Chemical analysis of dust produced in a N$_2$-CH$_4$ RF plasma discharge

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Abstract: In order to simulate the reactivity of Titan upper atmosphere, CCP RF plasma discharge in a N$_2$-CH$_4$ gas mixture is used. The soluble and the insoluble fractions in methanol and toluene are analysed. The soluble fractions are analysed by mass-spectrometry (APPI-TOF), whereas the total aerosols and the remaining insoluble fractions are analysed and compared by IR spectroscopy and SEM microscopy.

Keywords: dusty plasma, RF discharge, chemical analysis, mass spectrometry aerosols, Titan’s atmosphere

1. Introduction.
   In order to simulate the reactivity of Titan upper atmosphere, we have developed the experimental setup PAMPRE [1], a RF Capacitively Coupled Plasma (CCP) discharge in a N$_2$-CH$_4$ gas mixture allowing solid nitrogen rich particles production in suspension in the whole volume of the plasma. The solid particles produced during the experiment are called tholins and are considered as faithful analogues of Titan aerosols. The ACP experiment on Huygens probe is the only attempt to analyse in-situ the titan’s aerosols [2]. Now, only remote sensing measurements are available for the characterization of these aerosols. Very interesting results have been obtained by the DISR instrument on Huygens probe. Some optical properties of aerosols have been deduced from the study of scattered light [3]. Recent CIRS observation data from Cassini space probe around Titan shows an IR absorption signature at 3.4 µm [4]. With laboratory simulations, like the PAMPRE experiment, it is possible to produce analogues of Titan’s aerosols (names tholins) and the study their physical properties and chemical composition using high level analyse equipments. From comparison between observations and physical properties of aerosols produces in laboratory, it could be possible to reproduce real analogues of Titan’s aerosols. From chemical analysis of these analogues, the chemical composition of Titan’s aerosols could be found, and then, the chemical reactions chains leading to their formation in Titan’s atmosphere.

In this work we will present our recent results on the tholins chemical analysis.

2. Experiment.
   As mentioned before, tholins produced in CCP discharge at low pressure. In this device, the CH$_4$-N$_2$ gas mixture is injected continuously. Tholins are maintained in levitation between electrodes till their size reaches an upper limit. They are ejected out the plasma and are collected in a glass vessel to be analysed ex-situ.

In the present work; two different inlet percentages are chosen for the initial methane concentration in the plasma: 2% and 10%. Here after, the so produced sample are named respectively SA 98 and SA 90 referring to the initial amount of N$_2$ in the plasma. The latter concentrations simulate the range of methane abundances available in Titan atmosphere. Moreover these two initial concentrations allow us to study the competition between carbon and nitrogen in the plasma in order to explain a surprisingly important insertion of nitrogen in the dust particles.

Several analysis and observations are performed. The tholins are observed by SEM microscopy, their solubility is measured and the soluble fraction is analysed by high resolution mass spectrometry.

3. Solubility
   To determine their chemical composition, the produced particles have first been extracted in two different solvents: a polar one, methanol, and a non-polar one, toluene.

As expected, because of an important insertion of nitrogen in the particles quantified recently by elementary analysis [5], the aerosols are much more soluble in the polar solvent than in the non-polar one. However, we have been able to identify a small solubility of the dust in the toluene.

Moreover we have highlighted an important problem of definition of “solubility” in previous studies on tholins analysis [6-8]. It was defined as the soluble concentration obtained after partial dissolution of a tholins sample in a given solvent. This definition is adapted for a pure homogeneous compound but is inappropriate for heterogeneous samples. Tholins are strongly heterogenous. They are composed by thousands of
different species (as showed later by the APPI-TOF analysis) and each of them has its own proper solubility. We suggested then a better criterion to characterize and inter-compare the solubility of the solid heterogeneous samples which is to quantify the soluble mass fraction of the samples: i.e. the slope of the linear function (for low values) “dissolved mass” versus “total mass of the sample” (see figure 1).

We thus found a soluble mass fraction of respectively 20% and 35% for the samples SA 98 and SA 90 in methanol. In toluene a weak solubility of a few percents has been found, but is in the order of magnitude of the uncertainty on the value.

Even in a polar solvent such as methanol, most part of the organic matter remains insoluble (65% in the case of SA-90 and 80% in the case of SA-98). The reason for such an importance of the non-soluble fraction of the PAMPRE tholins comes likely from the growth process occurring in the plasma discharges. It seems that plasma process using levitation allows producing species containing molecules with strong chemical bonds, which are no longer soluble in any solvent. Hence PAMPRE tholins consist in molecules readily removable attached on a large and hardly insoluble nucleus.

4. Scanning Electron Microscopy (SEM) observations

In order to observe the effect of solubility on tholins morphology, they are observed by SEM. Same samples are observe before and after their dissolution in methanol. Figure 2 presents the SEM image obtained for samples produced with 2% and 10% of CH₄ into the plasma. The shape of the tholins is not modified by the previous liquid extraction and the sample shows again a regular distribution of spherical grains. The average diameter of the grains is possibly reduced in comparison with the initial sample before extraction (450 nm instead of 595 nm), but the reduction is not significant within the standard deviation on the size distribution. The preservation of the tholins global structure despite the application of an efficient extraction stress (35% of the organic matter has been pulled out in methanol for sample SA 90 for example) is in favour of the hypothesis of an external layer of soluble matter attached on a consistent insoluble nucleus. Indeed an interstitial localisation of the soluble matter would probably have affected the consistence of the grains when pulling them out of the structure.

5. Mass spectrometry analysis of the soluble fractions in toluene and in methanol

Taking into account solubility’s results, both soluble fractions (SF) of SA 98 and SA 90 in methanol and in toluene were analysed using APPI – QTOF mass spectrometer in positive ionization mode. SF in methanol analysis shows a complex spectrum (see figure 3) containing many massives made of regular clusters.
Similar clusters could be detected in toluene SF (Figure 4) at very low signal intensity. This might confirm a very small solubility in an apolar solvent.

For both SA.98 and SA.90 in methanol, the acquired mass spectra display ions from \( m/z \) 100 to \( m/z \) 800, organized in regular clusters, with a width of about 13.5-14 Da (see Figure 5). However as it can be shown on both spectra, the intensity of the observed massives are quite different. It seems that increasing CH₄ inlet percentage (SA.90) favours the formation of heavier species. Besides it appears that, the two samples consist in the same species but not with the same abundances.

5. Conclusion
We studied the chemical composition of aerosols produced by a RF Capacitively Coupled Plasma from a N₂ CH₄ gas mixture and representative of Titan’s atmospheric aerosols. We found that the produced particles are a strongly heterogeneous organic matter but that they present a very regular chemical structure. They consist in a hardly insoluble nucleus and a large amount of molecules almost insoluble in toluene but readily removable in methanol. No significant morphological change was noticed by Scanning Electron Microscopy (SEM) on the insoluble fraction after extraction by methanol, tending to prove that the extracted molecules were not supporting the solid spherical structures. Soluble fractions in both methanol and toluene solvents were analysed by mass spectrometry. It revealed a complex but well organised organic matter with a mass peak at every mass between 50 and 700 amu, regularly structured in mass clusters spaced out by about 13-14 amu.

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References