INVESTIGATIONS TOWARDS THE ANALYSIS OF COMPLEX ORGANIC AEROSOLS AND RELATED SOLIDS AS ANALOGUES TO TITAN HAZE MATERIALS. T. E. Munsch1, H. Imanaka1,2,3, and M. A. Smith1,3, 1Department of Chemistry, University of Arizona, Tucson, AZ 85721, 2SETI/NASA Ames Research Center, MS239-11 NASA Ames Research Center, Moffett Field, CA 94035, 3Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

Introduction: The complex organic materials (tholin) found on the surface and within the haze layer of Titan is attributed to chemistry occurring in its thick N2/CH4 atmosphere. The resulting organic aerosols contain a large mixture of nitrogen-rich organic molecules (i.e. substituted pyroles, nitriles, pyrimidines, amino acids, etc), as well as polyaromatic hydrocarbons.1,2 Several groups have been successful in simulating the believed Titan atmospheric aerosols,1,3 and the laboratory generated tholin materials have been characterized by several analytical methods including UV/Vis, fluorescence, IR, and MS, providing a wealth of information on the nature of these organic aerosols believed to be in Titan’s atmosphere.1,4,5 Despite these efforts, the complex tholin mixtures still holds several unanswered questions. Here, we report our continuing efforts to develop 1- and 2-dimensional spectroscopy (MS and NMR) and chromatography (LCMS) methods to analyze and separate tholin mixtures, respectively.

Mass Spectrometry: The recent installment of a dual ionization source, consisting of both electrospray (ESI) and laser desorption (LDI) ionization, has allowed us to carry out several ultra-high resolution MS experiments in both positive and negative ion modes using an FT-ICR instrument. Figure 1 demonstrates typical spectra obtained using the new dual ionization source. These spectra depict a very complex mixture of compounds, which is challenging to analyze, based solely on the MS. One can derive Van Krevelen diagrams (inset of Figure 1) both from the mass spectra, and this analysis provides functional group information.

2-Dimensional NMR Spectroscopy: NMR spectroscopy is a high resolution technique that can be used to analyze complex mixtures and large compounds. Compared to many analytical techniques used to characterize tholins, NMR is one of the few non-destructive methods that allows for structural analysis without resulting in structural degradation. Using a 500 MHz NMR, along with 13C and 15N isotopic labeling of the complex organic aggregates, we are able to report the first NMR spectra of tholin in the solution phase. Figure 2 shows the 1H and 13C NMR of an isotopically enriched tholin.

The complex nature of these organic aggregates is also demonstrated by the 1-D NMR spectra. Therefore, 2-dimensional NMR experiments (i.e. HSQC and Inadequate) are needed for the unique identification of the functional group inventories, and figure 3 shows examples of 2-D NMR of tholins.

Figure 1. Mass spectra of laboratory generated tholin in (a) positive and (b) negative ion mode using ESI and LDI. The corresponding Van Krevelen diagrams are shown as insets.

Figure 2. 1-Dimensional NMR: (a) 1H and (b) 13C spectra for tholin generated at -80ºC and dissolved in DMSO-d6.

Figure 3. 2-Dimensional NMR: (a) HSQC and (b) Inadequate spectra for tholin generated at -80ºC (solvent: DMSO-d6).
2-Dimensional Chromatography: 2-Dimensional chromatography is useful in separating complex mixtures such as tholins that would normally be unresolved using a 1-D approach. Both 1- and 2-dimensional GCMS have been used to analyze the volatile and semi-volatile components of tholin mixtures. To study the less volatile species in tholins, a few attempts have been made to utilize liquid chromatography methods, such as HPLC-MS, but these studies have been limited to 1-dimensional HPLC analysis. Here we also report our preliminary investigations to develop a two-dimensional liquid chromatography methodology in combination with mass spectrometry, which allows us to preselect the volatile compounds and reduce their interference from the organic polymeric components.