

How the feed gas composition influences the chemistry induced by non-thermal plasma in water solution



FINAL REPORT - ERASMUS+ INTERNSHIP

Author: Octavian Lombart
Supervisors: Dr. Cristina Canal, Dr. Francesco Tampieri
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1 - Introduction

We start by defining what a plasma is. It is one of the four fundamental states of matter (Fig. 1.1), first systematically studied by Irving Langmuir in the 1920s. It consists of a gas of ions - atoms or molecules which have one or more electrons stripped (or, rarely, an extra electron attached) - and free electrons [Wiki 2021].

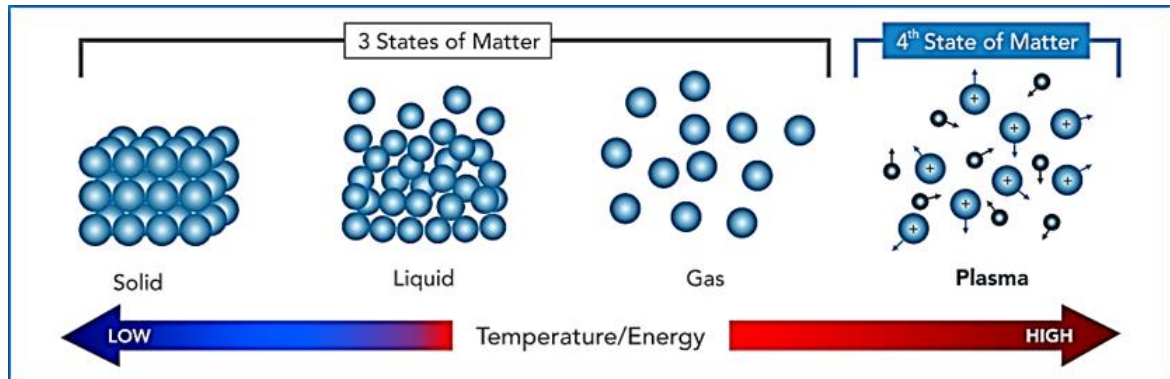


Figure 1.1: The four states of matter.

Plasmas can be artificially generated by heating a neutral gas or by subjecting it to a strong electromagnetic field. The presence of free charged particles makes plasma electrically conductive, with the dynamics of individual particles and macroscopic plasma motion governed by collective electromagnetic fields and very sensitive to externally applied fields. Plasmas can be natural or artificial. Some examples of natural plasmas are:

- Astrophysical plasma
- Stars, gas nebulae, quasar, pulsar
- Northern lights
- Lightning
- Ionosphere
- Solar wind
- Tail of comets
- Trail of shooting stars
- Heart of flames

Examples of artificial plasma are:

- The electrical discharges (arcs as in the high-voltage circuit breakers or torches, or other types of discharges as in gas lamps, microwave discharge, or the generators of X-ray)
- Treatment plasmas for deposition, etching, surface modification or doping by ion implantation
- Plasma televisions
- Propulsion plasmas
- Nuclear fusion

Plasmas can be classified in two types: thermal plasma and non-thermal plasma. The temperature of a plasma is given by the kinetic energy of electrons and heavy particles such as ions and neutral atoms and/or molecules. In this report, only non-thermal plasma will be considered, in which the temperature of the electrons is way higher than the temperature of ions and neutral species. Non-thermal plasmas can be generated at atmospheric pressure and room temperature by applying an

electric current produced by a high voltage generator. This excites the gas and causes it to pass from the gaseous to the plasma state. This excited state of the gas disappears as soon as the current supply is stopped.

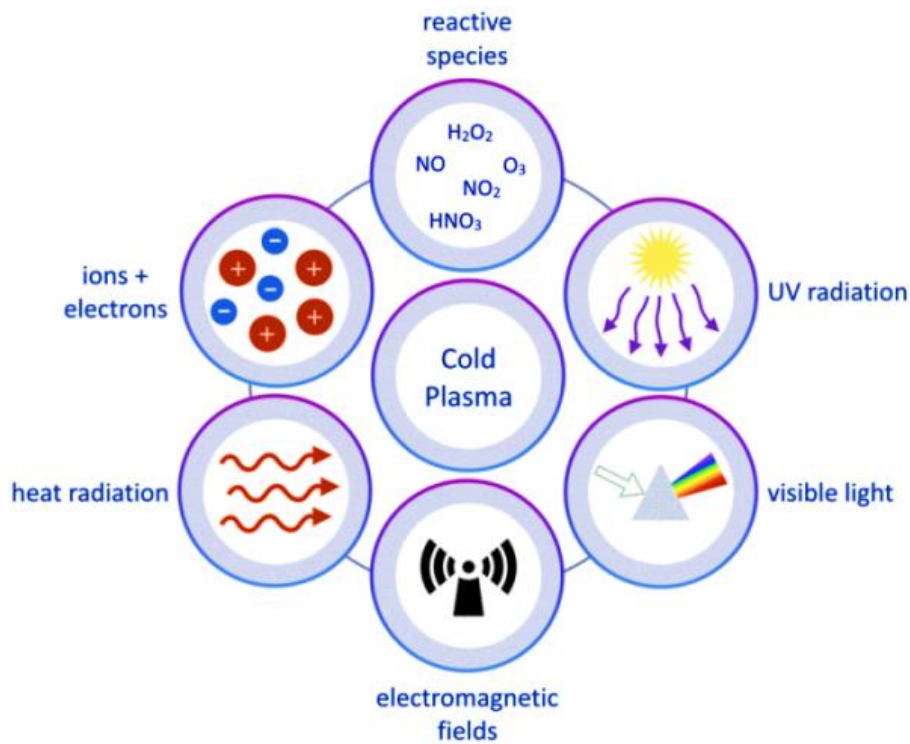


Figure 1.2: Components of non-thermal plasma.

A plasma is an extremely reactive environment (Fig. 1.2). The primary reactive species that are generated (free electrons and radical ions) quickly react to generate secondary reactive species or recombine to restore the original neutral atom/molecule. The nature of these primary and secondary reactive species depends on the plasma feed gas. When a plasma is generated in presence of air (or using air as a feed gas) a cocktail of reactive oxygen and nitrogen species (RONS) is generated. The most typical are ozone (O_3), atomic oxygen (O), singlet oxygen (1O_2), superoxide (O_2^-) and nitrogen oxides (NO , NO_2). If the plasma is generated in contact with an aqueous solution, or in presence of water vapour in the air, many RONS derive from the interaction with water. The most typical are hydroxyl radicals ($\cdot OH$), hydrogen peroxide (H_2O_2), nitrite (NO_2^-) and nitrate (NO_3^-) ions.

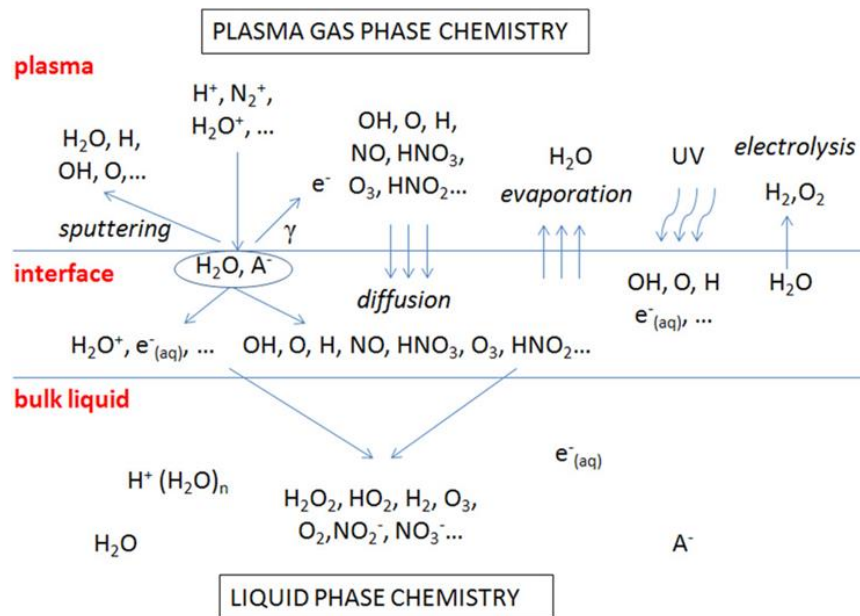


Figure 1.3: Typical Reactive Oxygen and Nitrogen Species generated when an air plasma is in contact with water [Samukawa 2012].

Thanks to the presence of these cocktails of RONS, whose nature and concentration can be tuned by changing some experimental parameters - like the applied voltage, feed gas flow rate and composition, atmosphere, plasma-to-target distance, etc - non-thermal plasmas find promising applications in many fields as energy production, agriculture, environment, manufacturing and medicine (Fig. 1.4).

