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► **To cite this version:**

Fanny Girard, Vasilica Badets, Sylvie Blanc, Neso Sojic, Franck Clement, et al.. Formation of reactive oxygen and nitrogen species including peroxyxynitrite in physiological buffer exposed to cold atmospheric plasma. International Conference on Plasmas with Liquids (ICPL 2017), Mar 2017, Prague, Czech Republic. <hal-02271089>

HAL Id: hal-02271089

<https://univ-pau.hal.science/hal-02271089v1>

Submitted on 4 Jan 2026

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Formation of reactive oxygen and nitrogen species including peroxyxynitrite in physiological buffer exposed to cold atmospheric plasma

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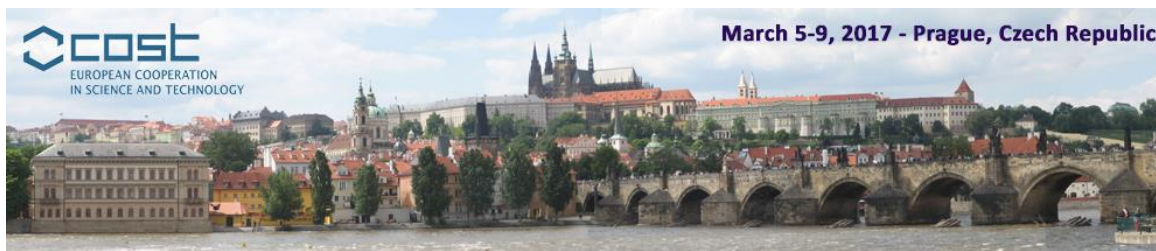
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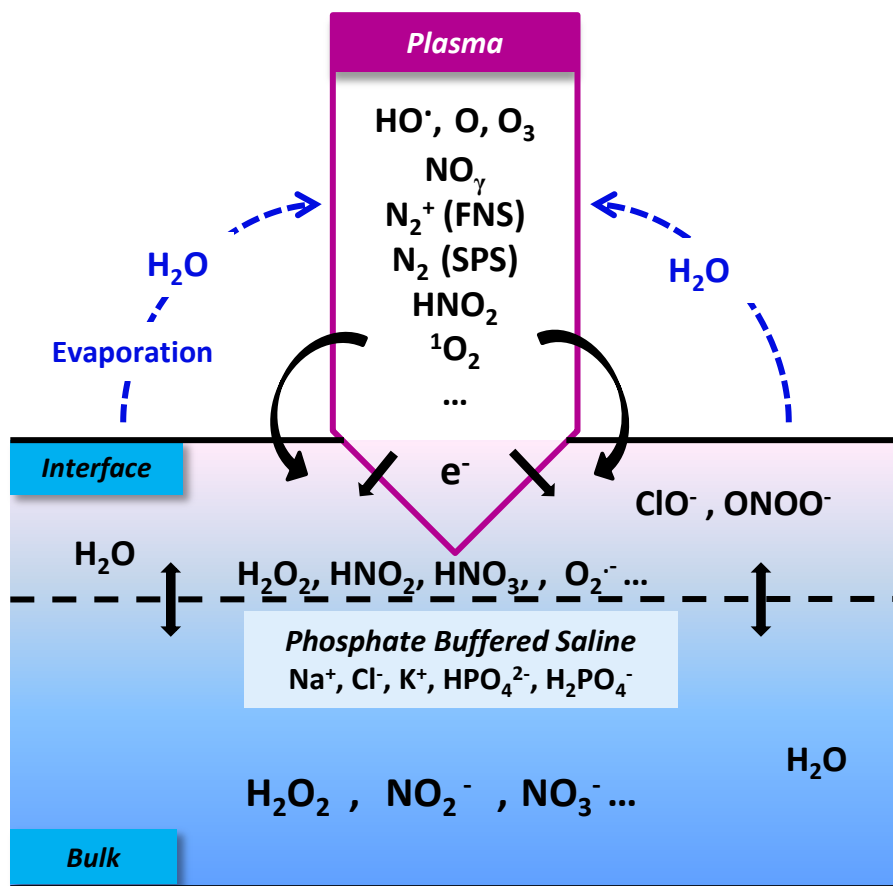
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stephane.arbault@enscbp.fr



INTERNATIONAL CONFERENCE ON PLASMAS WITH LIQUIDS (ICPL 2017)

Context and outline



1) Plasma generation

Physical parameters
Gas, Voltage, frequency, duty cycle...

2) Plasma characterization

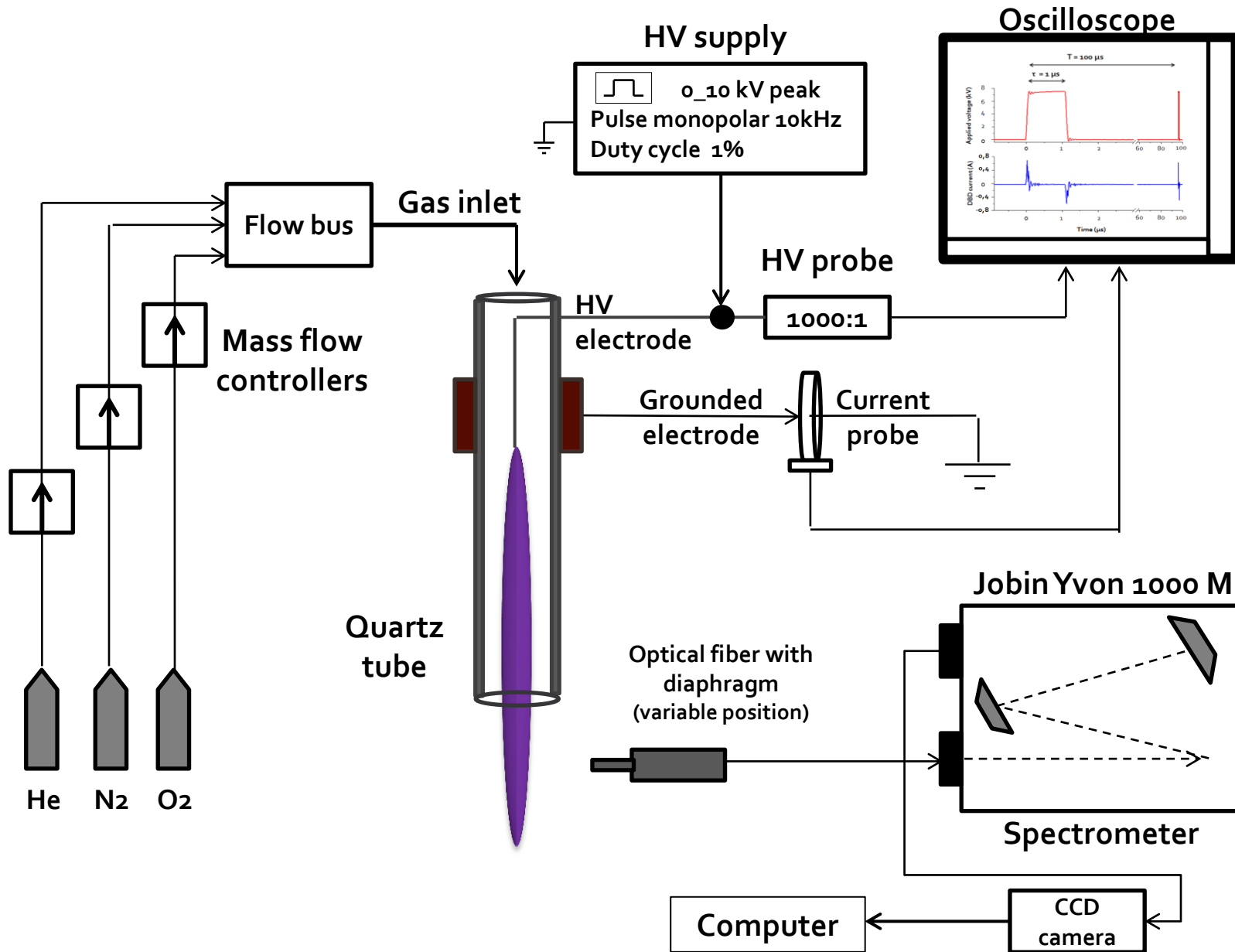
Plasma analysis
Physico-chemical components
(UV, e.m. fields, gaseous RONS)

