



## Comparison of soluble and insoluble organic matter in analogues of Titan's aerosols

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### ABSTRACT

Titan, the biggest moon of Saturn, has a thick atmosphere which presents similarities with the one thought to be on Earth at its beginning. The study of Titan's photochemical haze is thus a precious tool in gaining knowledge of the primitive atmosphere of Earth. The chemistry occurring in Titan's atmosphere and the exact processes at act in the formation of the hazes remain largely unknown. The production of analogs samples on Earth has proved to be a useful tool to improve our knowledge of the aerosols formation on Titan. Such solid organic analogs samples, named tholins, were produced with the PAMPRE experiment (French acronym for Aerosols Microgravity Production by Reactive Plasma). PAMPRE tholins were found to be mostly insoluble, with only one-third of the bulk sample that can be dissolved in methanol. This partial solubility limited the previous studies in mass spectrometry, which were done only on the soluble fraction. The goal of the present study is to compare the two fractions of PAMPRE's tholins (insoluble and soluble) using a ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometer (FTICR) equipped with a laser desorption/ionization source. Using modified Van Krevelen diagrams, we compare the global distribution of the molecules within the samples according to their Hydrogen/Carbon ratio and Nitrogen/Carbon ratio. Major differences are observed in the molecular composition of the soluble and the insoluble fraction. The soluble fraction of tholins was previously identified as a set of polymers of average formula  $(C_2H_3N)_n$ . In this work we observe that the insoluble fraction of tholins is comprised of a significantly different set of polymers with an average composition of  $(C_4H_3N_2)_n$ .

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## 1. Introduction

Titan, the largest satellite of Saturn, is surrounded by a thick atmosphere rich in nitrogen with a small percentage of methane. The chemistry in this atmosphere leads to the formation of a complex smog due to the radicalization and recombination of the two gases upon interaction with solar UV photons and charged particles from Saturn's magnetosphere. The observations of the Cassini mission and the information obtained during the landing of the Huygens probe provided partial information about the composition of the aerosols. Pyrolysis of the aerosols by the ACP experiment aboard Huygens released mainly  $NH_3$  and HCN but was not sufficient to further elaborate on the structural composition of the aerosols be-

cause of the detection limit of the instrument (Fulchignoni et al., 2005; Israel et al., 2005; Niemann et al., 2005).

Titan's aerosols also represent an interest in astrobiology (Sagan et al., 2002) due to their peculiar formation and their organic complexity. Some analogs, called tholins, were produced on Earth to investigate the formation processes and the structure of Titan's aerosols (Cable et al., 2012; Imanaka and Smith, 2010; Somogyi et al., 2005; Szopa et al., 2006; Toupance et al., 1975).

Infrared (IR) spectroscopy analyses have demonstrated that tholins structure includes nitrile, amine, hydrocarbon and unsaturated functions (Cable et al., 2014; Coll et al., 1999; Gautier et al., 2012; Imanaka et al., 2004; Sciamma-O'Brien et al., 2017). Primary amines were also identified in tholins using laser-induced fluorescence with nonaqueous capillary electrophoresis (Cable et al., 2014). Additional analyses were performed on the soluble fraction of the tholins by mass spectrometry showing a polymeric structure (Bonnet et al., 2013; Gautier et al., 2016; Vuitton et al., 2010). First analyses with ultra-high resolution mass spectrometry

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try also brought to light repetition patterns ( $\text{CH}_2$  and HCN) in the tholins' soluble fraction (Anicich et al., 2006; He et al., 2012; Somogyi et al., 2005).

However, some tholins are not completely soluble in solvents such as methanol (Carrasco et al., 2009). This is the case of the tholins synthesized with the PAMPRE experiment, described below (Szopa et al., 2006). The soluble fraction of tholins obtained from this experiment represents only one third of the total material. Only this soluble fraction was analyzed with mass spectrometry so far, using electrospray ionization and photoionization (Carrasco et al., 2009). The soluble fraction provided numerous information about the general structure of these samples. Several studies compared various tholins to a set of polymeric structures based on a  $\text{CH}_2$ -HCN repeating unit, spreading from  $m/z$  100 to  $m/z$  800, as emphasized by the Kendrick mass defect diagram using HCN or  $\text{CH}_2$  normalization (Hughey et al., 2001; Kendrick, 1963). This explained the periodic nature of the mass spectra of tholins showing repeating ion clusters (Gautier et al., 2014; Pernot et al., 2010).

A previous study emphasized that IR spectrum of the soluble and non-soluble fractions of tholins were nearly identical (Carrasco et al., 2009). As a consequence, it has been postulated that both fractions had a similar molecular content, and that the difference of solubility was only related to the difference of mass of the molecules composing tholins, as larger molecules are expected to be less soluble. In the present study, we reexamine this insoluble fraction at the molecular level by using ultra-high resolution mass spectrometry.

## 2. Experimental

### 2.1. Sample production

Tholins were produced using the PAMPRE experiment and following the procedure detailed in previous publications (Gautier et al., 2011; Szopa et al., 2006). In this setup, the reactor is composed of a stainless steel cylindrical reactor in which the Radio Frequency – Capacity Coupled Plasma (RF-CCP) discharge is established by an RF 13.56 MHz frequency generator. The gas mixture, containing nitrogen and 5% of methane, is injected in the chamber as a continuous flow through polarized electrodes and then extracted by a primary vacuum pump to ensure that gases are homogeneously distributed. The plasma discharge is maintained at a pressure of  $0.9 \pm 0.1$  mbar and at room temperature.

