

# REVIEW AND LATEST RESULTS OF LABORATORY INVESTIGATIONS OF TITAN'S AEROSOLS

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**Abstract.** Titan, the largest satellite of Saturn, has an atmosphere chiefly made up of N<sub>2</sub> and CH<sub>4</sub>, and including many organics. This atmosphere also partly consists of hazes and aerosol particles which shroud the surface of this satellite, giving it a reddish appearance. The aerosols observed in Titan's atmosphere are thought to be synthesized at high altitudes (>300 km) and fall to the surface. Varying with temperature profiles, condensation phenomena take place in the lower atmosphere, about 100 km below. These solid particles, often called 'tholins', have been currently investigated for many years by laboratory scientists and physics modellers.

This paper assesses past research and results in different fields (elemental composition, optical constants, pyrolysis, particle size), highlighting interests and questions aroused by these studies. It also presents the latest results and advances, and concludes with existing problems and future pathways.

## 1. Introduction

Among the several approaches for the study of the chemical evolution of a planetary atmosphere, benchwork experimental simulation is a powerful tool. The study of the gaseous phase generated during simulation can provide information on the nature and relative abundances of the minor trace species which are expected, given the main composition of the atmosphere. The study of solid phase products can also yield insights on the chemical composition of the solid particles constituting atmospheric hazes. Such information can then be used as a precious guide for observational campaigns, and for theoretical modelings of the studied atmosphere. Moreover, such experimental aerosol analogues are useful for developing and calibrating instruments for in situ analysis of extraterrestrial atmospheres. Much has been documented about the gaseous phase products ever since experimental simulations were started. Some of these were specifically devoted to Titan, the largest satellite of Saturn (Chang *et al.*, 1979; Raulin *et al.*, 1982; Sagan *et al.*, 1992; Cabane *et al.*, 1995). It turns out that very little work has been published about the solid phase. Hence a need for systematic studies of these solid products synthesised during simulation experiments. This is particularly important in the case of Titan's simulations, due to a host of new observational data available about its atmosphere or which will be presently available in a near future, from ground or Earth-orbit observations, and, at the start of the new millennium, from the Cassini-Huygens mission.

After a brief comment on how such studies were initiated, our paper will critically review past research and results derived as related to the many aspects of the solid products that formed during experimental mimicking of the chemical atmospheric evolution of planets. These fostered particular studies of elemental composition, spectral properties, pyrolysis, particle size and shape. Scientific benefits and questions aroused by these studies will be worth emphasizing. The latest results that were gained and subsequent advances will then be presented, together with the current problems and foreseeable trends future research.

## 2. A Research Survey on Solid Phase Products Laboratory Simulation Experiment: From Sticky Brownish Residue' to 'Tholins'...

The origin of experimental laboratory simulation laboratory of the chemical evolution of a planetary atmosphere was the now classical epoch-making experiment performed by Stanley Miller (1953,1955). For the first time, with a view to simulating a planetary atmosphere (that of the primitive Earth), a mixture of gases ( $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ) was submitted to an electrical discharge. Many organic compounds were identified in the resulting gas phase, and a 'sticky brownish residue' was observed on the walls of the reaction vessel.

The first organic synthesis in a  $\text{N}_2/\text{CH}_4$  mixture was performed by Dodonova (1966), using an hydrogen discharge lamp to produce hydrocarbons and HCN. However, Chang *et al.* (1979) could not confirm out Dodonova's results related to HCN. After UV irradiation of  $\text{N}_2/\text{CH}_4$  gas mixture, they produced hydrocarbons but they could not detect any N-organic compound. However, it must be noticed that they used different pressure and wavelengths conditions from those used by Dodonova (1966).

The first study on a  $\text{N}_2/\text{CH}_4$  gas mixture using electrical discharge was developed by Sanchez *et al.* (1966). They obtained the build up of many organics, in particular HCN and  $\text{HC}_3\text{N}$ . There followed a wide range of experiments of this kind, some of which were specifically devoted to the study of Titan's chemistry.

By the end of the seventies, it was well established (Woeller and Ponnampereuma, 1969; Khare and Sagan, 1973) that ultraviolet or electrical discharge irradiation of  $\text{CH}_4$  rich mixtures and other reducing gases can produce not only gaseous organics, but also a reddish brown solid supposed to be organic heteropolymer.

In 1978 Sagan and Khare (1979) dubbed 'tholins' the variety of brown complex solid organics they had produced over the last decade by the irradiation (UV or electrical discharge) of cosmically abundant gas mixtures:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HCHO}$  and  $\text{H}_2\text{S}$ . The first form of the persistent solid they studied was produced by a spark discharge in a  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  (2.5%) mixture. Using pyrolysis-GC-MS, they found that its thermal dissociation temperature was approximately  $900^\circ\text{C}$ . This dissociation led to aliphatic and aromatic hydrocarbons, abundant nitriles and other N-compounds. They clearly found that this solid was not a polymer (the repetition

of the same monomeric unit). This study was in fact the first detailed chemical investigation of tholins. It was obvious that the properties of tholins depended on the energy source employed and on the initial abundances of precursors, but general physical and chemical similarities among the various tholins were also observed.

During these years the interest of the scientific community for Titan, the largest satellite of Saturn, was on the increase: a detailed review of the pre-Voyager data on Titan was published by Burns (1977) but the main information on this satellite was obtained from the actual Voyager encounters in November 1980 (Voyager 1) and 1981 (Voyager 2) (Gehrels and Matthews, (1984); Burns and Matthews, (1986); ESA, (1985)...). The collected data confirmed the presence of an atmosphere, allowed the determination of its vertical temperature and pressure profile and of its main constituents ( $N_2$  and  $CH_4$ ), and further they helped detect several trace constituents. Voyager data also gave important clues on the hazes and aerosol particles which shroud the surface of the natural satellite. The first suggestion that the Titan aerosols are complex was made in Sagan (1974). This new interest has buttressed laboratory studies of complex organic solids produced in  $N_2/CH_4$  mixtures, which in turn, has made many advances, using pyrolysis, elemental analysis, and the establishment of optical and spectral properties.