3) Plasma-liquid interactions

Liquid analysis
RONS, pH, σ, evaporation

Links between chemical species in the plasma and induced liquid chemistry

Plasma setup



Plasma generation and characterization

Setup 1 : Air environment

❖ Fixed physical parameters :

7.5 kV

10 kHz

duty cycle : 1 %

2 slm

Various working gases

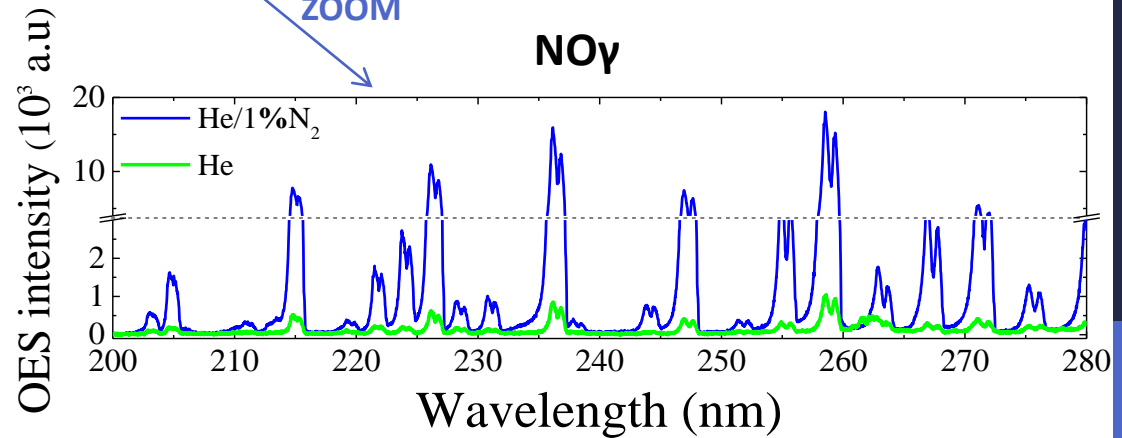
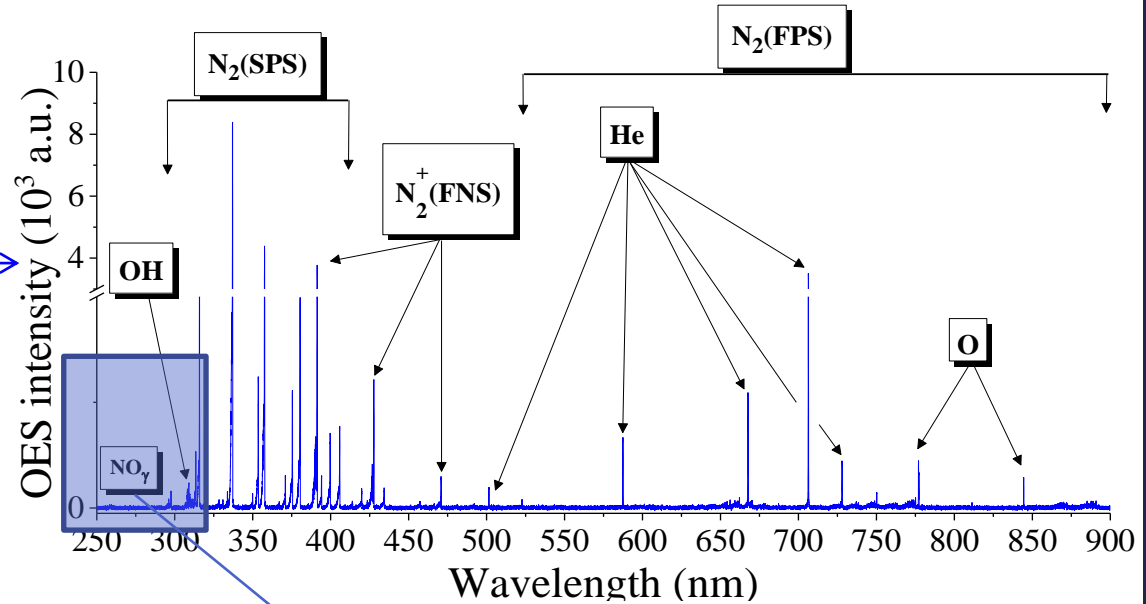
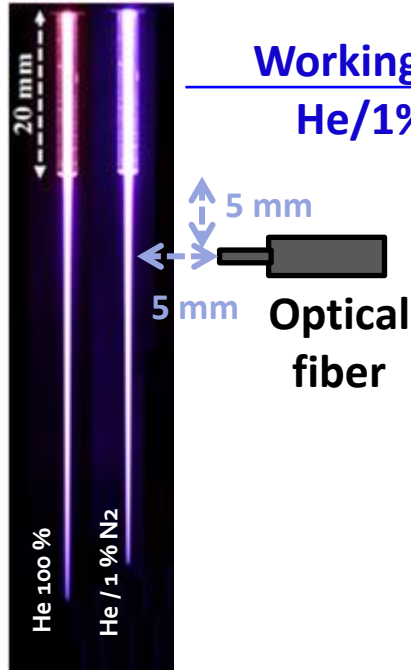


He
He/1%N₂

❖ Analysis by **Optical Emissive Spectroscopy (OES)**

Plasma generation and characterization

7.5 kV
10 kHz
duty cycle = 1 %



➤ Rotational structures of OH and $N_2(SPS)$ \longrightarrow $T_{gas} \approx 300 K^*$

*From Gazeli et al., *Journal of Applied Physics* 117, 093302. 2015

Plasma-liquid interactions

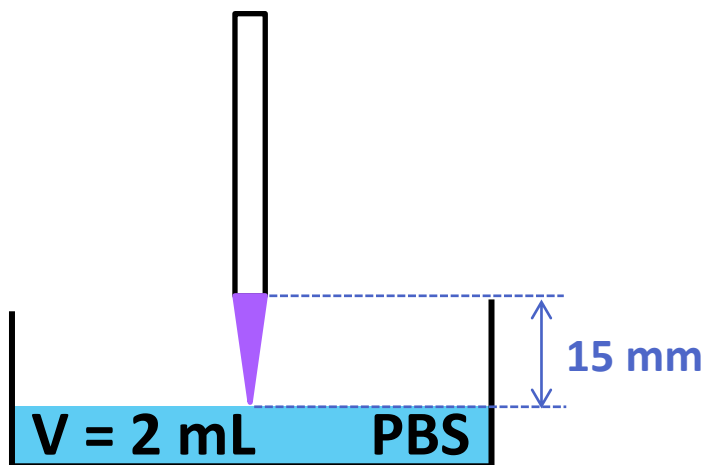
Excited chemical species in the plasma



What effects on liquid chemistry?

