

Surface analysis by plasma assisted desorption ionisation mass spectrometry (PADI-MS)

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1. Introduction

We have recently developed a novel approach to ambient surface analysis, termed plasma-assisted desorption ionization (PADI) [1]. The PADI source is a non-thermal atmospheric plasma jet which is allowed to interact directly with the analyte under study. The analyte is positioned close to the entrance of an atmospheric sampling molecular beam mass spectrometer (Hiden Analytical, Warrington, UK). Interaction of the plasma with the analyte produces ions (positive and negative) from the analyte material which are detected in real time by the mass spectrometer.

2. Apparatus

2.1. Atmospheric plasma source

The PADI source is a non-thermal 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 from the surface material which enter the gas phase and are readily detected by the molecular beam mass spectrometer, figure 1.

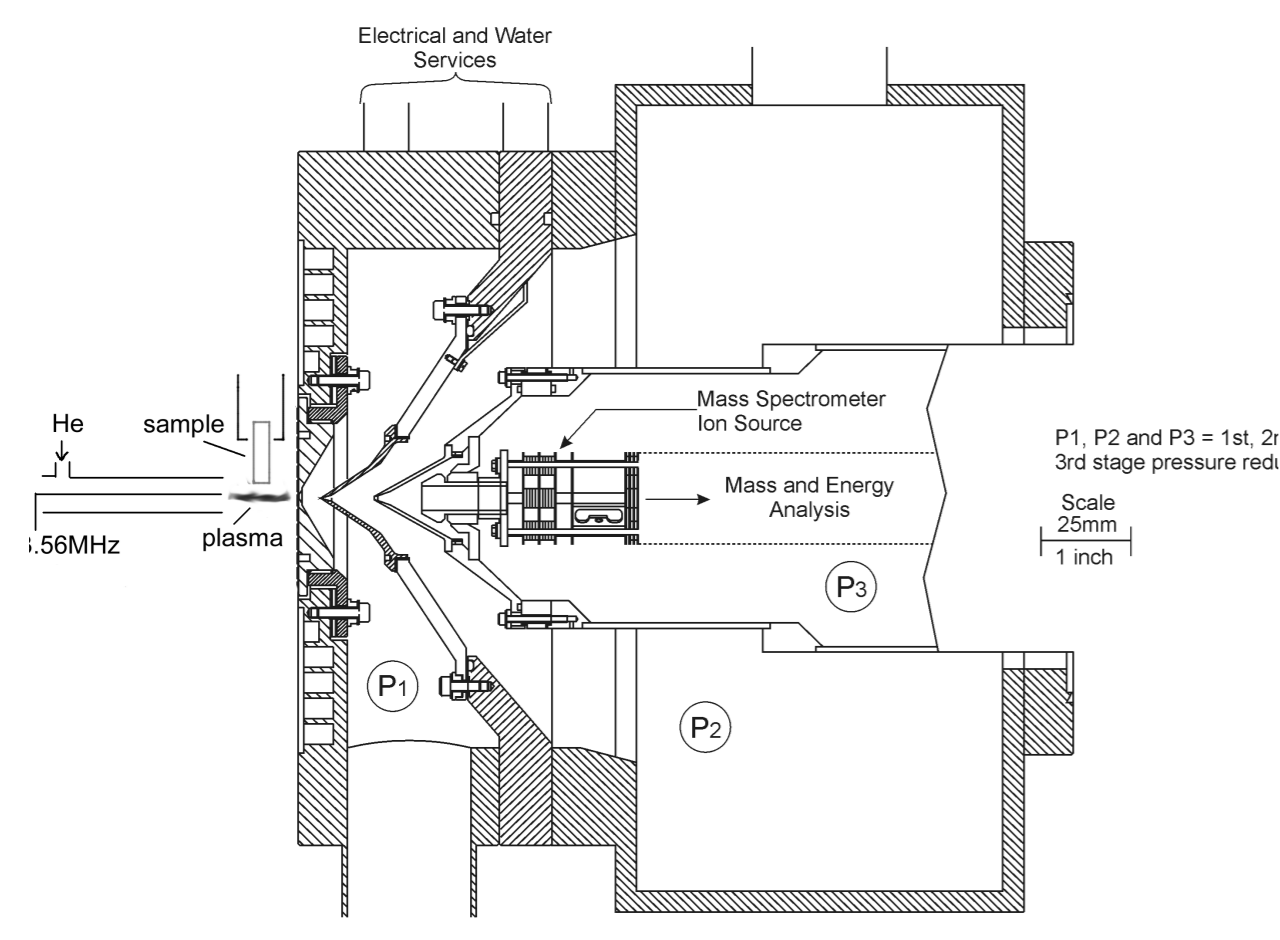


Figure 1. PADI-MS Analyser

2.2. Molecular beam mass spectrometer

An energy resolved molecular beam mass spectrometer (MBMS, Hiden Analytical, UK) is used to analyse the plasma species. The MBMS apparatus is detailed in [2].

It incorporates an EQP quadrupole mass/energy analyser. The EQP's inlet orifice is provided in the MBMS instrument by the final orifice of the differentially pumped, three-stage inlet system.

The plasma impinges upon the grounded entrance orifice (300 micrometer diameter) of the MBMS and subsequent expansion results in the formation of a molecular beam.

