WHICH THOLINS FOR SIMULATING TITAN'S AEROSOLS ? J.-M. Bernard[1], E. Quirico[1], G. Montagnac[2], B. Reynard[2], P. Mc Millan[3] Lydie Bonal[1], J.-N. Rouzaud[4], , P. Coll[5], and B. Schmitt[1], [1] Laboratoire de Planétologie de Grenoble (LPG), Bat. D de Physique, BP 53, 38041 Grenoble Cedex 9, France, jean-michel.bernard@ujf-grenoble.fr, [2] Laboratoire des Sciences de la Terre, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon Cedex 07, France, [3] Christopher Ingold Laboratories Department of Chemistry University College London 20 Gordon Street London WC1H 0AJ Great Britain, [4]Laboratoire de Géologie ENS Paris 75231 Paris France [5] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris XII-Paris VII, 61 av. du Gal de Gaulle, 94010 Créteil cedex, France.

Introduction: The exploration of Titan by the CASSINI-HUYGENS mission includes different spectrometers covering the visible and infrared ranges, which will probe the atmosphere (e.g. CIRS, DISR) and the surface (DISR). The analysis of these spectroscopic data requires the optical constant of analogues materials of Titan's aerosols. Titan's tholins, produced in laboratory from N_2:CH_4 mixtures in cold plasma, are considered as the best analogs available to date [1]. However, large compositional and morphological variations are reported among Tholins formed from different experiments, and even within the same experiment. Different attempts have been made in order to better constrain the factors controlling Tholin's composition, but no systematic studies have been performed for determining the links between the spectroscopic properties and the chemical composition [2]. This study focused on the chemical characterization of Tholins at the micrometric scale, by using different analytical techniques, and attempted to correlate the chemical information to the infrared spectral properties.

Samples: Tholins were produced at LISA. The experimental set-up (continuous gas flow, electrical discharge) is described in detail elsewhere [3]. Different Tholins were sampled from several experiments. In one experiment, two Tholins with very different colors (black and "yellow", "yellow" meaning a color ranging from bright yellow to dark orange) were recovered, respectively, close to the first electrod and at the middle of the tube. Visual observations under microscope and binocular microscope revealed an heterogeneous composition at the micrometric scale (Fig. 1). Black and yellow grains, with various morphologies were observed. The bulk color of macroscopic samples is due to the dominant of the black vs. yellow fractions. Chemical simple tests showed that the yellow fraction is soluble in H_2O and CH_2Cl_2, whereas the black one was mostly insoluble.

Analytical techniques: Samples were investigated by Laser Induced Fluorescence (LIF) [4] (457.9 nm excitation) and UV Raman micro-spectrometry (244 excitation), using two Labram HR800 Jobin-Yvon Raman spectrometers equipped with a microscope (x50 objective). Transmission Electron Microscopy was also carried out, in diffraction and high resolution modes [5] in order to detect an aromatic network in the insoluble black phases. Infrared spectra were performed on KBr pellets and using an FTIR Nicolet 800 spectrometer (spectral range 4000-400 cm^{-1}).

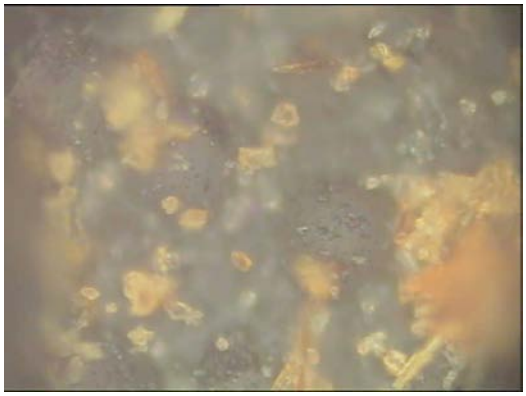

Figure 2: Tholin observed through a microscope (x50 objective; scale 200x155 µm). The picture reveals the two distinct phases : yellow and black.