1) Plasma treatment

- Working gas He/1%N₂
- Various exposure times



➤ PBS - - (10 mM) pH 7.4

2) Liquid analysis



UV-visible absorption spectroscopy

Electrochemistry

POST-TREATMENT Analysis

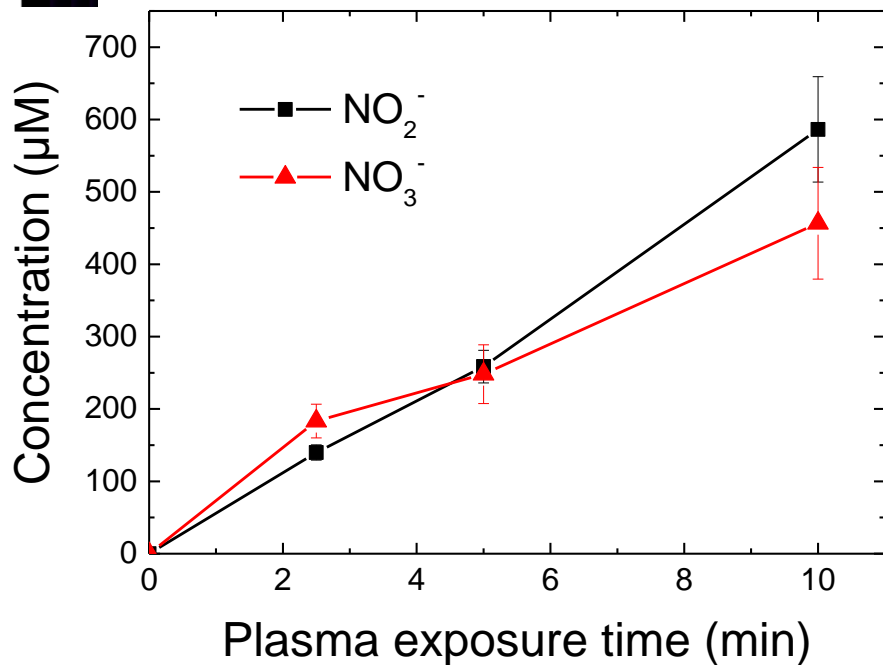


Plasma-liquid interactions

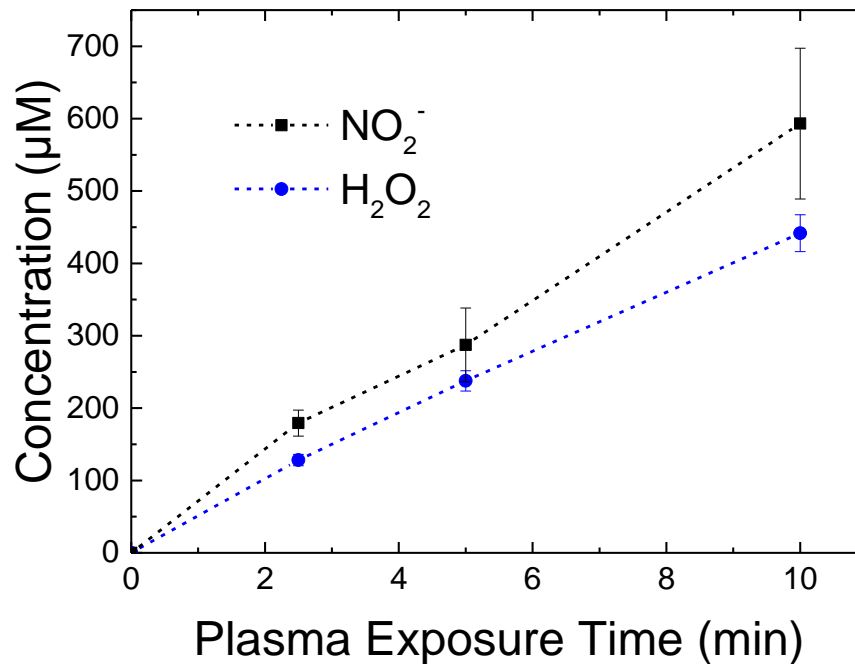
He/1%N₂

Stable Oxygen and Nitrogen Species

UV-visible absorption spectroscopy



Electrochemistry



NO₂⁻

NO₃⁻

Effects
on pH ?

