P33D-2677: Characterizing Water-soluble vs Water-insoluble Titan Haze Analogs

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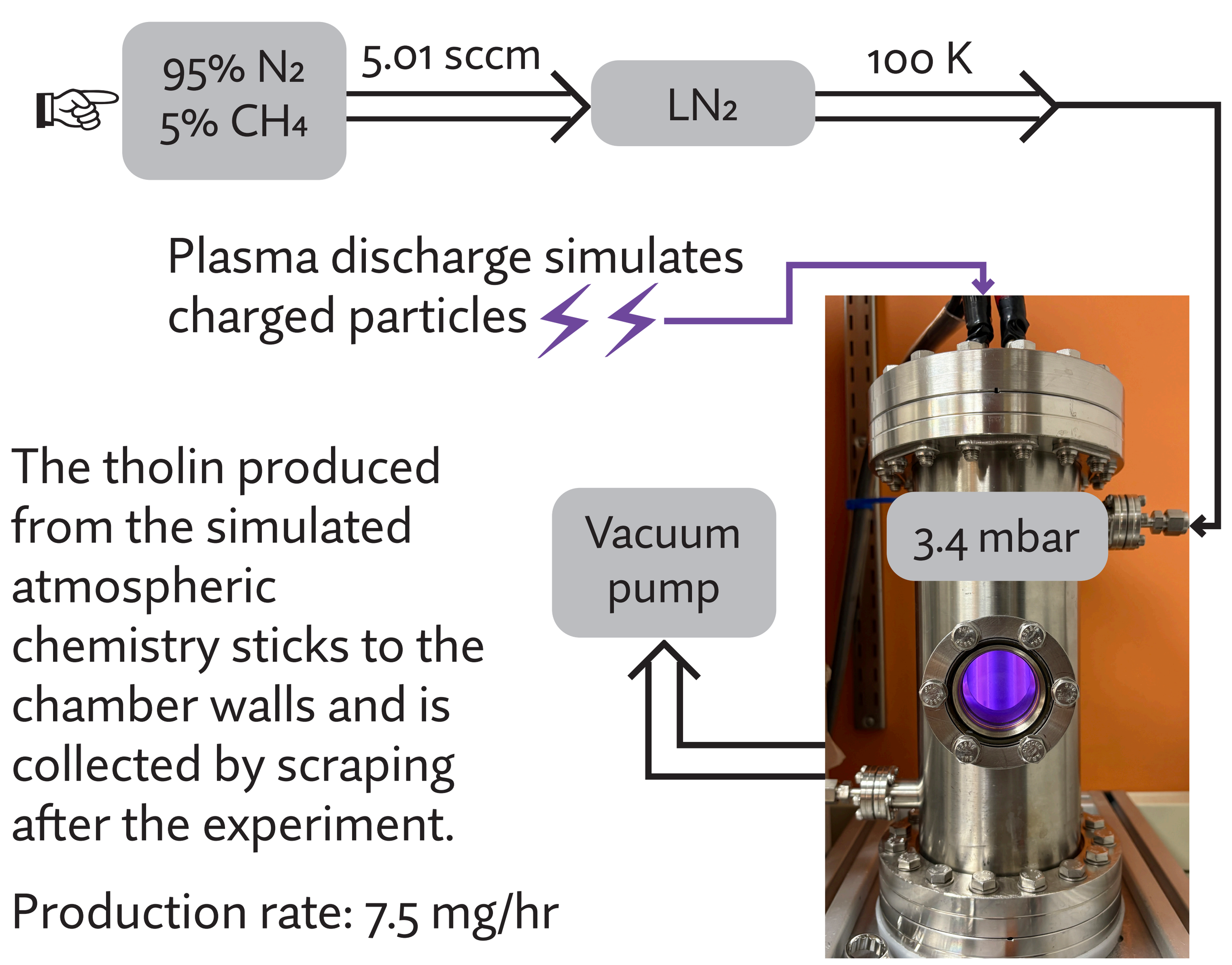
Motivation

- Complex organic molecules from Titan's photochemical hazes react with water to produce amino acids on the order of days to years (Neish et al., 2010, Hörst et al., 2012, Cleaves et al., 2014).
- As a surface material, some of Titan's haze particles may become hydrolyzed in liquid water and/or aqueous ammonia in impact melt pools, which last 10^2-10^3 years (Crósta et al., 2021, Wakita et al., 2023).
- Hydrolysis products may be later revealed and transported through erosional processes (Neish et al., 2015) and could be detectable by the Dragonfly relocatable lander (Barnes et al., 2021).
- **How do hydrolyzed haze particles change and how do we detect and identify their products?**

Methods: Tholin Production



The tholin produced from the simulated atmospheric chemistry sticks to the chamber walls and is collected by scraping after the experiment.