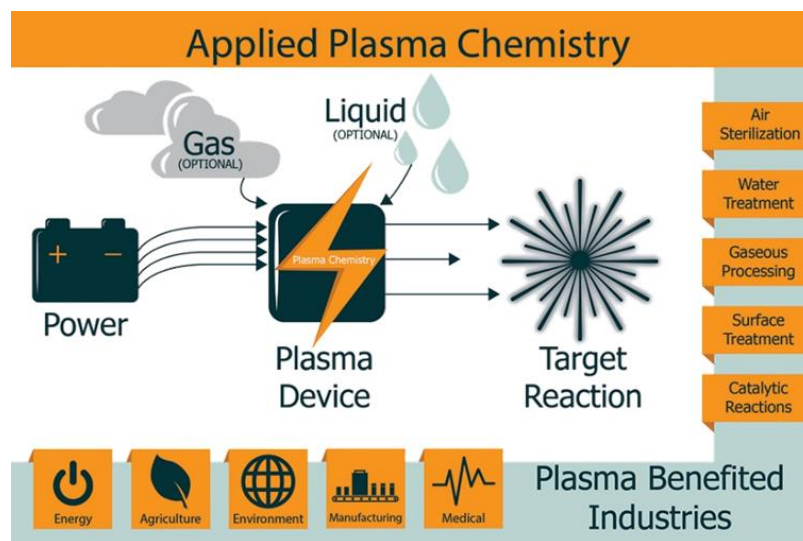


Figure 1.4: Application of non-thermal plasmas.

2 - Aim of the work

The nature and amount of plasma-generated reactive species in the gas-phase and in water solution are strongly dependent on many experimental parameters. According to [Neretti 2018], the helium flow rate has an impact on the reactive species observed. In a general way, the amount of the studied species (OH and N₂) increases with the flow. Some late studies analyzed the influence of the feed gas composition on the concentration of reactive species generated in water. A recent paper by B. Myers [Myers 2021] showed that the amount of OH radicals and O atoms generated by the same plasma source is strongly dependent on the addition of traces of molecular oxygen or water vapour to the feed gas (helium) and that this has a paramount influence on the subsequent water chemistry.

The objective of this work is to study the dependence of the plasma-generated reactive species in the gas-phase and in aqueous solution, as a function of the composition of the feed gas using an home-made atmospheric-pressure plasma jet that was previously studied only with pure helium. The gas composition will be modified by doping pure helium with small amounts of oxygen or nitrogen. At first qualitative experiments will be performed on the plasma plume in the gas-phase using optical emission spectroscopy (OES). These will allow us to analyze the excited species generated by plasma and their dependence on the gas composition. Then, using some selected gas compositions a detailed quantitative analysis of reactive species generated in the treated liquid as a function of the plasma treatment time will be performed.

3 - Experimental Section

3.1 - Materials

Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, >98.0%), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, >98.0%), sulfanilamide ($\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$, $\geq 99\%$), N-(1-naphthyl)ethylenediamine dihydrochloride ($\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$, >98%), hydrogen peroxide solution (H_2O_2 , 30%), sodium nitrite (NaNO_2 , >99.9%), potassium nitrate (KNO_3 , >99.0%), titanium(IV) oxysulfate - sulfuric acid solution (27-31% H_2SO_4 basis), 2-hydroxyterephthalic acid ($\text{C}_8\text{H}_6\text{O}_5$, 97%) and potassium indigotrisulfonate ($\text{C}_{16}\text{H}_7\text{K}_3\text{N}_2\text{O}_{11}\text{S}_3$) were purchased by Sigma Aldrich. Disodium terephthalate ($\text{C}_6\text{H}_4(\text{COONa})_2$, >99%) was purchased by Alfa Aesar. Nitrate test (Spectroquant, method: photometric, DMP) was purchased by Supelco. Ultrapure water was obtained by filtration using 0.22 μm pore size MILLEXGP filter unit (Merck Millipore Ltd., Ireland). Helium gas (99.998%), oxygen and nitrogen were provided by Praxair, Spain.

3.2 - Plasma source and treatments

The plasma source used in this work is an atmospheric pressure plasma jet (APPJ) that was already described in detail in previous publications [Zaplotnik 2015, Canal 2016]. The active electrode is a copper wire (0.1 mm diameter) embedded inside a quartz tube (ID = 1.2 mm) and connected to a high voltage power supply. The discharge was operated with a sinusoidal waveform at 23 kHz with (U) ~ 2 kV and (I) ~ 3 mA. The average power delivered to the discharge was 1 W. Helium (pure or doped with oxygen or nitrogen) flows through the tube and serves as plasma feed gas. Two Bronkhorst EL-FLOW Select flow controllers were used to set the flow rate of the gases.

All the treatments, if not otherwise stated, were done using the following conditions. He flow rate: 1 L min^{-1} (+ small contribution of the dopant gas); nozzle-to-target distance: 10 mm and 5 mm (fixed); sample volume: 1 mL in 24-well plate for liquid-phase analysis and 1.9 mL in 48-well plate for gas-phase analysis. Treatment time: between 60 to 600 s. The gas flow was started 15-20 min before each treatment in order to ensure the purge of the gas line. The plasma was started at least 5-10 min before the treatment to let it stabilize. Each plasma treatment was repeated three times to ensure reproducibility.

3.3 - Optical Emission Spectroscopy experiments

Optical emission spectroscopy experiments were performed using a StellarNet Black C-25 LT-14 Spectrometer equipped with an Ocean Optics QP600-2-SR optical fibre and SpectraWiz Software (Fig. 3.1). The head of the optical fibre was mounted perpendicular to the plasma plume, 3-4 mm horizontal distance. The distance was the lowest possible to maximize the signal without generating sparks. The vertical position of the optical fibre head was changed with respect to the plasma plume to explore different regions. During the optical emission spectroscopy measurements, 1.8 mL of water in a 48-well plate (full well) were positioned 5 or 10 mm below the plasma nozzle. The well was refilled when needed to compensate for the water lost due to evaporation.

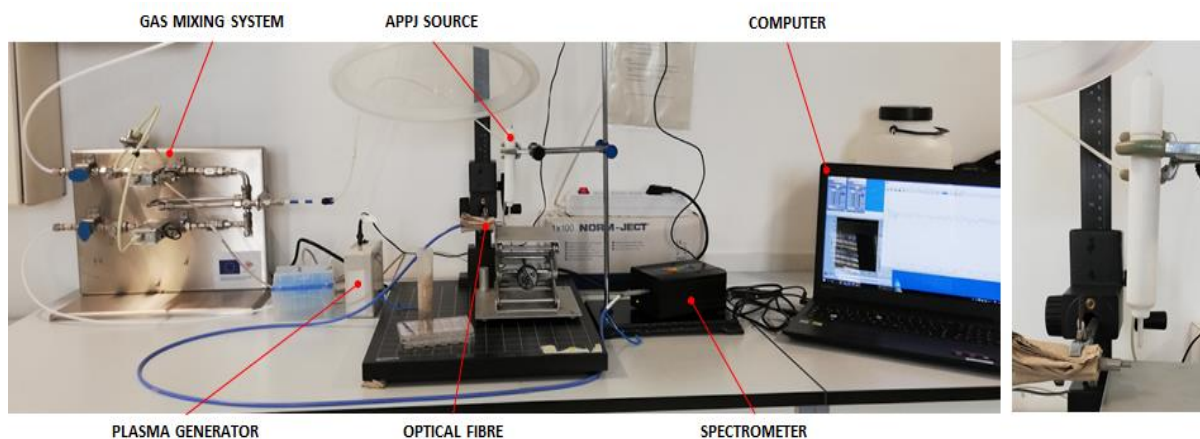


Figure 3.1:(left) experimental apparatus for OES experiments; (right) plasma source and optical fibre head.

Acquisition parameters: spectral range: 200-900 nm; spectral resolution: 0.5 nm integration time: 150 μ s; number of scans: 10. The background signal was subtracted before turning on the plasma. The following conditions were studied:

- Pure helium (1 L/min)
- Helium (1 L/min) doped with x% O₂.
x = 0.01 (0.1 mL/min), 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1 (1 mL/min), 0.12, 0.14, 0.16, 0.18, 0.20, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 (10 mL/min)
- Helium (1 L/min) doped with x% N₂.
x = 0.01 (0.1 mL/min), 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1 (1 mL/min), 0.12, 0.14, 0.16, 0.18, , 0.0.20, 0.25, 0.34, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 (10 mL/min)

The spectra were exported in excel files and then visualized and processed with the software Origin.

3.4 - Quantification of plasma-produced species in water

All the experiments to quantify the plasma-produced reactive species in solution were performed in a phosphate buffer. The buffer solution is prepared in order to fix the pH at 7 and not to have unwanted reactions if the pH changes during the plasma treatment. It is based on the following reaction:



To calculate the amount of acid and salt needed we use the formula:

$$\text{pH} = \text{pK}_A + \log \left(\frac{[\text{A}^-]}{[\text{AH}]}\right) \Leftrightarrow 7 = 7.20 + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right)$$

and the condition

$$[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = 1 \text{ mM}$$

Then the following masses were used to prepare 0.5 L of solution: $m(\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}) = 239 \text{ mg}$ and $m(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}) = 347 \text{ mg}$.

