Studies of Organics with the Cosmorbitrap, A HRMS Analyzer for Future Missions to Titan and other organic worlds

L. SELLIEZ[1,2], C. BRIOIS[1], N. CARRASCO[2]

laura.selliez@cnrs-orleans.fr [1]LPC2E, Orléans, France [2]LATMOS, Guyancourt, France

Scientific Context

Mass spectrometers are key instruments for the *in situ* detection and compositional analysis of organic matter within organic-rich environments of Solar System bodies. The Cassini-Huygens and Rosetta missions are among the best examples. The DFMS/ROSINA/Rosetta instrument has provided the best resolution in space with a m/Δm of 9,000 at m/z 28. The next steps in the future space exploration of organic-rich environments require the development of HRMS, with significantly higher mass resolution (Briois et al., 2016). Our group is developing a new generation of high resolution mass analyzer based on the Orbitrap™ technology called Cosmorbitrap (figure 1). The laboratory set-up is coupled with a laser ablation front-end (figure 2). In a context of a future *in situ* exploration of Titan, tests on organics have been performed in order to define the required performances of the instrument dedicated. Results obtained are non specific to Titan and can be extended to other organic worlds. Results on organic matter with the laboratory prototype are presented in this work.

Methods

What is Cosmorbitrap ?

- Development of a space mass analyzer based on the Orbitrap™ technology (sub system of a mass spectrometer) : Orbitrap™ cell, High Voltage, Pre amplifier, Acquisition and data treatment
- R&D development within a consortium of 5 laboratories in collaboration with ThermoFisher Scientific
- Current status: TRL 4-5

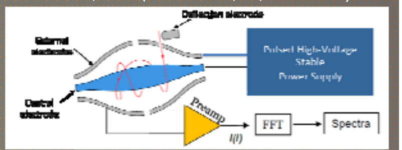
Laboratory set-up:

- Cosmorbitrap elements (figure 1)
- Nd-Yag laser at 266 nm for desorption/ionization
- Ion optics/Ionization chamber (around 10^{-8} mbar) and Orbitrap™ chamber (lower than 10^{-9} mbar)
- Frequency range: 100 kHz (M=2000) to 7 MHz (M=1)

About the Orbitrap™ cell:

- Two external electrodes, one central electrode. Ultra stable high voltage.
- Measure of ion oscillations along the central electrode
- Frequencies proportional to $(m/z)^{-1/2}$

Figure 1: Cosmorbitrap elements. Adapted with permission from Makarov et al, 2006 (Anal. Chem., 78, 2113-2120)



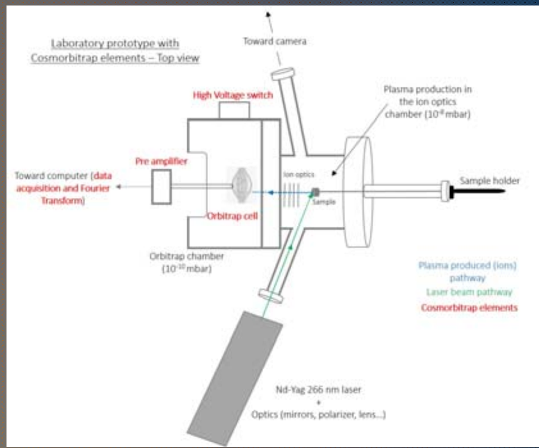


Figure 2: Laboratory set-up, top view

Results

1) A challenging identification

- Two unknown molecules sent by the JAXA team as part of a collaboration
- Tests performed with the Cosmorbitrap & signal processing with Attributor (software dedicated to UHRMS data analysis developed at IPAG, France)
- Methodology: Use of the mass accuracy; Mass Defect vs Exact Mass diagram (MDvEM) (figure 3) → Identification of positive and negative mass defects, then assumptions about possible structures present in the molecules; and final confirmation by the fragmentation pattern (figure 4)

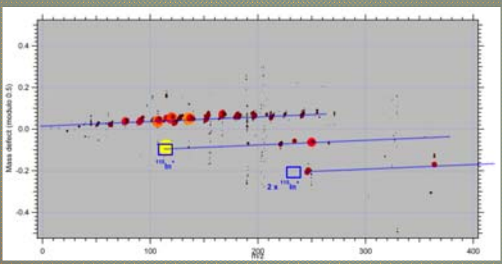


Figure 3 : MDvEM diagram for unknown molecule "B" (Cosmorbitrap team report).

