

A multi-jet Plasma Gun equipped with branching device for the treatment of liquids

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Abstract: The treatment of liquids by means of atmospheric pressure plasma jets (APPJs) leads to the formation of reactive oxygen and nitrogen species (RONS). In this perspective, three different plasma devices were used for the treatment of a liquid substrate: Plasma Gun (PG), PG equipped with a multi-jet array (PG-MJ) and PG equipped with a branching device (PG-BD). The effect of gap values and peak voltages on the production of RONS were investigated treating aqueous solutions with the three plasma sources.

Keywords: cold atmospheric pressure plasma, plasma activated liquids, Plasma Gun, multi-jet array, branching device.

1. Introduction

In the last years, APPJs are becoming increasingly important for their applications in the field of medicine thanks to their ability to generate high concentration of gas phase RONS. Moreover, the interaction of the plasma plume with a liquid substrates leads to the formation of RONS, like hydrogen peroxide (H_2O_2), nitrates (NO_3^-), nitrites (NO_2^-), peroxyxynitrites ($OONO^-$), ozone (O_3), singlet oxygen (1O_2), radicals $OH^\cdot$, etc... [1]. All these active agents can be successfully employed in many different plasma medicine applications; among others, wound healing [2], bacterial inactivation of root canal [3] and cancer treatment [4] [5].

Generally, an APPJ consists of a dielectric cylindrical tube of a few millimeters in diameter (used for the injection of plasma gas) with a central high voltage electrode and an external annular ground electrode [6]. Although this device can be used for the treatment of different types of substrates, the contact area does not exceed a few mm^2 since the interaction of the plasma with the underlying target has limited dimensions. To overcome this limit, several research groups have developed and studied plasma jet arrays connecting an arbitrary number of single-jet sources [7] [8] or using a single-jet primary plasma source with an additional perforated device [9].

In this work, a PG [10], a PG-MJ and a PG-BD were used for the treatment of a liquid substrate. Treated liquid phase concentrations of H_2O_2 , NO_3^- and NO_2^- were measured with semi-quantitative methods. In order to understand the correlation between RONS concentration and source operating conditions, tests were performed using two different peak voltages (PV) and different gaps between the tip of the plasma sources and liquid substrate.

2. Material and methods

2.1 Plasma devices

All plasma devices were driven by a micropulsed high voltage generator (AlmaPULSE, AlmaPlasma s.r.l.) delivering a peak voltage of 10 kV and 13 kV, pulse duration FWHM (Full Width at Half Maximum) of 8 μs and pulse repetition rate set at 2 kHz; these were used for the treatment of a liquid substrate (Fig. 1). The first one is a PG coaxial source (Fig. 1A), consisting of a hollow high voltage electrode through which helium is fluxed. The high voltage electrode is embedded in a borosilicate glass tube with an inner and outer diameter of 4 mm of 6 mm, respectively. This device was additionally equipped with a multi-jet array (Fig. 1B) and a branching device (Fig. 1C).

The multi-jet array of Fig. 1B consists of a polymethylmethacrylate (PMMA) structure which presents 16 holes of 1 mm diameter designed for splitting of plasma plume.

The branching device of Fig. 1C consists of a cylindrical support where a floating electrode is encased, with its central tip screwed on a brass support where 16 steel wires are fixed. Each wire is placed inside of a silicone tube with an inner and outer diameter of 1 mm and 2 mm, respectively. All the silicone tubes were fixed on a polymeric support which encases a cylindrical ground electrode.

Optical emission spectra have been collected with the use of Ocean optics MAYA Pro 2000 compact low resolution spectrometer. The spectrometer is equipped with a 1mm core diameter UV fiber cable set 1 mm above the liquid target top surface and set 3 cm away from the PG-BD axis. For these measurements, PG-BD device was powered with the PG power supply developed at GREMI, delivering peak voltage amplitude of 13 kV, pulse duration FWHM is 2 μs and pulse repetition rate set at 2 kHz.