Once the buffer solution is made, the pH has been verified using a PC80 Multiparameter pH-meter (XS Instruments, Italy) with a Crison 50 14 electrode (Crison, Spain).

The reactive species produced during plasma treatment were measured using colorimetric and fluorescent chemical probes. The methods used are reported in the literature [Khlyustova 2019, Labay 2019, Tornin 2021].

Nitrite ions were measured, using the Griess test [Tornin 2021]. It is a colorimetric procedure used for the quantification of nitrite ions in liquids. These ions are detected by producing a pink colour after adding the reagent. The principle of this method is based on two step diazotation reaction in which acidified NO_2^- produces a nitrosating agent that reacts with sulfanilic acid to generate the diazonium ion. This ion is then coupled to N-(1-naphthyl) ethylene diamine (NED) to form the chromophoric azo derivate which absorbs light at 540 nm.

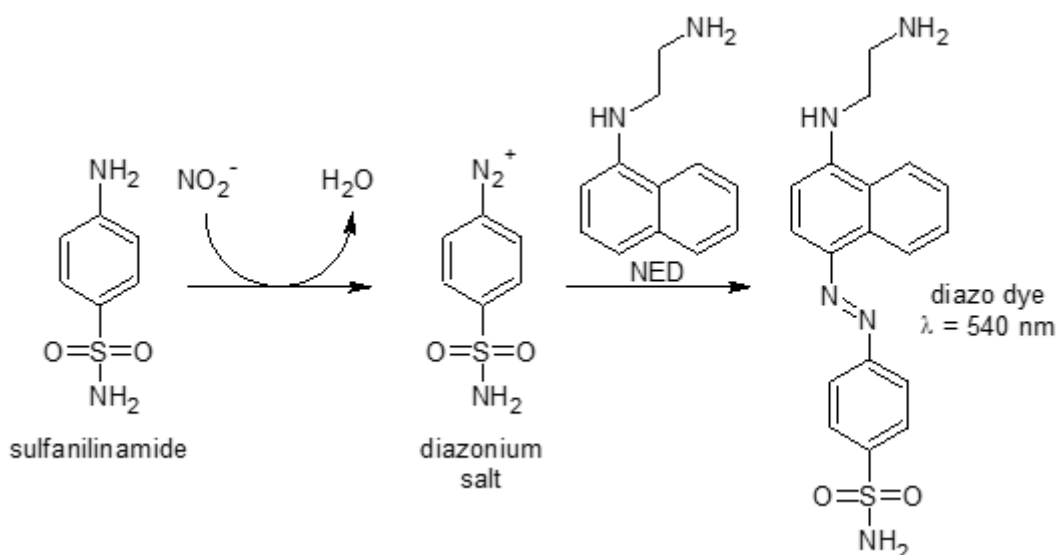
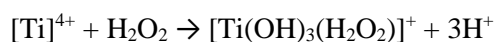


Figure 3.2 : Principle of Griess test to quantify nitrite ions

Aliquots of Griess reagent, containing sulphanilamide, NED and orthophosphoric acid were already prepared in the lab. To a 50 μL of plasma-treated solution 50 μL of Griess reagent were added. After incubating the sample at room temperature for 10 minutes the absorbance at 540 nm was measured in the microplate reader. All measurements were done in triplicate. Calibration lines were built using standard solutions of sodium nitrite prepared in the same media used during plasma treatment.

Hydrogen peroxide was quantified using the titanium(IV) oxysulfate method [Eisenberg 1943]. In presence of hydrogen peroxide, in sulfuric acid solution, Ti(IV) generates a yellow complex with absorption maximum at 410 nm.



To a 100 μL of plasma-treated solution 50 μL of Ti(IV) oxysulfate solution were added. The absorbance at 410 nm was measured in the microplate reader. All measurements were done in triplicate. Calibration lines were built using standard solutions of hydrogen peroxide prepared in the same media used during plasma treatment.

Nitrate ions were measured, using the 2,6-dimethylphenol (DMP) test [Tornin 2021]. It is a colorimetric procedure used for the quantification of nitrate ions in liquids. In a strong acidic mixture nitrate ions can nitrate DMP to generate 4-nitro-2,6-dimethylphenol that absorb at 320 nm.

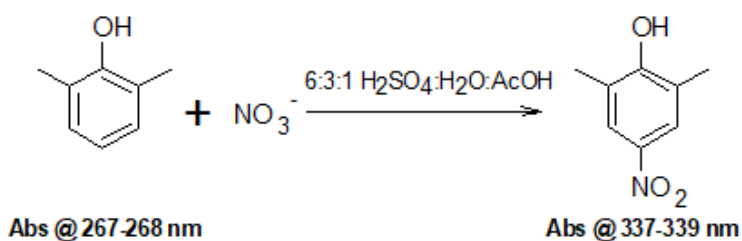


Figure 3.3 : Principle of DMP method to quantify nitrate ions

For this method we used a commercial nitrate detection kit (Spectroquant). In an Eppendorf vial we added 800 μL of Reagent 1, 100 μL of plasma-treated solution and 100 μL of Reagent 2. The vial was then mixed and incubated at room temperature for 10 minutes. Then 200 μL of solution were transferred to a UV-transparent 96-well plate and the absorbance at 320 nm was measured in the microplate reader. All measurements were done in triplicate. Calibration lines were built using standard solutions of nitrate ions prepared in the same media used during plasma treatment.

To detect *ozone* we used indigo trisulfonate [Bader 1981]. This molecule is blue (maximum absorbance 600 nm) and by reaction with ozone becomes colourless.

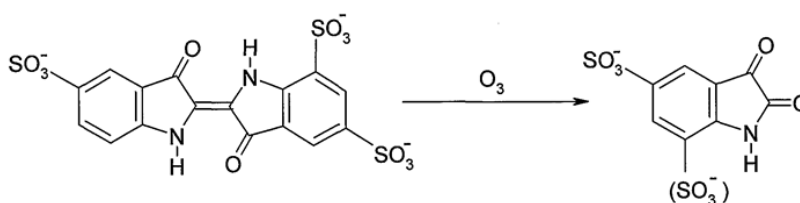


Figure 3.4 : Principle of indigo trisulfonate method to quantify ozone

100 μL of plasma-treated solution were added to 100 μL of indigo solution ($5 \cdot 10^{-4}$ M in phosphate buffer). Then the absorbance at 600 nm was compared with the absorbance of an untreated sample using the microplate reader. All measurements were done in triplicate.

To detect *OH radicals* we used sodium terephthalate (TPA). This molecule is non-fluorescent, but can react with OH radicals to give 2-hydroxyterephthalate (hTPA), that is fluorescent [Tampieri 2021].

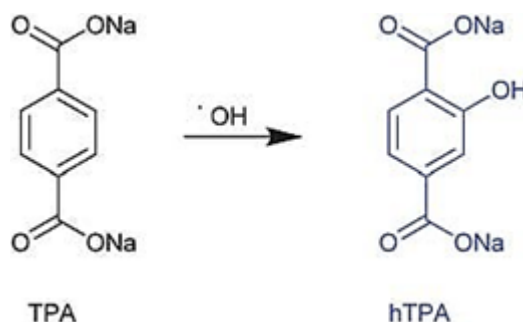


Figure 3.5 : Principle of terephthalate probe to quantify hydroxyl radicals

Since the lifetime of $\cdot\text{OH}$ in solution is considerably lower (hundreds of nanoseconds [Tampieri 2021]) compared to the previously reported species (more than days), it is necessary to have the probe in the solution during the plasma treatment. 1 mM solutions of TPA in phosphate buffer were treated by plasma. After the treatment 0.5 mL were transferred in a 48-well plate and fluorescence measurements were made in the microplate reader ($\lambda_{\text{EX/EM}} = 360/460$ nm, Gain = 100). All measurements were done in triplicate. Calibration lines were built using standard solution of 2-hydroxyterephthalate prepared in the same media used during plasma treatment.