The EQP is operated in energy resolved positive and negative ion modes for PADI-MS measurements. Neutral species can also be analysed via appearance potential and electron attachment mass spectrometry.

5. Conclusions

We have introduced a new technique for the ambient analysis and identification of a range of samples. The technique produces simple spectra with uniquely identifying peaks and is robust, fast and capable of high throughput analysis. Further work will expand the range of substances detected and investigate issues of quantification.

Plasma assisted desorption/ionisation mass spectrometry (PADI-MS) is a surface analysis technique that yields sample information under ambient conditions of pressure and humidity without any surface preparation. It is achieved by directing a non-thermal atmospheric plasma onto the surface of interest. Desorption occurs from the surface and the subsequent ionisation products are detected in real time by using an atmospheric sampling quadrupole mass spectrometer. We have demonstrated the detection of active ingredients in a range of pharmaceutical and other samples, demonstrating the potential of the technique for high throughput screening in a pharmaceutical or forensics environment.

3. Results

Typical data obtained for the detection of positive ions of the active ingredients from the indicated unprepared samples are shown in figures 2 a and 2b.

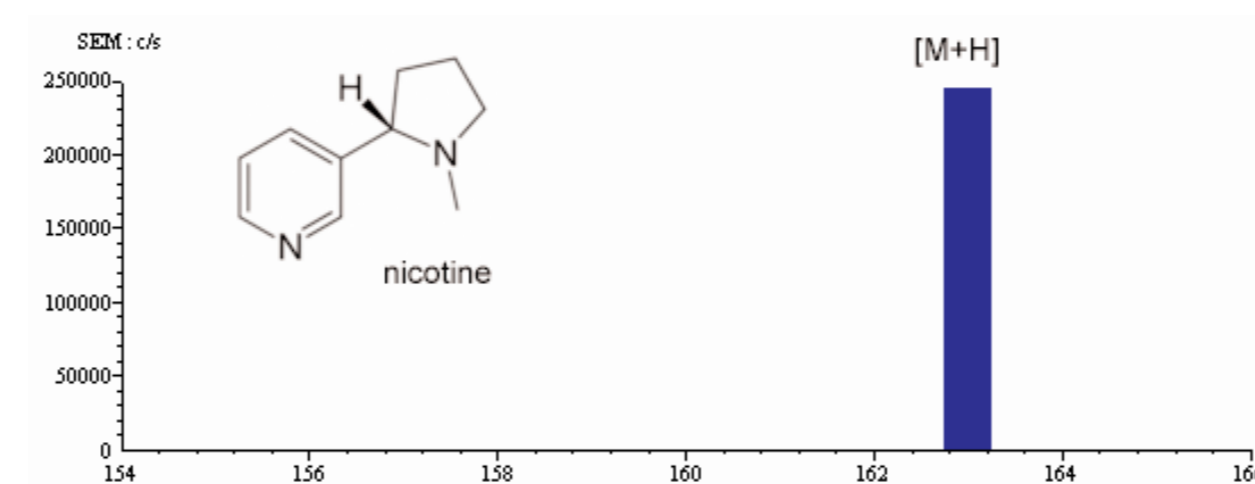


Figure 2a. Positive ion PADI-MS spectrum of nicotine from unprepared tobacco sample.