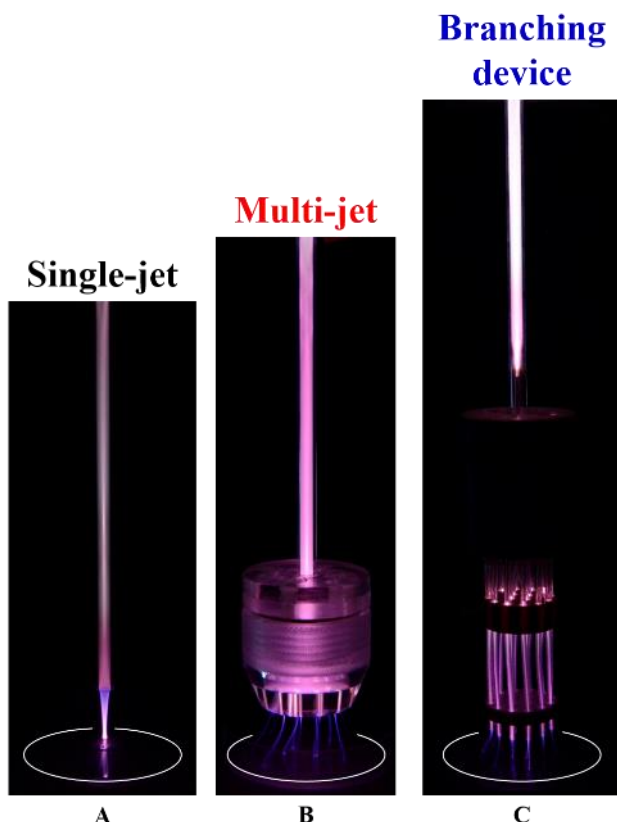


Fig. 1. **A)** PG, **B)** PG-MJ and **C)** PG-BD during the treatment of a liquid substrate. Operating conditions: 13 kV – 2 kHz – 3 slpm of He and a gap of 15 mm. The white ellipse highlights the contour of the surface of the liquid contained in a Petri dish.

2.2 Liquid substrate treatment

3 ml of phosphate buffer (PB) solution were exposed to plasma for 6 minutes. The pulse repetition frequency (PRF) was fixed at 2 kHz, while peak voltage (PV) was set on two different values, 10 kV and 13 kV, respectively. The gap between the outlet capillaries and the liquid surface has been progressively increased from 3 mm and 19 mm. After plasma treatment, semi-quantitative measurements of H_2O_2 , NO_3^- and NO_2^- were performed in duplicate using *Quantofix Peroxid* and *Nitrat/Nitrit* analytic strips.

3. Results and discussion

PB was exposed to PG, PG-MJ and to PG-BD using nine different gap values (from 3 mm to 19 mm) and two different PVs (10kV and 13 kV). After plasma treatment H_2O_2 , NO_3^- and NO_2^- concentrations were measured and subsequently mean value of each range was reported in histogram graphs (Fig.2 and Fig. 3).

Fig. 2A shows that H_2O_2 concentration depends strongly on the gap value. More specifically, PG produces 20 mg/l of H_2O_2 for small gaps (5 and 7 mm), while using PG-MJ and PG-BD lower values of H_2O_2 are induced in the treated liquids: 12,5 mg/l and 7,5 mg/l, respectively.

The gap dependence on H_2O_2 production is dramatically much more important when using PG-MJ or PG-BD

devices in comparison with the PG. It is suspected that in our experimental conditions, H_2O_2 is mostly generated in the liquid solution. As power delivered to plasma with either PG or PG-MJ or PG-BD setups is about constant, multi jet generation results in the distribution and so lowering of current flowing through each individual secondary jets. It results that the combination of H_2O_2 generation of each secondary jets is much lower than that achieved for a unique, high current plasma jet with the PG.