Hydrogen peroxide, nitrites, nitrates and ozone were measured using the same treated solutions. 1 mL of phosphate buffer was treated for a specific time with APPJ using the parameters described earlier. Then the following protocol was followed:

1. 50 μL were withdrawn for nitrites quantification (with 50 μL of Griess reagent)
2. 10 μL of sulfamic acid were added to the solution to eliminate remaining nitrites that could react with hydrogen peroxide and thus affect the concentration
3. 100 μL were withdrawn for hydrogen peroxide quantification (with 50 μL of Ti(IV) solution)
4. 100 μL were withdrawn for ozone quantification (with 100 μL of indigo solution)
5. 100 μL were withdrawn for nitrates quantification (with nitrate analysis kit)

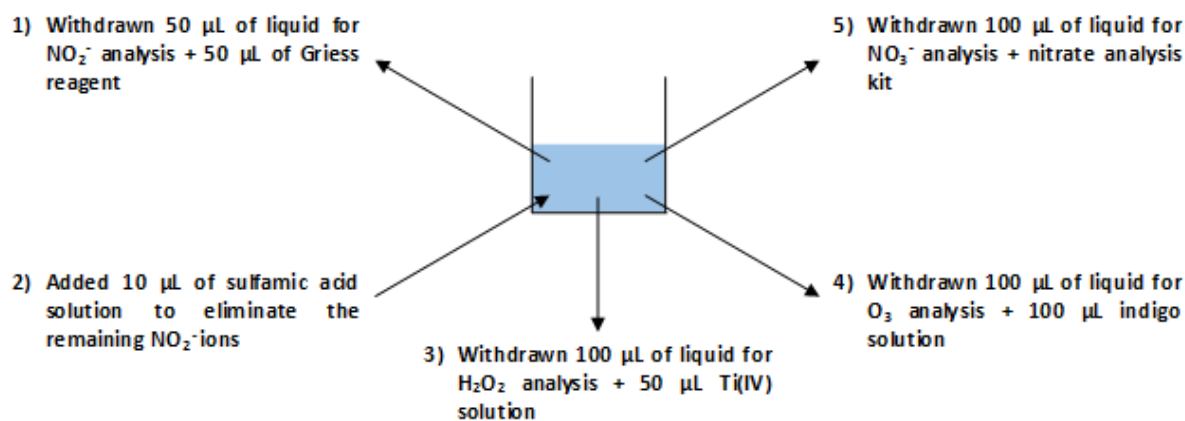


Figure 3.6: Experimental protocol for the quantification of plasma-generated reactive species in water solution.

The following conditions were studied:

- Pure helium (1 L/min)
- Helium (1 L/min) doped with x% O_2 . x = 0.1 (1 mL/min), 0.2 (2 mL/min) and 0.3 (3 mL/min)
- Helium (1 L/min) doped with x% N_2 . x = 0.2 (2 mL/min) and 0.5 (5 mL/min)

4 - Results and discussion

4.1 - Qualitative analysis of plasma-generated excited species in the gas-phase

Some effects of doping the plasma feed gas with molecular oxygen or nitrogen are evident visually by looking at the plasma plume. First, we can see that using pure He, the plasma plume is bright purple and covers all the distance between the plasma nozzle and the liquid surface (at both distances studied, 5 and 10 mm), and when we dope it, it becomes pink. Moreover, the plasma plume is brighter when it is doped with nitrogen. And with helium doped with nitrogen and helium doped with oxygen, the plasma plume is less bright when we increase the amount of the doping gas. The last thing we observe visually is that the plasma plume is brighter when the distance between the plasma nozzle and the water surface is decreasing in all conditions studied.

To analyze more in detail the effect of feed gas doping on the plasma generated by our APPJ source, OES experiments were performed. Figure 4.1 reports the OES spectra obtained at plasma-to liquid distance of 10 mm and with the optical fibre head positioned at vertical distance $z = 1$ mm and $z = 4$ mm from the plasma nozzle. A comparison between the spectra obtained using only He as feed gas and using He doped with 0.1% of O_2 and N_2 is reported. Thanks to the comparison with spectra previously reported in the literature [Neretti 2018], it was possible to identify all the components of our spectra. The following species were present: NO: 200-275 nm ; OH: 280-290 nm and 300-320 nm; N_2 SPS: 337.1, 357.7, 380.5, 405.9, 434 nm; N_2^+ FNS: 391.4, 427.5 nm; He: 501.6, 587.5, 667.8, 706.5, 728.1 nm; O(I) triplet: 777 nm.

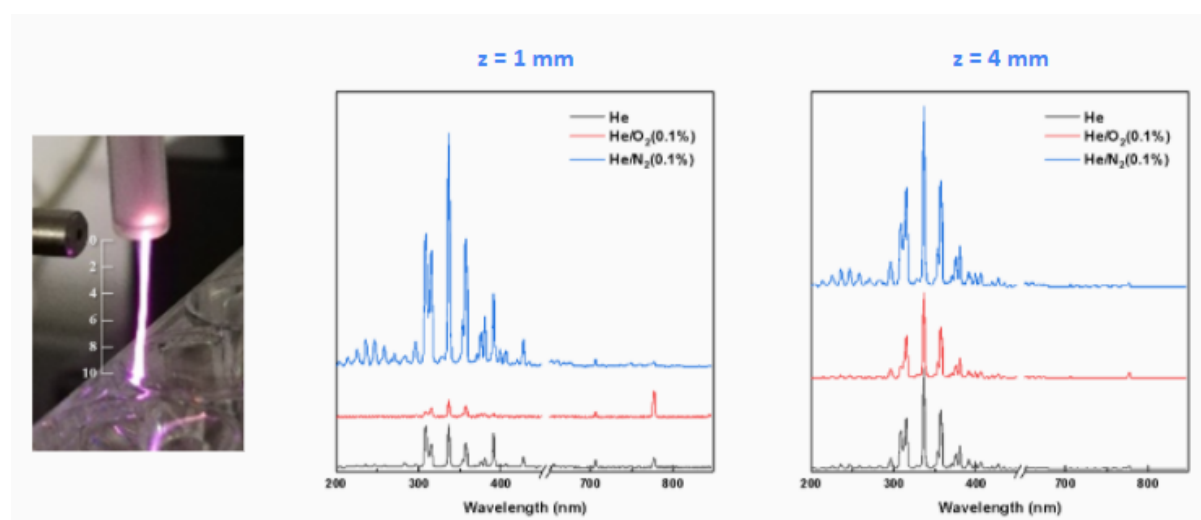


Figure 4.1: Comparison of OES spectra obtained using pure He (black) and He doped with 0.1% of oxygen (red) or nitrogen (blue). The spectra were collected at a plasma-to-target distance of 10 mm and with vertical position of the optical fibre head of 1 (left) and 4 mm (right).

From figure 4.1 it is clear that when helium is doped with oxygen, the nitrogen species (NO , N_2 and N_2^+) and helium are less intense than in pure helium, and the signal of triplet oxygen (777 nm) is more intense. And for helium doped with nitrogen, it is the opposite, the intensity of the signals of nitrogen species is more intense. Moreover, these effects decrease when the head of the optical fiber is positioned more distant from the plasma nozzle ($z = 4$ mm), which means that modification of the feed gas influence mostly the region of the plasma that is closer to the source.

Many OES spectra were collected varying the feed gas composition and the plasma-to-target distance. In the following figures are reported the intensity of the main species just described as function of the feed gas composition (increasing percentage of nitrogen or oxygen) in all the conditions studied. All spectra were acquired in duplicate and the intensity values reported in the figures are the average of the two experiments.

Helium doped with nitrogen

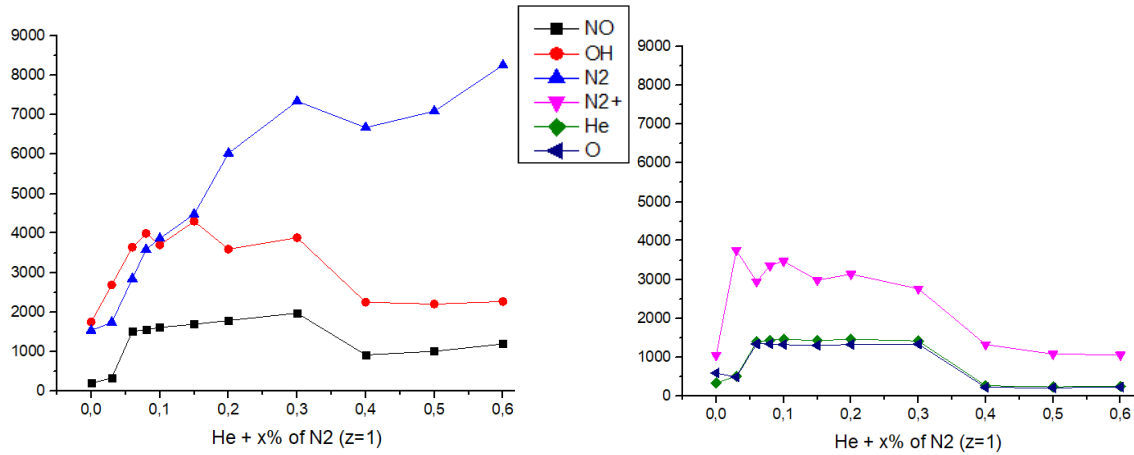


Figure 4.2: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: nitrogen; plasma-to-target distance: 5 mm; z = 1 mm.

For the helium doped with nitrogen at z = 1 mm with a plasma-to-target distance of 0.5 cm (Fig. 4.2), the intensity of NO signals increases a bit at low dopant percentage (0.05%) and stays constant until 0.3% and then decreases and stays constant. OH signals increase until 0.1%, then stay constant until 0.3% and then decrease. N₂ signals start to increase until 0.3% and then stay constant. N₂⁺ signals increase at 0.05% and then decrease slowly until 1%. He and O signals have the same profile: they increase for low doping percentage and then almost disappear at nitrogen content higher than 0.4%.

