# 20th Symposium on Application of Plasma Processes

# COST TD1208 Workshop on Application of Gaseous Plasma with Liquids

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Edited by P. Papp, J. Országh, L. Moravský, A. Ribar, Š. Matejčík

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Department of Experimental Physics, Comenius University, Bratislava, Slovakia
Society for Plasma Research and Applications, Bratislava, Slovakia

## Conference Topics

1. Electrical discharges and other plasma sources
2. Elementary processes and plasma chemical reactions
3. Plasma-surface interactions
4. Plasma treatment of polymer and biological material
5. Nanometer-scaled plasma technologies
6. Ion mobility spectrometry
7. COST TD1208 Workshop

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| Ivo Utke | Empa, Thun | Switzerland |
| Andreas Walte | Airsense Analytics GmbH, Schwerin | Germany |
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| Satoshi Hamaguchi | Osaka University, Osaka | Japan |
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## COST TD1208 Workshop on Application of Gaseous Plasma with Liquids

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| Malte Hammer | INP, Greifswald | Germany |
| Zdenko Machala | Comenius University, Bratislava | Slovakia |
| Eva Doležalová | Institute of Plasma Physics, Prague | Czech Republic |
| Fernando Brandi | INO and IIT, Pisa | Italy |

# WATER ELECTROSPRAY THROUGH AIR CORONA AND SPARK DISCHARGES AND INDUCED WATER CHEMISTRY

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Decontamination of water polluted with organic and microbial pollutants, and biomedical effects on cells mediated through aqueous solutions can be efficiently achieved by using various non-thermal plasma discharges. These effects can be further enhanced when air discharges are combined with water electrospray. The presence of the electrical discharge generating non-thermal plasma in the spraying area allows for very efficient mass transfer of plasma-generated species into the water [1, 2].
We investigated the effect of the electrospraying of water in combination with positive DC corona discharge. Our key finding is that the discharge has a significant effect on the electrospray behavior and vice versa [3-6]. Such water electrospray-air discharge system was demonstrated to be very efficient in inducing bactericidal and various chemical effects in treated water [1, 7].

## 1. Imaging of corona generation during the intermittent electrospray

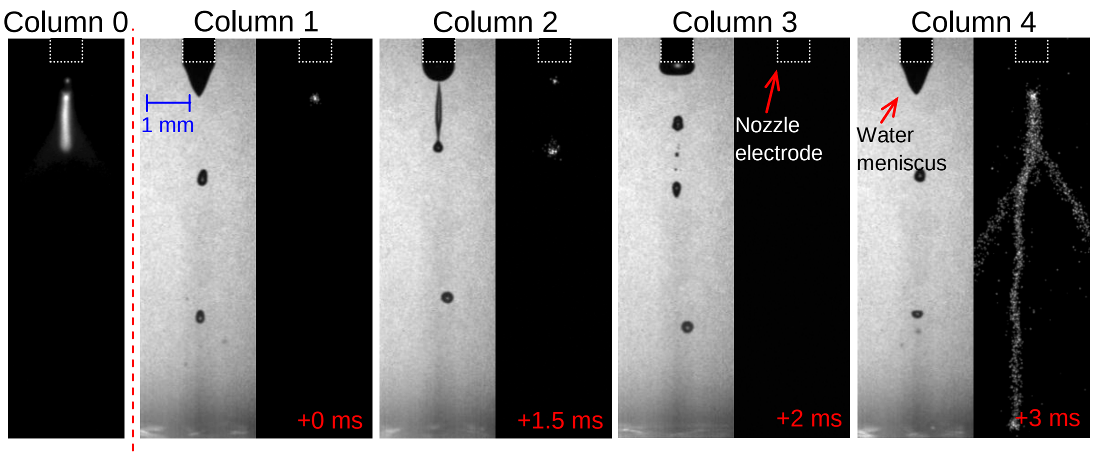


Fig. 1. iCCD time sequence images of electrospraying of water (illuminated, columns 1-4 with exposure time 10 μs) with corona discharge (dark, columns 1-4 with exposure time 100 μs) in spindle mode for water conductivity 500 μS/cm, + 6 kV, gap 1 cm, nozzle 0.8 mm o.d. and 0.6 mm i.d. iCCD dark image in column 0 with exposure time 5 s represent an integrated emission over the long period with many droplet formation cycles. [5]

The experimental setups, materials and methodology have been described in great detail in our previous papers. [1-2, 5-7]
We investigated the corona discharge generation during the electrospray of water. Fig. 1 shows different stages of the electrospraying event and the discharge propagation from 0 to 3 ms.
The glow corona is first visible at the tip of the water cone (column 1). As the water cone gradually elongates and creates the filament which propagates axially towards the grounded electrode, the bright spot of the glow corona remains present at the tip of this filament and propagates with it (column 2). After the detachment of the elongated water fragment, and the contraction of the water meniscus back towards the nozzle, the glow corona disappears (column 3). Finally, after a few ms, a new cone is formed, and the filamentary discharge occurs from the cone tip (column 4).
The dark image in column represent an integrated emission over the long period (5s) with many cycles of droplet formation and corona discharge on the water cone tip during this intermittent

electrospraying mode, and its movement with elongating water filament. The image also represents the visual appearance of the discharge during the electrospray.
We showed that the appearance of the corona on the water filament tip is primarily the electric field effect due to the various curvatures of this water filament tip [5].