### 3. Elemental Composition and Physico-Chemical Characteristics of $N_2/CH_4$ Tholins

One of the goals of elemental composition studies is to determine the C/N ratio of tholins, because this ratio is an important indicator of the chemical processes involved in tholins build-up. Its determination in the case of Titan should give important insights on the photochemical haze-making processes. For example, as already emphasized by McKay (1996), the C (contained in  $CH_4$ )/N (contained in  $N_2$ ) ratio in the upper atmosphere of Titan is known (0.01). The ratio of C (coming from  $CH_4$  photolysis)/N (coming from  $N_2$  dissociation) is approximately 15, because of the easiness of  $CH_4$  photolysis (Toublanc *et al.*, 1995). But the major part of carbon is converted into light hydrocarbons, which will eventually condense and will not form tholins. It is then possible, considering the transformation of high molecular weight hydrocarbons into tholins, to estimate the haze production rate (Yung *et al.*, 1984). Taking into account elemental stoichiometry of tholins determined in the laboratory, we can thus provide information on N-containing components for photochemical models.

Only three sets of simulation experiments as related to Titan's atmosphere have conducted a systematic determination of the elemental composition of the solid products (Sagan *et al.*, 1984; Coll *et al.*, 1995; McKay, 1996). The C/N values derived from the elemental analysis of their solid phase ranges from about 1.93 (Sagan *et al.*, 1984) to 11 (Coll *et al.*, 1995), as shown on Table I. The four

Table I  
Simulation conditions and elemental composition of different samples of tholins

Experiment	Gas-flow through system	Cold temperature ( $\approx 100$ K)	Low pressure (few mbar)	Airtight sampling	Gross formula	Ratio C/N
Sagan <i>et al.</i> (1984)	Yes	No	Yes	No	$(C_2H_3N)_n$	1.93
Coll <i>et al.</i> (1995)	No	Yes	No	Yes	$(C_{11}H_{11}N)_n$	11
McKay (1996)	Yes	No	No	No	$(C_{11}H_{11}N_2)_n$	5.5

experimental conditions as described in the table are these of an hypothetical experiment very close of the conditions of Titan's aerosols formation.

The great discrepancy of these results is certainly due to the different techniques used in the corresponding simulation experiments.

- (1) The energy source is of course a major point, but it turned out to be similar in these different discharge experiments. Although the energy flux and total energy deposition may vary from one to another.
- (2) The pressure used for the experiment is also a paramount factor in the build-up of tholins. Indeed, it is remarkable that the two higher C/N ratios are found for synthesized tholins made in the high pressure experiments (C/N = 11 and 5.5 for Coll *et al.* (1995) and McKay (1996) respectively). This suggests that carbon atoms are more available under high pressure conditions (higher number of atoms per  $cm^3$ ); hence, a greater quantity of carbon is integrated into tholins. So the gas phase quantity of carbon would then appear to be the limiting factor in low pressure experiments.

Taken as a whole it is impossible to explain the large range of C/N values because of the important differences in pressure and temperature between each experiment. Systematic studies of the dose and composition dependance of tholins for different pressure and temperature gradients of initial gas reactant mixture would be now of prime interest.

- (3) The third point worth considering is the possible contamination by oxygen which can induce oxidation, hydrolysis and carboxylation. Among the three experiments of Table I, only one (Coll *et al.*, 1995) benefits from a solid product sampling procedure avoiding contamination of the sample due to reactions with atmospheric  $O_2$  and  $H_2O$  (Figure 1). This precaution seems to play an important role as this experiment gave a resulting elemental analysis (and then another C/N ratio) clearly different from the others.
- (4) Another important factor is the low temperatures. It is likely that compounds that could change the C/N ratio would condense at 180 K (Titan's stratospheric

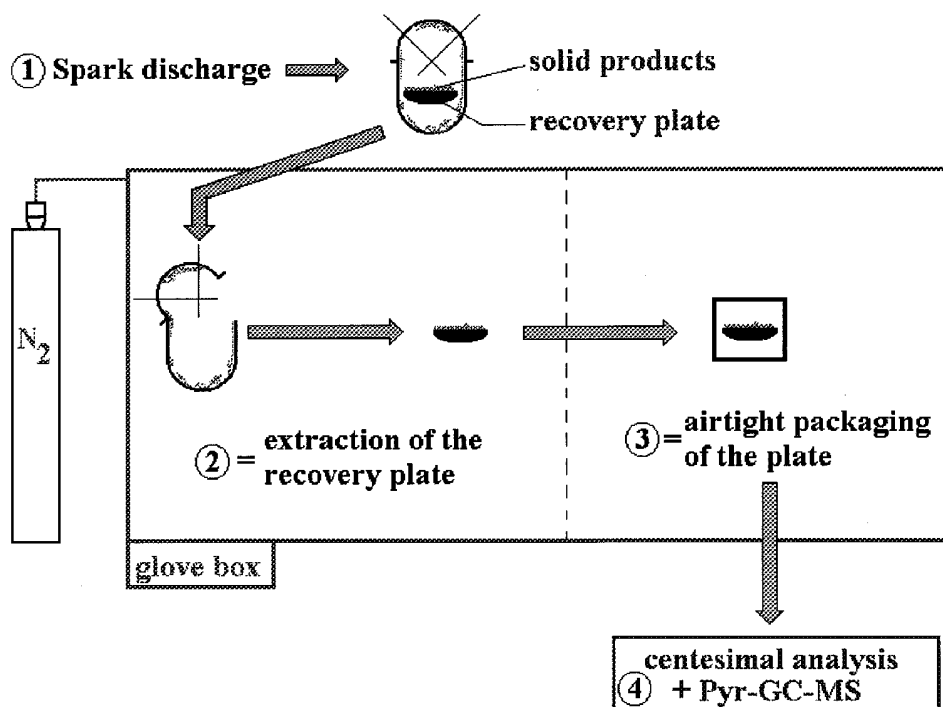


Figure 1. Description of the procedure for solid product sampling avoiding samples contamination with atmospheric gases

temperature) and not at room temperature. The Coll *et al.* results are the only low temperature results. However, it is probably more representative of Titan tholins.

As well as previous experimental simulations were performed with gas flow through the system, cold temperature and low pressure to be as closely as possible to Titan's environmental ones, future conditions will also need stringent procedures to avoid sample contamination due to reactions with atmospheric O<sub>2</sub> and H<sub>2</sub>O.

Another interesting point worth studying is the solubility of tholins, in particular in CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> liquids which are held as the constituents of the hypothetical lakes or ocean on Titan's surface. This physical characteristic is very interesting, because it is essential to model the behavior of Titan's aerosols, once they have reached the surface of the satellite, and in clouds.