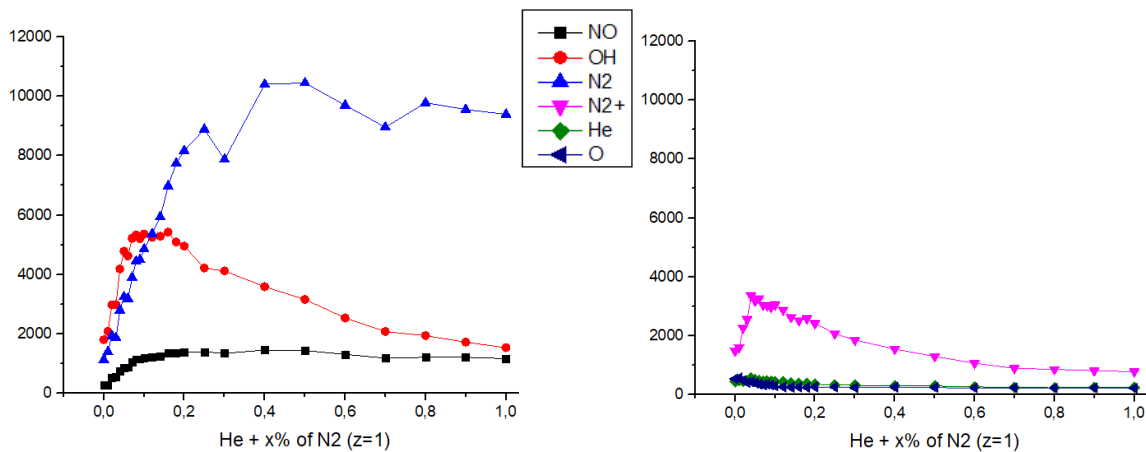


Figure 4.3: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: nitrogen; plasma-to-target distance: 10 mm; z = 1 mm.

By increasing the plasma-to-target distance to 1 cm (Fig. 4.3), all the nitrogen species show more or less the same trends. On the other side, the signals of He and O are very low, even at low dopant percentage.

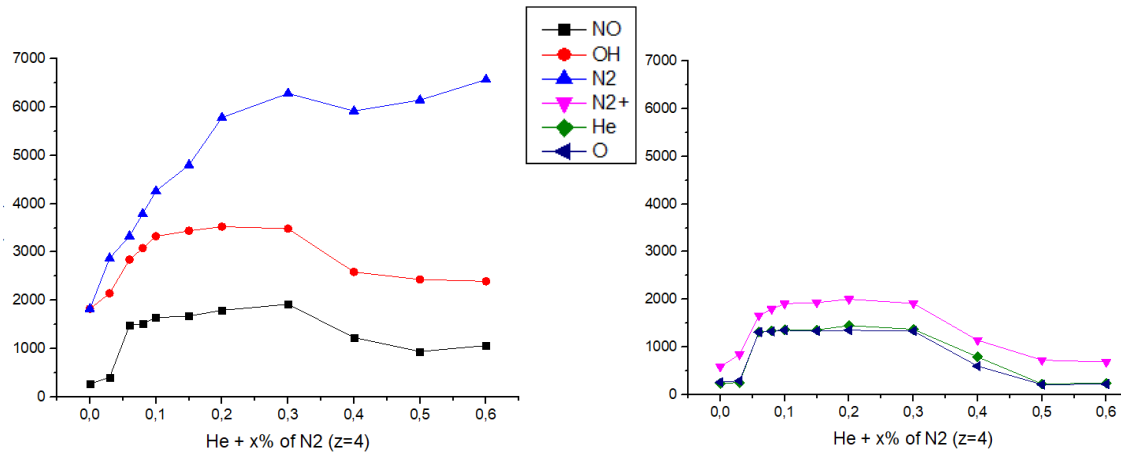


Figure 4.4: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: nitrogen; plasma-to-target distance: 5 mm; $z = 4$ mm.

For the helium doped with nitrogen at $z = 4$ mm with a plasma-to-target distance of 0.5 cm (Fig. 4.4), all the species show the same trend as with $z = 1$ mm.

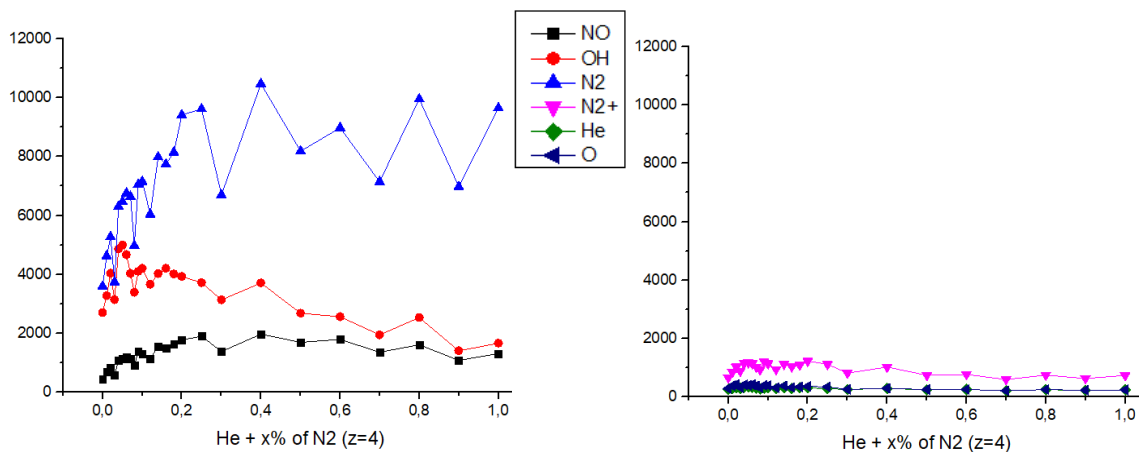


Figure 4.5: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: nitrogen; plasma-to-target distance: 10 mm; $z = 4$ mm.

For a plasma-to-target distance of 1 cm and $z = 4$ mm (Fig. 4.5), NO signals increase at low dopant percentage until 0.2% and then stay constant. OH signals increase until 0.5%, stay constant until 0.2% and then decrease by further increasing the dopant percentage. N_2 signals increase at low dopant percentage until 0.4% and then stay constant. N_2^+ signals increase from 0% to 0.05% and then decrease slowly by further increasing the dopant percentage. He and O signals stay at a low value (almost zero), regardless of the composition of the gas.

Helium doped with oxygen

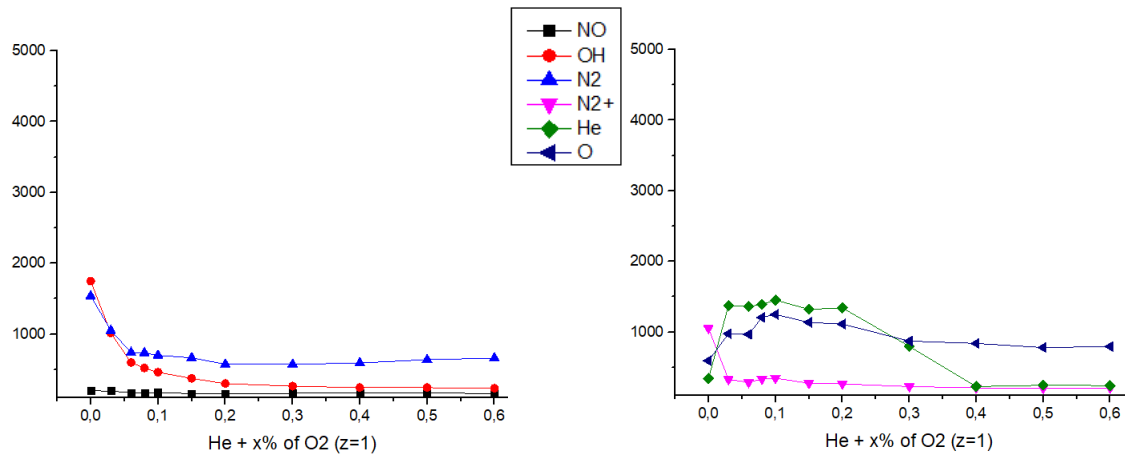


Figure 4.6: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: oxygen; plasma-to-target distance: 5 mm; $z = 1$ mm.

For the helium doped with oxygen at $z = 1$ mm with a plasma-to-target distance of 0.5 cm (Fig. 4.6), NO signals are very low and constant regardless of the gas composition. OH signals decrease quickly from the pure He condition until 0.2% oxygen and then stay constant. N_2 signals decrease quickly until 0.08% oxygen and then stay constant. N_2^+ signals decrease quickly until 0.03% and then stay constant. He signals increase from 0 to 0.03% oxygen, stay constant until 0.2% oxygen and then decrease until 0.4% and then stay at a low signal. O signal increases from 0 to 0.06%, stays constant until 0.2% and then decreases at 0.3% and then stays constant.

