STRUCTURAL ANALYSIS OF TITAN'S THOLINS BY ULTRA-HIGH RESOLUTION MASS SPECTROMETRY. V. Vuitton[1], M. Frisari[1], R. Thissen[1], O. Dutuit[1], J.-Y. Bonnet[1], E. Quirico[1], E. Sciamma O'Brien[2], C. Szopa[2], N. Carrasco[2], A. Somogyi[3], M. Smith[3,4], S. Hörst[4] and R. Yelle[4], [1]Laboratoire de Planétologie de Grenoble, CNRS, Université J. Fourier, Grenoble, France, [2]Laboratoire Atmosphères, Milieux, Observations Spatiales, CNRS, Université Versailles St-Quentin, Université P. et M. Curie, Verrières le Buisson, France, [3]Department of Chemistry and Biochemistry, University of Arizona, Tucson AZ, USA, [4]Lunar and Planetary Laboratory, University of Arizona, Tucson AZ, USA.

The structure, composition and formation processes of the aerosols constituting Titan's haze are largely unknown. In situ chemical analysis by the Huygens probe proved to be unsuccessful and remote optical data do not allow retrieving information about their molecular structure. As a consequence, analogs (called tholins) are produced in laboratories by depositing energy in a gas mixture of nitrogen and methane. Tholins have been extensively analyzed with various analytical methods (IR, UV and Raman spectroscopy, NMR, pyrolysis-GC/MS, etc.) and appear to be hydrogenated carbon nitrides with a very complex structure [1].

Tholins react rapidly in ammonia-water solutions at low temperature, producing complex organic molecules containing both oxygen and altered nitrogen functional groups [2]. On Titan, aerosols sediment to the surface where they could react readily in transient aqueous pools that might be generated from time to time by impacts and volcanic processes. It is therefore of potential prebiotic interest to further characterize the laboratory analogs of these aerosols.

While the techniques mentioned above provide information on the bulk tholins, ultra-high resolution mass spectrometry is necessary to determine the atomic composition of each individual molecule making up the samples [3]. Moreover, tandem mass spectrometry (MS/MS) experiments can provide complementary information on the functional group inventory in tholins [4]. However, the MS/MS fragmentation spectra gathered so far are insufficiently complete to allow the derivation of structural information. Based on these previous works, we propose here a systematic MS and MS/MS study in order to provide a more coherent and complete characterization of the structure of the molecules making up the soluble fraction of the tholins.

Our tholin samples are synthesized in a reactor called PAMPRE by exposing N_2-CH_4 gas mixtures with various CH_4 concentrations to a cold plasma discharge [6]. While tholins are usually synthesized on surfaces, in the PAMPRE reactor, tholins are produced in levitation in the plasma. This allows an excellent control over the growth conditions, and the tholins thus formed are very homogeneous.

The tholins are dissolved in CH_3OH [4, 5] and the soluble fraction is injected in a Fourier Transform LTQ-Orbitrap mass spectrometer by ElectroSpray Ionization (ESI). This method produces protonated (positive mode) and deprotonated (negative mode) ions. Several ions are selected and used as precursor ions in MS/MS experiments in the mass range of 50-300 amu. Collision Activated Dissociation (CAD) with He as collision gas in a quadrupole ion trap and High Collision Dissociation (HCD) with Ar as collision gas in an octupole are used to perform MS/MS experiments. Complementary MS/MS experiments will be performed with a Bruker 9.4 T FT-ICR mass spectrometer by laser desorption ionization (LDI) of the tholin powder. This technique will allow characterization of the entire sample and therefore confirmation that the chemical information retrieved when analyzing the soluble fraction provides a valuable insight of the bulk material.

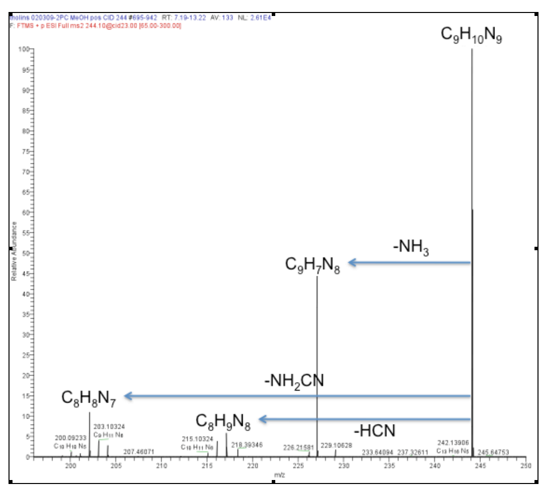

Fig. 1) Typical ultra-high resolution MS/MS (CAD) mass spectrum of tholins. The tholin sample was synthesized in the PAMPRE reactor from a mixture of N_2/CH_4 (98:2). The tholins were dissolved in CH_3OH and injected in the Orbitrap by ESI. The parent ion ($C_9H_7N_8^+$) fragments into 3 major daughter ions, showing loss of NH_3, HCN and NH_2CN.

Tandem mass spectrometry of standard molecules of general formula $C_xH_yN_z$ having structures (aliphatics, aromatics, heterocycles) and chemical functionalities (azines, nitriles, imines, amines, etc.) similar to those expected in the tholins will also be performed. Analysis of the fragmentation patterns will allow to retrieve some generic rules for the fragmentation of specific functional groups. These rules will be used as a basis to interpret the results of the tholins MS/MS experiments and will lead us to possible structures for the tholins.

These results highlight the importance and necessity of ultra-high mass resolution, accurate mass measurements and tandem mass spectrometry (MS/MS) experiments for a more coherent and in-depth characterization of complex organic solids. In the context of a return to Titan, development of ultra-high resolution ($m/\Delta m > 10^5$) mass spectrometers for spaceflight capable of *in situ* sampling of the atmosphere is mandatory.

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