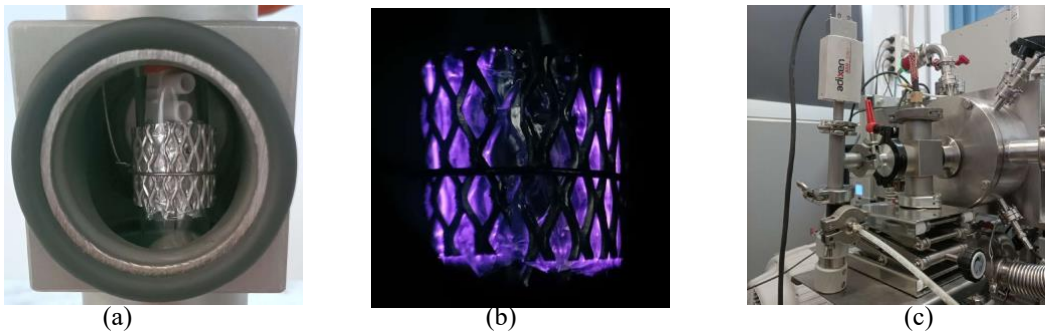
Mass Spectrometry of Atmospheric Pressure Plasma for Air Sanitation

D. Pal[1], R. Barni[1], C. Riccardi[1]

[1]*Dipartimento di Fisica G. Occhialini, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, I-20126 Milano, Italy*

Atmospheric pressure dielectric barrier discharges(DBD) generate strongly non-equilibrium plasmas which are characterized by high electron energies and with near ambient gas temperatures, making them efficient sources of reactive oxygen and nitrogen species(RONS) for air treatment applications. In this work, a double mesh DBD reactor consisting of two metallic grid electrodes separated by a glass or quartz dielectric barrier was investigated using a mass spectrometer. The discharge was operated in ambient air under high voltage AC, producing a plasma with transient microdischarges. Particular attention was given to identifying gas-phase species relevant for air sanitation including neutral molecules like (O_3,NO_2, NO, N_2O), positive ions (O_2^+, N_2^+, NO^+) and short lived radicals and metastable states. Species were sampled directly from the atmospheric pressure reactor into a differentially pumped quadrupole mass spectrometer via 200 μm orifice interface. Threshold ionsation analysis was used to discriminate between parent species and fragmentation products which allows improved selectivity in complex air plasma chemistry. The mass spectrometer enables direct detection of plasma generated ions as well as selective ionsation of neutrals using controlled electron impact energy (70 eV). Correlation between discharge conditions and species intensities were examined. This study demonstrates the capability of atmospheric pressure plasma with mass spectrometry to provide quantitative insight into plasma induced air chemistry, linking discharge physics to gas phase species dynamics. This approach establishes a diagnostic framework for real time charactersation of DBD driven reactive species relevant to plasma based air sanitation technologies. Recent TIMS measurements on an atmospheric-pressure SDBD plasma revealed possible evidence of metastable-assisted ionization. By scanning the electron energy in a quadrupole mass spectrometer and comparing plasma-off and plasma-on ionization curves, a significant shift of the appearance potential toward lower energies was observed. In particular, the onset of the m/z = 14 (N+) signal shifted from about 24.3 eV in neutral air to around 15.6 eV under plasma conditions, suggesting excited or metastable nitrogen species generated inside the discharge. Ongoing measurements for m/z = 16, 28, and 32 will further investigate excitation pathways in atmospheric-pressure plasma chemistry.

Atmospheric pressure plasma was generated using two dielectric barrier discharge reactors coupled to a Hiden HPR-60 quadrupole mass spectrometer for gas phase analysis. For the first reactor (Fig.1), plasma was generated inside a grounde metallic chamber using a homemade cylindrical surface dielectric barrier discharge(SDBD) source. The source consisted of an internal copper high voltage electrode, a quartz dielectric cylinder and an external grounded stainless steel mesh with rhomboidal openings of 4 x 3 mm and 0.8mm thickness. The source had an outer diameter of 18mm and a height of 4 mm. The reactor was powered by a high voltage supply developed by University of Bologna. The supply used a push-pull MOSFET configuration connected to a transformer, producing sinusoidal high-voltage signals with tunable frequency and a fixed duty cycle. In this experiment, an AC voltage at 25-30 kHz was applied to the inner electrode, generating localized microdischarges near the mesh openings and forming a non-thermal plasma layer on the dielectric surface. Pure humid air was introduced through a microvalve while the chamber pressure was monitered using a capacitance pressure guage (Adixen ASD 2001). The chamber was coupled to the Hiden HPR-60 mass spectrometer operated in RGA mode through a differentially pumped interface.



