# Molecular Beam Mass Spectrometry in Atmospheric Pressure Plasmas

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## Introduction

Atmospheric plasmas are becoming an important research field for its interest in different kinds of applications from material processing up to biomedical treatment. Non-thermal plasmas can have additional benefits compared to conventional methods for many applications including purification of water, the sterilization of surgical instruments, surface activation of plastics and polymers including woven and unwoven textiles, removal of pollutant and hazardous components, combustion enhancement and treatment of biological samples.

Many plasma diagnostics techniques exist for the study of atmospheric plasmas but the most direct technique to measure fluxes of ions and neutral species is molecular beam mass spectrometry. The main characteristic is that the identity of the sampled species is preserved from creation at atmospheric pressure to vacuum monitoring by the rapid expansion of the formed molecular beam that "freezes out" any chemical reactions occurring. This is crucial especially for highly reactive species such as radicals and ions. It can be used to measure both negative and positive ions including short lived radical species formed in the atmospheric pressure plasmas.

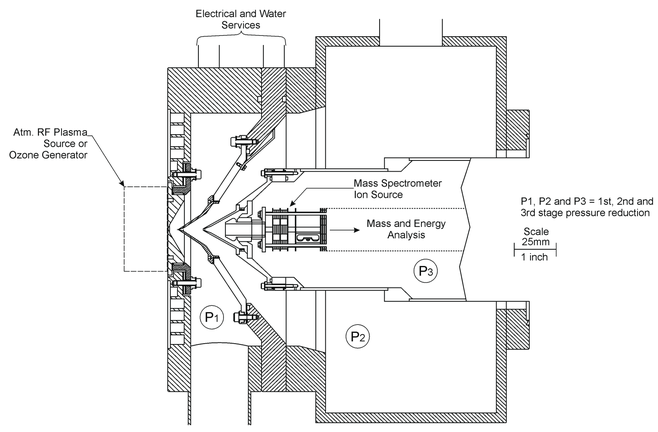
An overview of different atmospheric pressure plasma sources studied with a molecular beam mass spectrometer (MBMS) will be presented.

## MBMS

An energy resolved molecular beam mass spectrometer (HPR-60 MBMS, Hiden Analytical, UK) is used to analyse the plasma species. The MBMS incorporates an EQP mass/energy analyser. The pathway of the species to be analysed is generated in the MBMS instrument by the differentially pumped, three-stage inlet system.

The atmospheric plasma sources are directed at the grounded entrance orifice of the MBMS where it expands into the first pumping stage of the vacuum system. The sampling stages and associated pumping characteristics are designed to minimise collisions of the sampled species both with each other and with internal surfaces. The resulting molecular beam is collimated by the second and third vacuum stage skimmer cones before reaching the entrance to the EQP.

The EQP is operated in energy resolved positive and negative ion modes. Neutral species, radicals, can also be analysed via appearance potential and electron attachment mass spectrometry but are not reported in this work.



