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VOCs detection by Chemical Ionization Mass Spectrometry

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Introduction

Chemical ionization is the way to selectively ionize the volatile organic compounds present in air. As the major gases of air are not ionized the detector is not saturated and organic compounds at very low concentrations can be detected in real time.

It is a soft ionization technique leading to little or no fragmentation and thus well adapted for the identification of the VOCs present by the measurement of the ions mass to charge ratios.

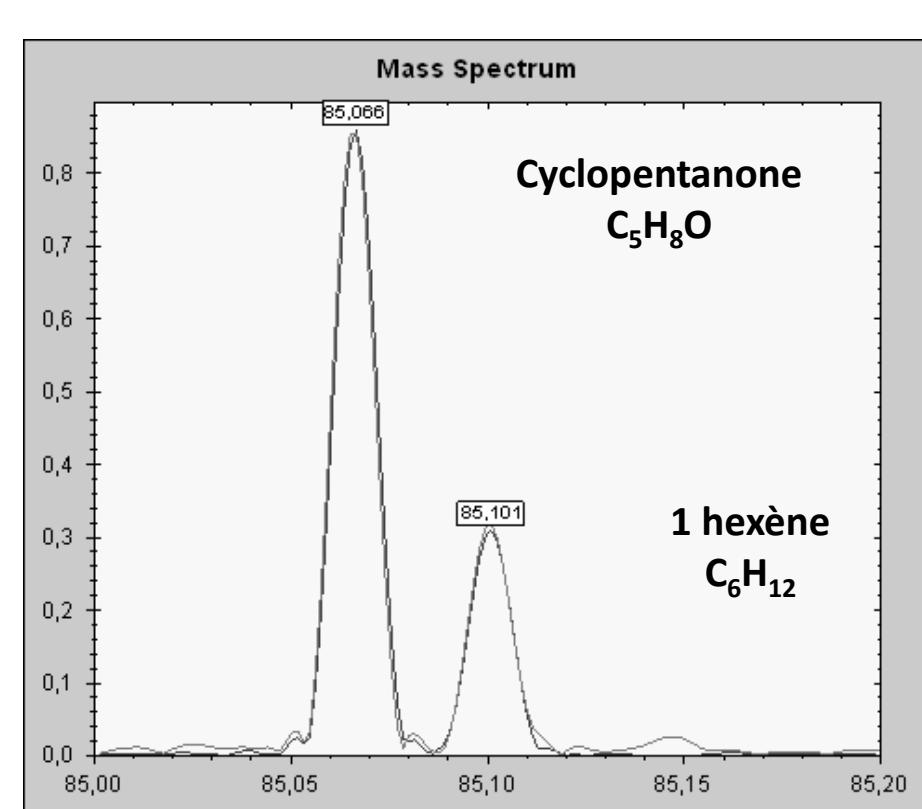
We have applied this ionization technique in transportable high resolution instruments : FTICR mass spectrometers fitted with permanent magnet assembly.

We actually work on a more compact portable drift tube instrument that will be coupled with cold plasma microjets, allowing analysis of both air or of less volatile species deposited on surfaces.

