



# Atmospheric Pressure Plasma Analysis by Modulated Molecular Beam Mass Spectrometry



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**ABSTRACT:** We describe a molecular beam mass spectrometer with automated beam modulation and present mass and energy resolved measurements from an RF plasma ‘needle’ operating at atmospheric pressure. The automation of the beam modulation allows the neutral components in the plasma to be rapidly and accurately measured by threshold ionisation techniques.

## 1. Introduction

Atmospheric plasmas are increasingly used to process materials that are otherwise unsuitable for vacuum processing. Highly functional surfaces can be produced on a number of materials including textiles, plastics, polymers and nonwovens. Other applications include cleaning of polluted water, sterilisation of surgical instruments and localised treatment of biological tissues.

In all cases an understanding of the gas phase and surface chemistry involved is important in order to develop and refine a particular process. Compared with optical techniques, mass spectrometry has the distinct advantage of being able to provide simultaneous identification of the various plasma species that impinge on the substrate or workpiece. When coupled with energy analysis a detailed understanding of the process can be quickly achieved.

Molecular beam inlet systems consist of several differentially pumped stages coupled by sampling/collimating apertures and have been used previously to determine reaction kinetics of high pressure combustion and pyrolysis processes [1]. More recently they have been developed for accurate measurement of radical densities in low pressure plasmas [2,3]. In this work we describe a molecular beam mass spectrometer system for atmospheric plasma diagnostics. The instrument incorporates beam modulation in the form of a software controlled rotating disk chopper.

## 2. Diagnostic Apparatus

### 2.1 Molecular Beam Mass Spectrometer

The discharge was generated by a radio frequency driven atmospheric plasma source, based upon the design of Stoffels et al [4]. This original design was adapted to include a second, concentric gas inlet in order to study mixtures of gases. The low power discharge, around 7W, was produced between the plasma source and the entrance of the Molecular Beam Mass Spectrometer (MBMS) analyser.

Species created in the atmospheric discharge were sampled using a triple stage differentially pumped molecular beam inlet system and subsequently detected with the Hiden EQP mass/energy analyser. A schematic of the arrangement is shown in Figure 1. The chopper mechanism is omitted for clarity

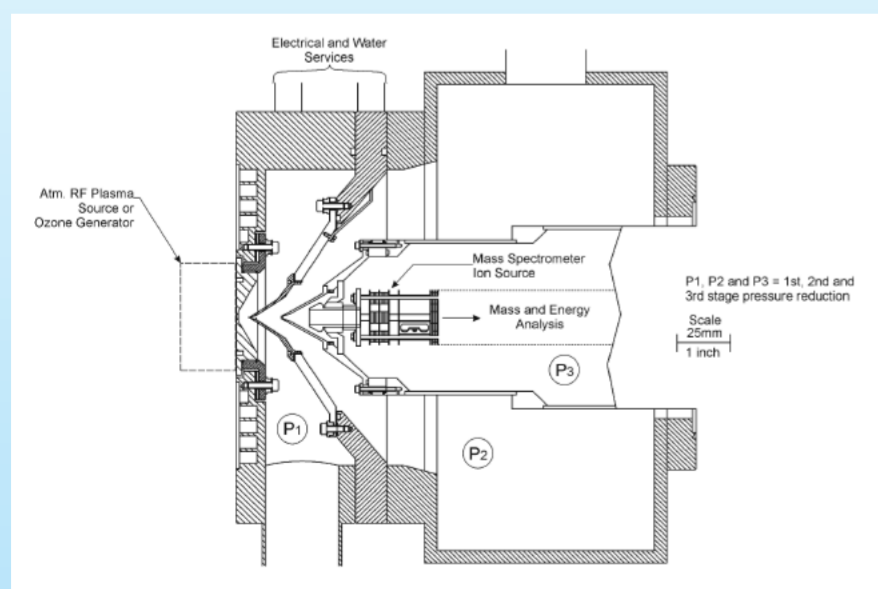


Fig 1. Schematic of MBMS Analyser

### 2.2 Automated Beam Modulation Control

The beam chopper mechanism incorporates an opto-detector positioned on the opposite side of the rotating disk to the molecular beam aperture. This generates a synchronisation signal that is phase locked to the chopper movement and used by the mass spectrometer as two virtual detectors, *foreground* and *background*.