(a) (b) (c)

Fig.1 – A picture of the discharge setup inside the metallic chamber (a) together with the pattern of light emission (b) and the whole experimental setup(c).

For the second reactor(Fig. 2), a flat SDBD geometry and the same sorce was used. Two tin-clad copper adhesive tape electrodes were placed on opposite sides of a 3 mm thick flat dielectric plate. Each electrode was approximately 60 μm thick, 4 cm wide, 12 cm long and two electrodes were laterally shifted by about 0.5cm. The exposed electrode was grounded, while the covered electrode was connected to the high voltage supply.When the applied voltage exceeded the air breakdown threshold, a thin non-thermal plasma layer formed near the exposed electrode edge. The discharge was self- limiting due to charge accumulation on the dielecric surface, and therefore AC excitation was required for sustained plasma operation[1]. The applied voltage, discharge current and the transferred charge were measured using

Tektronix P6015A(bandwidth 75 MHz), Tektronix CT1(bandwidth 1 GHz), 9.83 nF capacitor and a large bandwidth oscilloscope (Agilent MSO8104A, 1 GHz bandwidth, 4 GSample/s rate).

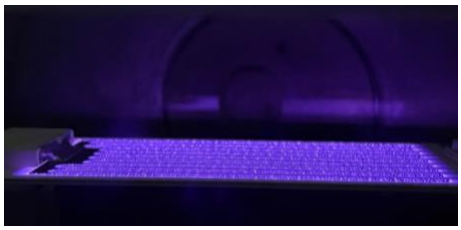


Fig. 2 – A picture of the discharge of the surface dielectric barrier discharge

Gas- phase species were analysed using a Hiden HPR-60 quadrupole mass spectrometer. The gas was sampled through a 200 μm orifice. Then the gas passes through two skimmer cones of 300 μm and 700 μm aperture. The three stage pumping interface enabled molecular beam like sampling while reducing collisions and wall losses[2]. Mass analysis was performed using an RF quadrupole mass filter, with ion transmission optimized by tunable ion optics and a 45° electrostatic sector energy analyser[3].

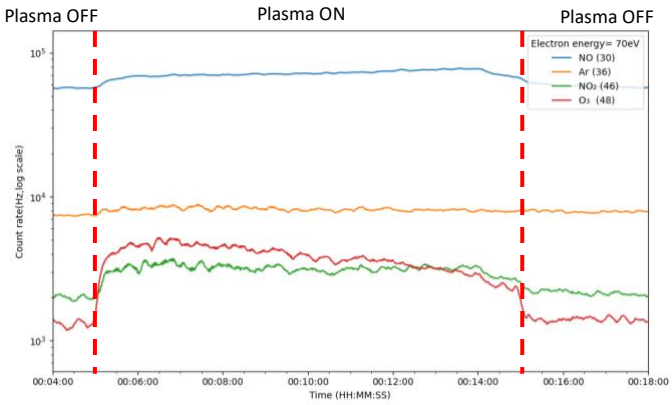


Fig. 3 – Time-resolved MID signals of selected RONS-related mass channels

Fig. 3 showed time resolved MID measuremnts of plasma induced changes in selected RONS channels. The Ar-36 reference signal remained nearly constant, indicating stable sampling conditions. In contrast, O_3, NO, NO_2 showed different temporal behaviours after plasma ignition. The ozone signal initially increased and then decayed over time while No and NO_2 increased later, suggesting a transition from ozone dominated oxidation toward notrogen oxide. Fig. 4 describes the threshold ionization measurements of a significant plasma induced shift in the appearance potential of m/z 14 channel. In plasma-off air, N^+ is mainly produced by dissociative ionization N_2, requiring an appearance energy of about 24.3 eV[4]. Under plasma-on conditions, the onset shifts to14.5 eV, close to the ionization energy of atomic nitrogen [5]. This indicates the presence of atomic nitrogen and electronically excited nitrogen