High resolution transportable FT-ICR instruments

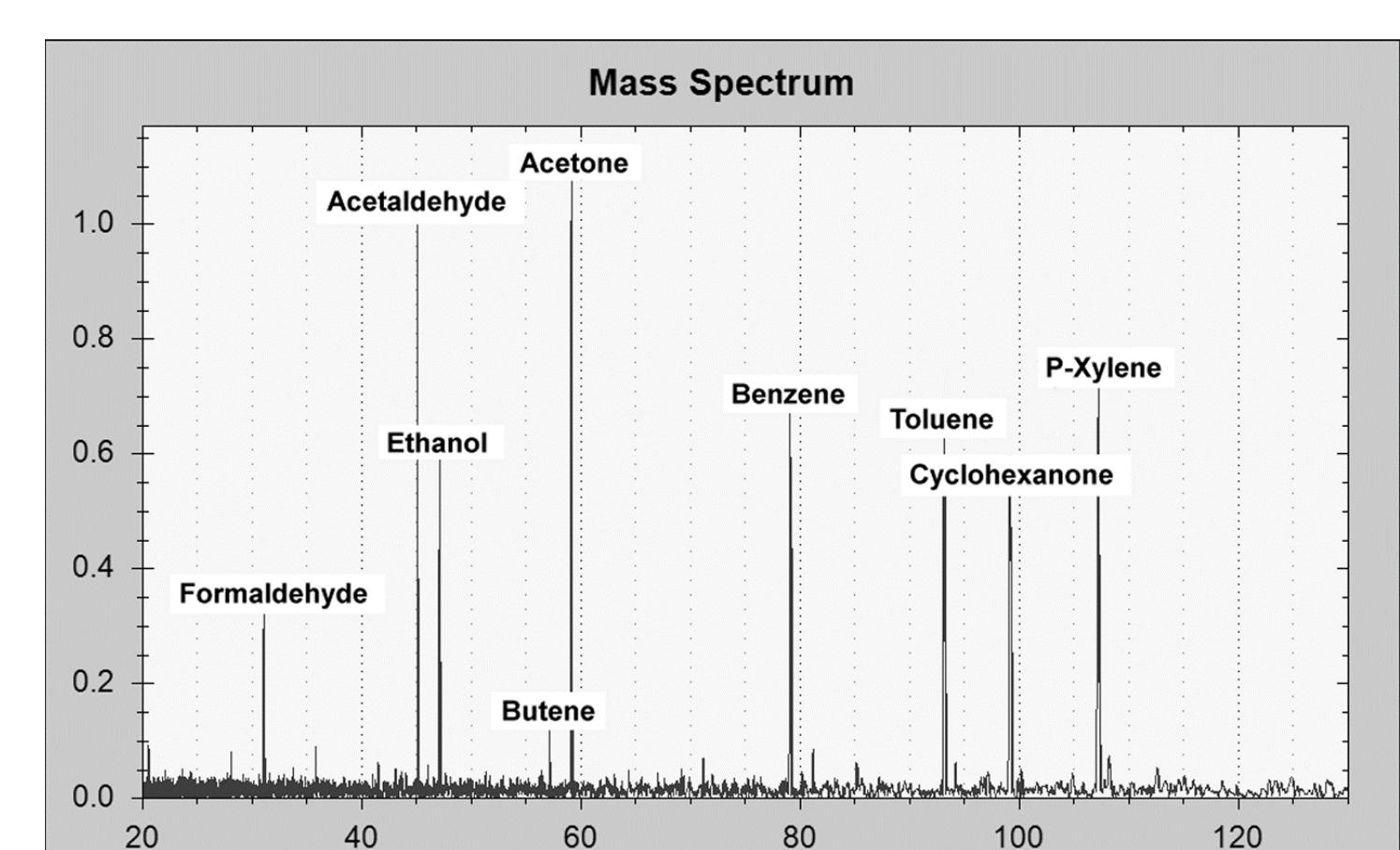


We have developed compact FTICR mass spectrometers ; first in the LCP lab, now commercialized by AlyXan. Our instruments use permanent magnets in order to generate the magnetic field (nominal field up to 1.5 Tesla).



The high resolution allows a precise identification of the organic molecules that are present, even when they are at very low concentrations.

Species differing by their molecular formula are separated and identified, even when they have the same nominal mass.