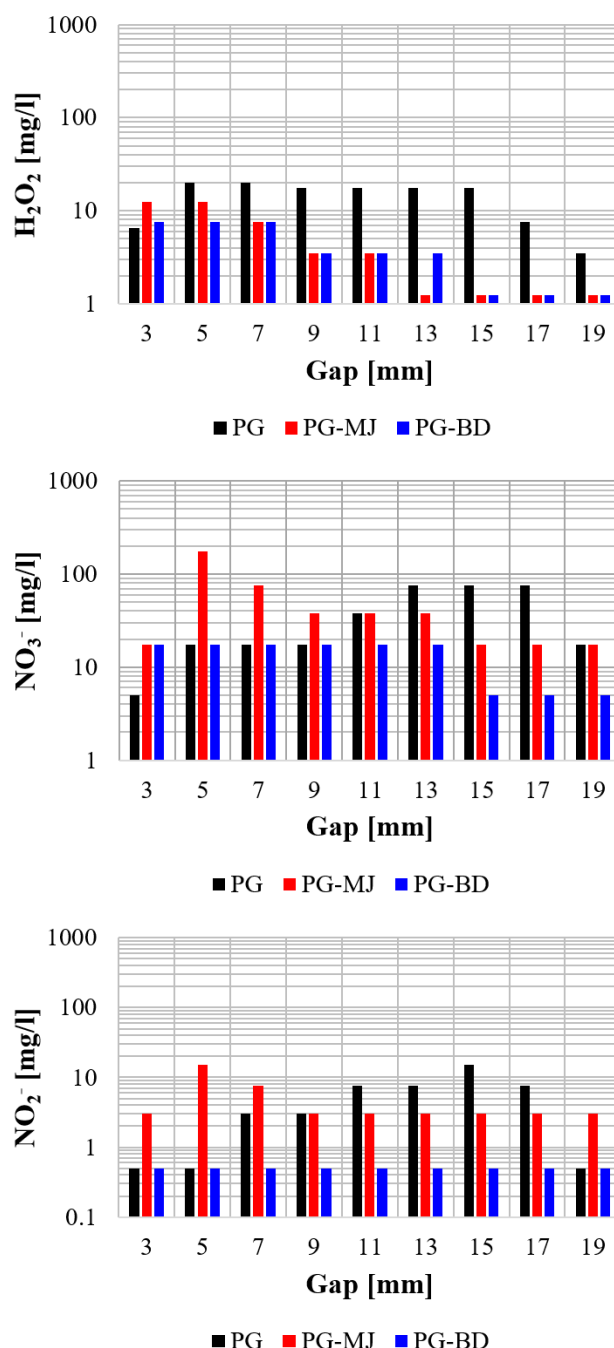


Fig. 2. Concentrations of **A)** H_2O_2 , **B)** NO_3^- and **C)** NO_2^- in a PB solution treated with single-jet, multi-jet and branching devices: 10 kV (PV) - 2 kHz (PRF) - 3 slpm (He) - 6 min of treatment

After PG treatments, NO_3^- and NO_2^- concentrations (Fig. 2B and C) reach a maximum value of 75 mg/l and 15 mg/l, respectively. On the other hand, the use of PG-MJ leads to the formation of higher concentration of NO_3^- (175 mg/l) and the same concentration of NO_2^- . Finally, NO_3^- and NO_2^- produced by PG-BD treatment do not appear to be influenced by the gap values. More specifically, NO_2^- concentration results to be the lowest among all measured values.

Conversely to the impact of gap modulation on H_2O_2 generation, it is measured that nitrite/nitrate concentrations achieved for the largest gaps is about the same as that obtained for small gaps when using the PG-MJ setup. This is probably largely associated with the key impact of plasma jet mixing with surrounding ambient air for the generation of reactive nitrogen species (RNS). Here, distribution of plasma power in secondary jets is much less influential on the global nitrite/nitrate transfer to the liquid target, as RNS are mostly generated in the gaseous phase above the liquid.