McKay (1996) has found that the organic tholins are insoluble in liquid ethane, and probably in liquid methane. Although such tholins have not been obtained under low temperature and pressure conditions of Titan's stratosphere, these preliminary experimental results are of great interest. They show that the integration of nitrogen

atoms in the tholins could be an irreversible sink for gas phase nitrogen elements, because the sedimentation of aerosols in the reservoir at the surface does not release those atoms.

#### 4. Spectral Properties of N<sub>2</sub>/CH<sub>4</sub> Tholins

Since tholins obtained from experimental simulation with N<sub>2</sub>/CH<sub>4</sub> gas mixture provide good laboratory analogues of Titan's aerosols, the study of their spectral characteristics (in a very wide range of wavelengths) is of prime importance. It is, thus far, the only way to retrieve information on Titan's particles necessary to develop models and interpret the optical data already available on Titan.

In 1977, Scattergood and Owen found that the infrared spectrum of a reddish-brown condensed material produced in a N<sub>2</sub>/CH<sub>4</sub> mixture by irradiation showed characteristics of complex hydrocarbon mixtures, but in the presence of compounds containing nitrogen. The study of the ultraviolet-visible spectrum (250-700 nm) of these products confirms the presence of a nitrogen-containing material.

Podolak *et al.* (1979) have studied the photolysis of many mixtures, which all produced solid material. Using computerized models, they have tried to reproduce Titan's geometric albedo as a function of wavelength. They found that C<sub>2</sub>H<sub>4</sub> polymers present the best fit with the observed Titan's values. However corrected values of Bar-Nun *et al.* (1988) showed that Titan's aerosols could also be acetylene polymers. But Khare *et al.* (1994) recently show that neither ethylene or acetylene polymers can explain the observed optical properties of the Titanian haze.

The most complete study of optical properties has been achieved by Khare *et al.* (1984a). From soft X-rays to the far IR region they determined the spectral characteristics of organic tholins produced in a simulated titanian atmosphere (10% CH<sub>4</sub>-90% N<sub>2</sub>, pressure of 0.2 mbar, continuous electrical discharge). This pressure condition corresponds to the altitude of detection of the reddish aerosol haze in the upper atmosphere of Titan. However the temperature condition of Titan (170 K) was not used in the laboratory experiment which was carried out at room temperature. Under such conditions, a thick film of tholins, up to 20 μm thick, is produced in 3 days of continuous sparking. They determined real and imaginary values of the complex refractive index of Titan's tholins as a function of wavelength, from 0.01 to 1000 μm. The interpretation of the infrared spectrum permitted detection only of the signatures of C-H and N-H stretching, and the characteristic one of the nitrile group (C≡N).

Recently McDonald *et al.* (1994) studied in detail the tholins generated from N<sub>2</sub>(90%)/CH<sub>4</sub>(10%) mixtures, submitted to plasma discharges. After a DMSO treatment of the solid products, they collected its infrared spectrum. It presents the signatures of C-H bonds, probably due to CH<sub>2</sub> or CH<sub>3</sub> groups, N-H bonds, likely formed by primary and secondary amino-groups, with the possibility of C=N-H amino-group. From the same IR spectra, the authors also reported the presence of

the nitrile group  $C\equiv N$  and maybe of the isocyano group ( $C=N-$ ), together with that of acetylenic group ( $C\equiv C$ ), conjugated nitriles, alkenic group ( $C=C$ ), and dinitro group ( $N=N$ ).

More recently McKay (1996) has provided experiments in which initial mixtures have different  $N_2/CH_4$  ratios. An increase of  $CH_4$  percentage in the gas mixture produces solids which are darker and darker in the ultra-violet and violet, though transparent in the visible and near infrared. He observed an inconstancy in the optical properties (more than a factor 2 between experiments reproduced with the same initial gas mixture), like in the work of Khare *et al.* (1987) in which they reported optical properties of film made in pure  $CH_4$  at 0.13 mbar using a radio-frequency discharge: they also found that the results varied by factors of more than 2. McKay also observed a difference between these results and those from Khare *et al.* (1984a) which demonstrate that the optical properties of Titan tholin depend on the experimental conditions under which it is produced.

## 5. Molecular Analysis of $N_2/CH_4$ Tholins

This section assesses results of all indirect analytical techniques used to characterize Titan's tholins laboratory analogues.

First of all, Khare *et al.* (1986) corroborated the presence of complex nitriles ( $-C\equiv N$  group) in tholins. They obtained urea and amino-acids ( $RCH-COOH-NH_2$ ) when they submitted tholins ( $N_2/CH_4$ ) to an acid treatment ( $-C\equiv N + 2 HCl \rightarrow -NH_2 + Cl_2\dots$ ).

Analytical pyrolysis is a more recent technique used to analyze relatively high molecular weight compounds, such as oligomers or polymers, which are very difficult to study by other techniques. It has been extensively developed in parallel with powerful techniques of chemical analysis such as gas chromatography (GC) and mass spectrometry (MS) and is now widely used (Irwin, 1982). In analytical pyrolysis, samples are pyrolysed by rapid heating. Usually, the organic samples are heated at temperatures in the range 600–800 °C. The main goal of the pyrolysis is to form enough fragments of the volatile sample to be qualitatively and quantitatively analyzed by other techniques. The use of GC or GC-MS allows the separation of the pyrolysis fragments, their identification and the determination of their relative concentration. The distribution of the fragment helps identify the nature and structure of the initial sample.

Khare *et al.* (1984b) carried out the first published pyrolysis of Titan's tholins, although they included oxygen atoms. They found alkanes, alkenes, many nitriles, aromatic hydrocarbons, alkylbenzenes and other compounds (indene, pyrrole...) in the pyrolysis compounds. The complete table is reported in Figure 2.