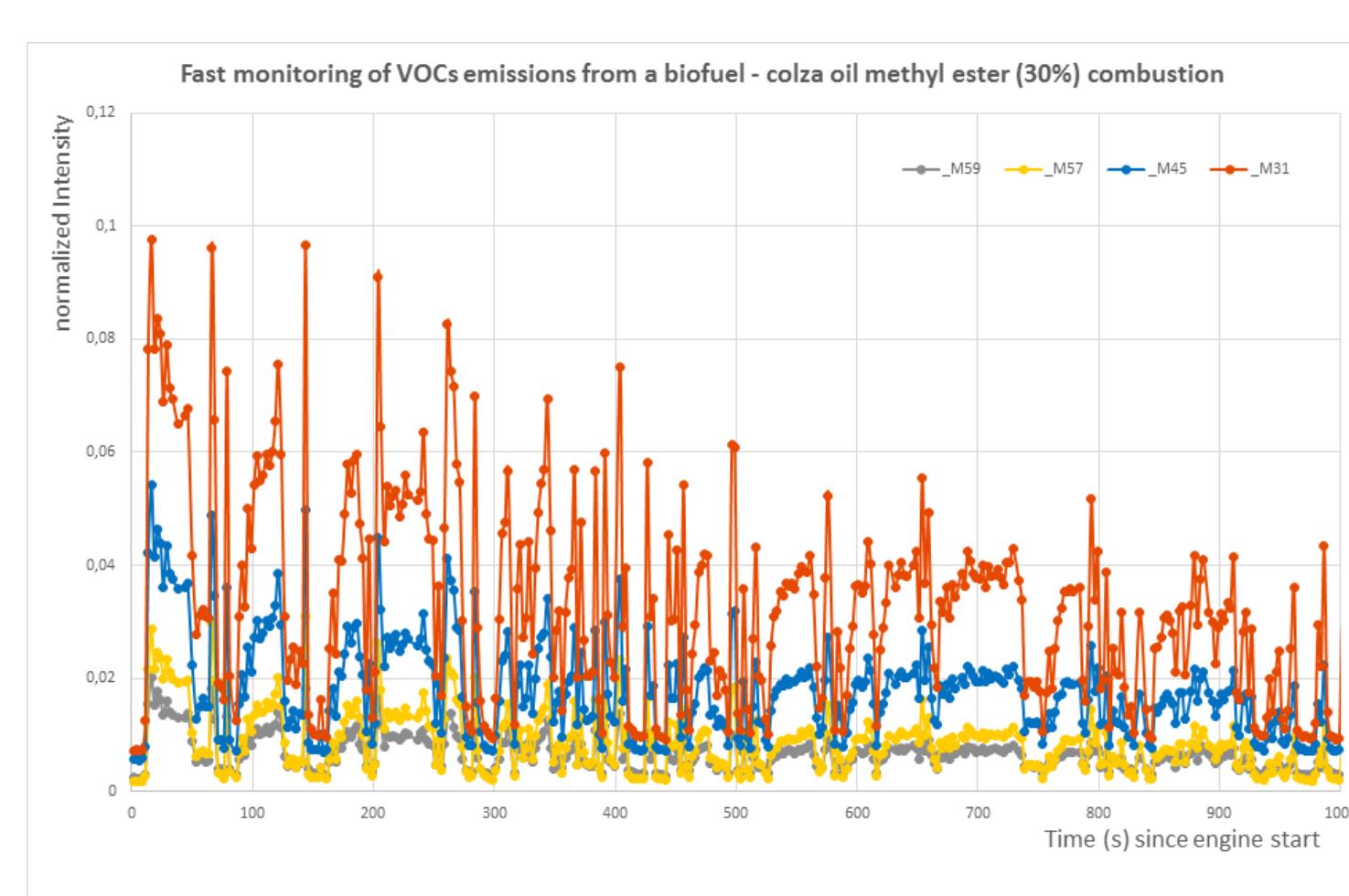


When using chemical ionization (here proton transfer from H_3O^+ ions) one peak is observed for each species present.

Here for a mixture of 9 compounds at low concentrations in air 9 peaks are observed on the mass spectrum.