The mass spectrometer has one physical electron multiplier detector (SEM), which may be connected to either the foreground or background virtual detectors under the control of the gating system. The detectors are presented as separate inputs by the control software and related as follows;

$$\text{SEM} = \text{foreground} + \text{background} \quad (1)$$

$$\text{foreground} = \text{SEM} - \text{background} \quad (2)$$

$$\text{background} = \text{background} \quad (3)$$

The chopper synchronisation signal cannot be used to directly gate the mass spectrometer as its duty cycle does not exactly match the instrument’s response to the beam chopper, and this would tend to reduce its differential sensitivity. To overcome this, two internal delayed pulse generators (100nsec resolution) are used to match the beam chopping cycle to the foreground and background gating, as shown in Figure 2.

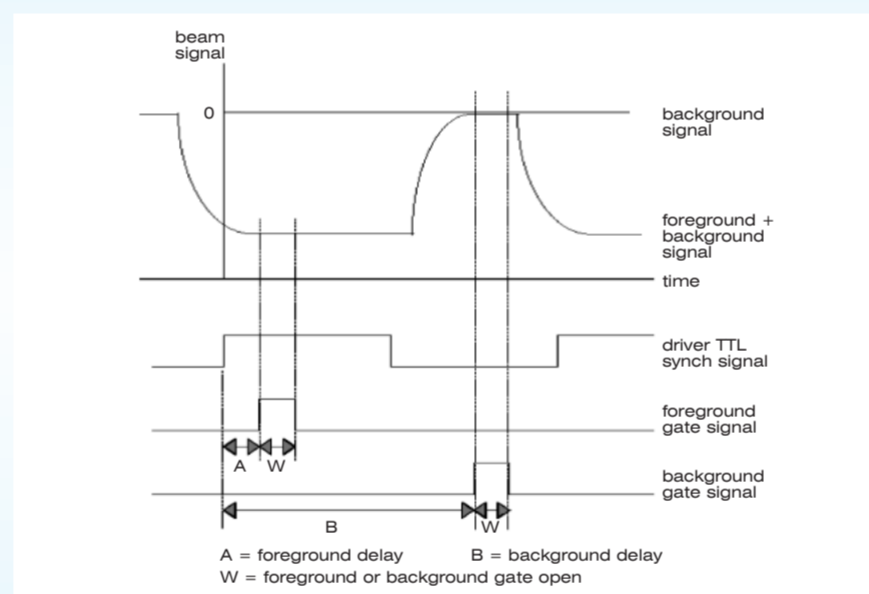


Fig 2. Modulation timing diagram

## 3. Results & Discussions

Figure 3 shows the measurement and display of SEM and background signals for N<sub>2</sub><sup>+</sup> for plasma on and off conditions. The foreground (beam) signal is derived in real time from (2).