## 2. Measurements of the electrosprayed droplet size and time of flight

The fast camera image sequences also enabled us to estimate the average time of flight (time between the water filament disintegration and the droplet fall on the grounded electrode) in 1 cm gap and the sizes of the sprayed water droplets between the electrodes. For instance, in the case of low conductivity water (2 μS/cm) this average time of flight is ~100 μs for the first incoming droplets from the head of the filament, and ~2.5 ms for the last one. The characteristic size of the water droplet (approximating to a spherical shape) vary approximately from <10 μm to ~250 μm in diameter. The droplet size becomes larger with higher liquid conductivities (from ~190 μm to ~280 μm for 400 μS/cm). The same applies to the time of flight which becomes longer (from ~2.7 ms to ~6.3 ms for 400 μS/cm). Since the droplets are formed by disintegration of the thin water filament, the sizes of droplets are determined by this filament thickness. The time of flight is related with the velocity of filament propagation and its length before disintegration. Both of these parameters (filament size and filament velocity) depend on the water conductivity, as also described elsewhere [6].
Knowing the typical droplet size and time of flight is important in water decontamination applications when considering the mass transfer of plasma generated active species into the water droplets while they are sprayed through the discharge. Our results on bio-decontamination of water in streamer corona or transient spark showed that even such short times of flight enable efficient mass transfer of air plasma generated reactive oxygen and nitrogen species in the sprayed water to induce significant bactericidal effects [1,7]. In addition, water activated by the electrospray with very low flow rates (~0.05 ml/min) demonstrated enhanced bactericidal effects when sprayed on the surfaces [2]. The key is probably in very high surface to volume ratio of the droplets.

## 3. Influence of the water conductivity on the corona properties

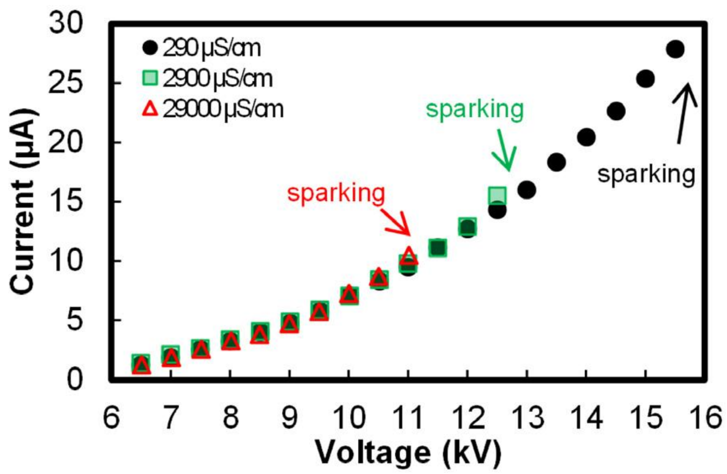


Fig. 2. I-V characteristics of the electrospray with corona discharge. Different breakdown voltages for corona-to-spark transition are due to different conductivity effect.

Depending on the conductivity, various spray properties were observed: pointy, prolonged, and fast spreading water filaments for lower conductivity; in contrast to rounder, broader, and shorter quickly disintegrating filaments for higher conductivity. When the conductivity increases, the breakdown voltage for corona-to-spark transition decreases (Fig. 2).
Since the highly conductive liquid acts as a good conductor, the electric field is stronger on the highly conductive water meniscus. The discharge is thus permitted to occur at the liquid surface and the

discharge activity on the water filament tip is then enhanced as the filament proceeds toward the ground electrode.
For poorly conductive liquids, the liquid acts more as an insulator and the electrical resistance of the growing water filament suppresses the corona activity on its surface. So the discharge is forced to occur on the metal electrode. Subsequently, the spark does not occur until the higher voltage [6].

## 4. Chemistry induced in water electrosprayed through air discharges

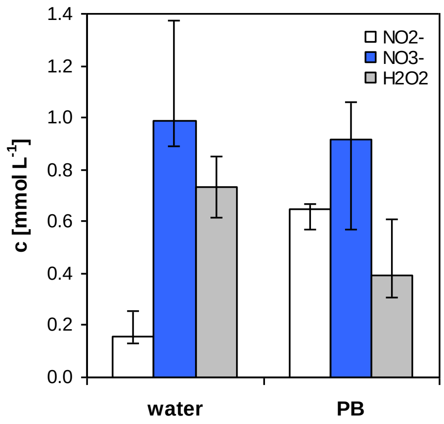


Fig. 3. Nitrite ($NO_2^-$), nitrate ($NO_3^-$) and hydrogen peroxide ($H_2O_2$) concentrations measured in modeled tap water (acidification occurs) and *phosphate buffer* (no acidification occurs) solutions air transient spark plasma treatment via electrospray. [1]

Chemical and bactericidal effects induced by plasma in water upon electro-spraying through DC-driven positive transient spark discharge in air were investigated. Inactivation of *E. coli* bacteria in water was determined in dependence on pH (controlled by buffers) and correlated with chemical changes induced in water, namely generation of reactive oxygen and nitrogen species (RONS) that play significant roles in cell physiology and many medical therapies [8]. The discharges in humid air (or air with water microdroplets) produce OH radicals, nitrogen oxides and in some cases ozone, resulting in the formation of hydrogen peroxide, nitrites, nitrates, peroxynitrites and pH changes in the sprayed water. The degree of inactivation and oxidative damage of bacteria increased with the increasing acidity of the solution. Acidified nitrites interacting with hydrogen peroxide were determined as the most important bactericidal ROS/RNS agents in plasma-treated water leading to peroxynitrites (peroxynitrous acid) [1, 9].
In the specific case of low power corona discharge with water electrospray, the bactericidal effect of ozone dissolved in water may play an important role. Since the diffusive solubility of ozone in water is relatively low, the interaction of non-thermal plasma with the micrometric droplets of water in the spraying area allows for very efficient mass transfer of ozone into the water.

## 5. Acknowledgement

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