### 2.2. Sample treatment for mass spectrometry analysis

In order to separate soluble and insoluble fractions, 4 mg of tholins were dissolved in 1 mL of methanol in a vial under ambient atmosphere. The vial was vigorously stirred for 3 min to dissolve the maximum amount of species. The brown mixture was then filtered using a 0.2  $\mu\text{m}$  polytetrafluoroethylene (PTFE) membrane filter on a filter holder. Of the filtered solution, the soluble fraction, was transferred in a glass vial. Half dilution with a 50/50 water/methanol mixture was performed just before analysis in order to be analyzed using similar conditions as previous studies by electrospray ionization. The PTFE membrane was then recovered, placed in a vial and left open under a neutral atmosphere of Nitrogen to evaporate the remaining methanol and avoid contamination. The insoluble fraction, recovered as a black powder from the membrane, was then analyzed by mass spectrometry. The global sample was directly analyzed avoiding any contact with solvents.

### 2.3. Mass spectrometry analyses

Different ionization methods can be used for the analysis of molecules in their solid state, especially Laser Desorption Ioniza-

tion (LDI). LDI-MS has already been used for the analysis of tholins (Gautier et al., 2017; Imanaka et al., 2004; Mahjoub et al., 2016; Sagan et al., 1993; Somogyi et al., 2012). It has also been used for the analysis of asphaltene, a fraction of petroleum non-soluble in pentane or heptane (Pereira et al., 2014; Sagan et al., 1993; Tanaka et al., 2004). In this work a LDI source is coupled with a Fourier transform ion cyclotron resonance mass spectrometer (FTICR) to compare the soluble and non-soluble fractions of tholins at the molecular level. A comparison between electrospray and LDI sources using the same analyzer parameters can be found in the supporting information (Figs. S1 and S2). In addition, LDI-FTICR was compared to LDI-TOF analyses (Fig. S1).

Previous works have demonstrated the significant differences in the molecules detected in tholins depending on the ionization mode used (Carrasco et al., 2009; Somogyi et al., 2012). For this work we chose to investigate only positive ionization as this is the one most widely used in the community for tholins analysis.

All analyses were performed on a FTICR Solarix XR from Bruker equipped with a 12 T superconducting magnet and a laser desorption ionization source (laser NdYAg 355 nm). The mass spectrometer was externally calibrated with a solution of sodium trifluoroacetate. Mass spectra were afterwards internally calibrated with confidently assigned signals yielding a mass accuracy below 300 ppb in the considered mass range. The soluble fraction was deposited on a LDI plate using the dry droplet method ( $5 \times 1 \mu\text{L}$  to ensure a good concentration of the sample). Insoluble fraction and the global sample were deposited using a solvent-free method, following a previously published procedure (Barrere et al., 2012). Mass spectra were recorded in positive mode at 8 million points with a sum of 500 scans, yielding a resolution of 1 500 000 at  $m/z$  150 and 500 000 at  $m/z$  500. The following instrumental parameters were implemented for the insoluble and total fractions: Plate offset 100 V, Deflector plate 210 V, Laser power 19%, Laser shots 40, Frequency of laser shots 1000 Hz, Funnel 1 at 150 V, Skimmer 1 at 25 V. The same parameters were used for the soluble fraction, except the laser power that was raised to 29% and the number of shots increased to 150. Fraction responses to the laser ionization were different for each fraction of the sample due to the molecular differences between each fraction, especially the hydrogen/carbon ratio. To obtain sufficient signal for the soluble fraction, it was necessary to increase the laser power compared to the parameter used for the non-soluble fraction spectra. A comparison between the global intensity of the spectra and the laser power used for the ionization is given in the supplementary material (Fig. S3). We then defined a laser power value for each fraction in order to obtain similar signal intensities. We fixed the value at 5% of laser power above the determined threshold – 19% and 29% for the insoluble and soluble fraction respectively. Peak picking was done with a signal/noise ratio of 5 and 0.01% of intensity. Molecular formulas were obtained using the SmartFormula tool from the Bruker Data Analysis 4.4 software with the following parameters: molecular formula  $\text{C}_{0-x}\text{H}_{0-y}\text{O}_{0-2}$ , even and odd electron configuration allowed, 0.5 ppm error tolerance.

It should be noted that while we try to limit oxygen contamination, tholins are known to be prone to oxidation when exposed to oxygen. Numerous discussions can be found in the literature on this point (see for example Carrasco et al., 2016 for a discussion on PAMPRE tholins). In our case, oxidation principally happens when tholins are exposed to the air during their collection after production. This exposition is intrinsic to the experimental setup used. Studies on plasma produced organic materials have shown that this oxidation happens within seconds of exposition of the sample to ambient air (Hörst et al., 2018; McKay, 1996; Swaraj et al., 2007; Tran et al., 2003). In the case of the sample analyzed here, the amount of oxygen contamination can be estimated through the detection of oxygenated molecules in the samples from the LDI-FTICR

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