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DraMS-like molecular extraction and analysis of Titan analog materials exposed to gamma and proton irradiations

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Dragonfly is a NASA New Frontiers mission to Titan (Saturn's largest natural satellite [1]), scheduled to arrive in the mid-2030s [2,3]. The main objectives of the Dragonfly rotorcraft and the onboard DraMS instrument (dual mode Laser Desorption and Gas Chromatography Mass Spectrometer, or LD/GC-MS) are to identify the organic matter produced on Titan's surface, and to understand the prebiotic chemistry that arises from the high productivity of organic aerosols in the atmosphere and their interaction with gamma/cosmic-rays and energetic particles on the surface [4–6]. DraMS-GC will analyze organic compounds present in Titan's surface materials. Processing within the sample cups in the DraMS oven will be used prior to GC-MS analysis to volatilize and analyze polar or refractory compounds. Three different treatments are planned: pyrolysis, derivatization using dimethylformamide dimethyl acetal (DMF-DMA) reagent [7,8] and thermochemolysis using tetramethylammonium hydroxide (TMAH) [9,10].

We simulated the radiative conditions (γ -rays at 1-300 krad equivalent to 6 months-1000 Titan years' simulation or protons at 200 MeV or a few Titan months) and chemical environment that tropospheric aerosols or surface deposits may undergo on Titan. With this aim, we conducted DraMS-like extraction and analysis on 3 sets of samples: i) non-irradiated dry tholins and shales; ii) 20 mg irradiated tholins or natural shale samples in a dry or 5% NH₃ aqueous environment; and iii) irradiated standard bioindicators and biosignatures. The two first sets of samples are dedicated to help understand the prebiotic chemistry that could be happening on Titan and how efficiently DraMS will be able to extract, derivatize, and analyze compounds from these organic materials. The last set of samples are standard molecules (L-alanine, lignoceric acid, and uracil) and the objective of the experiment was to measure the kinetics of transformation/degradation of building blocks of life on Titan (and might refer to other ocean worlds as well).

Pyrolysis (at 600 °C for a few seconds) enabled the most effective detection and identification of compounds from the pure tholin or shales' samples. However, derivatization with DMF-DMA and thermochemolysis with

TMAH/TMSH were efficient for prebiotic organic molecules detection and quantification. DMF-DMA was much more efficient to detect amines and amino acids while TMAH and TMSH were primordial to detect carboxylic acids and alcohols. This study helps to validate DraMS processing and parameters and to establish analysis strategies for different samples on Titan. Further, the molecular analysis highlights the transformation of organic matter composing tholins, from a primary composition of mostly amine and nitrile molecules to an enrichment in O-bearing and aromatic compounds because tholins interacted with the atmospheric or liquid water only during radiations. No amino acids were detected in irradiated tholins. Indeed, the kinetics' study conducted on standards confirmed the complete degradation of L-alanine over 50 krad by γ -rays, for instance. The overall results helped to begin a list of organic molecules/bioindicators/biosignatures and the mechanistic pathways between some of them due to aqueous/ammonia/gamma/proton alterations (Figure 1).

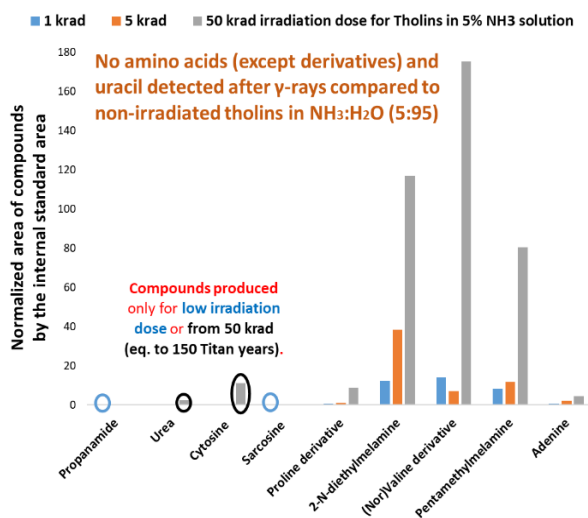


Figure 1. Some of the molecules detected and quantified with DraMS-like devices in Titan analog samples partially solubilized in a 5% NH₃ solution after γ -ray irradiations (at the GSFC-NASA radiation facility).

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