DEVELOPMENT OF THE *DRAGONFLY* MASS SPECTROMETER (DRAMS) FOR TITAN. J. C. Stern[1], M. G. Trainer[1], W. B. Brinckerhoff[1], A. Grubisic[1], R. M. Danell[1,2], D. Kaplan[1,3], F. H. W. van Amerom[1,4], X. Li[1], W. Suero Amparo[5], C. Freissinet[6], C. Szopa[6], A. Buch[7], S. Teinturier[1,8], V. Moulay[6], D. Boulesteix[7], C. A. Malespin[1], P. W. Barfknecht[1], P. R. Stysley[1], D. B. Coyle[1], M. W. Mullin[1], B. L. James[1], E. I. Lyness[1,9], R. S. Wilkinson[1,10], P. Coronado[1], E. P. Turtle[11], and the *Dragonfly* Team. [1]NASA Goddard Space Flight Center, Greenbelt MD (melissa.trainer@nasa.gov), [2]Danell Consulting, Winterville NC, [3]Kapscience, Tewksbury MA, [1,4]Mini-Mass Consulting, Hyattsville MD, [5]New Jersey Institute of Technology, Newark NJ, [6]LATMOS/IPSL, UVSQ Université Paris-Saclay, CNRS, Guyancourt, France, [7]LPGM, CentraleSupélec, Gif-sur-Yvette, France, [8]Catholic University of America, Washington DC, [9]Microtel, Greenbelt MD, [10]Aerodyne Industries, Greenbelt MD, [11]Johns Hopkins University Applied Physics Laboratory, Columbia MD.

Introduction: Titan's abundant complex carbon-rich chemistry, interior ocean, and past presence of liquid water on the surface make it an ideal destination to study prebiotic chemical processes and habitability of an extraterrestrial environment [*e.g.*, 1-4]. NASA's *Dragonfly* New Frontiers mission is a rotorcraft lander [5] designed to perform wide-ranging *in situ* exploration on this moon of Saturn by flying to different geologic settings up to ~180 km apart. Multidisciplinary science measurements at each landing site will reveal the compositions of the solid materials on Titan's surface, which are still essentially unknown [6-8].

Two primary science goals of the *Dragonfly* mission are to identify chemical components and processes at work that may produce biologically relevant compounds, and to search for potential molecular biosignatures. These objectives are addressed by the *Dragonfly* Mass Spectrometer (DraMS), which performs molecular analysis on surface samples that are acquired and delivered by the Drill for Acquisition of Complex Organics (DrACO).

The *Dragonfly* Mass Spectrometer (DraMS): DraMS is a linear ion trap mass spectrometer, most closely related to the Mars Organic Molecule Analyzer (MOMA) [9], part of the ExoMars *Rosalind Franklin* Rover set to launch in the late 2020's. For solid sample analysis, DraMS features two modes: Laser Desorption Mass Spectrometry (LDMS) for the broad compositional survey of surface materials including refractory organics, and Gas Chromatography Mass Spectrometry (GCMS) for the separation and identification of key prebiotic molecules and measurement of enantiomeric excesses (if present). LDMS mode allows for structural disambiguation of surface molecules using ion isolation and tandem mass spectrometry (MS/MS). GCMS mode uses pyrolysis or derivatization to volatilize, separate, and identify molecules of interest. Much of the gas processing system (valves, pyrolysis oven, etc.) and electronics are also inherited from the Sample Analysis at Mars (SAM) instrument onboard *Curiosity* [10].

Hardware Developments: The DraMS instrument completed Preliminary Design Review (PDR) in September, 2022. Significant progress in the technical design of the instrument and associated systems has taken place to lead up to this milestone review. Much of the development has focused on areas in which the unique aspects of the Titan environment and *Dragonfly* science [11] differed from the heritage Mars investigations. Here we will present the current status of the DraMS investigation and instrument development.

Table 1. DraMS Specifications

Characteristic	Predicted Performance
Mass Sensor	Linear Ion Trap
Mass Range	**15 – 1950** Da [a]
Mass Resolution	**0.4** – 3 Da (FWHM) [b]
Mass Accuracy	**± 0.4 Da**
Ion polarity	Positive and Negative ion detection [c]
Limit of detection	**100 ppbw** organics in surface sample
GC Columns	Two; General and Chiral separation

Bold = Exceeds requirements
[a] Composite range, individual modes access a subset of this range
[b] Resolution decreases above required maximum mass range (550 Da), impacts LDMS mode.
[c] Negative ion detection only in LDMS mode

Laser Desorption Mass Spectrometry (LDMS). Solid surface samples are acquired by the DrACO sample handling system [12] in specialized sample cups and delivered to the relevant ports on the DraMS instrument; one for LDMS and one for GCMS. In the LDMS cups, the sample resides behind a fine mesh covering a slit-like window in the side of the cup. For analysis, the LDMS cup is inserted into a small chamber, with the mesh window positioned only a few mm away from the ion inlet tube of the DraMS instrument. The laser impinges on the sample through the mesh at Titan sub-ambient pressure (< 50 mbar) and sample temperature < 165 K, with the resulting ions ingested into the mass spectrometer [13]. The influence of mesh geometry parameters on LDMS detection of organic analyte coronene was quantified, with signal level observed to be proportional to percent sample area visible to the laser.

