

**Characterization and Detection of Hydrolyzed Titan “Tholins” for *Dragonfly*.** B.A. Hadnott<sup>1</sup>, S.M. Hörst<sup>1</sup>, Chao He<sup>1</sup>, M.G. Trainer<sup>2</sup>, and X. Li<sup>2</sup>, <sup>1</sup>Johns Hopkins University, Department of Earth and Planetary Science Olin Hall, 3400 N. Charles St. Baltimore, MD, 21218, bhadnot1@jhu.edu, <sup>2</sup>NASA Goddard Space Flight Center 8800 Greenbelt Rd-Code 690 Greenbelt, MD 20771, melissa.trainer@nasa.gov

**Introduction:** Saturn’s largest moon, Titan, is a complex ocean world with abundant organic molecules ranging from liquid alkanes within the seas to hazes in the stratosphere [1]. *Dragonfly*, a proposed dual-quadcopter sampling mission to Titan and New Frontiers finalist, will carry a variety of instruments to detect complex organics and search for prebiotic molecules [2]. The instrument suite will include a laser desorption mass spectrometer (LDI), based on components of the Mars Organic Mass Analyzer (MOMA) for ExoMars. Photochemical processes initiated by UV and plasma excitation fragment the CH<sub>4</sub> and N<sub>2</sub> within the ionosphere; the dissociation products combine in the stratosphere to form higher order hydrocarbons and nitrogenous organics, then combine further to produce aromatic compounds and polymers in the troposphere. Large organic particles eventually settle out onto the surface, where they may have interacted with small pools of liquid water from impact melts or ammonia water from cryovolcanism. By sampling frozen-over impact melt ponds or potential cryomagmas, *Dragonfly* may be able to identify the products of hydrolysis reactions on Titan.

The Planetary HAZE Research (PHAZER) experimental set-up simulates atmospheric photochemical processes, producing Titan organic analogs called “tholins”, which can then be added to liquid water or ammonia-water solutions for hydrolysis studies [3-4]. Using commercially available mass spectrometers (Thermo MALDI LTQ XL and Bruker Autoflex Speed MALDI TOF/TOF) at NASA Goddard, we characterized the soluble fraction of tholin-water-ammonia mixtures in order to identify newly formed molecules. This study will lay the groundwork for determining the detectability limits for prebiotic molecules and aid in providing a characterization library for the flight-ready mass spectrometer instrument.

**Methods:** Two tholin samples were produced in PHAZER chamber from two different gas mixtures—95% N<sub>2</sub> and 5% CH<sub>4</sub>; 94.9995% N<sub>2</sub>, 5% CH<sub>4</sub>, 500 ppm CO [Further detail in 5]. Five milligrams of the solid samples were placed in glass vials, which were filled with either 2 milliliters of HPLC grade water or a mixture of HPLC grade water with 28-30% NH<sub>3</sub> (ACS grade) cooled to the 3 reaction temperatures. The solutions were then wrapped in foil to prevent light exposure, stored at 21.1° C (294 K, room temperature), -3.6° C (269 K, refrigerator), or -33.0° C (240 K,

freezer), and allowed to sit for 90 days. After 90 days, the samples were analyzed with MALDI-MS (Thermo LTQ XL), MS/MS (Thermo LTQ XL), and TOF-MS (Bruker) at NASA Goddard Space Flight Center. Pure tholin samples were dissolved in acetone and allowed to dry immediately before MS analyses. This study is unique, in that it characterizes hydrolysis for two different tholin compositions (with or without O) in water and ammonia-water mixtures at a wide range of temperatures (294 – 240 K). This work also analyzes the dependence of tholin solubility with varying composition and solvent type.

**Results:** While several experiments have studied the hydrolysis of tholins at a range of temperatures, solvent compositions, and reaction times [6], this study will also measure the effects of oxygen on tholin formation and hydrolysis. Here, we present preliminary data analysis for room temperature data:

*Data processing.* Thermo LTQ XL data was processed in Jupyter, version 4.3.1. The raw text files from the mass spectrometer were imported as numerical arrays, and the total integrated area for each data file was calculated using the composite trapezoidal rule. The raw data was then divided by the calculated total integrated area in order to standardize each data set. The standardized data was divided by each file’s global maximum intensity in order to normalize all values from zero to one. The resultant values were plotted against the raw data to check for any artifacts or errors from processing. In order to account for the instrument’s unit *m/z* resolution, the molecular mass was binned such that each local maximum intensity value within a bin corresponded to a single integer. Two binning procedures were used: one generated bins dynamically by calculating the number of data points for each bin with a width of 1 amu; the second method grouped a pre-set number of data points into bins. For the dynamical method, the bin width was set to 1 amu, from (N-0.5) amu to (N+0.5) amu, where N is an integer. Based on a quick comparison, the dynamical method was shown to be more accurate and preserve finer data structure (Figure 1).