Thompson and Sagan (1989) have argued that tholins can be formed by polymerization reaction of nitriles with unsaturated and radical species. This hypothesis can lead to a substructure shown on Figure 3. In fact there is evidence of a central

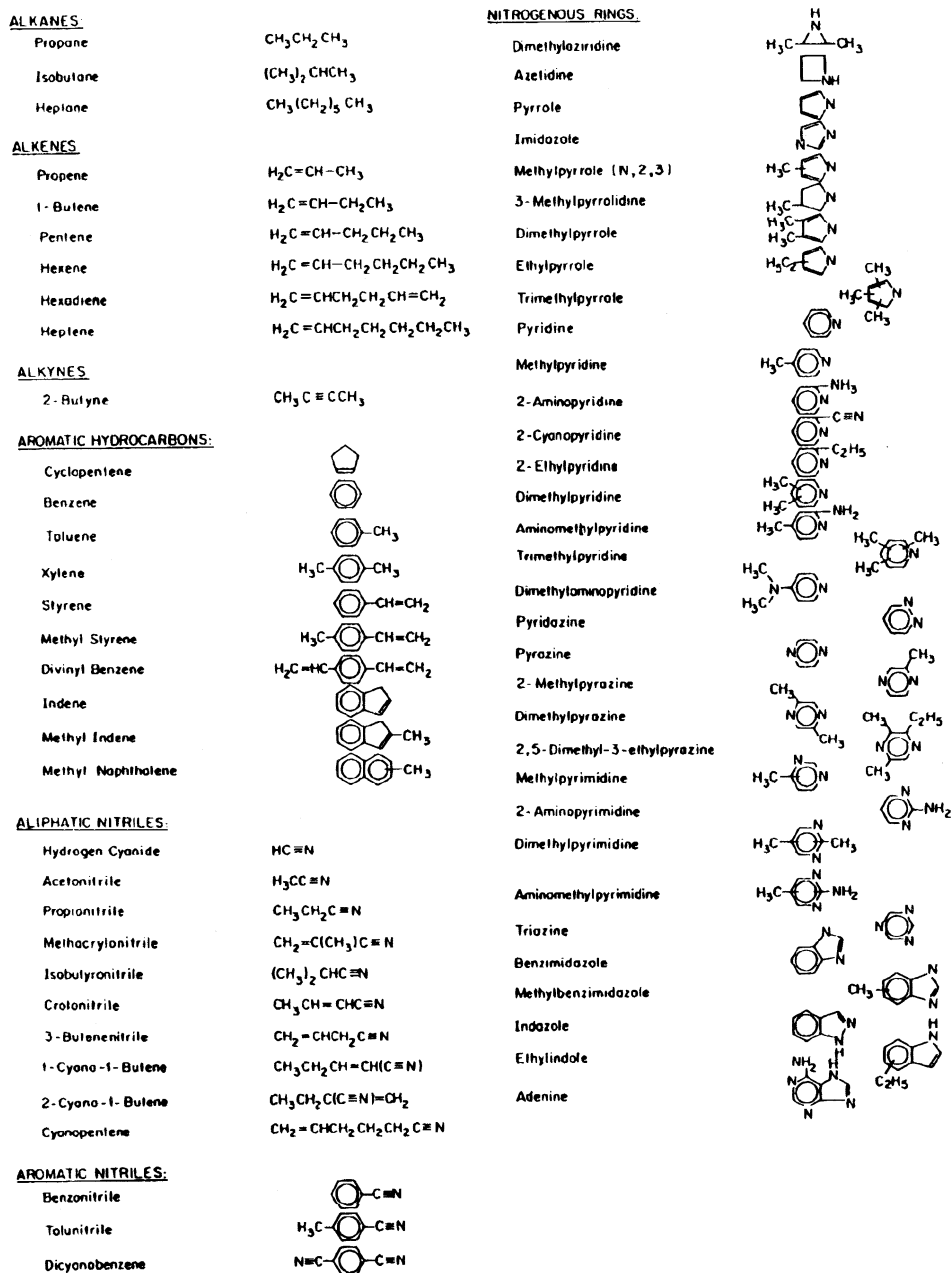


Figure 2. Results of PY-GC-MS from Khare *et al.*, *Adv. Space Res.* 4, 59.

moiety with the empirical formula  $(\text{HCN})_n$  in Titan tholin (McDonald *et al.*, 1994) although this is not poly-HCN (Khare *et al.*, 1994). But this synthetic scheme was not intended to take into account the presence of many hydrocarbons in gaseous



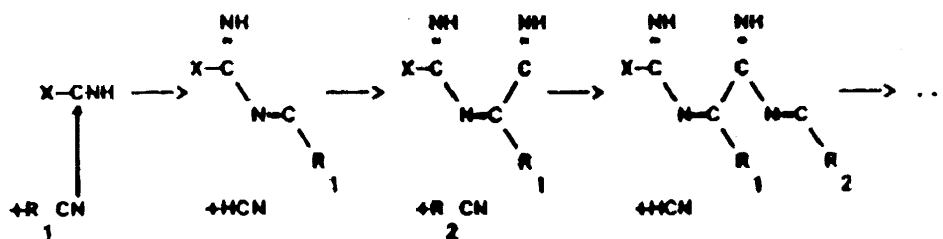


Figure 3. Theoretical reaction scheme of the 'polymerization' for a  $N_2/CH_4$  tholin proposed in W. R. Thompson and C. Sagan (1989), *Origins of Life* 19, 503.

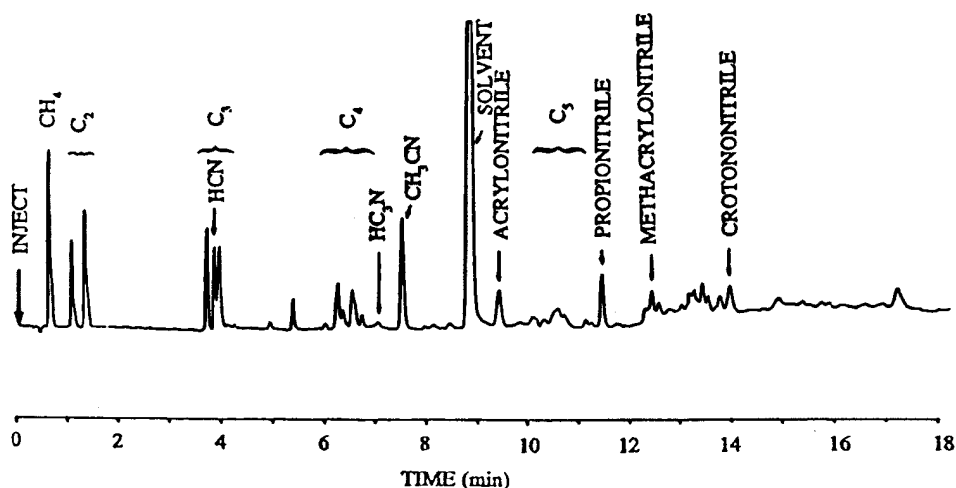


Figure 4. Pyrolysis gas chromatography of solid product obtained after 4 hr sparking in  $N_2/CH_4$ . Pyrolysis:  $600^\circ C$  for 5 s. From F. Raulin *et al.*, (1992), *J. of Brit. Interplanetary Soc.* 45, 257.

phase, like  $C_{2n}H_2$  molecules (deVanssay *et al.*, 1995). This will require separate, but not implausible, pathways.