Results: Tholins are highly fluorescent materials which prevent from getting Raman features using visible excitation. The LIF spectra have a spectral shape which is correlated to the color of the phase (black vs. yellow) [4]. The UV Raman spectra are features-rich. The first- and second-order carbon bands are observed and indicate widespread sp^2 bonds throughout the samples. The feature around 2200 cm^{-1} is assigned to CN sp^1. The shape of the first-order carbon band is different between black and "yellow" phases : in the former it would point to a ta-CNx material, in the latter to a ta-C:H:Nx material. However, the splitting of the CN sp^1 bands is not observed in these amorphous films [6]. Other features are observed : two narrow bands at 686 cm^{-1} and 983 cm^{-1}, which can be assigned to breathing modes of aromatic compounds. Such features definitely demonstrate the presence of aromatic compounds, either as free HAPs or rings within aromatic units composing a polyaromatic network. A broad feature seems also present around 980 cm^{-1} (sp^3 T peak ?), as well as substructures in the broad first-order band. A consistent spectroscopic analysis is still required. HRMET images reveal a very disordered or amorphous material. Diffraction patterns may however suggest a polyaromatic network in the black tholins.

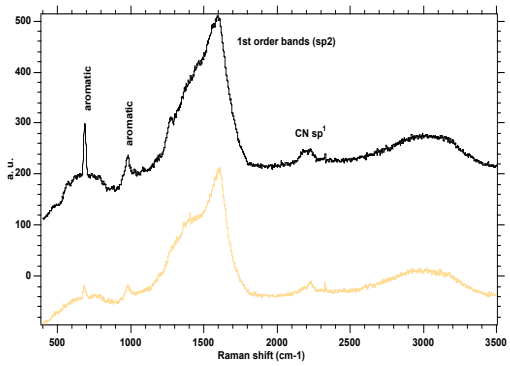

Fig. 2: UV Raman spectra of black and "yellow" Tholins. The spectra are consistent with CNx or CHNx amorphous films, but other features, such as the breathing modes of aromatic compounds, are clearly observed.

Infrared spectroscopy. The IR spectra in the 4000-400 cm-1 spectral ranges of each phases very close, but with significant differences (Fig. 3). Three chemical functions are easily identified : nitrile (CN) function around 2200 cm^{-1}, CH functions between 2700 and 3000 cm^{-1} and amines (NH) functions around 3200 cm^{-1}. The general form of spectra are identical for both tholins, but we observe the lack of CH_2/CH_3 functions in the black tholins. Moreover, the CN band in "yellow" tholins exhibit subcomponents.

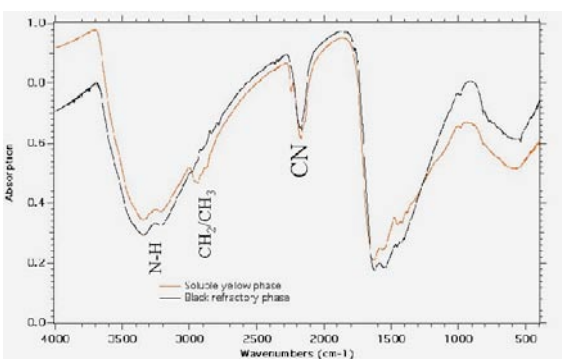

Figure 3 : infrared spectra of both Titan's tholins (yellow and black ones) synthetised at LISA.

These results are striking as huge variations of optical properties in the visible range are observed along with subtle spectral variations in the mid-IR. They raise the question of how using these data for simulating Titan's aerosols. The chemical and optical heterogeneity at the micrometric scale of the Tholins formed in laboratory calls for the determination of different set of optical constants, determined from homogeneous micrometric phases. Having a large set of optical constants in the visible and near-infrared ranges will be particularly crucial for analyzing DISR spectroscopic data.

It is not clear yet whether or not the color variations observed in laboratory Tholins may occur in Titan's aerosols. The forthcoming CASSINI-HUYGENS data will be of help to answer this question.

References: [1] McKay C. P. et al. (2001) *Planet. Space Science, 49*, 1,79-99 ; [2] Bernard J.-M et al. (2002) *ESA SP-518*, 623-625; [3] Coll P et al. (1999) *Planet. Space Sci. 47*, 1331-1340 ; [4] Bonal L. et al. (2005) *LPSC XXXVI*, Abstract #1858 This volume. ; [5] Rouzaud et al. (2005) *LPSC XXXVI*, This volume. ; [6] Rodil et al. (2002) *Thin Solid Films, 420-421*, 122-131