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Mass Spectrometry of Atmospheric Pressure Plasma for Air Sanitation

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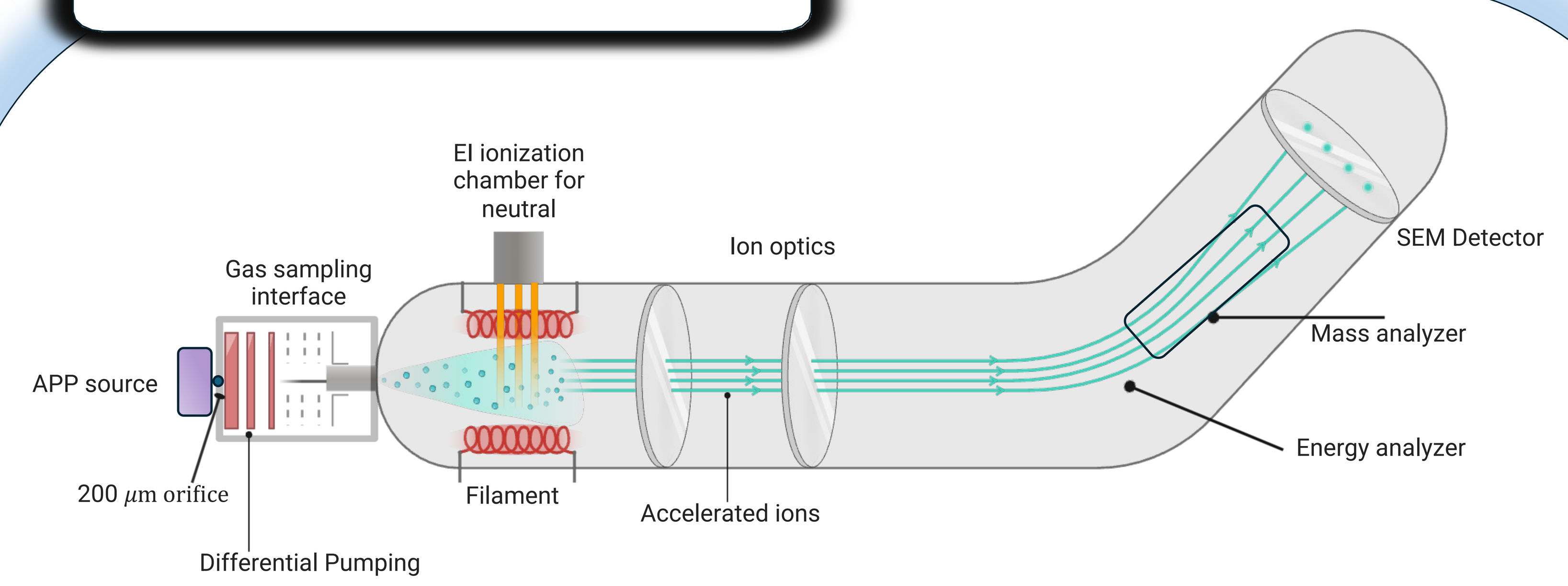
INTRODUCTION

- **Capability:** Mass spectrometry provides **real-time, in situ monitoring** of plasma generated **neutral and ionic species** through selected m/z channels.
- **Limitation:** Atmospheric-pressure sampling can cause species **loss, fragmentation, recombination, or neutralisation** before detection.
- **Relevance:** Air plasmas generate **O_3, NOx, radicals, metastables, and ions** involved in air sanitation chemistry.
- **This work:** A **DBD air-plasma reactor** is coupled to a **Hiden HPR-60 EQP** Mass Spectrometer to study neutral species, metastables and preliminary positive-ion signals.