Similar studies have been made by Raulin *et al.*, (1992). Figure 4 shows a GC-pyrogram, obtained after heating solid products at  $600^\circ C$  resulting from sparking  $N_2/CH_4$  gas mixtures. It includes N-containing groups but at a relatively low concentration. The carbon chains are saturated and unsaturated. These results show that the main part of N included in tholins comes from nitriles.

More recently, Ehrenfreund *et al.* (1995) performed the pyrolysis of solid products synthesized at Cornell University from high energy electrons beaming of  $N_2-CH_4$  gas mixture. Measurements were carried out by Curie-point-GC-MS and by temperature-resolved in-source Pyrolysis-MS to reveal the composition and evolution of the products dissociation temperature, and to understand the relationship between the gaseous atmosphere phase and the solid products. Such pyrolyses, in the case of the solid residue from the irradiation of a  $N_2(90\%)/CH_4(10\%)$  mixture, results in the primary pyrolysates being (Figure 5) HCN, acetonitrile, acrylonitrile,

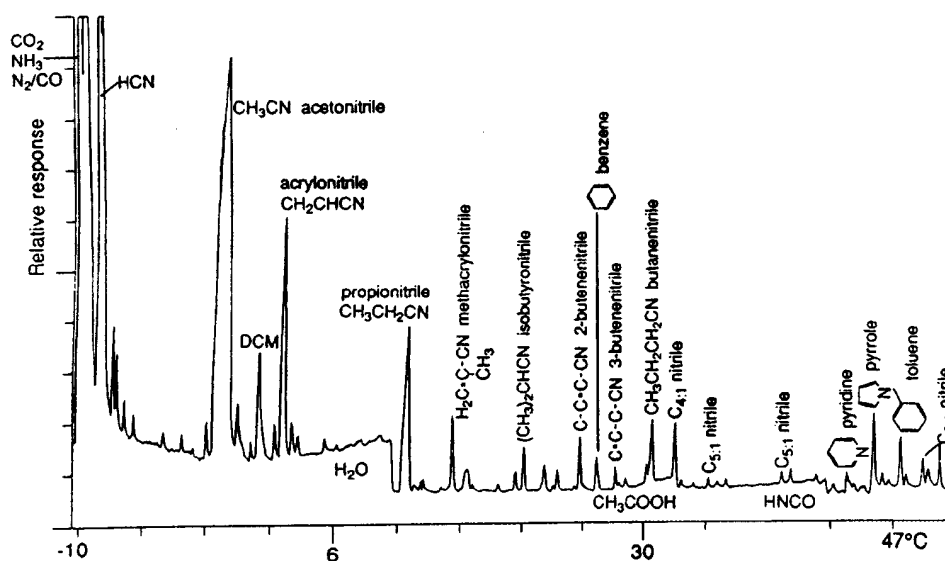


Figure 5. High resolution PyGC/MS of  $N_2/CH_4$  tholin. From Ehrenfreund *et al.*, *Adv. Space Res.* **15**(3), 335.

propionitrile and many longer branched chain and unsaturated isomeric nitriles. No saturated hydrocarbons are present, but benzene, pyrrole, pyridine, pyrazine, pyrimidine and alkylated homologues as small components have been observed. Several O-compounds such as  $H_2O$ , acetic acid and  $HNCO$  are also detected; this indicates that the solid sample has been contaminated by air during its recovery and when sampled in the Pyr-GC-MS system.

A similar program is under development at LISA (Coscia *et al.*, 1995). Pyrolysis-GC-MS technique is used to determine the nature of the organics in condensed phases, obtained after electron bombardment of  $N_2-CH_4$  gas mixtures. Pyrolysis is performed with ovens which are models of the ACP (Aerosol Collector Pyrolyser) experiment (Israël *et al.*, 1991; Raulin *et al.*, 1992). This instrument will fly on the Huygens probe of the Cassini-Huygens mission which will reach the Saturn system in 2004.

In particular, the last sets of experiments were carried out with a mini-oven especially designed to perform scientific validation and laboratory investigation of the ACP oven subsystem. This mini-oven has a volume of 6 ml. It is heated by a thermocoax, with a maximum temperature of  $900\text{ }^\circ\text{C}$ ; this gives a maximum temperature of  $600\text{ }^\circ\text{C}$  for the metallic filter which retains the sample to be pyrolysed. This maximum temperature can be reached within 3 min. Using the glass reactor described above, five irradiations of about 4 hr each were performed. Between each irradiation, the gas phase was removed from the reactor and replaced by a new gas mixture of  $N_2(90\%)/CH_4(10\%)$  at 900 mbar total pressure. During all irradiations, the bottom part of the reactor was cooled by liquid nitrogen.

After irradiation, the reactor was opened in a glove box overpressurized with nitrogen and where the filter has been previously introduced. The collected solid samples were crushed on the filter, and the filter was kept in confinement in the oven. This oven was pumped out after being connected to the GC-MS. Because of the use of this glove box filled with nitrogen and because of the low leak rate ( $10^{-3}$  mbar l s<sup>-1</sup>) of this oven model, we can be sure that no contamination on the filter coming from oxygen ever persists.

The chromatographic conditions were chosen to analyze mainly hydrocarbons from C4 to C10 and N-compounds. A Saturn II GCMS from Varian Company was used with helium, as a carrier gas, at an inlet pressure of 1.6 bar. The chromatographic capillary column was a CP-Sil-5 CB column of 25 m length, 0.15 mm inside diameter and 1.20  $\mu$ m thickness from Chrompack Corporation. The column temperature was:

- 30 °C during 20 min.
- From 30 to 150 °C during 30 min (heat rate: 4 °C min<sup>-1</sup>).
- 150 °C during 10 min.

The chromatogram of the synthesized solid phase obtained by GC-MS analysis, previously pyrolysed and transferred to the GC-MS system, shows the presence of many organic compounds: hydrocarbons (mostly unsaturated, including cyclic and aromatic), nitriles and pyrroles (Figure 6). According to their mass spectra, 23 gross formulae of more than 25 GC peaks, labeled on the pyrogram by a given number, are reported and the possible isomers according to their mass spectra are presented.

It immediately appears that no oxygenated compound can be detected. The laboratory process, by the use of a glove box filled with nitrogen and an airtight pyrolyser, is efficient in preventing oxygen contamination of the synthesized solid phase.