Plasma-liquid interactions

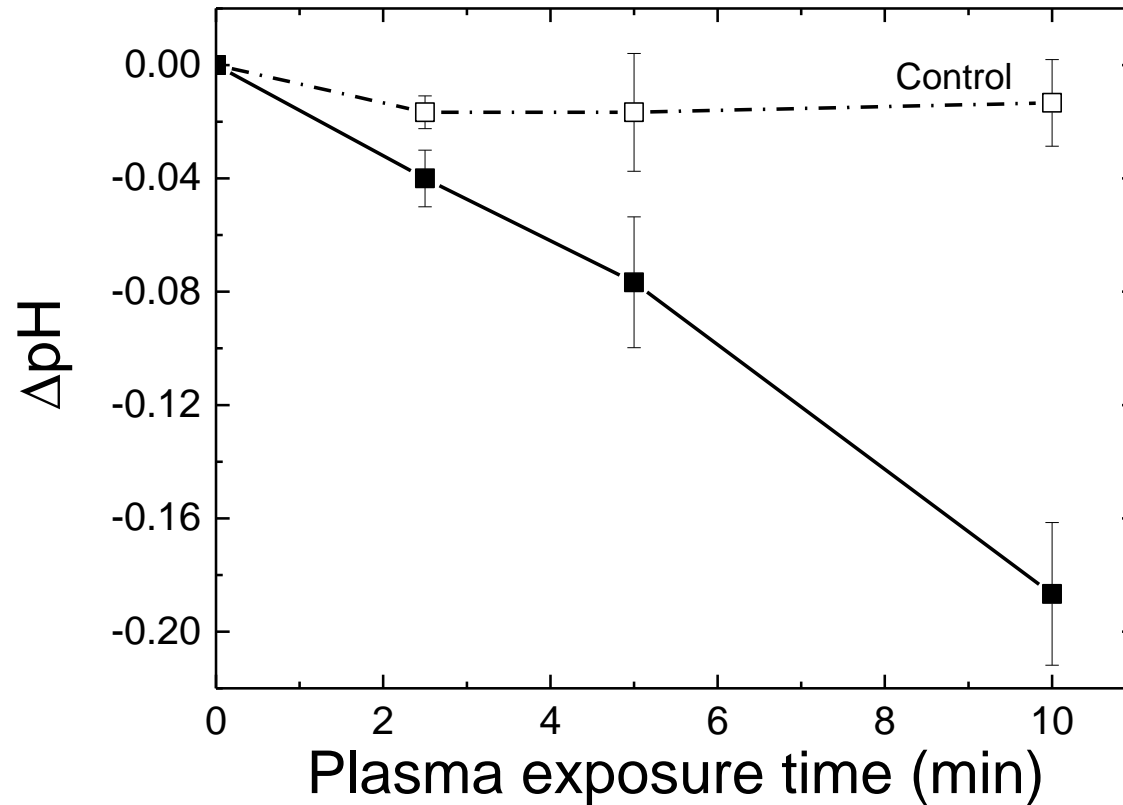
7.5 kV
10 kHz
duty cycle = 1 %

pH measurements

He/1%N₂



Initial pH : 7.4



➤ Acidification

➤ Hypothesis : HNO₂ and HNO₃

Plasma-liquid interactions

- H_2O_2 , NO_2^- and NO_3^- : stable species in solution

**What strategies to detect
Reactive Oxygen and Nitrogen Species (RONS)
in liquids ?**

**Switch the pH of PBS
to alkaline values**

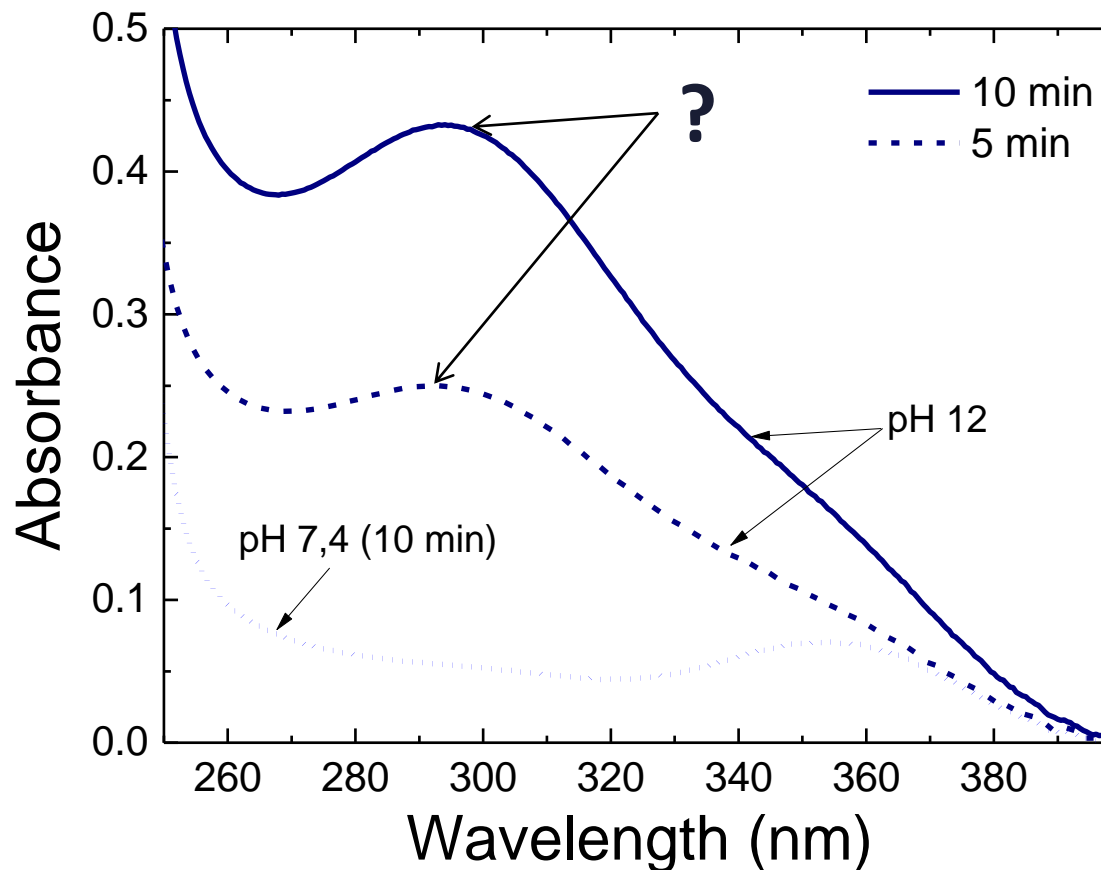
**Stabilize basic anionic
species**

Plasma-liquid interactions

7.5 kV
10 kHz
duty cycle = 1 %

PBS pH 12, UV-visible absorption spectroscopy *

He/1%N₂



➤ Hypothesis : ONOO^- ($\epsilon_{302\text{nm}} = 1670 \text{ M}^{-1} \cdot \text{cm}^{-1}$)

*Girard *et al.*, RSC Adv., 2016, 6, 78457–78467

Plasma-liquid interactions

7.5 kV
10 kHz
duty cycle = 1 %

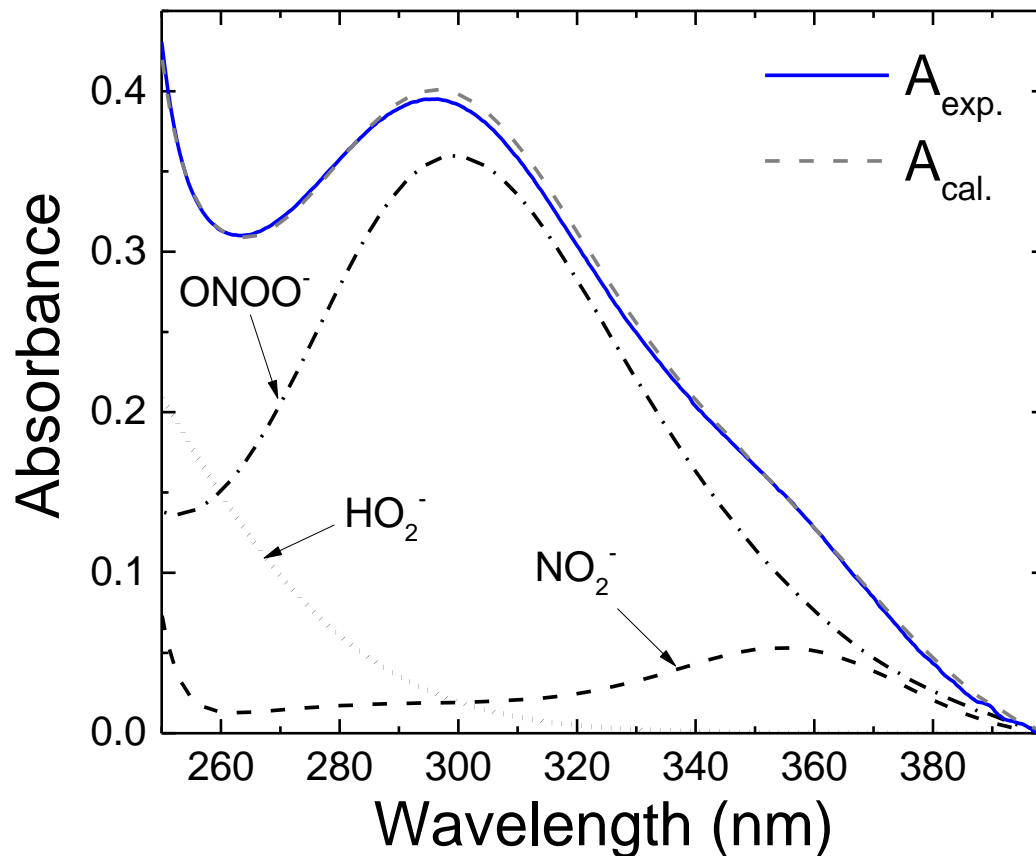
PBS pH 12, UV-visible absorption spectroscopy *