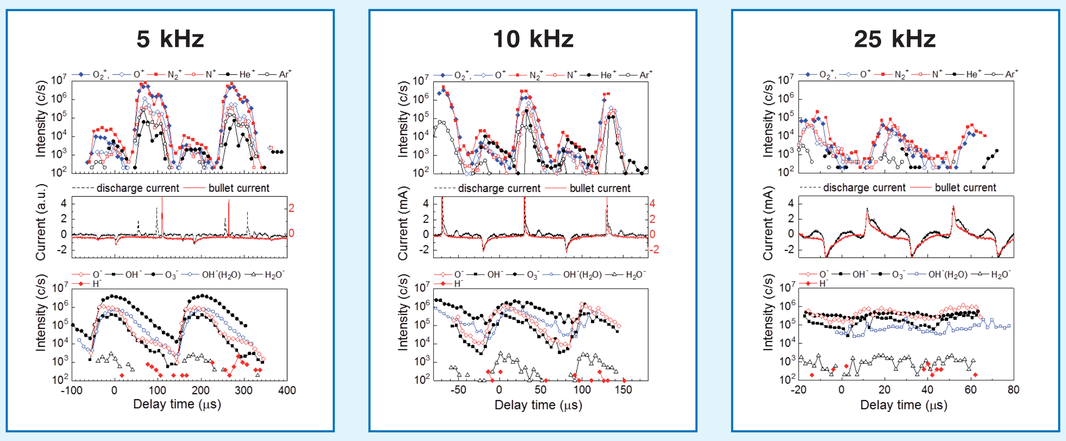

## Micro plasma jets; time resolved measurements

Atmospheric pressure plasma jets are normally are operated at an excitation frequency of several tens of kilohertz (ac or pulsed mode) or in radiofrequency (rf) range. Detailed measurements obtained with ICCD images revealed that these jets are not continuous plasmas but consist of "plasma bullets". This is the first time that measurements of positive and negative ions generated in the plasma jet is presented by means of time-resolved molecular mass spectrometry (MBMS) [2].

The plasma jet used in this study was produced by a bipolar high voltage ac with a variable repetition rate of 5, 10 and 25 kHz. The recorded peak to peak voltage is generally 8 kV and is independent of the frequency applied. The plasma generated is produced in a quartz glass tube of 1mm diameter with an electrode around the glass tube.

The time-resolved measurements by MBMS reveal the evolution of the main species, positive and negative, during the applied ac for the different repetition rates applied. The main positive species observed are $O_2^+$, $O^+$, $N_2^+$, $N^+$ and $He^+$. These positive ions were found to follow the applied voltage and for higher frequency or repetition rate, a decrease in the number of species present in the plasma was observed. For negative ions there is a strong presence of $O^-$, $OH^-$, $H_2O^-$, $H^-$, $OH^-(H_2O)$ and the behavior of these ions with respect to the repetition rate is different than for positive ions. At higher frequency the signal of negative ions tends to be constant in the active part of the applied voltage. That could be an indication of the origin of negative ions and it shows clearly that the dynamics and chemistry associated with positive and negative ions are different.

**Time-resolved positive and negative ion fluxes for selected species measured at a fixed distance of 7 mm from the nozzle at different frequencies:**

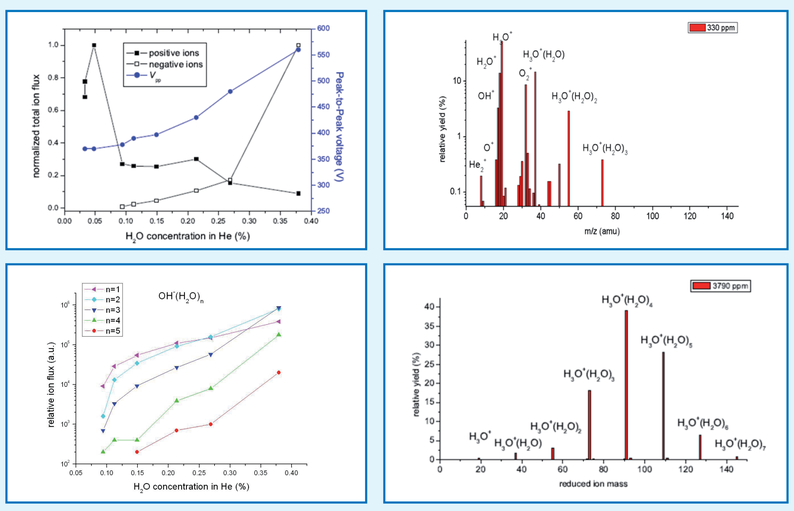



## Capacitively coupled atmospheric RF; Atmospheric plasma glow discharge

An RF (13.56 MHz) excited APGD between two parallel bare metal plate electrodes in He-$H_2O$ mixtures has been investigated by molecular beam mass spectrometry [3]. The electrode system consist of a water cooled circular copper electrode with a diameter of 20.5 mm interfaced to the inlet plate of the HPR-60 molecular beam mass spectrometer (MBMS) with a fixed inter-electrode distance of 0.5 mm. The power was kept constant at 20W for experiments conducted with different water concentrations.