The main pyrolyzates are monoaromatic hydrocarbons: benzene (12), toluene (16), C2 substituted benzene (17 and 18) and C3 substituted benzenes (19, 21, 22). Two explanations can be put forward for such distribution:

- These monoaromatic hydrocarbons could be the major constituents of the solid phase.
- Observing a bi-aromatic hydrocarbon on our pyrogram (23) and considering the chromatographic conditions (no correct observation of the polyaromatic hydrocarbons is possible), these monoaromatic hydrocarbons could be the pyrolysis products of polyaromatic hydrocarbons constituting the solid products. This hypothesis is supported by the presence of bi-aromatic hydrocarbons on the chromatogram, and the possible presence of higher molecular weight HAP, which are not detectable under the chosen chromatographic conditions. It is also confirmed by the results of previous studies with anthracene. With the

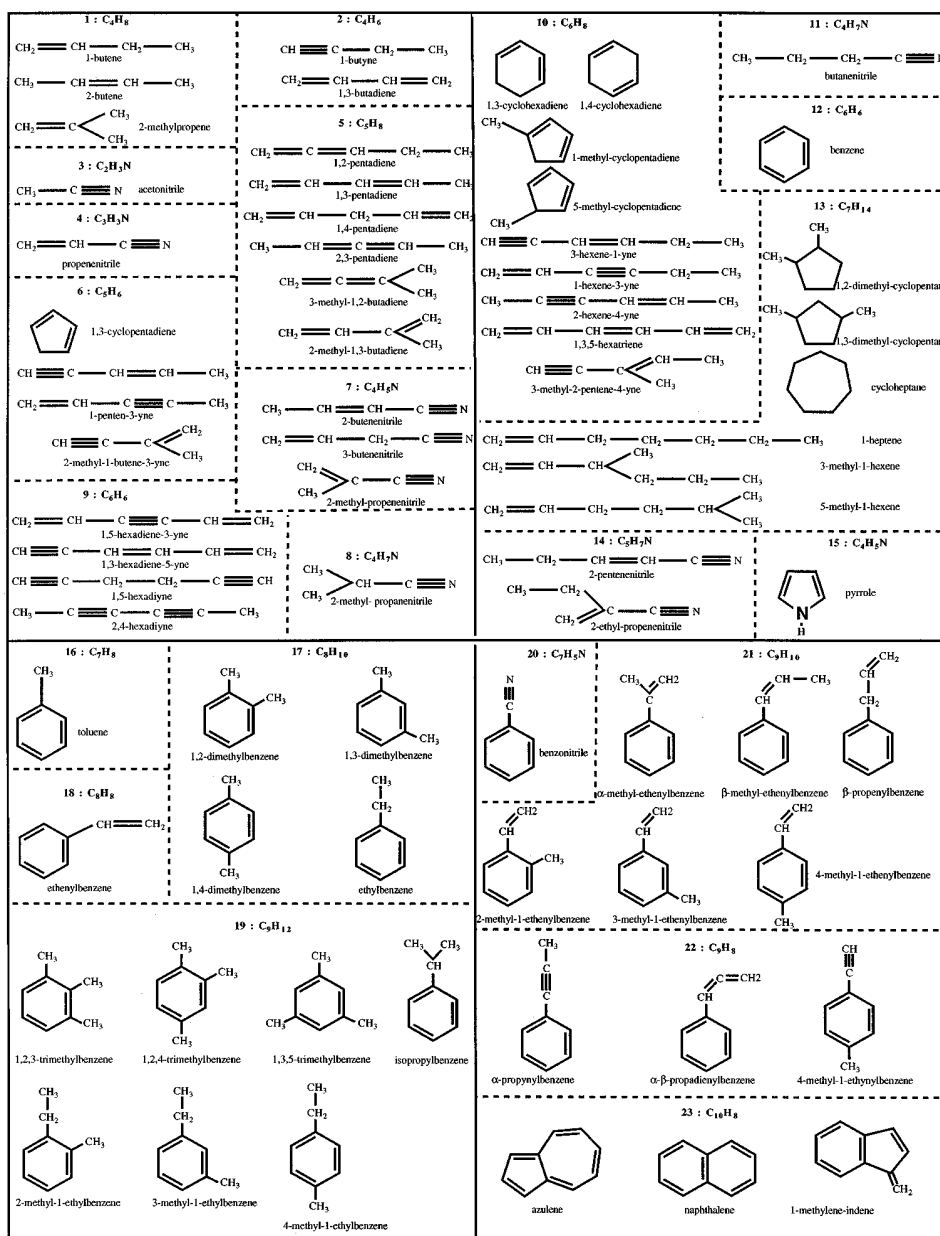


Figure 6. Gross formulae of the compounds detected by Pyr-GCMS and possible isomers according to their mass spectra.

same pyrolyser, anthracene is broken down at 600 °C into benzene, toluene, ethenyl-benzene and C<sub>8</sub>H<sub>10</sub> isomers. Polyaromatic hydrocarbons are decomposed at 600 °C into benzene and into monoaromatic hydrocarbons.

A small amount of benzonitrile is also present in the pyrolyzates. It can be, like all monoaromatic hydrocarbons, produced by the thermal breakdown of polyaromatic compounds including nitrogen atoms. Most of the other nitriles detected have also been identified in the gas phase after irradiation. However, it is difficult to determine whether the source of these compounds is thermal desorption from solid phase or thermal decomposition of heavier molecules. Nevertheless, it is interesting to note that Sagan *et al.* (1993) found that laboratory tholins contained  $\sim 10^{-4}$  g of polycyclic aromatic hydrocarbons per gram of tholins by using a specific PAHs detection system.

## 6. Structure of Aerosols Particles

Bar-Nun *et al.* (1988) experimentally studied the shapes and the sizes of photochemically produced aerosol particles of polyacetylene, polyethylene, and polyhydrogen cyanide. They diluted 10 torr of  $C_2H_2$ ,  $C_2H_4$  or HCN in 200 torr of argon, at room temperature. The irradiation was made by a low pressure Hg-lamp (184.7 and 253.7 nm).

All of the individual particles produced were found to be perfectly spherical and semi-liquid. The size distribution of the polyacetylene particles (Figure 7a) shows a radius range between 0.1 and 1  $\mu m$ . The absence of polyacetylene particles radii smaller than 0.1  $\mu m$  suggests a rapid growth of the spherical polymer particles by addition of monomers, or by agglomeration of the smaller, more liquid, particles into perfect large spheres. The polymerization of  $C_2H_2$  is faster than the one of  $C_2H_4$  or HCN: when six spherical particles may be found in acetylene polymer particles, no aggregates are formed with HCN and  $C_2H_4$ .