He/1%N₂



Beer-Lambert law :

$$A_{\lambda} = \sum_i \epsilon_{\lambda,i} l C_i$$



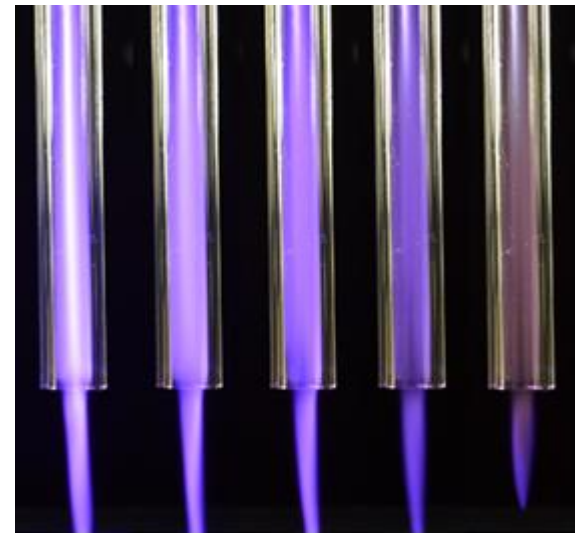
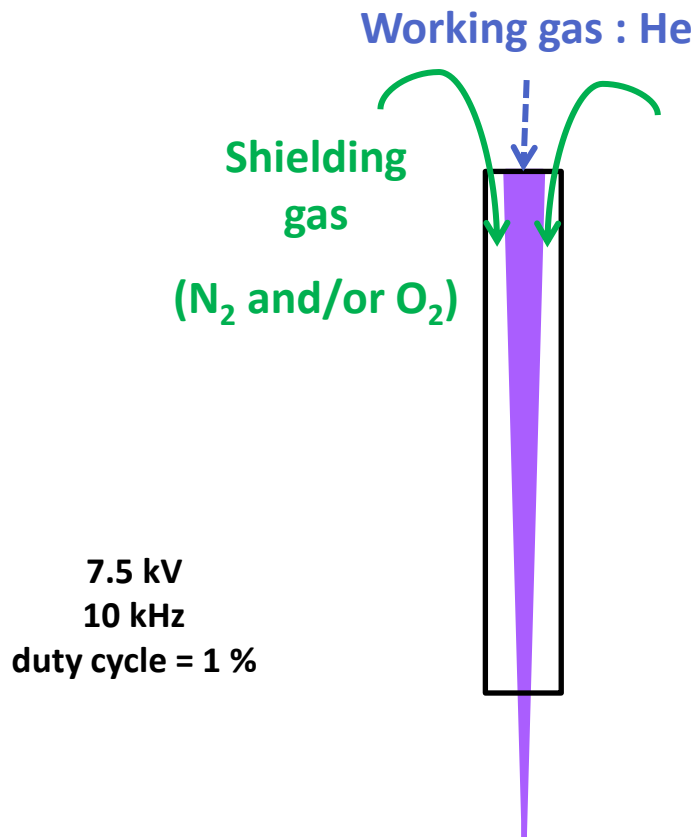
- ✓ ONOO⁻ : hypothesis validated
- ✓ [ONOO⁻] ≈ 50 μM (10 minutes of treatment)
- ✓ Stabilized at pH 12 but probably also exists at pH 7.4

*Girard *et al.*, RSC Adv., 2016, 6, 78457–78467

Plasma generation and characterization

Influence of the surrounding atmosphere on chemical species ?

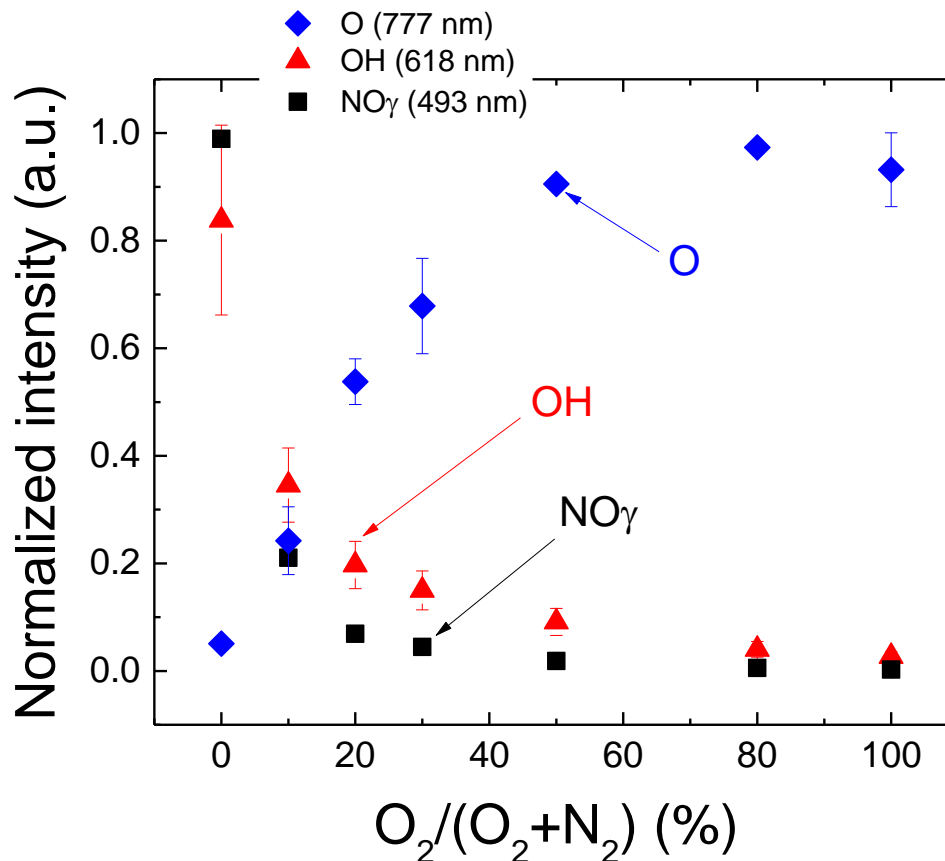
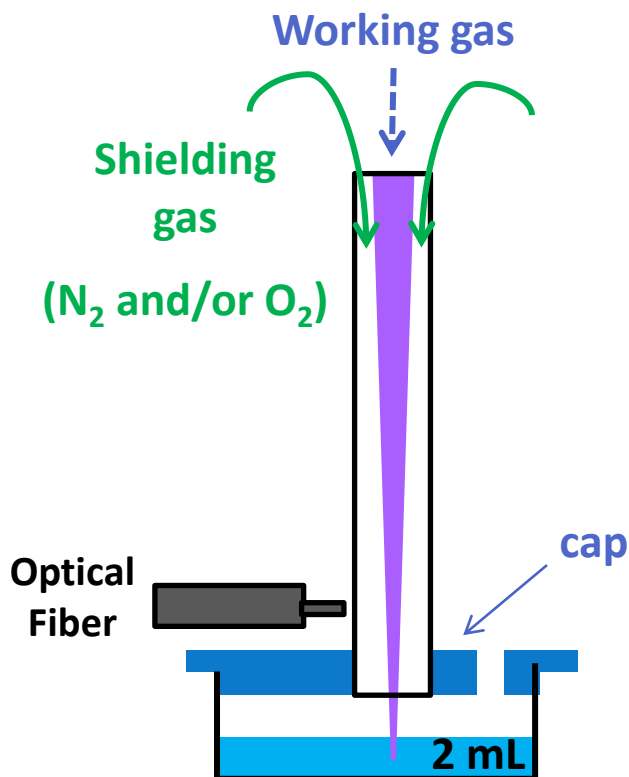
Setup 2 : Shielding gas device