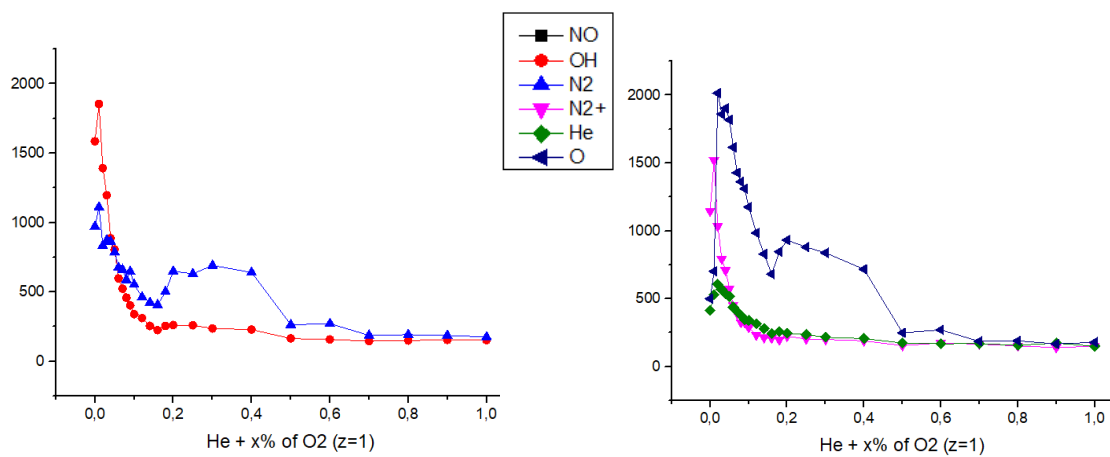


Figure 4.7: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: oxygen; plasma-to-target distance: 10 mm; $z = 1$ mm.

For a plasma-to-target distance of 1 cm (Fig. 4.7), no NO signal was evident in the spectra. OH signals decrease at the beginning until 0.2% and then stay constant. N_2 signals decrease at the beginning until 0.15% and increase until 0.2% and stay constant until 0.4% and then decrease and stay constant from 0.5%. N_2^+ signals decrease from 0 to 0.2% oxygen and then stay constant at a low signal. He signals increase slightly until 0.05% and then decrease until 0.2% and stay at a low signal. O signal increases with the presence of oxygen and decreases from 0.2% until 0.5% and stays at a low signal.

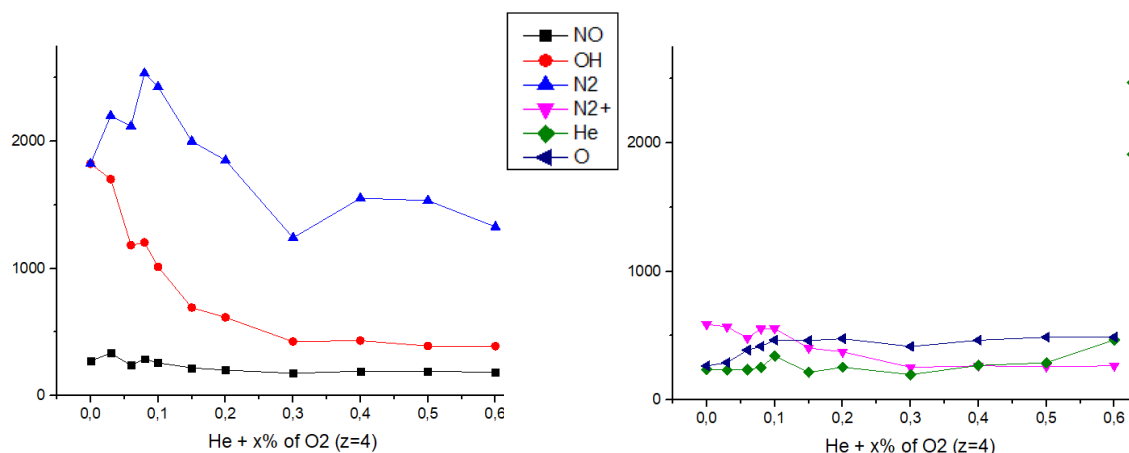


Figure 4.8: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: oxygen; plasma-to-target distance: 5 mm; $z = 4$ mm.

For the helium doped with nitrogen at $z = 4$ mm with a plasma-to-target distance of 0.5 cm (Fig. 4.8), NO signals are constant at a low value, regardless of the composition of the gas. OH signals are decreasing until 0.3% and then stay constant at a low value. N_2 signals are increasing until 0.06% and then decrease until 0.3% and then stay constant until 1%. N_2^+ , He and O signals are constant at a low value, regardless of the composition of the gas.

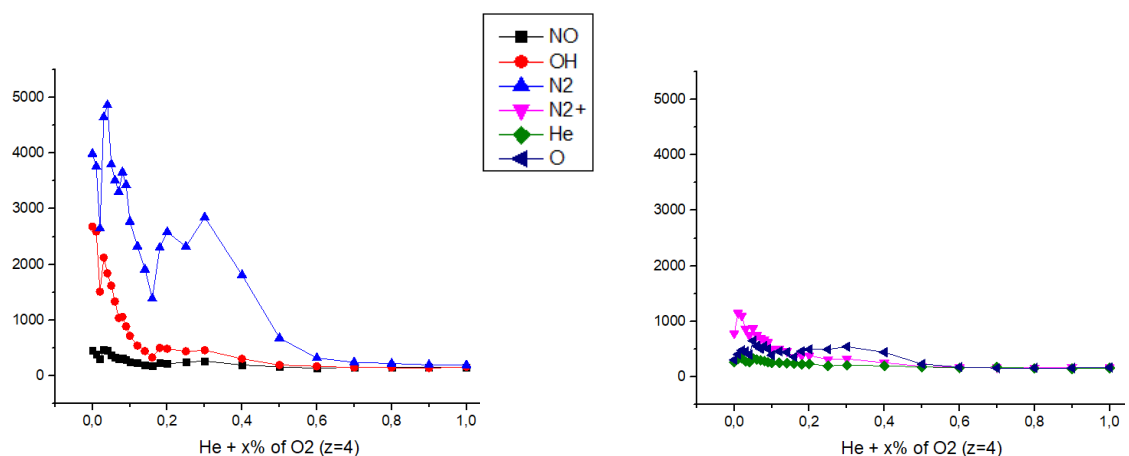


Figure 4.9: Intensity of the main excited species in the plasma plume as function of the feed gas composition. Dopant: oxygen; plasma-to-target distance: 10 mm; $z = 4$ mm.

For a plasma-to-target distance of 1 cm (Fig. 4.9), no NO signal was evident in the spectra. OH signals decrease until 0.2% and then stay constant at a low value. N_2 signals decrease with the oxygen percentage until reaching a low value. N_2^+ signals increase a bit with oxygen but decrease from 0.02% and then stay at a low signal. He and O signals are constant at a low value, regardless of the composition of the gas.

All the data presented in this section allow us to select some interesting conditions for the subsequent quantitative analysis of plasma-generated species in water solution:

- For helium doped with oxygen, 0.1 and 0.3 % are selected because they correspond to a higher generation of oxygen atoms with respect to the pure helium condition.
- For helium doped with nitrogen, 0.2 % is selected because it corresponds to a maximum in the N_2^+ trend and 0.5 % because it corresponds to maxima in N_2 and NO trends.

4.2 - Quantitative analysis of plasma-generated species in water solution

We know from previous studies [Tampieri 2021] that the evaporation rate of water due to plasma treatment for a plasma-to-target distance of 10 mm is $(2.10 \pm 0.09) \cdot 10^{-4} \text{ s}^{-1}$. We obtained the same parameter for 5 mm distance. We treated 1 mL aliquots of phosphate buffer solutions in a 24-well plate with plasma source and we weighted the liquid at the end of the treatment. All measurements were done in triplicate. We plotted the relative evaporation as a function of the plasma treatment time (Fig. 4.2) and we obtained the evaporation rate by fitting the experimental data with a linear function. For a plasma-to-target distance of 5 mm we obtained an evaporation rate of $2.282 \times 10^{-4} \text{ mL}\cdot\text{s}^{-1}$. The evaporation rates have been used to correct the data of concentration of RONS in water solution.

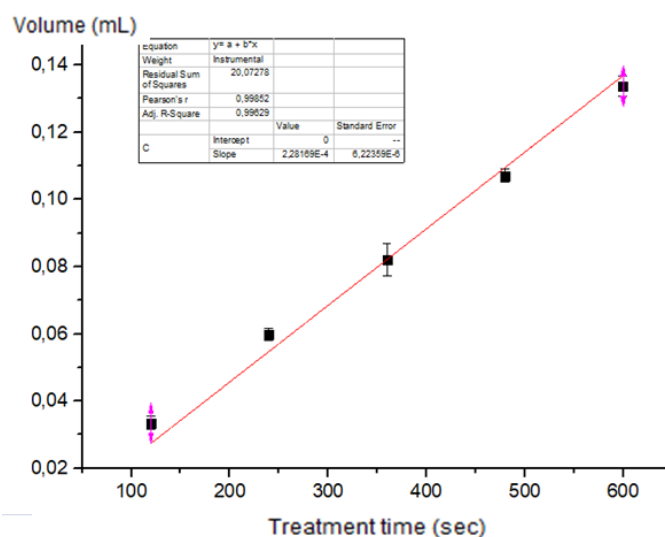


Figure 4.10: Evaporation as function of the treatment time for experiments with plasma-to-target distance of 0.5 cm.