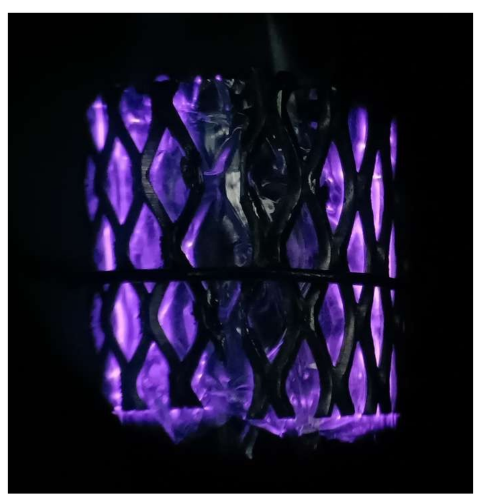
OBJECTIVE

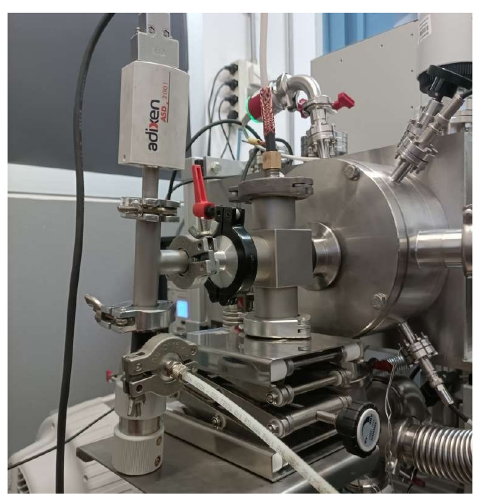
- **Couple** an atmospheric-pressure **DBD air-plasma reactor** to a **Hiden HPR-60 EQP mass spectrometer**.
- **Evaluate** the feasibility of detecting **positive-ion and neutral signals** from the plasma.
- **Monitor** plasma induced changes in selected **m/z channels** related to O_2, N_2, O_3, NO, NO_2, and other RONS and their behaviour chemistry.
- **Compare plasma ON/OFF conditions** to identify species whose signals are modified by plasma operation.
- **Assess how reactor geometry, sampling distance, gas flow, and MS detection mode** influence RONS-related mass signals relevant to **air-sanitation chemistry**.

EXPERIMENTAL SETUP

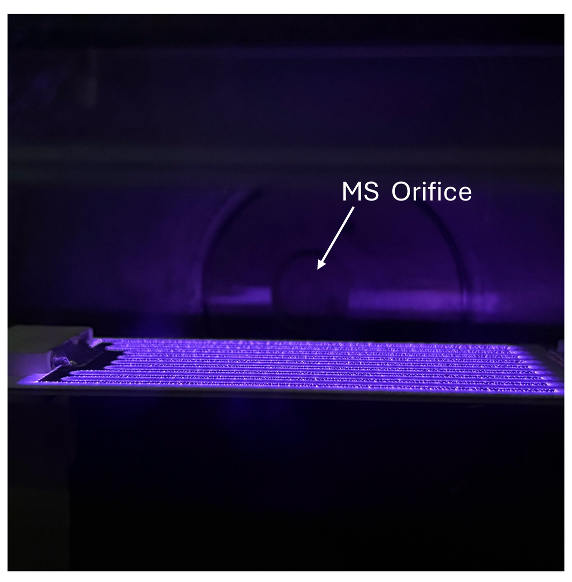


(a) Reactor 1: Co-axial DBD Source





(b) Reactor 2: Finger-type DBD Source



Neutral, metastable mode:
Plasma neutrals → EI ionisation → mass analyser → detector
Positive-ion mode: (Filament OFF)
Plasma ions → ion optics → mass analyser → detector

Feature	Reactor 1	Reactor 2
Configuration	Mesh DBD with quartz dielectric	Ceramic finger type
Plasma location	Around dielectric tube	Along electrode fingers,
Sampling style	Directly near MS orifice	Plasma-treated air sampled from chamber
Main use	Neutrals,Metastables, RONS monitoring	Positive-ion feasibility
Working gas	Ambient air	Ambient air
Dimension	16 mm length, 15 mm outer diameter	77 mm × 43 mm active area

KEY RESULTS

Fig. 1: Plasma induced changes in selected gas-phase m/z channels:

- Plasma operation produces measurable changes in selected **RONS** related m/z channels.
- **m/z 30 NO** remains the strongest reactive-species channel.
- **m/z 46 (NO_2)** and **m/z 48 (O_3)** show clear plasma-related transient behaviour, suggesting formation, conversion, and possible loss during sampling.
- Ar (m/z 36) was used as a reference channel to check signal stability.