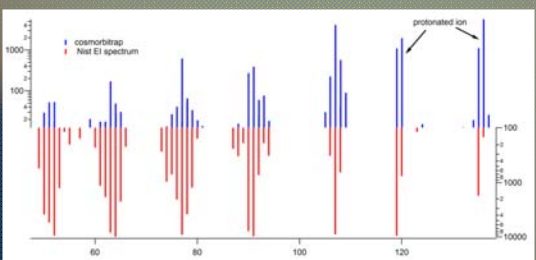
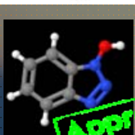
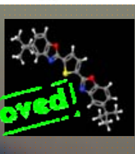


Figure 4 : Similarities between the fragmentation pattern observed with the Cosmorbitrap (laser ablation) and the one referenced in the NIST database (electron impact). Production of radical ions leading to the same fragments.

Sample « A » is HOBt 1H-Benzotriazole, 1-hydroxy- $C_6H_5N_3O$





Sample « B » is BBOT 2,5-Bis(5-tert-butyl-2 benzoxazolyl)thiophene $C_{26}H_{26}N_2O_2S$

- **SUCCESSFUL IDENTIFICATION !**
- Similarities observed in the fragmentation between laser ablation and electron impact become a very useful tool as a final step in the identification process.
- **PAPER IN PREPARATION**

2) Bringing in light the analytical performances

This work is presenting performances of our laboratory prototype using a laser ablation ionization and not the ones of a commercial instrument

- 150 spectra recorded for two organic species: HOBt (m/z ≈ 136) and BBOT (m/z ≈ 431)
- Mass accuracy: between -5 and 5 ppm
- Isotopic ratios (figure 5): Less than 10% of error for the major part of the FFT time used.
- The FFT duration acts on the mass resolving power and the isotopic abundance

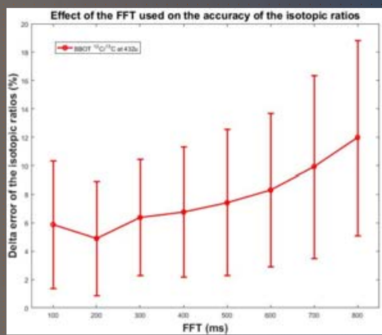


Figure 5 : Accuracy of the first Carbon exchange of BBOT as a function of the FFT length used.

3) Work in progress about the Pressure in the Orbitrap™ chamber related to the mass resolving power

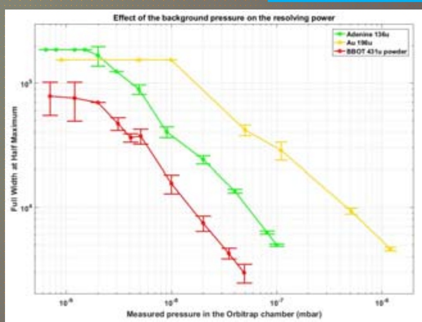


Figure 6 : Effect of the background pressure on the mass resolving power of organics and comparison with metal. Experiments performed with Dylan Chateigner during his internship

- At low pressure (10^{-9} mbar), resolution decreases with the m/z
- Mass resolving power at 10^{-9} mbar: m/Δm= 183,070 at m/z 136 and m/Δm= 88,407 at m/z 431
- Resolution decreases with higher pressure inside the Orbitrap™ chamber
- A plateau is observed at low pressure. For organics, the decrease starts at lower pressure ($2*10^{-9}$ mbar) than metals (10^{-8} mbar)
- No data detection at 10^{-6} mbar for organics.

Future work

- Continue with mixtures of molecules.
- Test the quantification capability of the Cosmorbitrap: determination of proportion of molecules in a mixture
- Test more complex molecules like tholins, analogs of Titan aerosols synthesized with the PAMPRE experiment at LATMOS, France.