

# Laboratory studies of tholins, analogues of Titan aerosols, with the LAB-CosmOrbitrap

Laura Selliez (1,2), Barnabé Cherville (1), Christelle Briois (1), Nathalie Carrasco (2), Julien Maillard (2,3), Thomas Gautier (2), Laurent Thirkell (1), Bertrand Gaubicher (1) and Jean-Pierre Lebreton (1) (laura.selliez@cns-orleans.fr)

- (1) Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), Orléans, France  
(2) Laboratoire ATmosphères, Milieux, Observations Spatiales (LATMOS), Guyancourt, France  
(3) Laboratoire Chimie Organique et Bioorganique – Réactivité et Analyses (COBRA), Rouen, France

## Abstract

Instruments on the Cassini-Huygens mission have allowed the collection of a big amount of data about Titan and revealed part of the complex organic chemistry in the dense atmosphere of this moon. Complementarily to the data received, analyses of laboratory analogues of Titan aerosols help the understanding of chemical mechanisms occurring on Titan. These analyses are also preparing the new generation of space mass spectrometer, such as the LAB-CosmOrbitrap, new high-resolution mass analyser based on the Orbitrap™ technology and coupled with laser ablation ionisation.

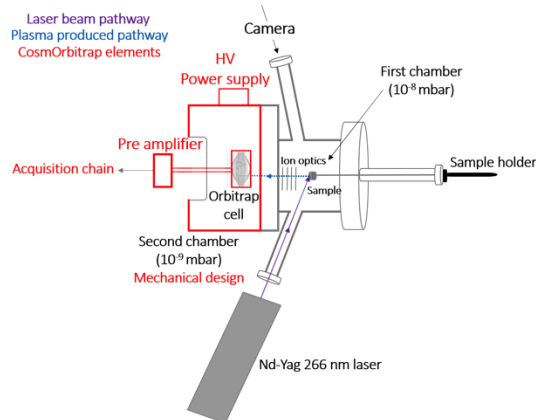


Figure 1: The LAB – CosmOrbitrap

## 1. Introduction

Among the discoveries about Titan allowed by the Cassini-Huygens mission, we can cite detections made by INMS (Ion and Neutral Mass Spectrometer) and CAPS (CASSINI Plasma Spectrometer). They have highlighted the presence of (i) positive ions and neutral up to 100 mass units [1] and (ii) very heavy positive and negative ions [1]. Instrumental limits, in terms of mass range and mass resolving power, don't allow to decipher the composition of the organic molecules detected nor the growth chemical pathways leading to the formation of aerosols.

### 1.1 The Laser-CosmOrbitrap: a new mass spectrometer dedicated to space exploration

Ultra-high-resolution mass spectrometer is needed to go further in the *in situ* chemical analysis of, for instance, Titan atmosphere. This work aims to show the potential of a new generation of simple mass spectrometer concept, the Laser Ablation - CosmOrbitrap (Figure 1) as future space exploration instrument of complex organic worlds. For that purpose Titan aerosol analogues have been studied.

Ionisation of the sample is provided by a Nd-Yag laser at 266 nm. Mass analysis is then performed by the CosmOrbitrap [2] high-resolution mass analyser, which is a space version of the Orbitrap technology [3], currently developed by a consortium of laboratories (LPC2E, LATMOS, LISA, IPAG and CSNSM) in close collaboration with ThermoFisher Scientific, with the support of CNES. This instrumental concept has demonstrated its potential for the identification of organic molecules [4].

### 1.2 Analogues of Titan aerosols

To go further in the chemical analysis of Titan aerosols started by the Cassini-Huygens mission, different experiments allow the synthesis of analogues of Titan aerosols called "tholins". One of them, the PAMPRE experiment [5] uses a radio frequency reactive plasma to produce solid particles in the volume, limiting wall effects and mimicking the coupled ion-neutral chemistry occurring in Titan ionosphere [1]. Particles studied are produced with gas mixture of 5% of CH<sub>4</sub> and 95% of N<sub>2</sub>.

## 2. LAb-CosmOrbitrap analysis of tholins and comparison to other laboratory techniques

Fresh solid tholins particles have been gently pressed on the sample-holder indium surface. This simple deposition method allows adducts formation between the organic sample and the indium surface [4] that could help for the identification of compounds. To refresh the sample area destroyed under the laser ablation conditions, location of the laser beam on the sample-holder was set regularly. Energy of the laser shot has been explored. Under nano-pulsed single laser shot, patterns of organic molecules, polymeric structures and adducts with indium have been observed.

These results have been compared to previous studies made by LDI-FTICR (Figure 2, [6]) on the same tholins sample.

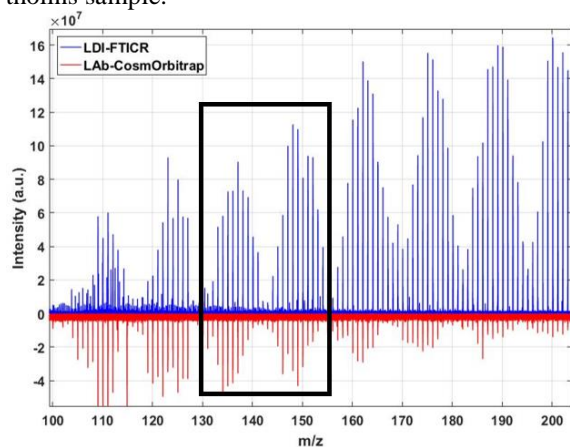


Figure 2: Comparison between LDI-FTICR mass spectrum (upper panel – in blue) and LAb-CosmOrbitrap mass spectrum (lower panel – in red) on the same tholins sample.

Different analytical representation such as the Mass Defect versus Mass diagram [7] and the Kendrick mass defect diagram ([8] and [9]) have been used for further data treatment. Interesting similarities such as the importance of HCN and CH<sub>2</sub> molecules as polymeric structures involved in the growth processes of tholins but also in the location and identification of chemical formula of tholins, have been highlighted.

These similarities demonstrate the possible ionisation and detection of tholins with the LAb-CosmOrbitrap, with mass accuracy better than 2 ppm and mass resolving power up to 350 000 (FWHM) in the  $m/z$  range 20 to 250. The relevance of our instrumental configuration as a future mass spectrometer for space exploration of ocean worlds is also evidenced.

## 3. Perspectives of this work

One of the main perspectives will be to switch the LAb-CosmOrbitrap in the negative ion mode due to the CAPS negative ions detection and as the use of both positive and negative ion modes is an important requirement, from an instrumental development point of view.

### Acknowledgements

We gratefully acknowledge the financial support by the Centre National des Etudes Spatiales (CNES), the Région Centre-Val de Loire and the Labex Exploration Spatiale des Environnements Planétaires (ESEP). We also thank the CosmOrbitrap consortium and Dr Titaina Gibert for lending the Nd-Yag laser. N.C. thanks the European Research Council for funding via the ERC PrimChem (grant agreement No. 636829).

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