Detailed information about the behavior of different reactive species can be obtained by comparison of the OES spectra with results of more thorough plasma characterization with other techniques reported in the literature. Several authors have reported detailed studies using more expensive and demanding characterization techniques but similar discharges. Such a comparison is useful for the interpretation, but one should beware of huge discrepancies summarized in this paper.

The APPJ is often sustained in Ar without the intentional addition of a reactive gas. It was shown that the traces of water (that have been adsorbed in the discharge or connecting tubes) might play a dominant role in surface reactions. Any APPJ plasma operating in the atmosphere thus contains OH radicals. The emission from OH radicals is much stronger in pure Ar plasmas than in pure He plasma. The OH radicals are among chemicals of the highest oxidation potential; therefore, they interact intensively with a material surface causing rapid activation. Furthermore, the OH radicals have a rather large internal energy (the vibrational temperature often exceeds 1000 K) what contributes to the chemical reactivity of these radicals. Various OH densities and its rotational and vibrational temperatures were reported by different authors, but as a general rule, the OH density decreases quickly with increasing distance from the APPJ powered electrode. Some authors reported the OH densities well over $10^{20} \text{ m}^{-3}$ what should be sufficient for saturation of a polymer surface with functional groups. The optical emission spectroscopy will not give the absolute density of the OH radicals in the ground state but will rather represent a useful technique for detection and estimation of the density, as explained in appendix A. For the determination of the absolute values, the optical absorption spectroscopy is the method of choice. The absorption spectroscopy comes in various configurations. Because the absorption cross-section for 4 eV photons from a laser on OH radicals is rather small, multiple passes are needed to obtain reliable results. An alternative is the simultaneous absorption of two or three photons of lower energy and observation of the fluorescence. The technique is known as two-atom LIF (TALIF). These techniques operate very well at low pressures, but at atmospheric pressure, one should take into account the final shelf-time of excited states and quenching. In any case, the OES will indicate the presence of the radicals useful for tailoring surface properties of solid materials.

The APPJ sustained in pure noble gases is also a rich source of VUV radiation. The penetration depth of radiation with a wavelength of approximately 100 nm in a polymer is short (of the order of 10 nm); therefore, extensive bond scission occurs in the surface layer upon the interaction of the APPJ with a polymer sample. The dangling bonds interact
with oxygen even at ambient conditions, so the surface of any polymer exposed to APPJ sustained in pure noble gas is activated. As already mentioned, the radiation in the VUV range can be probed only with special instruments, but a comparison of the OES spectra with VUV spectra reported by other authors may be useful for interpretation of the observed surface finish. Even a small addition of reactive gases to Ar or He causes significant suppression of VUV radiation from dimers and the appearance of radiation of O or N atoms. The VUV radiation from plasma sustained in a noble gas with approximately 0.1–1% of a reactive gas (water vapor, air, or alike) is governed by reactive species, not Ar or He dimers.

The exact surface finish depends on the fluences of both radiation and reactive plasma species. Several authors cited in this paper have probed both parameters what represents a solid background for interpretation of the observed results. The OES is a qualitative technique, so it will not reveal the fluxes or fluences, but the comparison of measured results with reports of other authors that have used more sophisticated techniques for plasma characterization helps to understand the complex mechanisms involved in surface treatment of materials by atmospheric plasma jets.

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