In the following figures are reported the concentration of plasma generated reactive species in water obtained using the method reported in the previous chapter. All experiments have been done in triplicate and the data were corrected taking into account for the evaporation. The experimental data have been interpolated with straight lines and the slopes of these lines have been collected in tables. The slopes represent the rates of formation of the reactive species.

Ozone

Quantitative analysis for ozone was performed as described in the experimental section but in all the conditions studied the amount of ozone generated was lower than the detection limit of our quantification method. In all cases the absorbance of indigo solution after addition of plasma treated solution was not different from the one after addition of untreated solution. Therefore, no figure or table is presented in this section.

Hydrogen peroxide

Hydrogen peroxide in water is generated by recombination of OH radicals.

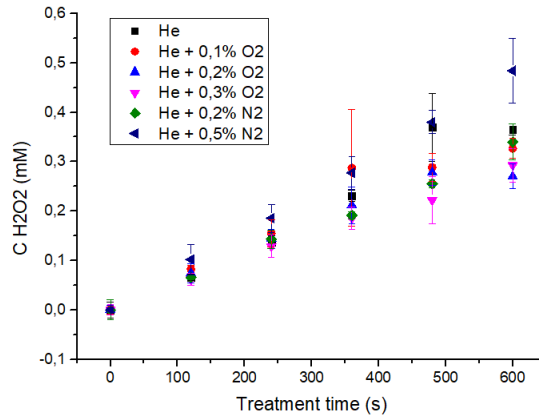


Figure 4.11: Concentrations of hydrogen peroxide as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 0.5 cm

H2O2		
Condition	Slope ($\mu\text{M/s}$)	Error ($\mu\text{M/s}$)
Pure He	0,66	0,04
He + 0,1% O2	0,63	0,03
He + 0,2% O2	0,58	0,01
He + 0,3% O2	0,51	0,02
He + 0,2% N2	0,53	0,01
He + 0,5% N2	0,79	0,01

Figure 4.12: Generation rate of hydrogen peroxide for different feed gas conditions at a plasma-to-target distance of 0.5 cm

In the case of the 0.5 cm plasma-to-target distance (Fig. 4.11 and 4.12), the amount of hydrogen peroxide generated is nearly the same in each gas composition, and it is increasing with the treatment time, in the same way (slopes are similar), but a bit more in the case of He +0.5% of N₂.

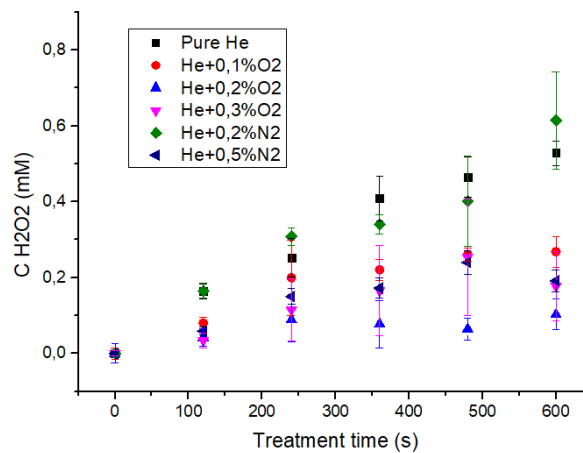


Figure 4.13: Concentrations of hydrogen peroxide as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 1 cm

H2O2		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	1,09	0,09
He + 0,1% O2	0,55	0,03
He + 0,2% O2	0,13	0,05
He + 0,3% O2	0,38	0,06
He + 0,2% N2	1,06	0,12
He + 0,5% N2	0,52	0,03

Figure 4.14: Generation rate of hydrogen peroxide for different feed gas conditions at a plasma-to-target distance of 1 cm

In the case of the 1 cm plasma-to-target distance (Fig. 4.13 and 4.14), the concentrations of hydrogen peroxide in the case of pure He and He + 0.2% of N₂ are increasing linearly with the treatment time up to 10 min treatment, and they reach approximately the same value (about 0.6 mM), which are the highest that we could quantify between all the conditions studied. In the case of He + 0.1% of O₂ and He + 0.5% of N₂, the concentrations are increasing slower with the treatment time compared to the previous ones, and they reach a plateau condition after 5 min treatment. For He + 0.2% of O₂, the concentration of hydrogen peroxide remains very low for all treatment times. Regarding the distance, it appears that with pure helium or adding a small amount of nitrogen, the concentration of hydrogen peroxide is higher if the plasma is 10 mm from the water surface. For all the other conditions (addition of oxygen or high amount of nitrogen) the concentration is higher when the plasma is closer to the water surface.

Nitrite ions

Nitrite ions are generated by the reaction of NO with water. In this way nitrous acid is produced and it can dissociate in water to generate nitrite ions.

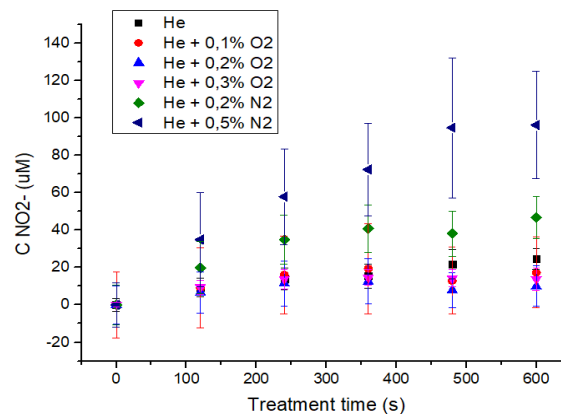


Figure 4.15: Concentrations of nitrite ions as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 0.5 cm

NO ₂ ⁻		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	0,05	0,01
He + 0,1% O ₂	0,06	0,01
He + 0,2% O ₂	0,04	0,01
He + 0,3% O ₂	0,05	0,01
He + 0,2% N ₂	0,12	0,02
He + 0,5% N ₂	0,21	0,02

Figure 4.16: Generation rate of nitrite ions for different feed gas conditions at a plasma-to-target distance of 0.5 cm

In the case of the 0.5 cm plasma-to-target distance (Fig. 4.15 and 4.16), the concentration of nitrite in the case of pure He and He doped with oxygen, is very low, even at high treatment time. When doping He with N₂, the concentration of nitrites increases with respect to pure helium is increasing. The increase is much higher in the case of 0.5% nitrogen.

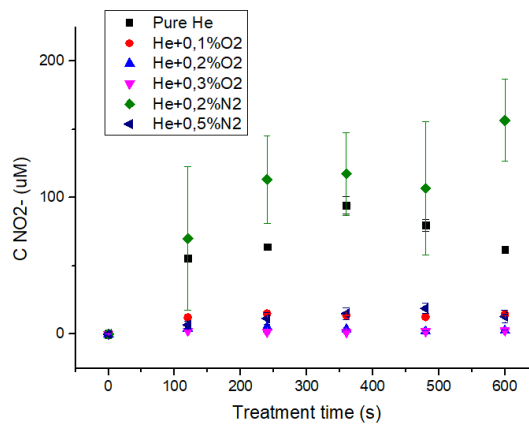


Figure 4.17: Concentrations of nitrite ions as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 1 cm

NO ₂ ⁻		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	0,37	0,07
He + 0,1% O ₂	0,05	0,02
He + 0,2% O ₂	0,01	0,01
He + 0,3% O ₂	0,003	0,004
He + 0,2% N ₂	0,37	0,05
He + 0,5% N ₂	0,04	0,004

Figure 4.18: Generation rate of nitrite ions for different feed gas conditions at a plasma-to-target distance of 1 cm

For 1 cm plasma-to-target distance (Fig. 4.17 and 4.18), the concentrations of nitrites in the case of He doped with oxygen and He + 0.5% of N₂, is very low for all treatment times. For pure He, the concentration is increasing until 6 min of treatment and then reaches a plateau (about 80 uM). For He + 0.2% of N₂, the concentration is increasing with the treatment time and is the highest one (150 uM at 10 min treatment).

In general, the amount of nitrites obtained at a plasma-to-target distance of 1 cm are higher for the pure He and He doped with a small amount of nitrogen. In all the other conditions, the short distance gives higher concentration.

Nitrate ions

Nitrate ions are generated by the reaction of NO_2 with water. In this way nitric acid is produced and it can dissociate in water to generate nitrate ions. Nitrates can also be generated as a product of the reaction of nitrites and hydrogen peroxide in presence of an acid.