species generated in the discharge. Direct positive-ion measurements were performed by comparing plasma-off and on spectra(Fig. 5). With the plasma off, the ion signal was negligible. When the discharge was ignited distinct ion signals appeared around m/z=28, 30, 32, assigned respectively N_2^+, NO^+, O_2^+. The broad and fluctuating peak structure indicates that further optimization of ion optics, ion energy selection and plasma-orifice distance is required for stable mass-resolves detection.

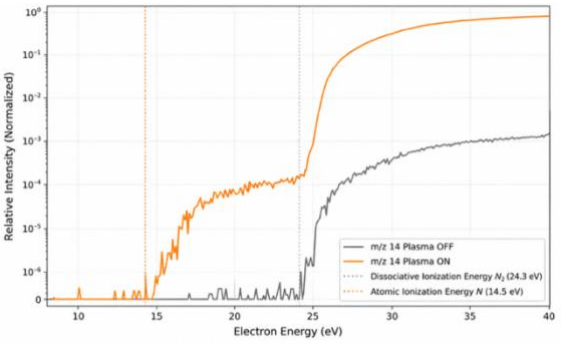


Fig.4 – Threshold ionization curves of the m/z = 14

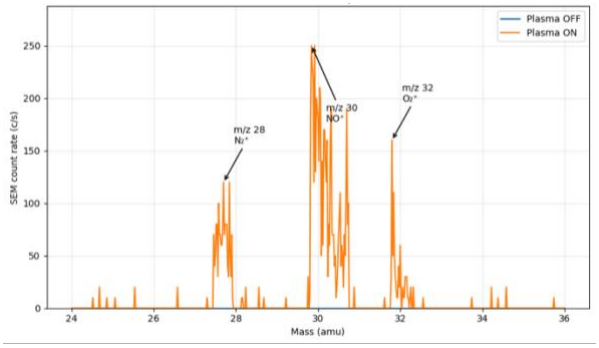


Fig. 5 – Positive-ion mass spectra

A kinetic simulation of atmospheric pressure air DBD chemistry was used to support the interpretation of the MS trends. The simulation shows that O and N atoms, molecular ions, excited states and metastables are produced during the early microdischarge phase, while O_3 and NO_x evolve later through post-discharge reactions. [6].

Acknowledgments

This work was partially funded by the National Plan for NRRP Complementary Investments (PNC, established with the decree-law 6 May 2021, n. 59, converted by law n. 101 of 2021) in the call for the funding of research initiatives for technologies and innovative trajectories in the health and care sectors (Directorial Decree n. 931 of 06-06-2022) - project n. PNC0000003 - AdvaNced Technologies for Human-centrEd Medicine (project acronym: ANTHEM). This work reflects only the authors views and opinions, neither the Ministry for University and Research nor the European Commission can be considered responsible for them.

References

[1] C. Piferi, R. Barni, H.E. Roman and C. Riccardi, Appl. Sci. 11, 2079 (2021)

[2] S. Große-Kreul et al., Plasma Sources Sci. Technol. 24, 044008 (2015)

[3] Hiden Analytical Ltd., HPR-60 MBMS: Molecular Beam Mass Spectrometer for Reactive Gas and Plasma Analysis, Technical Data Sheet TDS-158-1, Hiden Analytical, Warrington, UK

[4] NIST Chemistry WebBook, molecular N_2 appearance energy for N^+ formation

[5] A. Kramida, Yu. Ralchenko, J. Reader and NIST ASD Team, NIST Atomic Spectra Database, National Institute of Standards and Technology, Gaithersburg, MD

[6] R. Barni, P. Alex and C. Riccardi, Plasma 6, 735–752 (2023)