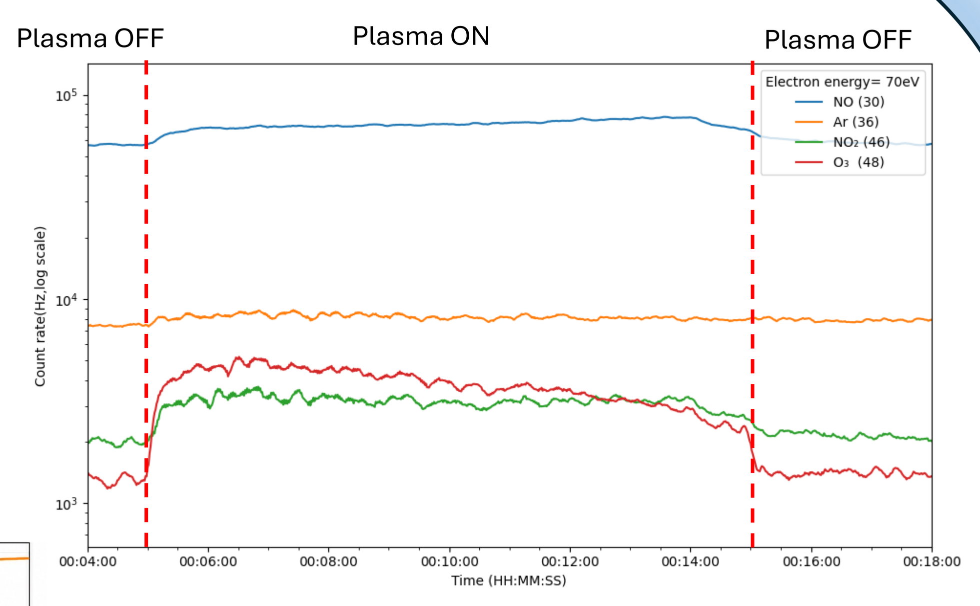


Fig. 1

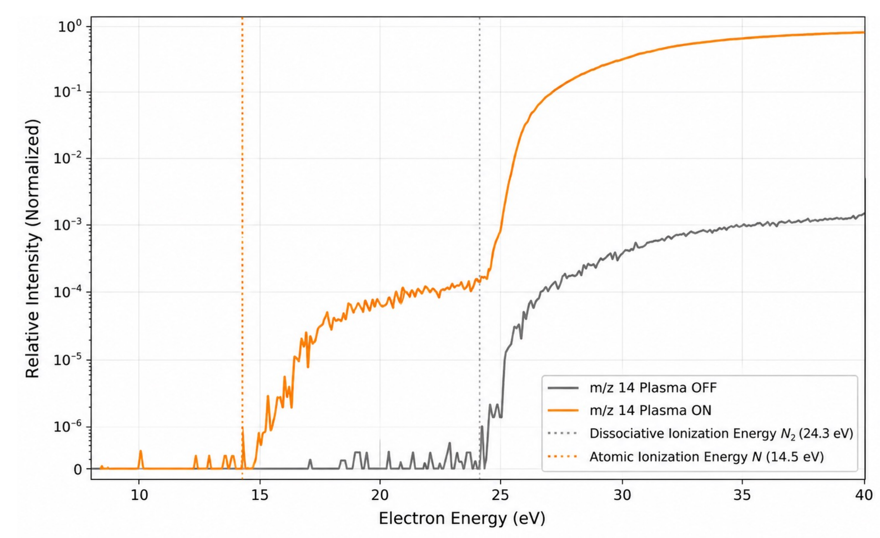


Fig. 2

Fig. 2: Low-energy electron-impact scan of nitrogen m/z 14 signal:

- Plasma ON strongly increases the **m/z 14 nitrogen-related signal**.
- The enhanced response at lower electron energies suggests contribution from **excited or dissociation-related nitrogen species**.
- This measurement is treated as **low-energy / metastable-sensitive detection**
- Threshold comparison helps separate ordinary EI ionisation from plasma-assisted processes.