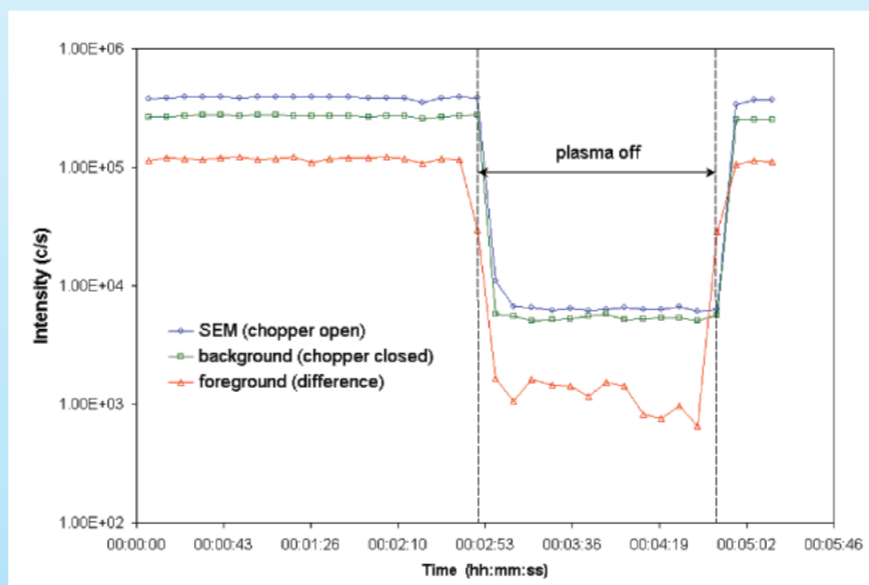


Fig 3. Raw (SEM, background) and derived (foreground) signal intensities for N<sub>2</sub><sup>+</sup> for plasma on/off conditions

Figure 4 shows the corresponding appearance potential scans for N<sup>+</sup> when the plasma is on. Again, the threshold ionisation foreground (beam) data is generated automatically. The two observed thresholds correspond to the direct and dissociative ionisation processes;

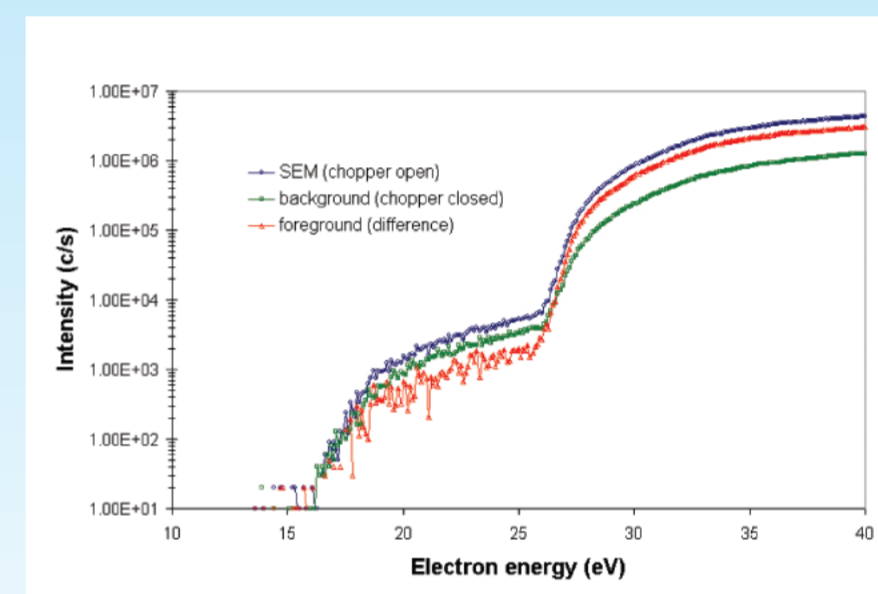
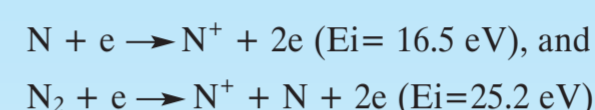


Fig 4. Threshold ionisation curves for N<sup>+</sup>

The beam-to-background ratio can be calculated from the slope of the linear fits between the above thresholds and gives a figure of merit for the sensitivity of the overall apparatus to the beam component [2]. This in turn determines the accuracy of absolute radical density calculations [3]. The value of 0.95 is obtained for the N<sup>+</sup> case above, clearly demonstrating the sensitivity of this apparatus for absolute radical density determination from atmospheric plasmas.

## 4. Conclusions

We have described a modulated molecular beam mass spectrometer that is suitable for diagnostics of atmospheric plasmas. Automatic control and processing of the modulated molecular beam signals allows rapid and accurate determination of beam/background components which are required to determine absolute radical densities.

## 5. References

- [1] D. Dayton, W. Frederick, Energy & Fuels **10** (1996) 284.
- [2] H. Singh et. al., JVST A **17** (5) (1999) 2447.
- [3] S. Agarwal et. al., JVST A **22** (1) (2004) 71.
- [4] E Stoffels et. al., Plasma Sources Sci. Technol, **11** (2002) 383.