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# Titan tholins analysed by in situ mass spectrometry

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## Abstract

The main objective of the whole project developed in collaboration is to provide a better understanding of the chemical composition of Titan Tholins produced in the PAMPRE reactor (LATMOS) and thereby of their formation pathways.

## 1. Introduction

Numerous efforts are made in the community to determine the composition as well as to analyze the production pathways of Titan's aerosols laboratory analogs, called tholins. In the simulation chamber PAMPRE, built at LATMOS, such particles are generated in levitation (wall effects are thus limited) in a low pressure radiofrequency plasma. Up to now, the determination of the physical and chemical properties of these laboratory-produced tholins was achieved after their collection and their ex-situ analysis by several methods.
As a first example, as reported in [1], tholins were dissolved in a polar solvent and the soluble fractions analyzed. Their bulk composition was then determined but their insoluble part is still unknown. That is the reason why, a campaign at synchrotron SOLEIL on the DESIRS beamline has been performed in order to acquire fragment-free mass spectra of the chemical constituents of the tholins particles. Indeed, VUV soft-ionization technique was used to analyze the chemical composition of these complex organic particles
Other examples of studies of Titan's tholins can be mentioned. All of them were performed after the transfer of the aerosols to different analytical instruments ([4], [5]). Therefore, possible artifacts could have influenced the results. A challenging issue of our work is to perform the PAMPRE tholins' analysis in real time and in situ. With that purpose, a new device is currently developed at LATMOS in the frame of the SMARD program.

## 2. Preliminary approach: PEPICO and TPEPICO spectroscopy on the DESIRS beamline

A first campaign has been led on the DESIRS beamline. Tholins were analyzed ex-situ, but with setup presenting some analogies with the future online SMARD project.
The experiments on chemical analysis of tholins aerosol using tunable VUV photons on the DESIRS beamline were carried out in january 2012. Tholins produced in the PAMPRE reactor with a $N_2$-$CH_4$ gaseous mixture containing 5.0±0.1% of methane at a flowrate of 55.0±0.1 sccm were studied. First, number, concentration and size distribution of tholins aerosol were determined by Scanning mobility particule Sizer (SMPS). A bimodal size distribution was highlighted with 2 median diameters at 50 and 360 nm. As in a previous study performed on other solid particles [2], after sampling the tholins via a lens system, those were vaporized using a thermal desorption module (TDM) of the DELICIOUS 2 spectrometer. At the reached temperature (553 K), mass spectra have been recorded at different photon energy between 8 and 12 eV (Figure 1). For a specific ion signal, different isomers can be identified whose structure can be determined. Indeed, a comparison between the experimental and the calculated ionization energies (IE) of the main constituents of the tholins particules as well as their experimental/calculated photoelectron spectra can be done. Such work has been done for the m/z = 97 fragment obtained from the PEPICO spectrum. This

structure has been attributed to the NcyanoNNdimethylformamidine.
A first step concerning the molecular identification of the tholins insoluble fraction is then realized.

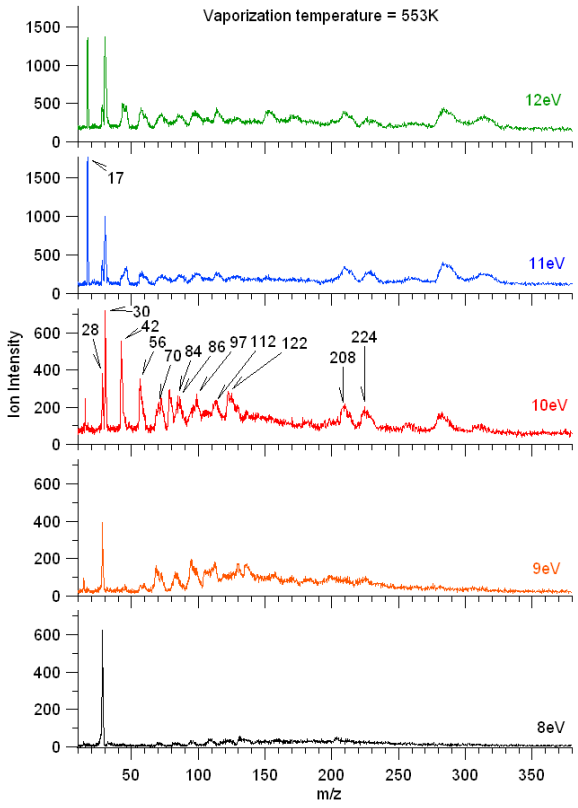



Figure 1: Mass spectra of Tholins aerosol recorded between 8 and 12eV (mass spectrum acquisition time = 11min) using a vaporization temperature of 553K.

This work appears to be nicely complementary to the following program also dedicated to the study of Titan's tholins. The later involves a new experimental device, based at LATMOS.

## 3. The SMARD program

A unique instrument (SPLAM- Single Particle Laser Ablation Mass Spectrometry) has been developed at LISA [2]. It allows determining in real time and in situ the characteristics (chemical composition together with granulometry) of nanometric aerosols. The later are introduced in the instrument using an aerodynamic lens system. Their detection and sizing are realized by using two continuous diode lasers operating at $\lambda$ = 403 nm. They are vaporized using a 10 µm $CO_2$ pulsed laser. The gas produced is then ionized by a 248 nm excimer laser. The formed ions are analyzed by a 1 m linear time-of-flight mass spectrometer in order to access to the chemical composition of individual particles. Recently, the instrument has been moved at LATMOS in order to determine the nature of insoluble part of the tholins created inside the PAMPRE simulation chamber. The whole program is named SMARD (a French acronym for Mass Spectrometry of Aerosols by InfraRed Desorption Laser).

## Acknowledgements

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