The sample temperature and range of matrix compositions will also strongly influence the spectra and signal within DraMS. We have studied the LDMS of powdered icy samples – “CryoLDMS” – to determine whether a water ice or other icy matrix will drastically change detection or identification of organic materials. Figure 1 demonstrates that LDMS of trace organics in frozen water ice samples have high sensitivity and are largely consistent with analyses at room temperature. Additionally, we are exploring the influence of high salt concentrations, potentially introduced by emplaced materials originating from Titan’s subsurface ocean.

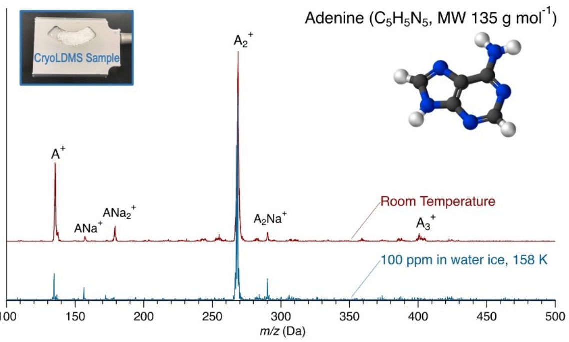

Figure 1. CryoLDMS of adenine in water ice at relevant sample temperatures shows that the spectra is remarkably similar to that of the pure molecule at room temperature.

Ultraviolet (UV) Laser. DraMS LDMS is accomplished using the Titan Hydrocarbon Analysis Nanosecond Optical Source (THANOS) UV laser, a compact solid-state 266-nm pulsed Nd:YAG laser. The THANOS engineering model (EM) has been developed and successfully put through environmental testing. Performance testing has shown that all requirements can be met, including lifetime, emission of precise laser bursts (0–50 pulses at up to 100 Hz), and energy attenuation capability [14]. The EM unit achieved TRL 6 in early 2022.

Gas Chromatography Mass Spectrometry (GCMS). The varied and largely unknown molecular composition of Titan surface materials requires DraMS to have a flexible analytical strategy. For GCMS analysis, the pyrolysis and derivatization processes need to accommodate the potential range of molecular abundances and compositions found in the samples. Early testing of analog materials has commenced to aid in the determination of operational parameters.

DraMS carries two GC columns, one for general analysis and one chiral column for the separation of enantiomers. A comprehensive study was conducted to select the optimal general column to robustly analyze the wide range of molecules likely to be present at Titan (nitriles, amines, amino acids, etc.). Figure 2 shows the performance of four candidate columns that were considered for DraMS, as detailed in Moulay et al [14]. The RTX-5 column was selected due to its ability to separate compounds bearing up to 25 carbon atoms in run duration consistent with DraMS in situ analysis.

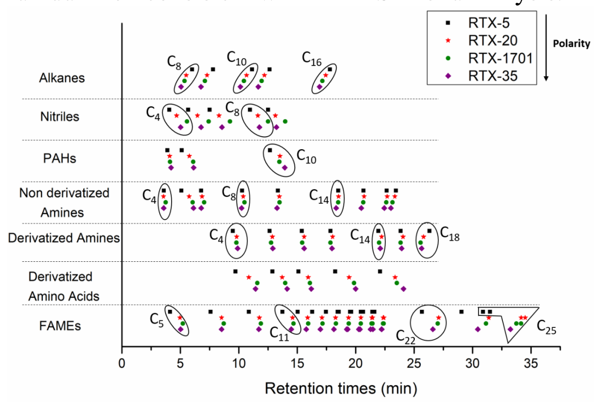

Figure 2. Distribution of the retention times (min) for the chemical family standards tested for candidate general columns. Each point represents a single compound. The RTX-5 column was chosen for DraMS.

DraMS derivatization efficacy in organic-rich samples was studied using Titan analogs – “tholins” – as well as other relevant compounds. These studies to optimize in situ derivatization of Titan surface materials using DMF-DMA and TMAH will also be presented.

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