Scattergood *et al.* (1992) have irradiated the same molecules (0.13-1.3 mbar) diluted in  $N_2$  ( $\approx 70$  mbar) with same energy source. The results obtained are similar to those of Bar-Nun *et al.* (1988): only acetylene irradiation produces aggregates of spherical particles. The mean diameter of the particles is 0.6  $\mu m$ , and the aggregates may contain two to ten spherical particles. However 80% of the particles found in these aggregates are non-spherical but near-linear.

DeVanssay (1994) performed observations by electron microscopy of tholins produced during  $N_2/CH_4$  simulation experiments. The novelty of these observations was that the observed particles were directly produced in a  $N_2/CH_4$  mixture, and not synthesised from pure compounds identical to those produced during the irradiation of this gas phase mixture, such as  $C_2H_2$ , HCN... as in previous studies (Bar-Nun *et al.*, 1988, Scattergood *et al.*, 1992). Two analytical techniques have been used: transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Because TEM has a higher resolution power than SEM, it is possible to observe particles smaller than 0.1  $\mu m$ . SEM provides a better access to the morphology and the granulometry of micronic size particle.

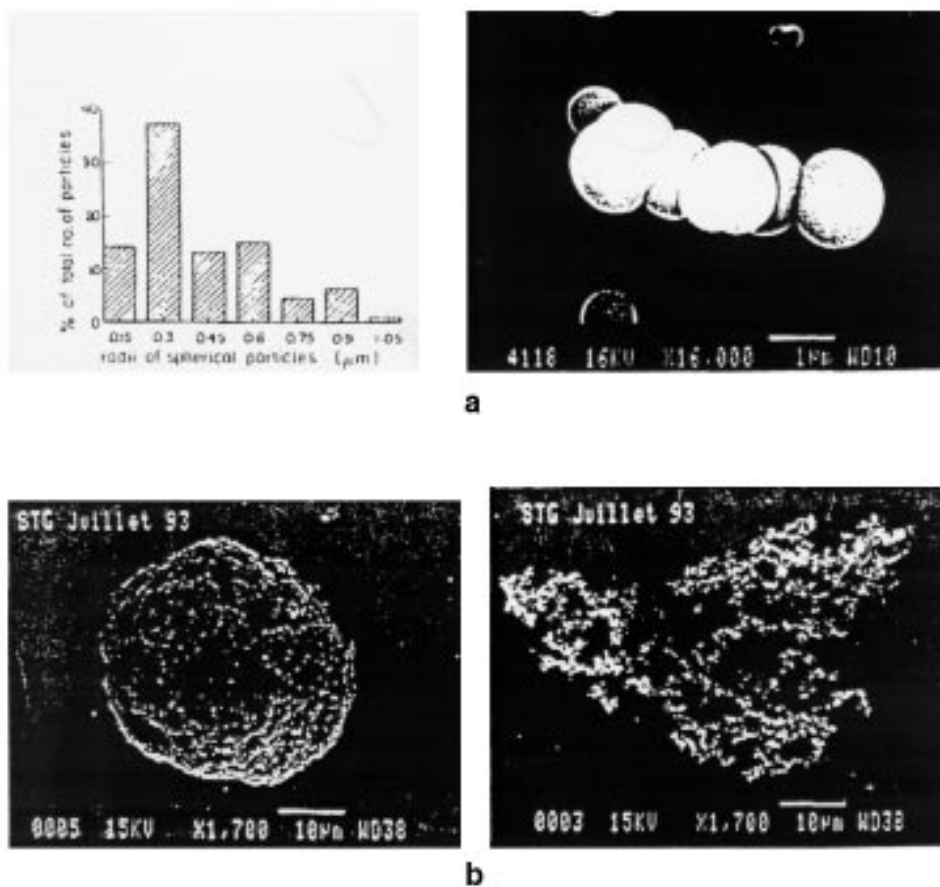


Figure 7. (a) Size distribution of the photochemically produced single polyacetylene aerosol particles and an aggregate of such a particle. From Bar-Nun *et al.*, *J. Geophys. Res.* **93**, 8383. (b) Two types of aggregates observed by de Vanssay (1994).

These observations have first demonstrated that elemental particles are spherical or quasi-spherical, seldom individual but often in ramified or linear aggregates. Their mean diameter is in the 0.05 to 0.5  $\mu\text{m}$  range, and their structure looks like those described by Scattergood *et al.* (1992). The data have also demonstrated that the solid products obtained during simulations are mainly a pile of quasi-spherical particles. These piles have two possible appearances (Figure 7b):

- One is a big spherical structure (diameter  $\approx 40 \mu\text{m}$ ) of micro-spherical particles, covered by a filamentous veil.
- In the second case the structure is more linear and smaller than in the previous case.

## 7. Assessment of Research

The aerosols observed in Titan's atmosphere are thought to be synthesised photochemically at high altitudes ( $>300$  km) and fall to the surface. According to the temperature profile, condensation phenomena take place in the lower atmosphere, below about 100 km.

Laboratory simulation of Titan's aerosols is complementary to modeling and remote sensing; the latter give information about distribution, particle size and optical properties of the photochemical aerosols, both in the upper and the middle atmosphere of Titan (Hunten *et al.*, 1984; Samuelson *et al.*, 1985). Modeling is a powerful tool to approach the micro-physical processes which govern the behavior and evolution of the particles, i.e.: condensation, coagulation, diffusion and sedimentation. However the development of such models requires the availability of many physical and chemical data on the aerosol particles. These necessary data can be obtained from experimental simulation in the laboratory, as described above, several are, indeed, already available. They concern:

**Solubility:** as discuss before, we know that tholins are insoluble in liquid ethane, and probably in liquid methane (McKay, 1996). These results are in good agreement with Raulin's thermodynamic modeling (1987) of the solubility of organic compounds, interesting Titan's environment, monomers as well as polymers, in  $C_2H_6/CH_4/N_2/Ar$  liquid mixtures. Such results have direct implication on the modeling of condensation phenomena.