The consideration of all data documented in Fig. 2, indicate that PG-MJ device could represent an efficient option to deliver high RNS concentration over large surfaces and not in a single spot when using the PG assembly. This would be a relevant indication when treating tissue and solid surface and not a liquid solution where mixing of reactive species delivered at the impact zone of each secondary jets will necessarily occur.

Using a higher PV (13 kV) for the treatment of PB, an increase in the concentrations of RONS was induced for all the investigated cases. In particular, as reported in Fig. 3A, H_2O_2 maximum concentration (225 mg/l) was measured after treatments with PG and PG-BD, for a gap of 3 mm; while the maximum values of NO_3^- and NO_2^- concentrations (500 mg/l and 450 mg/l respectively) were measured after treatment with the PG-BD, for a gap of 3 mm.

Fig. 4 present optical emission spectra collected for two gap values (3 and 15 mm wide) when using the PG-BD device. Plasma emission is the average over about a 5 mm high zone above the liquid top surface. Spectra have been averaged over 50 acquisitions, each being 100 μs exposure time. From raw spectra (top graph) it is measured that for larger gap, emission from nitrogen bands from N_2C to N_2B but also from N_2B to N_2A levels is much stronger. While hardly visible from Fig. 4, it is also measured that NO^* bands are recorded for this larger gap setting. From Fig. 4 bottom graph where both spectra were normalized to the nitrogen second positive band emission at 337 nm amplitude, it is measured that small gap setting promotes much intense emission of helium lines (e.g. 703 nm), nitrogen ion bands (N_2^+ detected at 491.4 and 427 nm), and also atomic oxygen lines at 777 nm while no significant difference is measured for the OH^* band radiation around 310 nm. All this confirms the stronger mixing of helium plasma with ambient air for the larger gap, resulting in lowering of nitrogen ion population at the benefit and nitrogen neutral levels. The mixing with the air

is not beneficial for atomic oxygen radiation and has finally no impact on hydroxyl radiation. These species being probably quenched at the benefit of nitric oxide generation.

Emission spectra while being only indicative for excited state population during plasma generation on microsecond time scales, correlate with the in-liquid reaction species measurements, showing that larger gaps allow for efficient RNS production while being detrimental to hydrogen peroxide generation.

