Comparative Study of Chemical Probes for Ozone Detection

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Introduction

Plasma composition is typically studied by absorption and emission spectroscopy, mass spectrometry and computational studies. While these techniques provide valuable information about the chemical species in the gas phase, in many applications it is desirable to have a direct measurement of the dose of chemical species delivered to a particular target. For this purpose, chemical probes are particularly interesting as they can provide an inexpensive means for determining the dose of a particular compound.

A number of chemical probes have recently been used by the plasma community, particularly those working in plasma medicine and with plasmas interacting with liquids. Generally, however, these probes were not initially intended for use in plasma environments and therefore, it is important to assess their suitability and identify any selectivity issue that could affect the correct interpretation of the measurements. Here, we report on a comparative study of three chemical probes aimed at the quantitative detection of ozone (Table 1): Indigo Carmine and two DCF-derived fluorescent probes.

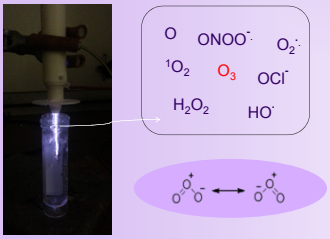


Figure 1: Plasma jet interacting with liquid (left). Some of the reactive species present in oxygen containing plasmas (right). Equilibrium structures of ozone (down).

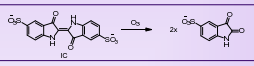
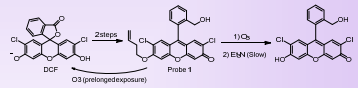
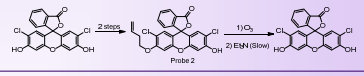
Probe	Reaction scheme	Detection
Indigo Carmine		Absorbance. λ= 610 nm
Probe 1 [1]		Fluorescence λ_{ex}= 502 λ_{em}= 522 nm
Probe 2		

Table 1: Scheme of the reaction between IC, Probe 1 and 2 with ozone (Left). Optical properties measured to quantifying ozone (Right).

[1] A. L. Garner et al. *Nature Chem*, 2009, **1**, 316-321

Selectivity study

Figure 2 shows the results of a selectivity study in which the three probes are exposed to a number of reactive species. Probe 1 and 2 (table 1) show increased fluorescence only when exposed to ozone, as desired for ozone probes. The fluorescent product resulting from the ozone exposure of probe 1, however, can further undergo reaction with ozone, and this could compromise the quantitative interpretation of experimental results. This was one of the motivations for developing Probe 2. Large amount of singlet oxygen or peroxynitrite, however, break down the fluorescent probes. The use of indigo carmine as a probe, however, can be quite problematic as its absorbance is affected by multiple reactive species (Figure 2).

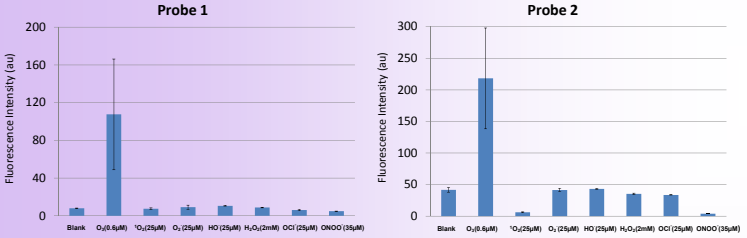


Figure 2: On the left and middle: Fluorescence of Probe 1 and Probe 2 respectively after adding different RS. On the right: Absorbance of an Indigo Carmine solution after adding different RS.

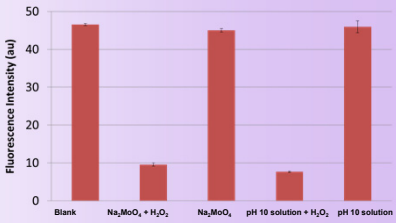


Figure 3: Fluorescence of Probes 2 after being exposed to different conditions.

As performed in [1], singlet oxygen was initially generated by adding sodium molibdate in pH 10 buffer solution and hydrogen peroxide. Further analysis of this technique, however, reveals that the destruction of the probes was due to hydrogen peroxide in basic conditions (Figure 3) and not singlet oxygen. Probe 2 was also exposed to singlet oxygen generated externally with a singlet oxygen generator with no chemical changes observed in the ^{1}H NMR spectrum after 2 hour exposure (Figure 4). The generation of peroxynitrite is also in basic conditions, which could (in part) explain the decrease of the fluorescence.

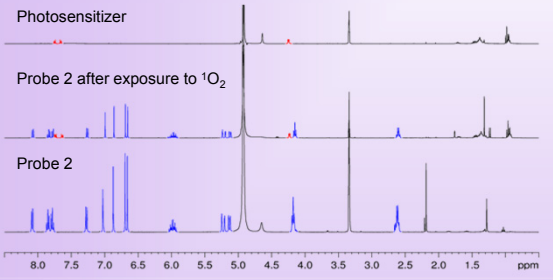


Figure 4: ^{1}H NMR of Probe 2, Probe 2 after singlet oxygen exposure and photosensitizer used for the singlet oxygen generation. The spectrum show no degradation after $^1O_2$ exposure.

Stability of DCF: Fluorescent product of Probe 2

The stability of DCF, product of the reaction between Probe 2 and ozone, in the presence of reactive species is shown in figure 5. Good stability is observed except for peroxynitrite.

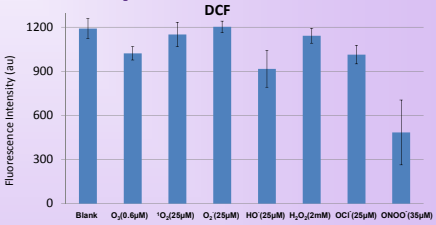


Figure 5: Fluorescence of DCF after exposure to various reactive species.

Conclusions and future work

- The use of Indigo Carmine as a chemical probe in a plasma environment is likely to be problematic due to its poor selectivity.
- A novel DCF-derived fluorescence probe has been developed for the detection of ozone.
- The two fluorescent probes studied in this work show good selectivity against a range of reactive species often generated in plasmas.
- Degradation of the fluorescent probes previously attributed to singlet oxygen is likely to be caused by the presence of H2O2 in a basic environment.
- Further research is needed to determine if peroxynitrite degradation of the probes is due to peroxynitrite or the conditions in which this is prepared.
- The end product of Probe 2 (DCF) is more stable than the product of Probe 1[1], as the latter further reacts with ozone.
- As part of the future work, we will compare measurements obtained with the chemical probes with data obtained by absorption spectroscopy (~260nm).

P3G Plasma and Pulsed Power Group

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