100% N₂
80% N₂/20% O₂
50% N₂/50% O₂
20% N₂/80% O₂
100% O₂

Plasma generation and characterization

Optical Emissive Spectroscopy



- ✓ O emission higher for 100% O_2
- ✓ OH and NO_γ emissions higher for 100% N_2

➔ Different ratios of RNS and ROS in solution

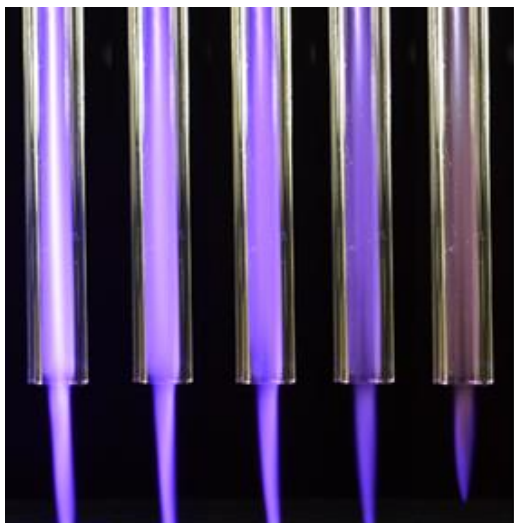
Plasma-liquid interactions

7.5 kV

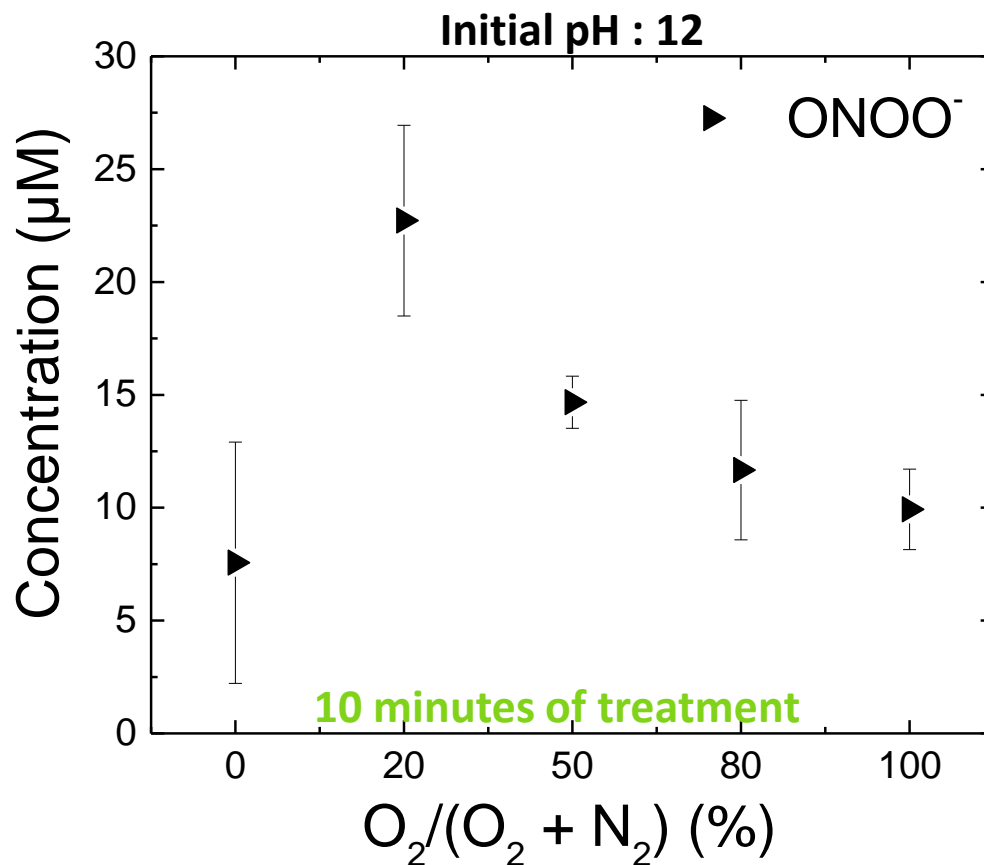
10 kHz

duty cycle = 1 %

ONOO⁻ quantification



100% N₂
80% N₂/20% O₂
50% N₂/50% O₂
20% N₂/80% O₂
100% O₂



✓ [ONOO⁻]_{max} for 20% O₂/80% N₂ in the shielding gas ("air shielding")

What about the stable oxygen and nitrogen species ?