Real time measurements:

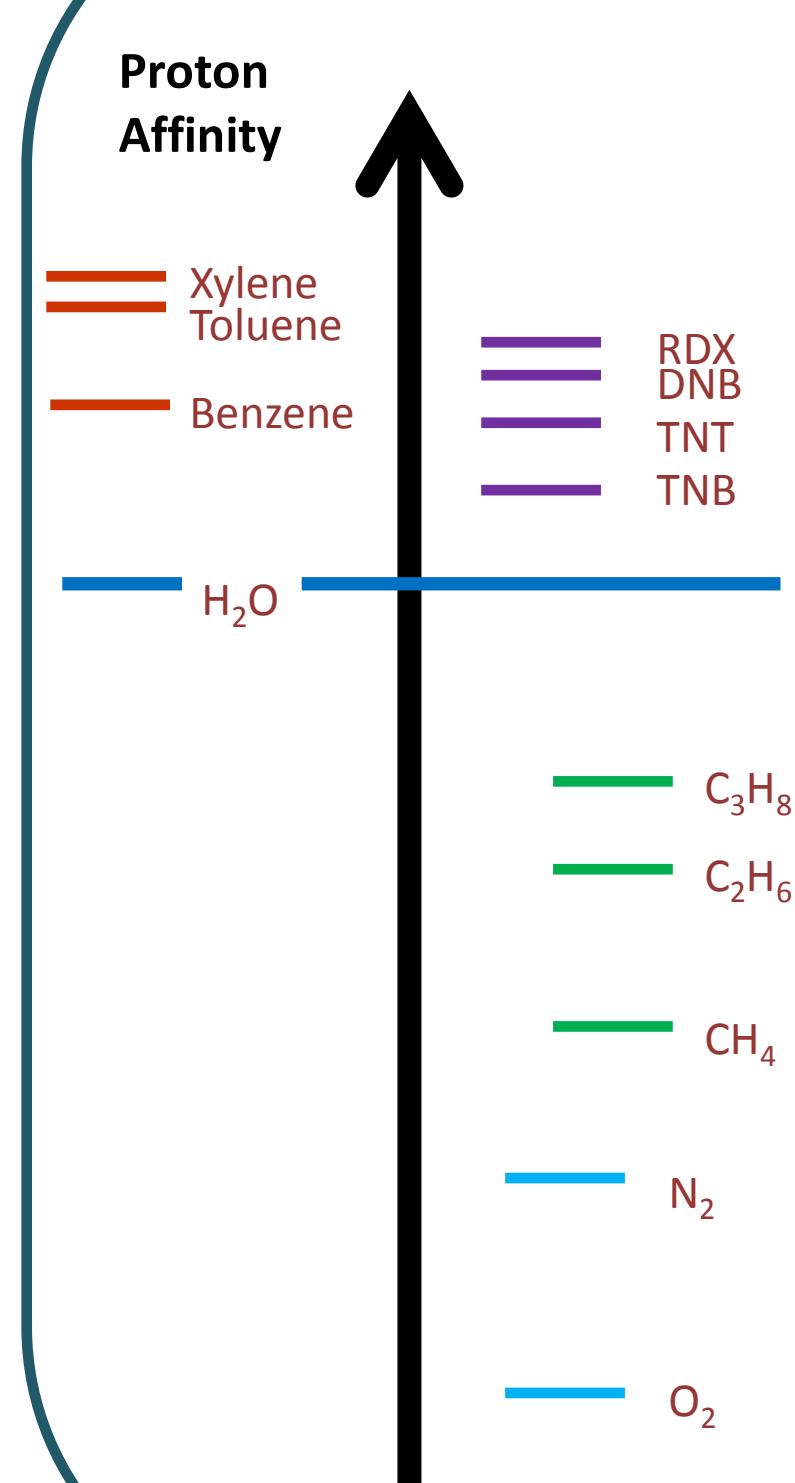
The time variations of selected VOCs are followed on an engine test stand while the engine using biofuels is submitted to a Common Artemis Driving Cycle (a cycle conceived to be close to real driving conditions).