*Spectral Interpretation.* Owing to the complexity of the spectra and uncertainty in relative peak intensity due to sample roughness, the processed and binned spectra of the pure tholin samples are subtracted from the hydrolyzed samples to identify new peaks or peaks that reacted away. Positive values in the difference

plots suggest the formation of new products; negative values suggest the decrease/disappearance of molecules only present in the pure tholin due to chemical reactions or dissolution. Moderate changes are identified by dividing the hydrolyzed tholin spectrum by the pure tholin spectrum. However, it should be noted that for  $m/z$  greater than 1500, the identified changes are likely due to slight differences in noise rather than chemistry. The resultant division plots indicate peak growth (greater than 1) or a decrease in peak intensity (less than 1). Using the difference and division plots, it is possible to identify reaction products from tholin hydrolysis and find corresponding reactants in the pure tholin spectra (Figure 2). Based on simple water addition reactions and potential ammonia reactions, reaction products are expected to be heavier than reactants. Water addition products should be 16 or 18  $m/z$  heavier depending on the order (single vs double bond) of the carbon bond broken. Ammonia reaction products should be 15 or 17  $m/z$  heavier than the reactants. Complex reactions involving greater changes in  $m/z$  still need to be identified.

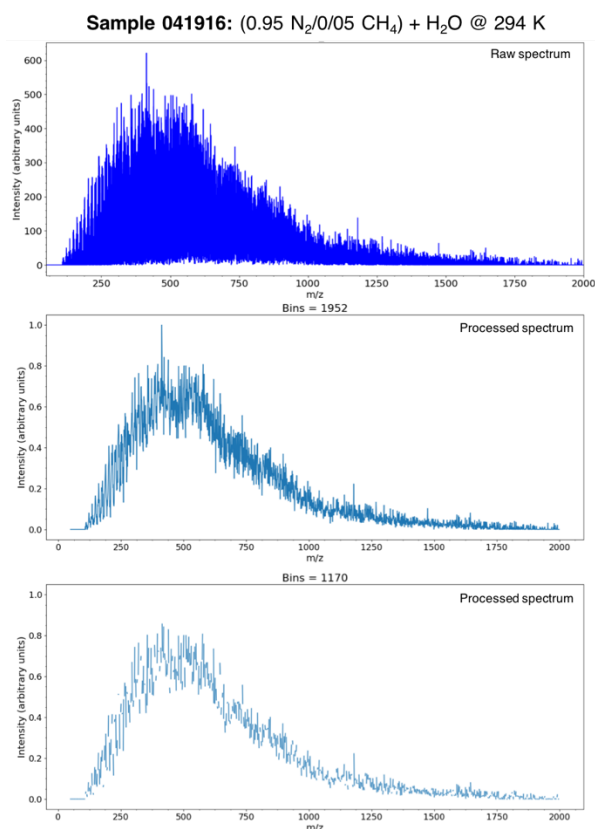


Figure 1. Comparison of raw spectrum (top) for tholin composed of 0.95  $N_2/0.05 CH_4$  added to pure water at room temperature, and processed spectra using dynamic (center) and static (bottom) binning methods.

**Discussion:** Follow up work will involve systematically determining the peaks with the greatest positive change in difference plots and with values greater than one in the division plots. Peaks that meet both of these criteria are most likely to correspond to new reaction products. The peaks will be identified in the hydrolyzed tholin spectrum, and the pure tholin spectrum will be analyzed for water or ammonia addition parent products with  $m/z$  values that are fifteen to eighteen less than the daughter products. Additionally, peaks with the greatest positive change will be analyzed with fragmentation studies (tandem mass spectrometry, MS/MS) to better determine potential molecular formulas and structures. Ideally, by finding the molecular formulas of new peaks, it will be possible to determine the formulas of peaks with the greatest negative change, which represent molecules that reacted away to form new products. This information will aid in developing a comprehensive library of molecules that comprise tholin and tholin hydrolysis products.

Sample 041916: (0.95  $N_2/0/05 CH_4$ ) +  $H_2O$  @ 294 K

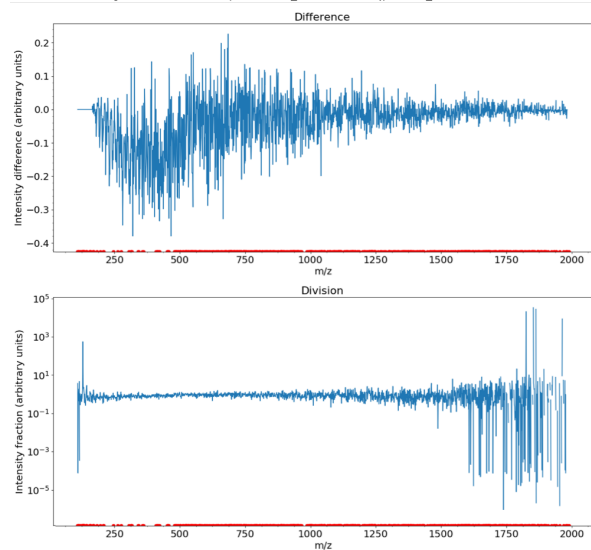


Figure 2. Difference/division plots of the hydrolyzed tholin spectrum (Figure 1) subtracted/divided by the pure tholin spectrum; red marks show peaks identified for further study based on criteria described above.

**References:** [1] Hörst, S. M. *JGR Planets* 122.3 (2017): 432-482. [2] "Dragonfly." dragonfly.jhuapl.edu accessed Sep. 25, 2017 [3] Hörst, S. M. The University of Arizona (2011). [4] Coustenis, A. *Métode Science Studies Journal-Annual Review* 6 (2015). [5] He, C., Hörst, S. M., et al. *ApJL* 841 (2017): L31. [6] Cable, M.L., et al. *Chemical Reviews* 112.3 (2011): 1882-1909.