Production rate: 7.5 mg/hr

Figure 1: Tholin production in the Planetary HAZE Research (PHAZER) Chamber as described by He et al (2017.)

Methods: Hydrolysis

1. Samples were prepared as 1.5 wt% solutions of tholin in either HPLC water or aqueous ammonia (30 wt%).
2. Tholin was added to centrifuge tubes in a nitrogen-filled glove box. The solvent was then added to the tubes in fume hoods under ambient conditions, then the tubes were sealed.
3. The solutions were constantly agitated on a nutating shaker (Figure 2) for 3 weeks.
4. After 3 weeks of hydrolysis, the solutions with aqueous ammonia are visibly darker and differ in color from the samples in pure water.

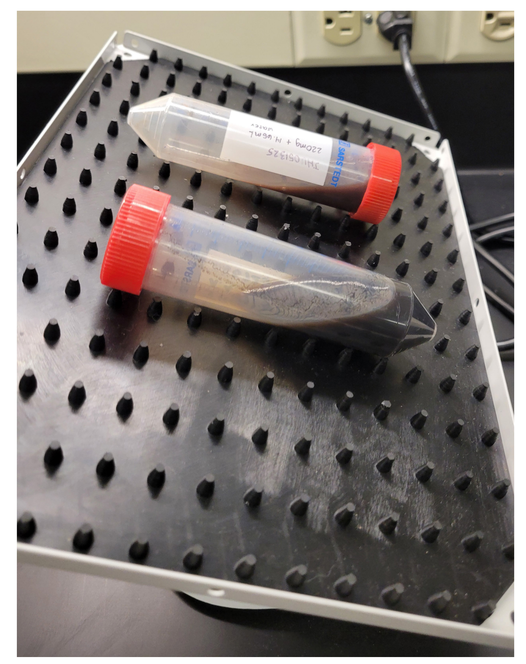


Figure 2: Hydrolysis samples on a nutating shaker

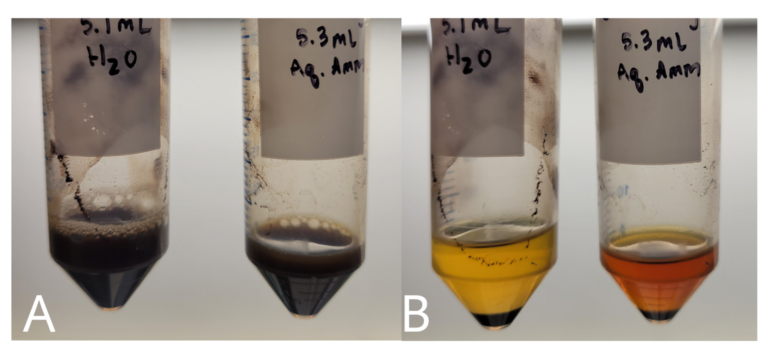


Figure 3: Visual comparison of tholin hydrolyzed in pure water vs. in aqueous ammonia. A: Before separation in centrifuge (water is on the left). B: After centrifuge (water is on the left).

5. The samples are put into a centrifuge at 4200 rpm for 20 minutes. The solid, insoluble fraction of hydrolyzed tholin is pulled to the tip of the tube, while the soluble liquid fraction floats above.
6. To separate the two fractions, the liquid fraction is siphoned off with a pipette, then filtered and transferred into a vial with a 20-μm filtered syringe. The liquid can then be dried under N_2 in an 80° C oven, and a sticky film of the soluble fraction remains.
7. To ensure no soluble fraction is left in the insoluble fraction, the solids are rinsed with the original solvent (pure water or aqueous ammonia) using a Hirsh vacuum filtration funnel.