Acknowledgements

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Chemical ionization

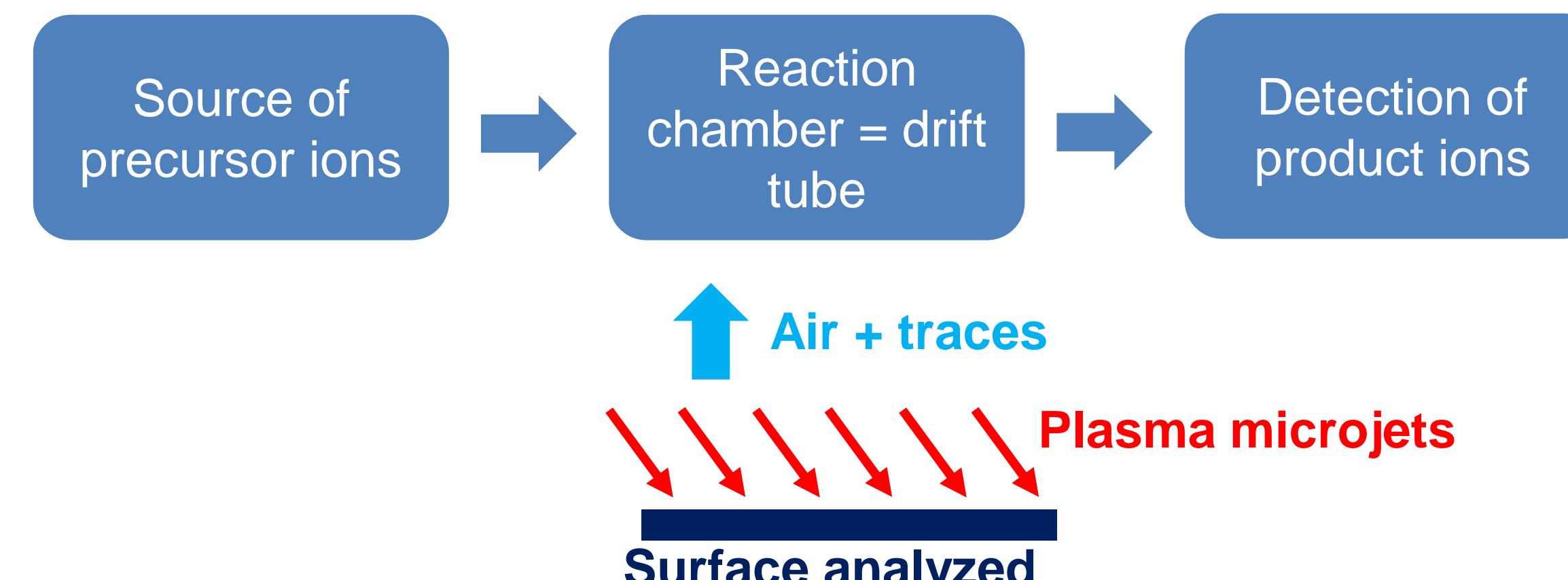


For detection of VOCs in air the most often used reaction is proton transfer from H_3O^+ ions