For all the investigated concentrations of He-$H_2O$ mixtures the dominant positive ions are $H_2O^+$, $OH^+$, $O^+$, $He_2^+$, $HeH^+$, $O_3^+$ and $H_3^+$. Hydration of the ions increases with increasing water vapour concentration and decreases with increasing discharge power. For concentrations of 900 ppm water in He and above, negative ions can be detected. It was observed that the detected negative ion flux increases with increasing water concentration. The dominant ion is $OH^-$ and its clusters. With the emergence of the negative ions, there is a drop in positive ion flux to the mass spectrometer together with a significant increase in applied voltage indicating increasing electron loss by attachment and ion loss by mutual positive and negative ion recombination. Positive and negative ion cluster formation increases with decreasing discharge power and increasing concentration of water.

**Variation of the Voltage discharge and the positive and negative ion flux in function of the $H_2O$ concentration in He**

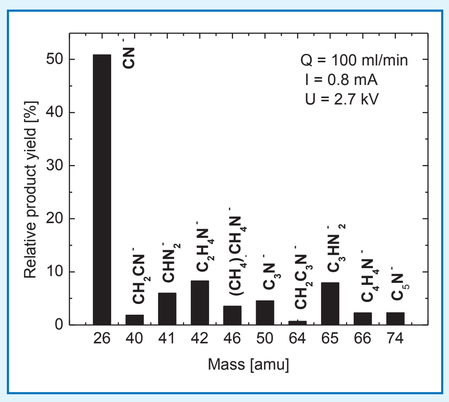



## Corona Discharge; Astrophysics studies

The formation of negative ions produced in a negative point-to-plane corona discharge fed by a $N_2$(88%)/Ar(8%)/$CH_4$(4%) gas mixture has been studied using mass spectrometry [4]. The same anions have been detected in Titan's atmosphere from the results of the Cassini Huygens space mission.

The measurements were carried out in a flowing regime at ambient temperature, at a current discharge of 0.8 mA and a reduced pressure of 460 mbar. The $CN^-$ anion has been found to be the most dominant negative ion in the discharge and is believed to be the precursor of heavier negative ions such as $C_3N^-$ and $C_5N^-$.

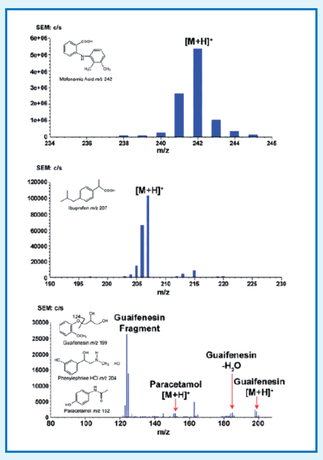
The most likely pathway of their formation is H-loss dissociative electron attachment to HCN, $H_3CN$ and $H_5CN$ formed in the discharge.




## DBD for plasma assisted desorption ionisation (PADI); ambient surface analysis

Plasma Assisted Desorption Ionization (PADI) is a novel approach to ambient surface analysis that coupled with atmospheric pressure sampling mass spectrometry provides a technique capable of rapid surface analysis without the requirement for sample preparation [5-6].

The PADI source is a non-thermal dielectric barrier discharge (DBD) 13.56 MHz RF plasma 'needle' operating at atmospheric pressure. The plasma is around 1mm in diameter and may extend up to 10 mm from the tip. The plasma is generated in flowing helium and operates in open air. It can be brought into direct contact with any of the surfaces under study. The action of the plasma at the sample surface produces ions (positive and negative) from the surface material which enter the gas phase and are readily detected by the molecular beam mass spectrometer MBMS in real time.




## Conclusions

It has been demonstrated that molecular beam mass spectrometry (MBMS) is the most direct technique to determine fluxes of ions and neutral species. Several source configurations of atmospheric plasma discharges have been studied with a molecular beam mass spectrometer and it is a valuable diagnostic technique for the investigation of atmospheric pressure plasma processes.

## Acknowledgments

The authors would like to thank all the collaborators, in particular Professors Bradley, Bruggeman, Mason, Matthews and McCoustra for the joint work on the presented results.

## References

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Poster Ref: 2013/01