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

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Abstract

The study of Titan's photochemical haze is thus a precious tool to gain knowledge on the primitive atmosphere of Earth. The simulation in the laboratory of analogs of this haze has proved itself to be a useful tool to improve our knowledge of the aerosols formation on Titan. Tholins (analogues of aerosols) produced by PAMPRE experiment were found to be mostly insoluble, with only a third of the bulk sample that can be solubilized in methanol [1]. This partial solubility limited the previous studies by mass spectrometry, which were done only on the soluble fraction. In this work, we compared both soluble and insoluble fraction of tholins in methanol using an ultra-high resolution mass spectrometer equipped with a Laser desorption ionization (LDI) source, to get full insights on these complex samples. Major differences are observed in the molecular composition of the soluble and the insoluble fraction [2].

1. Introduction

It was postulated that soluble and insoluble fractions of Titan's aerosols analogues might be identical at the molecular level and differed on their mass value [3]. Thanks to laser desorption ionization (LDI) source, which allows an ionization of both liquid and solid state, it is possible to compare all fractions.

The goal of this work is to highlight differences between each fractions of analogues of Titan's aerosols.

2. Method

2.1. Sample preparation for analysis

Tholins were produced using the PAMPRE experiment and following the procedure detailed in previous publications [4]. 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 minutes to dissolve the maximum amount of species. The brown mixture was then filtered using a 0.2 µm 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 mass spectrometry. 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.

2.2. Mass spectrometry analyses

All analyses were performed on a FTICR Solarix XR from Bruker equipped with a 12 Tesla superconducting magnet and a laser desorption ionization source (laser NdYAg 355 nm).

An extremely complex matter is revealed and graphical analysis is necessary to simplify the visualization of the data. Using modified Van Krevelen diagrams, the global distribution of the molecules is observed in each fraction according to

their Hydrogen/Carbon ratio and Nitrogen/Carbon ratio (Figure 1). From these experiments it appears that the molecular composition is very different between each fraction with the formation of different polymeric structures. Soluble and insoluble fractions while emerging from the same set of molecules at low m/z actually represent two families of compounds that are totally uncorrelated at higher m/z values.

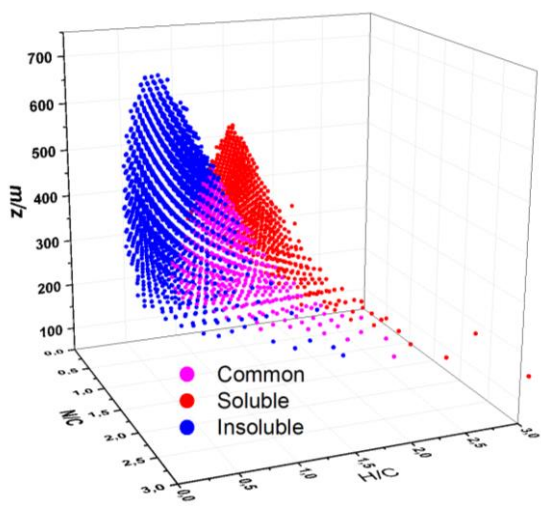


Figure 1: 3D modified Van Krevelen diagrams showing the comparison of (red) soluble species, (blue) insoluble species and (purple) common species in Tholins [2].

3. Summary and Conclusions

This work highlighted, for the first time, major differences between soluble and non-soluble part of analogues of Titan's aerosols. Thanks to the comparison of spectra and global data visualization, we proved that non-soluble fraction is much less hydrogenated than soluble one.

In addition, we bring to light a phenomenon which can occur on the surface of Titan: the fragmentation of aerosols due to their interaction with liquid lakes present on the surface.

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