Initial Results

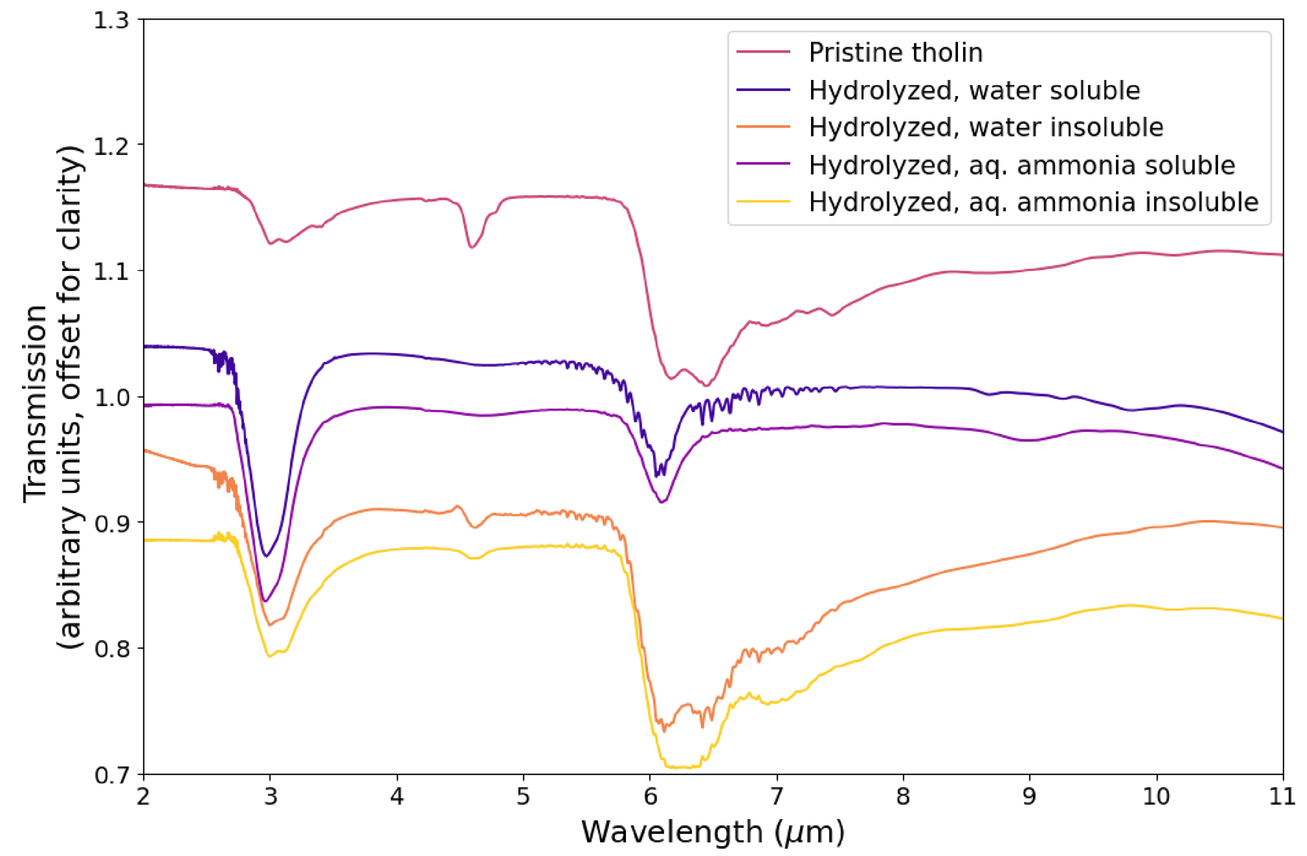


Figure 4: Transmission spectra comparing pristine tholin (non-hydrolyzed and not exposed to air), and the soluble and insoluble fractions of tholin hydrolyzed in water and tholin hydrolyzed in 30 wt% aqueous ammonia. The absorption feature at seen at ~4.6 μm in the pristine tholin becomes broadened and nearly absent in both soluble fractions; the same feature remains narrow but shallower in both insoluble fractions. Similarly, the absorption feature at 6.5 μm is absent in both soluble fractions.