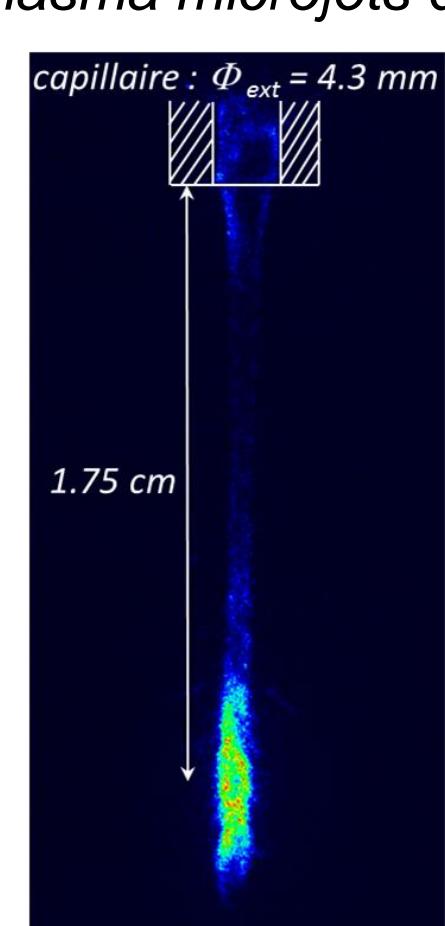


This reaction will efficiently protonate all molecules having a proton affinity higher than water (such as aromatic compounds, aldehydes, nitrated explosives, narcotics,...) but will not protonate the major gases of air (N_2 , O_2 , Ar, CO_2 , Ne, CH_4 ..) as well as alkanes and most CFCs.

Development of a portable instrument coupling plasma microjets and mass spectrometry

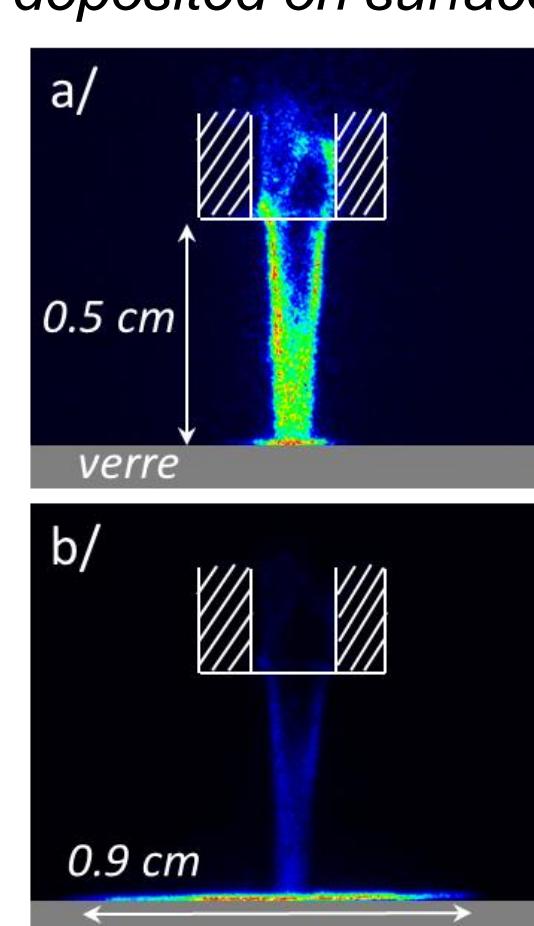


Plasma microjets developed at the LPGP lab will be applied to the desorption of species deposited on surfaces