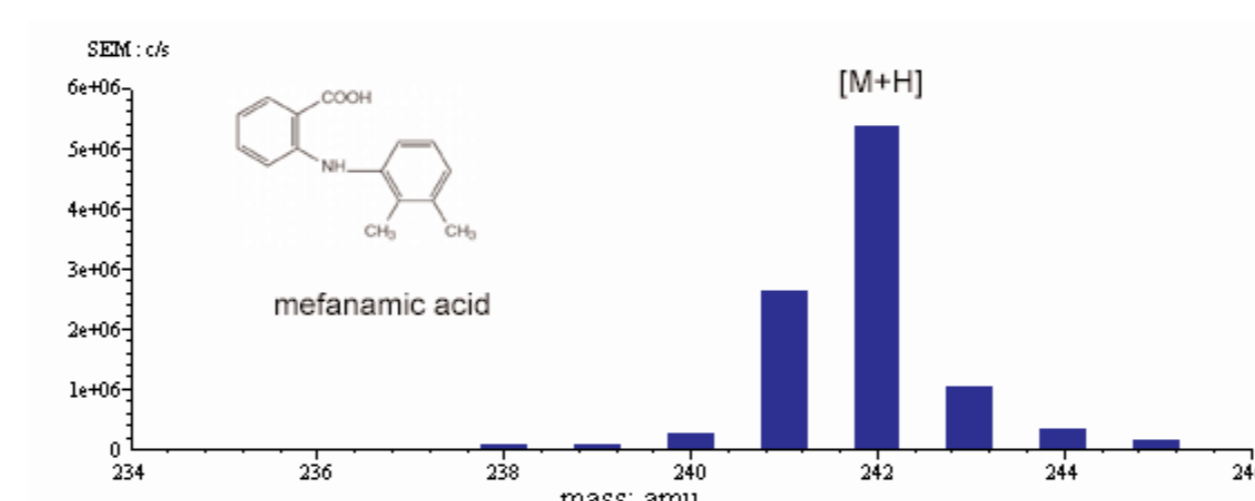


Figure 2b. Positive ion PADI-MS spectrum of mefenamic acid, a common anti-inflammatory drug.

Each sample was analysed without any prior preparation and the resulting spectra contained uniquely identifying peaks for each of the substances under study.

Negative ions, appearing mainly as [M-H] fragments, are also measured by simply switching the MS detection mode, i.e. without disturbing the plasma. Switching between modes can be achieved in a sequential loop type scan with millisecond interval providing rapid confirmation of correct identification.

Figures 3a and 3b show respectively the positive and negative ion PADI-MS spectra for paracetamol.

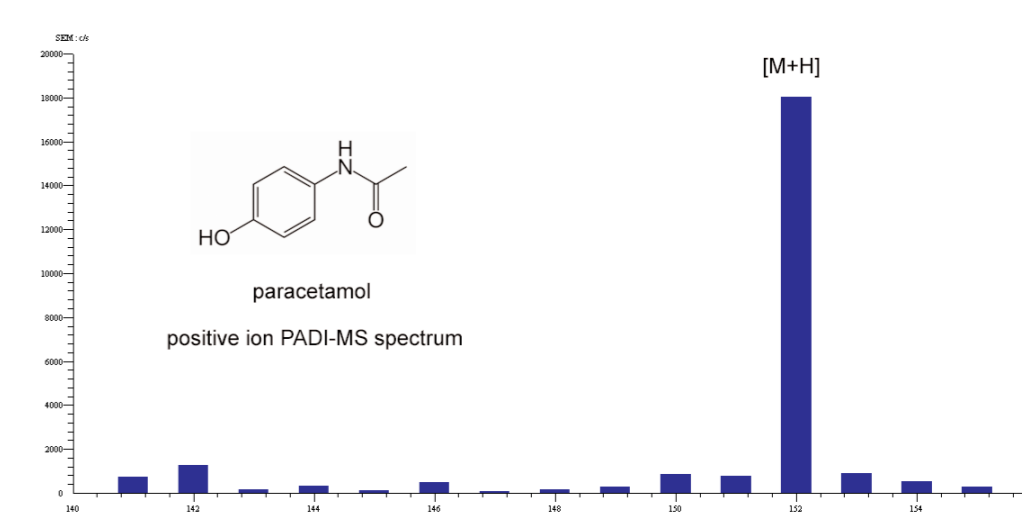


Figure 3a. Positive ion PADI-MS spectrum of paracetamol from a popular over-the-counter pain reliever.