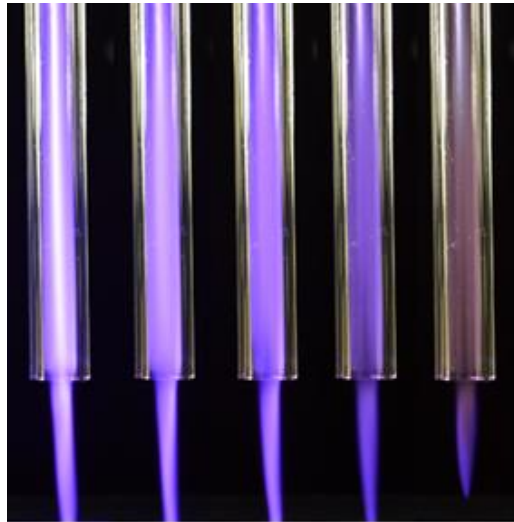
Plasma-liquid interactions

7.5 kV

10 kHz

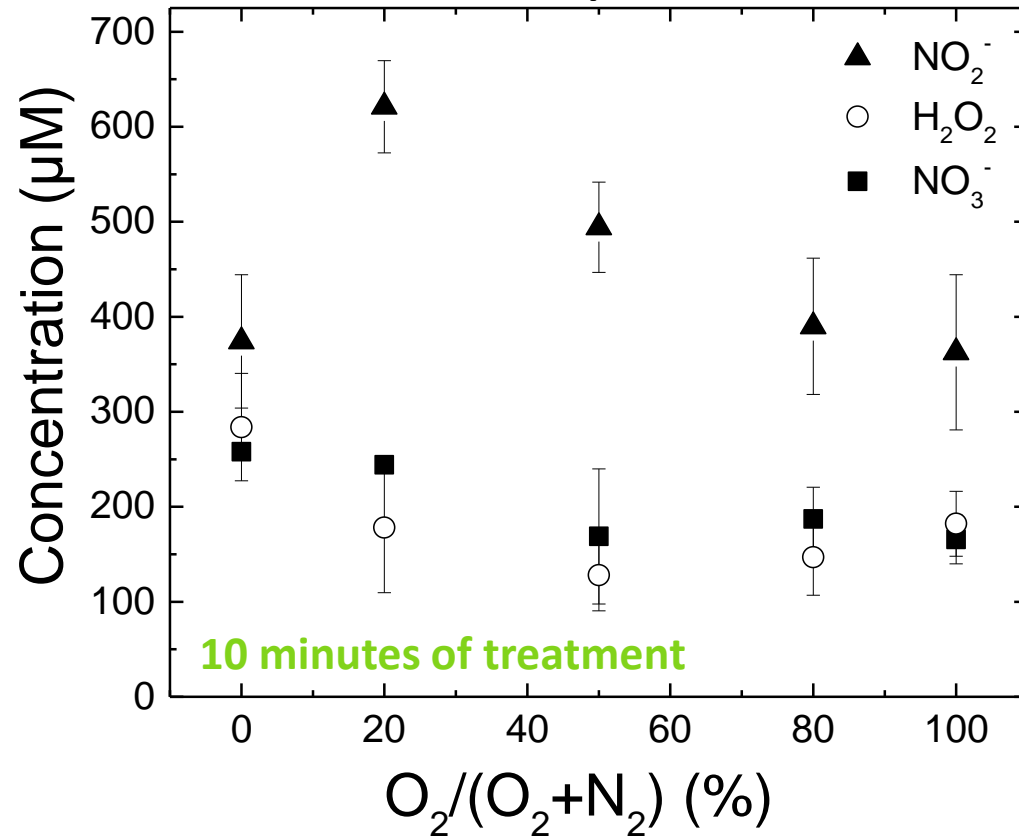
duty cycle = 1 %

NO_2^- , H_2O_2 and NO_3^- quantification



100% N_2
80% N_2 /20% O_2
50% N_2 /50% O_2
20% N_2 /80% O_2
100% O_2

Initial pH : 7.4

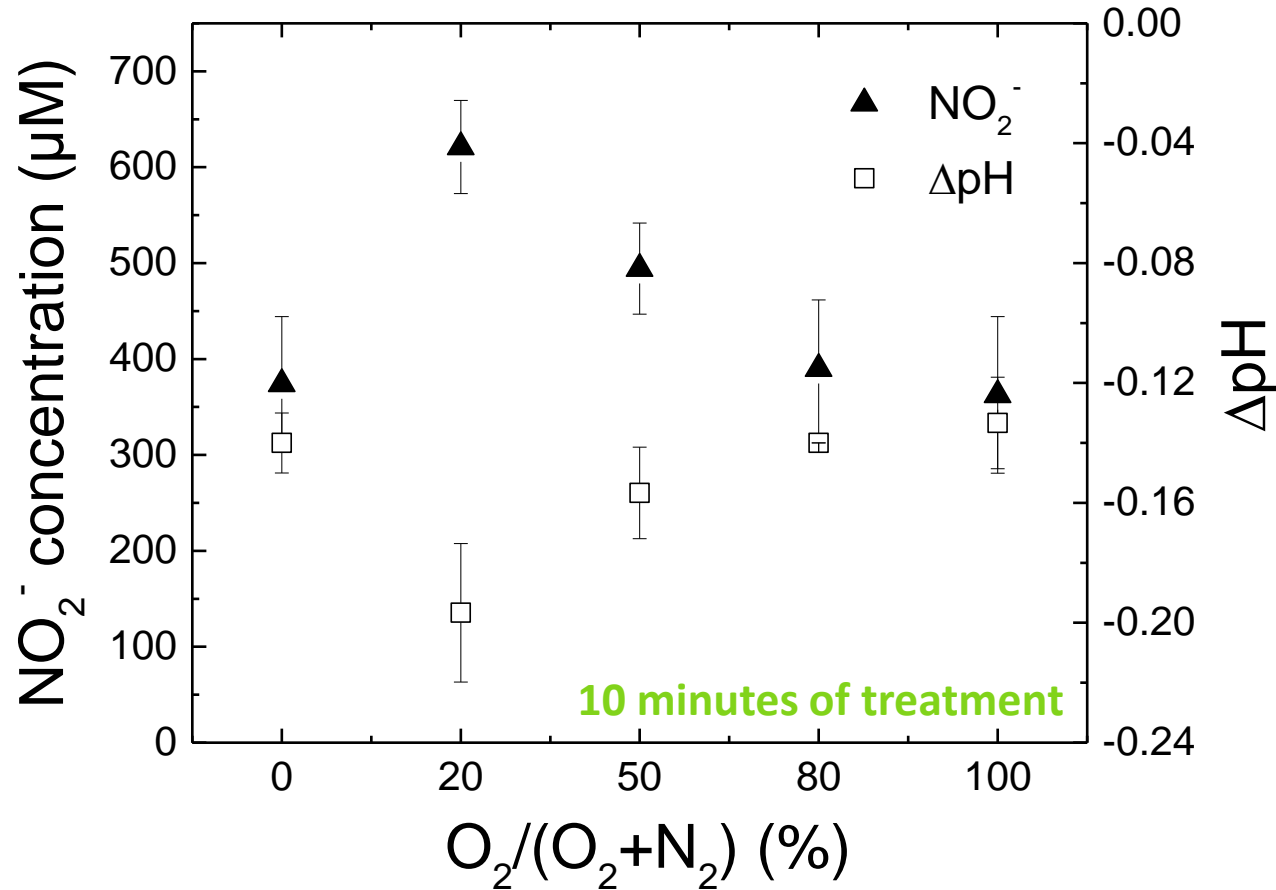


- ✓ $[\text{NO}_2^-]_{\text{max}}$ for the “air shielding” (20% O_2 /80% N_2)
- ✓ $[\text{H}_2\text{O}_2]_{\text{max}}$ and $[\text{NO}_3^-]_{\text{max}}$ for 100% N_2 in the shielding gas

Importance of the N_2 and air shielding gases, already observed by
H. Tresp, M. U. Hammer, K.-D. Weltmann and S. Reuter, *Plasma Med.*, 2013, 3.