**Chemical composition:** as indicated above, the knowledge of C/N ratio of the material constituting Titan's haze is of prime importance for understanding the process which drives its formation. It provides useful constraints in the development and solving of photochemical models. In addition the number of N-atoms by tholin molecule is an interesting parameter, because the production of tholins on Titan is a major sink for gaseous N but not for gaseous C (McKay, 1996). Vertical atmospheric profiles of the concentration of species like HCN, for example, could be modified by such a sink. But chemical composition seems to be very dependent on aerosols initial conditions of creation.

**Optical properties:** the determination of the optical properties of Titan's tholins by Khare *et al.* (1984a) had very strong implication in Titan's aerosols modeling. These laboratory data have been widely used for radiative transfer calculations and photochemical models. However, it must be emphasized that the optical properties of tholins vary considerably from one simulation experiment to another. Comparison between Scattergood and Owen (1977), Khare *et al.* (1984a), Sagan *et al.* (1984) and McKay (1996) data show that optical properties of the solid products formed during the experimental simulation strongly depend on the nature of the energy source and  $CH_4/N_2$  ratio in the initial gas mixture. In addition, it would be better to carry out such optical measurements in absence of any air-contamination ( $O_2$ ,  $CO_2$  and  $H_2O$ ) of the solid sample, because it is not fully demonstrated that

such potential contamination could not markedly change the optical properties of the studied solid.

Some microphysical models (McKay *et al.*, 1989, Toon *et al.*, 1992, Rannou *et al.*, 1996), using observations, computed the geometric albedo of Titan and determined the optical properties of the haze. The results obtained for the refractive indices of tholins produced in laboratory (Khare *et al.*, 1984a) are similar (Sagan *et al.*, 1992). The Titan laboratory analogues are then well representative of the titanian haze material.

Particle size: many measurements by remote sensing (spectroscopy, polarization) gave information about particle sizes of Titan's hazes. One of the problems concerning the aerosols has been to reconcile polarization and brightness measurements. Pioneer 11 and Voyager have measured large single-scattering polarization near  $90^\circ$  phase angle which, for spherical particles, implies a radius lower than  $0.1 \mu\text{m}$  (Tomasko and Smith, 1982; West *et al.*, 1983). On the other hand, Voyager 1 observations of high phase angle brightness have indicated that particles at the top of the haze must have radii greater than  $0.2 \mu\text{m}$ , this size limit being relatively insensitive to the particle detailed shape (Rages *et al.*, 1983). West and Smith (1991) have calculated that the presence of aggregates of small number ( $\approx 8$ ) of spherical particles, which they called monomers, can account for most of those observations with a diameter of  $\approx 0.12 \mu\text{m}$ . Aggregates observed by Bar-Nun *et al.* (1988), Scattergood *et al.* (1992) and deVanssay (1994) are compatible with these values.

Cabane *et al.* (1992; 1993) have then elaborated a micro-physical model of Titan's aerosols (above the condensation region) in which aggregate particles are considered. In their model, the growth of the particles can be divided into two stages. First, in a region near the altitude of photochemical synthesis, spherical particles ( $< 0.1 \mu\text{m}$ ) are formed by accretion of newly-synthesized very small particles ( $\approx 1 \text{ nm}$ ). In the second stage, the settling becomes effective. Below the region of synthesis, the aerosols distribution is close to semi-modal (a single size at each altitude) and coagulation occurs mainly between particles of about the same size, thus forming aggregates of the type of West and Smith (1991), corresponding to aggregates observed during laboratory simulations. The retrieved profile of the effective radius as a function of visible optical depth is in good agreement with Voyager observations.

## 8. Conclusions

Several of the conditions of a real planetary atmosphere cannot be accurately reproduced in the laboratory. Due in particular to the absence of vertical temperature and pressure gradients, and to the presence of wall effects, laboratory experiments have strong limitations in simulating a real atmosphere. Nevertheless, experimental approaches provide useful information on the nature and relative abundances of



trace compounds likely to be present in the studied atmosphere. Moreover, the solid products, also formed during the experiments can efficiently mimic the atmospheric aerosols. This is particularly relevant in the case of Titan's tholins. The role of atmospheric particles in the behavior of Titan's atmosphere is so crucial that studies on laboratory analogues of Titan's aerosols are of prime importance to model the observation of the satellite, through the use of their optical properties and structure. Until the ACP and GC-MS experiments on board the Huygens probe of the Cassini-Huygens mission respectively collect and analyze Titan's aerosols, they are so far the only way of getting such data.

All the investigation fields have not made the same advances; the results of Sagan *et al.* (1984), Cabane *et al.* (1995) and McKay (1996) demonstrate that there is significant diversity in tholins production. In fact it appears that the diversity of tholins production modes is a barrier to the complete understanding of the organic aerosol phase of Titan. This diversity takes into account:

- The CH<sub>4</sub>/N<sub>2</sub> ratio in initial gas mixture.
- The choice of energy source and its intensity.
- The pressure and temperature of the initial mixture.
- The contamination of the samples by the ambient atmosphere of the laboratory (oxygen, carbon dioxide and water vapor).

In addition, it is clear that detailed chemical analysis of tholins should require more diversified, soft and efficient tools. In that field, the systematic involvement of techniques like those used by Liebman *et al.* (1995) for organic analysis of HCN polymers: solid-state nmR spectroscopy (<sup>13</sup>C and <sup>15</sup>N), FTIR-PAS (Fourier Transform Infrared – Photoacoustic spectroscopy), SFE (Supercritical Fluid Extraction) with interface to FTIR-mic (FTIR-Microscopy), DIP-MS (analytical Pyrolysis Direct Insertion Pyroprobe) could bring many new and complementary information on the molecular structure and processes of formation of tholins.

The first step in the building up of a systematic experimental protocol needed to perform the chemical and physical analysis of these laboratory analogues, is the development and optimization of experimental tools allowing the formation, recovery and analysis of tholins in conditions avoiding any contamination of the samples. In the frame of the Cassini-Huygens mission, and of the research program of the InterDisciplinary Scientist project 'Titan's Chemistry and Exobiology', we have developed and optimized such an experimental tool. We are currently developing a Titan aerosol generator, in order to get production of Titan's aerosol analogues within conditions closer to those of the Titanian atmosphere (in term of energy, pressure and even temperature). We will then determine the elemental composition, and obtain the molecular weight of Titan's tholins, using state of the art techniques like SI-MS or ICP-MS. We also want to better characterize the structure of tholins. Then we will be able to measure optical constants. It will be then of crucial impor-

tance to re-examine the many data of Titan's observation, in the light of these new laboratory data.

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