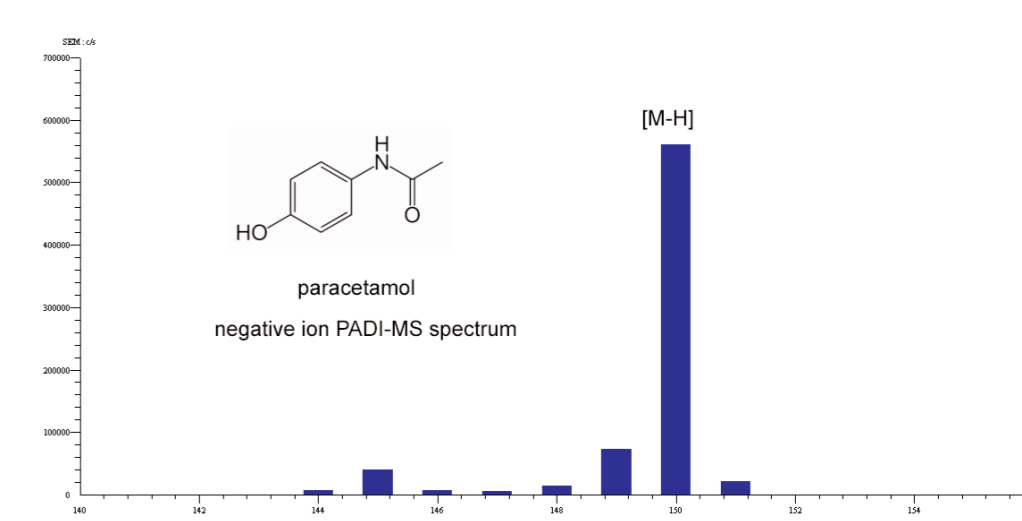
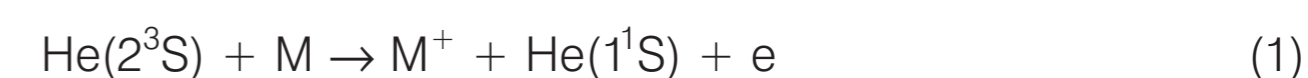


Figure 3b. Negative ion PADI-MS spectrum of paracetamol from a popular over-the-counter pain reliever.

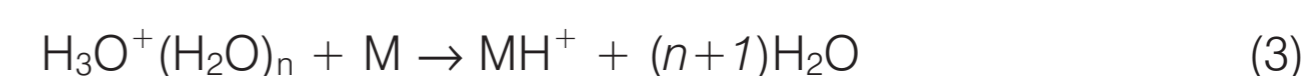
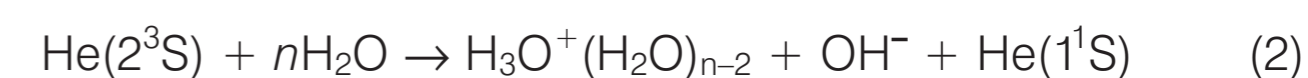
4. Discussion

Positive ionisation mechanisms are thought to include a combination of direct electron impact ionisation, metastable Penning ionisation and ion molecule reactions.

The He(2³S) metastable state has an energy of 19.8eV and will ionise molecules with ionisation potentials lower than this;



The reaction of the helium (2³S) state with water is very efficient [3] and the analyte ionisation mechanism proceeds via a combination of ionised water cluster formation and proton transfer reactions;



We have measured both M⁺ and [M+H]⁺ fragments and also H₃O⁺(H₃O)_n clusters from the PADI source and expect that each mechanism plays a part in the ionisation of analytes in this technique.

Negative ion formation is thought to proceed via direct and dissociative electron attachment to oxygen species which then react with analyte molecules to produce predominantly [M-H]⁻ groups.

Desorption processes are less well understood but we believe that a combination of energy transfer from metastable helium, ion impact and radical-surface interactions all contribute.

6. References

- [1] L. Ratcliffe et. al., accepted for publication in J. Anal. Chem.
- [2] Y. Aranda-Gonzalvo et. al., JVST A 24(3) 2006
- [3] J. Q. Searcy and J. B. Fenn, J. Chem. Phys., 61 12 (1974) 5282-5288