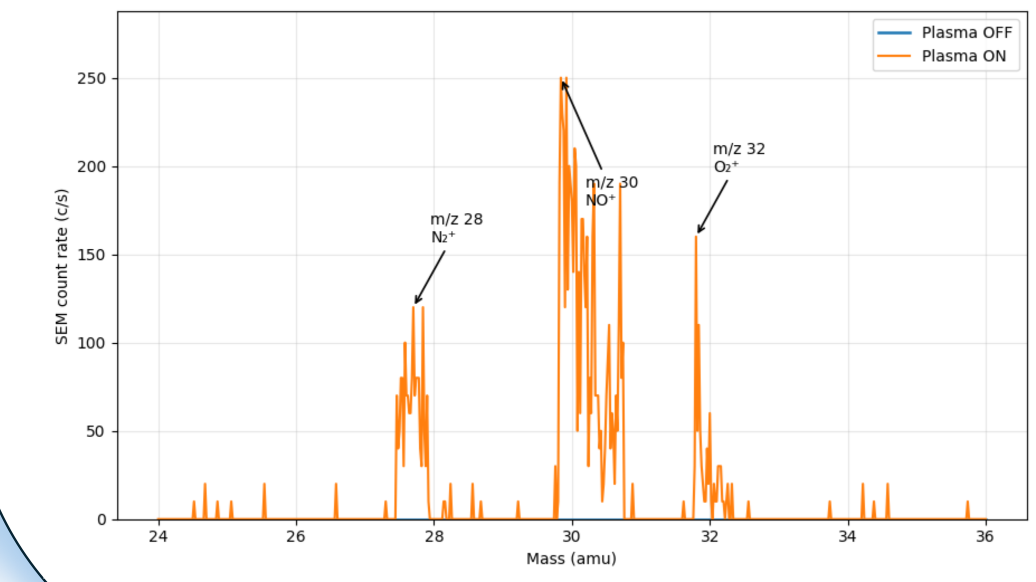


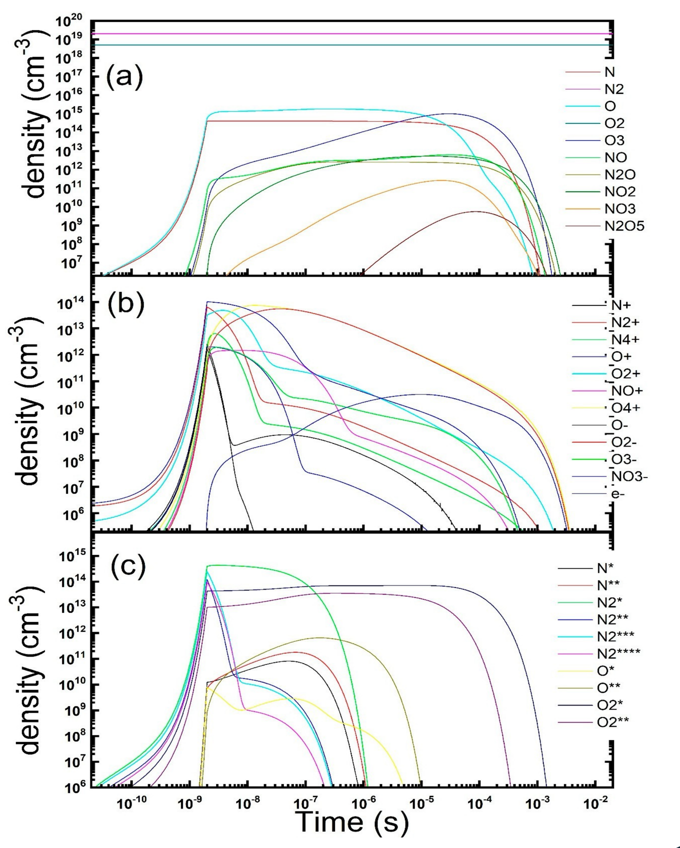
Fig. 3

Fig. 3: Preliminary positive-ion mass spectrum:

- Peaks near **m/z 28, 30, and 32** indicate possible detection of **N_2^+, NO^+, and O_2^+** from the DBD air plasma.
- The flat plasma OFF baseline confirms that these signals are mainly associated with plasma operation.
- The strongest response appears around **m/z 30**, suggesting a significant contribution from **NO^+, nitrogen–oxygen ion chemistry**.
- The assignment at **m/z 28** should be treated cautiously because **N_2^+ and CO^+ overlap** at the same nominal mass.

DISCUSSION

- The MID(Multiple Ion Detection) scan shows that DBD operation modifies selected gas-phase signals. The transient rise and decay indicate that the MS signal is governed by species formation, gas-phase conversion, residence time, wall losses, and sampling effects.
- The enhanced m/z 14 signal during plasma ON indicates that nitrogen-related species are strongly affected by plasma excitation and dissociation processes.
- With the **EI filament OFF**, the plasma ON spectrum shows positive-ion peaks around m/z 28, 30, and 32, assigned to possible N_2^+/CO^+, NO^+, and O_2^+ channels.
- Kinetic simulations of pulsed DBDs show that radicals, ions, and excited species are produced rapidly during the discharge pulse. Stable products such as O_3 and NO_x continue to evolve during the post-discharge phase through slower gas-phase reactions. This supports our interpretation that the MID signals are controlled by plasma chemistry, residence time, diffusion, and sampling losses.



FUTURE WORK

- Optimise sampling distance, reactor alignment, ion optics tuning for stable positive-ion detection.
- Compare MS signals with **O_3/NO_2 sensors, OES, and optical diagnostics** for stronger species validation.
- Use complementary diagnostics such as **TALIF** to detect short-lived **O atoms, OH radicals, and oxygen metastables**.
- Combine experimental MS data with **numerical simulations** to interpret neutral, ionic, radical, and metastable pathways.

References:
[1] S Große-Kreul et al 2015 Plasma Sources Sci. Technol. 24 044008," Mass spectrometry of atmospheric pressure plasmas".
[2] Barni, R.; Alex, P.; Riccardi,C. Pulsed Dielectric Barrier Discharges for Gas-PhaseComposition Control: A SimulationModel. Plasma 2023, 6, 735–752.https://doi.org/10.3390/plasma6040050