Plasma-liquid interactions

Nitrite-pH correlation



➤ Acidification

➤ Hypothesis : HNO_2

Plasma-liquid interactions

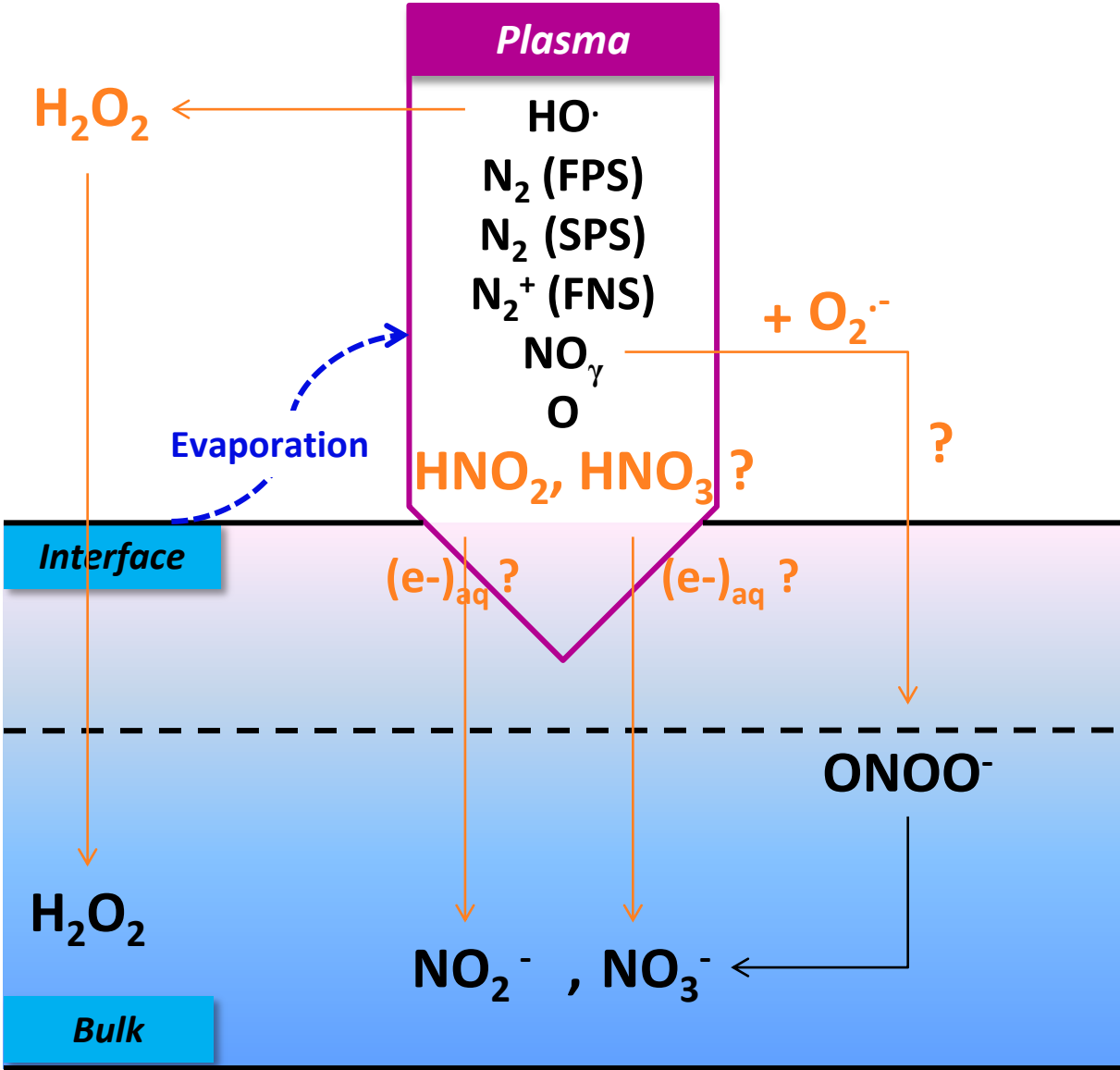
- The concentrations of species depend on the shielding gas composition
- The final ratios of species in the liquid are different

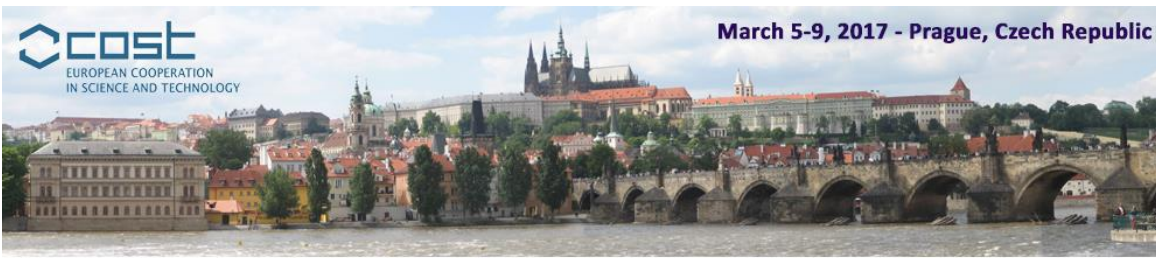
What really happens during the plasma treatment ?



***in situ* electrochemistry
has to be performed**

Conclusions and hypotheses...





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Thank you for your attention

- **Particular thanks to Laurent Marlin, Natacha Dumont, Mathieu Peret and Kristaq Gazeli for their respective contribution**

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Additional slide

Plasma-liquid interactions

7.5 kV

10 kHz

duty cycle = 1 %

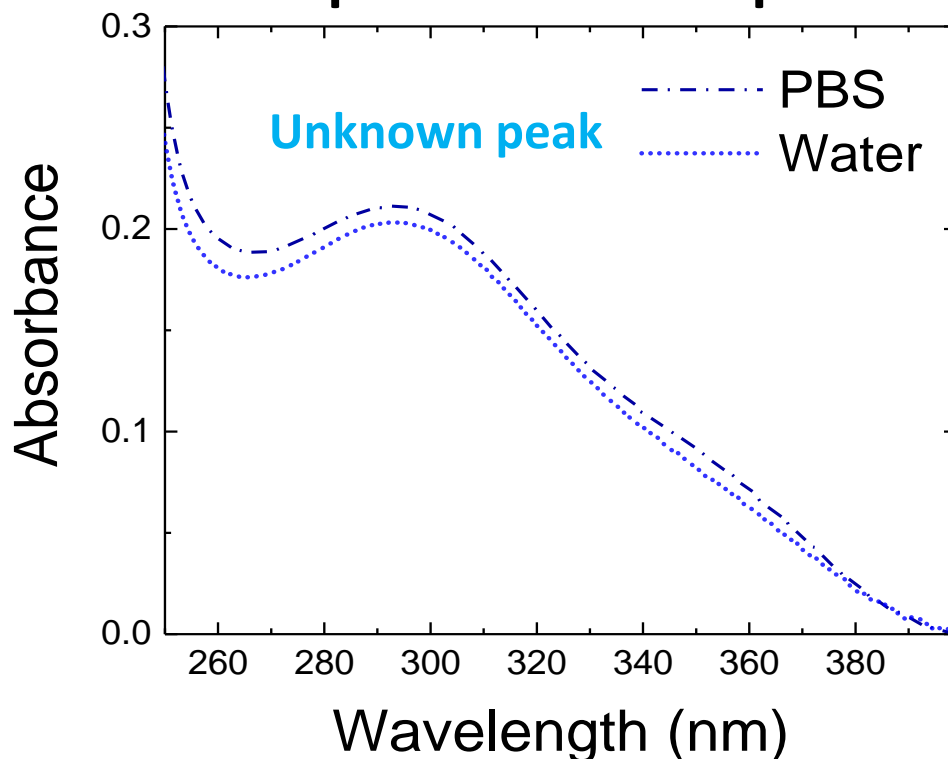
Switch to alkaline values : PBS pH 12 *

UV-visible absorption spectroscopy

He/1%N₂



PBS pH 12 vs. water pH 12



Same spectra

~~ClO⁻~~

➤ 1st Hypothesis : hypochlorite ClO⁻ ($\epsilon_{292\text{nm}} = 365 \text{ M}^{-1}\cdot\text{cm}^{-1}$)

➤ 2nd Hypothesis : ONOO⁻ ($\epsilon_{302\text{nm}} = 1670 \text{ M}^{-1}\cdot\text{cm}^{-1}$)

*Girard *et al.*, RSC Adv., 2016, 6, 78457–78467