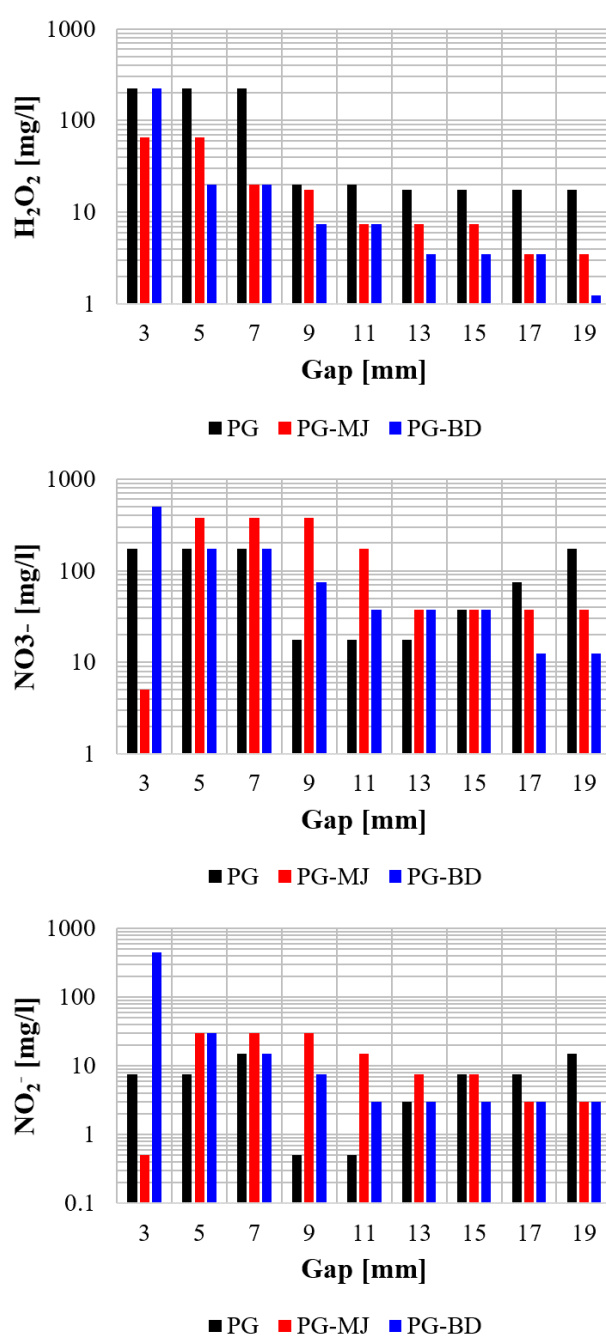


Fig. 3. Concentrations of A) H_2O_2 , B) NO_3^- and C) NO_2^- in a PB solution treated with single-jet, multi-jet and branching devices: 13 kV (PV) - 2 kHz (PRF) - 3 slpm (He) - 6 min of treatment

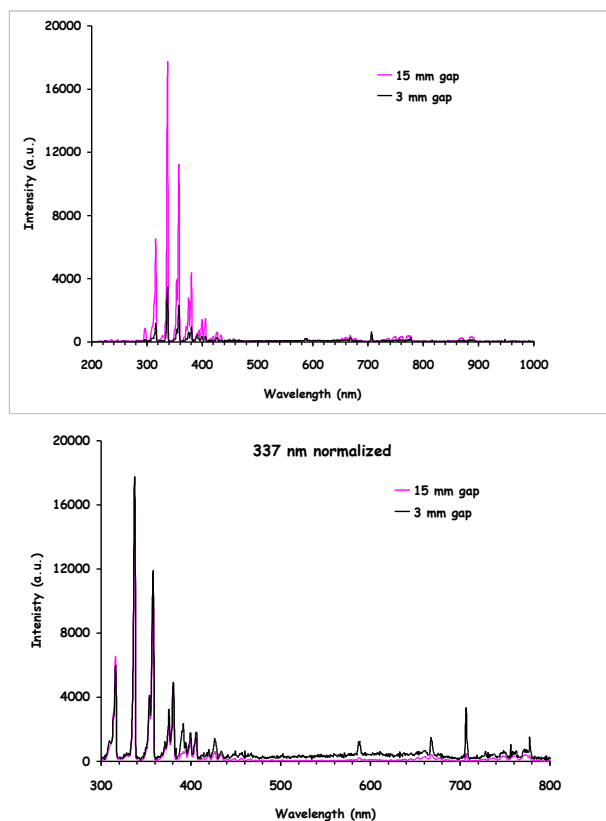


Fig. 4. Optical emission spectra for 3 mm (dark trace) and 15 mm (light trace) gaps with PG-BD powered at 13 kV, 2 kHz. Top graph: raw spectra, bottom graph: zoom on 300-800 nm wavelength range with normalization of both spectra to the same second positive emission of nitrogen at 337 nm.

4. Conclusions

This work was focused on the parametric study of H_2O_2 , NO_3^- and NO_2^- concentrations in a liquid substrate after 6 min of plasma treatment using two different operating conditions (10 and 13 kV) and a wide range of gap values (between 3 and 19 mm) with three different plasma devices: PG, PG-MJ and PG-BD. It is evident that the concentrations of RONS are strongly influenced not only by the gap values but also by the PV. Moreover, it has also been demonstrated that the use PG-BD device enables an improvement of PG performance in terms of RNS concentration in the liquid solution. In fact, according to the reported data, it is possible to keep constant H_2O_2 concentration obtained by PG and increase the NO_3^- and NO_2^- ones for a gap of 3 mm using a PG-BD.

Future research will focus on the investigation of RONS concentration induced by plasma generated in bubbles and subsequently the bactericidal effect of the plasma treatment.

5. References

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