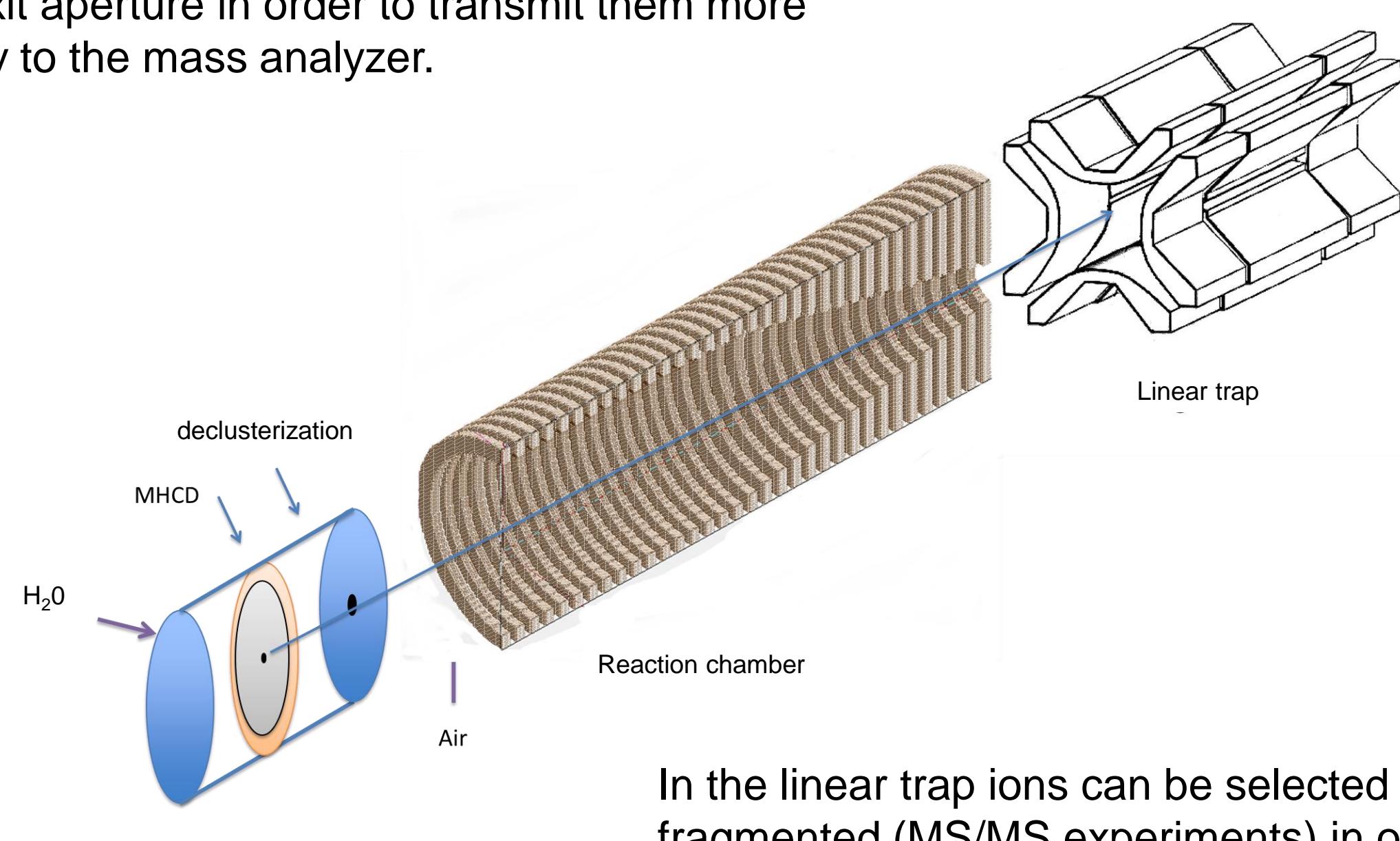


Fluorescence of the plasma in the argon microjet is here recorded with an intensified CCD camera. (acquisition time 20ns, 10 accumulations).

Effect of the presence of a glass surface placed 5mm away from the capillary exit At longer times the plasma spreads on the surface.



Precursor ions produced in a micro hollow cathode discharge (MHCD) will react with the air to analyze in a drift tube where the application of radiofrequency fields will help in focalizing the ions on the exit aperture in order to transmit them more efficiently to the mass analyzer.



In the linear trap ions can be selected and fragmented (MS/MS experiments) in order to get more information for a better identification.

Conclusion

We have implemented chemical ionization in different kind of mass spectrometers. The FTICR instrument has the advantage of high resolution, the exact mass allowing for a precise identification. With the drift tube a better sensitivity is obtained. For the first tests we are using a linear quadrupole to analyze the ions. In a second step we will use a linear trap, allowing for a more compact design and in which MS/MS will help in identifying the compounds present in air. For the less volatile compounds difficult to detect directly in air as they are present at extremely low concentrations cold plasmas will help in desorbing them from the surfaces on which they can be deposited in a gentle manner so that the fragile molecules will still be intact for mass spectrometric analysis.