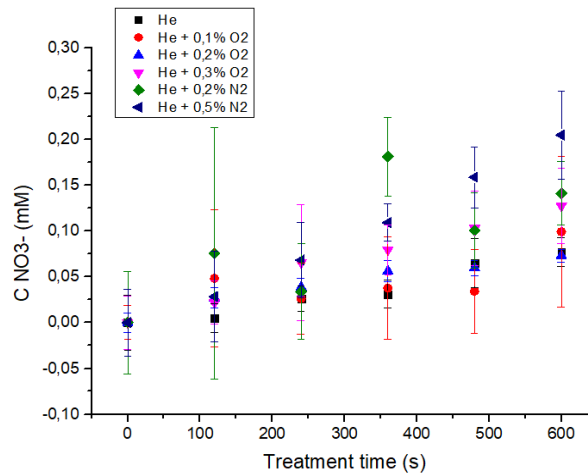


Figure 4.19: Concentrations of nitrate ions as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 0.5 cm

NO ₃ ⁻		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	0,10	0,03
He + 0,1% O ₂	0,11	0,04
He + 0,2% O ₂	0,15	0,02
He + 0,3% O ₂	0,23	0,02
He + 0,2% N ₂	0,27	0,17
He + 0,5% N ₂	0,31	0,01

Figure 4.20: Generation rate of nitrate ions for different feed gas conditions at a plasma-to-target distance of 0.5 cm

In the case of the 0.5 cm plasma-to-target distance (Fig. 4.19 and 4.20), all the concentrations are increasing with treatment time. In the case He doped with oxygen, the concentrations are increasing slower than pure He, and in the case of He doped with nitrogen, the concentrations are increasing faster. But for He + 0.2% of N_2 , the concentration is increasing until 6 min of treatment and then reaches a plateau. For He + 0.5% of N_2 , the concentrations are the highest keep increasing with the treatment time.

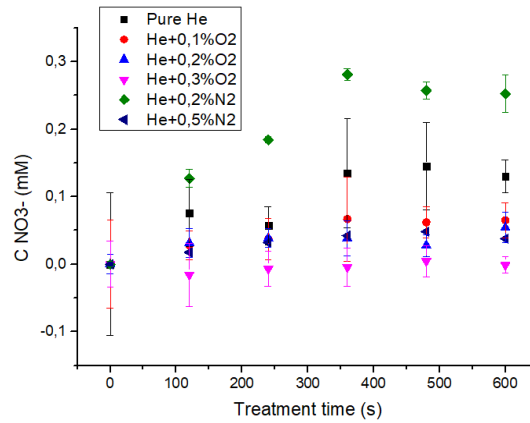


Figure 4.21: Concentrations of nitrate ions as a function of plasma concentration treatment time with different feed gas conditions and a plasma-to-target distance of 1 cm

NO ₃ ⁻		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	0,25	0,11
He + 0,1% O ₂	0,10	0,02
He + 0,2% O ₂	0,06	0,04
He + 0,3% O ₂	0,02	0,02
He + 0,2% N ₂	0,69	0,09
He + 0,5% N ₂	0,10	0,01

Figure 4.22: Generation rate of nitrate ions for different feed gas conditions at a plasma-to-target distance of 1 cm

For 1 cm plasma-to-target distance (Fig. 4.21 and 4.22), the concentrations in the case of He doped with oxygen and He + 0.5% of N₂, are very low and stay constant with the treatment time. But for pure He and He + 0.2% of N₂, the concentration is increasing until 6 min of treatment and then reaches a plateau. The concentrations with He + 0.2% of N₂ are higher than with pure He. The highest concentration of nitrates have been observed for 1 cm plasma-to-target distance.

OH radicals and O atoms

A recent published work [Myers 2021] reported that the product of the reaction between hydroxyl radicals and terephthalate and the product of the reaction between O atoms and terephthalate are the same, hydroxyterephthalate. Therefore, using TPA as a probe during the plasma treatment should allow us to indirectly quantify the sum of the contribution of both species.

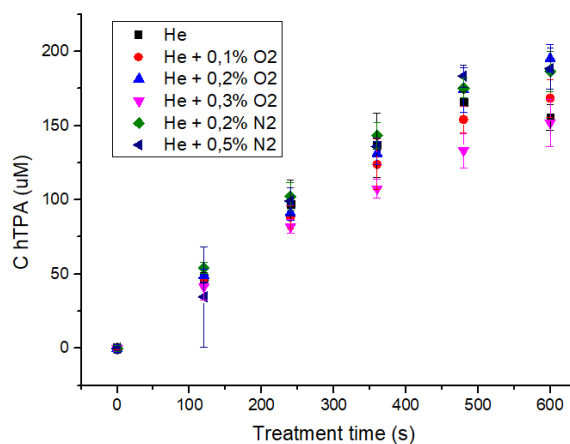


Figure 4.23 : Concentrations of hTPA as a function of plasma treatment time with different feed gas conditions and a plasma-to-target distance of 0.5 cm

OH		
Condition	Slope (uM/s)	Error (uM/s)
Pure He	0,39	0,01
He + 0,1% O2	0,38	0,01
He + 0,2% O2	0,37	0,01
He + 0,3% O2	0,32	0,02
He + 0,2% N2	0,42	0,02
He + 0,5% N2	0,38	0,01

Figure 4.24: Generation rate of hydroxyterephthalate for different feed gas conditions at a plasma-to-target distance of 0.5 cm

The quantitative analysis for OH radicals has been done only for 0.5 cm plasma-to-target distance (Fig. 4.23 and 4.24). The amount of hydroxyterephthalate (hTPA) generated is nearly the same in each gas composition, even if pure He and He +0.5% of N₂ have the biggest amounts. Moreover, the amounts are increasing with the treatment time, in the same way (slopes are similar) in every composition of the gas.

5 - Conclusions

In this work we studied the effect of doping the plasma feed gas on the production of reactive species in the gas phase and in water solution. The plasma source used in this work has previously been characterized only using pure helium as feed gas and therefore the results reported in this work started exploring new working modes and possible applications that follows.

Qualitative/semiquantitative experiments in the gas phase were performed using optical emission spectroscopy. Most of the differences were observed in the plasma region close to the plasma nozzle. Moving far from it, the optical emission spectra become similar, meaning that the nature of the feed gas influences the plasma mostly in the proximity of the active electrode and then external contributions become dominant (ambient air, water, humidity). By doping the feed gas (He) with small amounts of molecular oxygen or nitrogen we observed some general effects. The stability of the plasma is higher when the gas is not doped. The length and intensity of the plasma plume generally decrease by increasing the amount of dopant gas. The effect is more evident with oxygen than with nitrogen but happens in both cases. This effect is also more pronounced at a higher plasma-to-target distance. By normalizing the intensity of the signals of excited species by the signals of helium, we could observe that doping the feed gas with oxygen turned into a higher relative intensity of the O triplet signal at 777 nm. This signal, in case of pure He is very low and is due to interaction with air oxygen, while in the case of doping with nitrogen, it is not detectable. On the other hand, doping the feed gas with nitrogen results in a very high increase of the relative signals of nitrogen-containing species (NO, N₂ and N₂⁺) and to the almost disappearance of the oxygen signal.

Quantitative analysis of RONS in water solution was performed using well-established chemical probes. We quantified hydrogen peroxide, nitrite and nitrate ions, ozone and hydroxylated terephthalate that is the product of the reaction between OH radicals or O atoms with terephthalate (we couldn't detect directly the short lived reactive species due to their high reactivity). OH radicals are mostly generated by the interaction of primary plasma reactive species with water molecules, so they are not expected to be strongly dependent on the presence of nitrogen or oxygen in the feed gas. The same happens for hydrogen peroxide that comes from the recombination of OH radicals. Nitrites and nitrates come mostly from the reaction of NO and NO₂ with water molecules and these two species depend on the presence of nitrogen in the plasma region. On the other hand, O atoms and ozone molecules depend on the presence of oxygen.

The results that we obtained with nitrogen as a dopant are in line with these considerations: the amount of nitrites and nitrates is higher in water when a small amount of nitrogen is added to the feed gas. High amounts of nitrogen (0.5%) cause the plasma plume to be less intense and therefore the amount of all the species decreases. Also the results obtained for hydrogen peroxide are in this line. At short plasma-to-target distance we didn't observe high differences between the different experiments. Some differences were observed at high distance because the intensity and length of the plasma plume decrease when a high amount of dopant is added.

The amount of ozone produced and transferred in solution was below the detection limit in all cases, so we were not able to observe any dependence on the feed gas composition.

In the case of short-lived species, we didn't observe any evident difference by modifying the feed gas. This is expected for OH radicals, but not for O atoms, that should be higher in presence of oxygen. This can mean that, using our APPJ source, even in presence of molecular oxygen in the feed gas, the amount of atomic oxygen generated remain negligible with respect of the OH radicals or that the possible higher contribution of O atoms is counterbalanced by the lower intensity of the plasma plume that we observed by doping the feed gas with oxygen.

All the experiences that were done allow us to draw some conclusions about the effects of the gas composition. The information that we obtained will allow us to tune the plasma parameters more finely in following studies and more specifically for the desired application. What can be interesting is to study other parameters like for example the total flow or the speed of the gas when it hits the liquid surface. This change could be done by modifying the diameter of the plasma nozzle. Transfer properties could be influenced by this parameter.

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