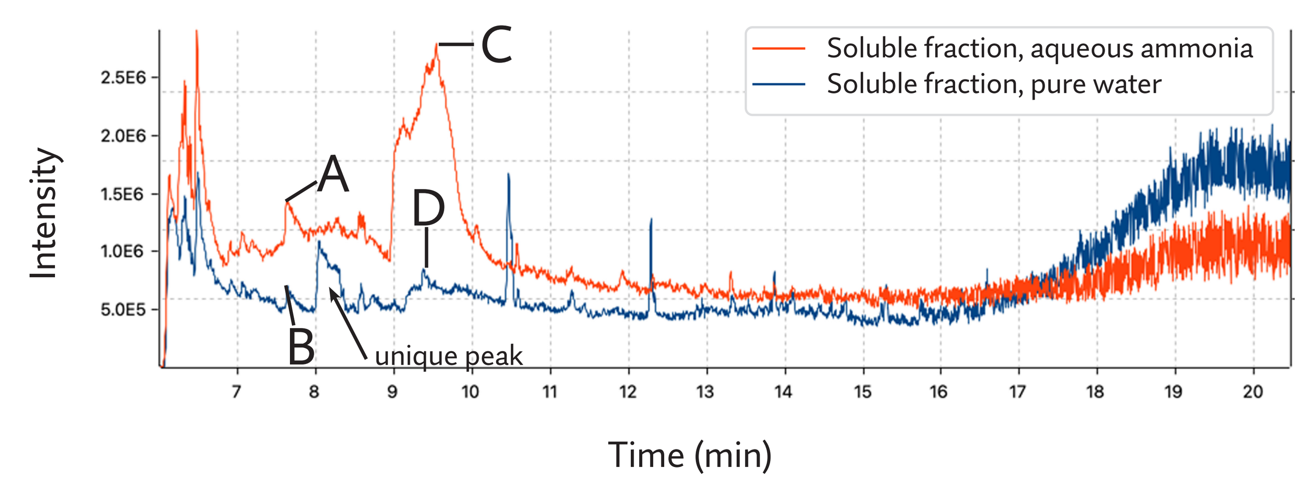


Figure 5: Gas Chromatography comparison of the chromatograms of both soluble fractions. Some peaks, like the ones at ~7.6 min (A, B) and ~9.4 min (C, D) are shared across both but with differing intensity. Other peaks, like the one at ~8 min in the water-soluble chromatogram are unique to the sample. Figure 6 (below) compares the ion scans of two peaks from both samples.

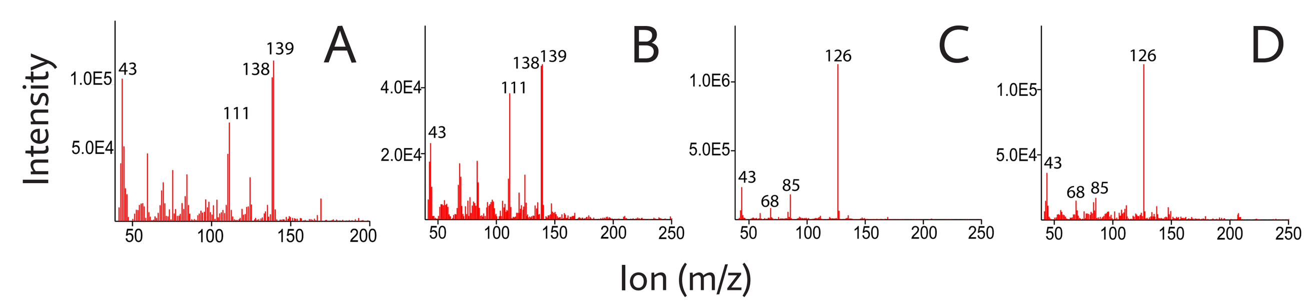


Figure 6: GC-MS Ion scans of peak 7.6 of (A) the ammonia-soluble and of (B) the water-soluble samples, and peak 9.5 of (C) the ammonia-soluble and of (D) the water-soluble samples

Next Steps

- Identify peaks in GC-MS for soluble and insoluble fractions in pure water and aqueous ammonia hydrolysis.
- Compare ions across samples and identify shared features vs. species that are unique to samples.
- Quantify distinguishing features in transmission spectra and mass spectra.

Acknowledgments

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