Introduction: NASA’s Dragonfly mission is scheduled to land a rotorcraft on Titan in the mid-2030s within the Shangri-La organic sand sea and traverse to the Selk impact structure [1]. Determining the chemical composition of samples acquired from the surface of Titan will be critical to accomplishing multiple Dragonfly mission science goals [2]. The Dragonfly Mass Spectrometer (DraMS) will be the primary means of investigating the chemical composition of samples analyzed in situ on Titan using both laser desorption mass spectrometry (LDMS) and pyrolysis/derivationization–gas chromatograph mass spectrometry (pyr/der-GCMS) modes [3,4]. LDMS will be the initial measurement mode applied to all samples collected for DraMS [3]. DraMS LDMS is a direct sampling technique requiring little-to-no sample preparation that can be used to analyze moderate-to-low volatility compounds [4]. If potential compounds of interest are detected in LDMS mode, samples can be analyzed in pyr/der-GCMS modes for more information on specific chemical structures, repeating patterns of molecules, and enantiomeric excess of any chiral molecules [3].

Organic material in the Shangri-La region is likely to be composed of CHN compounds with potentially complex and diverse chemical structures similar to laboratory produced tholins [see 5]. The Selk impact likely generated interactions between CHN compounds and liquid water capable of forming prebiotic CHNOPS compounds such as amino acids [6,7]. CHNOPS compounds explicitly targeted for detection by Dragonfly include amino acids, sugars, and lipids that may form abiotically or may represent organic molecular biosignatures [2,8].

Here, we highlight LDMS spectra of CHNOPS compounds as described by [2] produced on the current DraMS LDMS board instrument at the NASA Goddard Space Flight Center (GSFC). We describe distinct features of the LDMS spectra from multiple CHNOPS classes that will be useful for identification of such compounds on Titan, including through the use of machine learning.

Samples and Methods: LDMS boardroom experiments were designed to closely simulate DraMS LDMS. Laser desorption and ionization was achieved using a 266 nm Nd:YAG laser with a ~2 ns pulse duration and a focal spot size of ~50 × 100 µm [4]. DraMS-type LDMS analysis induces minimal damage to material outside of the laser focal spot enabling repeated analyses on the same sample [9]. Laser desorption was performed at 25 Torr of gas of Titan atmospheric composition (95% N2, 5% CH4). To ensure that differences in spectra produced from CHNOPS compounds are the result of chemical variation rather than laser power, all analyses were performed with a constant, low laser energy of 30 µJ/pulse and 5 laser pulses per spectrum.

Ions produced via LDMS were directed into an ion trap mass spectrometer (ITMS). The DraMS breadboard ITMS was operated in both positive and negative ion polarities with a scanned mass range of 80 – 1000 Da. The scan-to-scan cadence for LDMS experiments (cycle time to produce one mass spectrum) was 4.26 s. The rate of LDMS spectrum collection with the ability to perform multiple analyses on each sample enabled the collection of hundreds of spectra for each compound. The rate of data production is important to produce sufficient quality data for the future development of machine learning models to recognize and discriminate such CHNOPS compounds on Titan.

As such, all samples were carefully prepared to minimize contamination and maximize the quality of spectra produced for each compound. CHNOPS compound classes selected for analysis include amino acids, nucleobases, fatty acids, sugars, phospholipids, and organo-sulfur compounds. Individual standard compounds were dissolved at 100 mM concentrations. Four µL of each solution were spotted onto individual stainless steel sample plates for an average coverage of ~10 mM/mm2. The sample plates were then dried and introduced to the LDMS chamber for analysis.

Results and Discussion: LDMS spectra of CHNOPS compounds are distinct from spectra produced via electron impact (EI) ionization. Unlike EI spectra, LDMS spectra of CHNOPS compounds often contain molecular ions ([M]+) with little-to-no molecular fragmentation, clusters of multiple molecular ions ([M]+), and molecular ions with adducts (e.g., [M+Na]+). Figure 1 highlights representative LDMS results from three of the six CHNOPS compound classes targeted for this analysis. Notably, the observable patterns of both ion cluster and ion adduct formation are distinct between these compound classes.

In positive polarity MS mode, the nucleobase uracil produces ion clusters of [M2+ + adduct]+ throughout a large portion of the scanned mass range, primarily with
Na and Na$_2$ adducts (Fig. 1). In contrast, the fatty acids myristic acid and stearic acid, as well as the sugar glucose produce positive spectra that contain [M$_{1.2}$ + adduct]$^+$ ions, both with Na and K adducts (Fig. 1).

Negative ion patterns are also distinct for each compound class in Figure 1. Uracil, myristic acid, and stearic acid all produce detectable [M$_{1.3}$ $\pm$ adduct]$^-$ ions, but the pattern of uracil negative ions is distinct from the pattern of fatty acid ion clusters and adducts. Further, the negative ion patterns of myristic acid ([M-H]$^-$ at m/z 227 with additional ions [M$_2$-H]$^-$, [M$_2$+90]$^-$, [M$_3$+55]$^-$) exactly match the ion patterns of stearic acid ([M-H]$^-$ at m/z 283; Fig. 1) suggesting an LDMS ionization pattern diagnostic of the fatty acid compound class. Similarly, negative ion patterns observed via LDMS of glucose ([M+45]$^-$, [M+70]$^-$, and [M$_2$-H]$^-$) exactly match the ion cluster and adduct patterns observed from LDMS analysis of ribose (150 Da; data not shown), also suggesting a potentially diagnostic pattern. Future analyses will explore the applicability of the positive and negative LDMS ion patterns observed here for similar compounds with varying sizes and molecular structures.

The results presented here indicate that DraMS LDMS is capable of characterizing CHNOPS compounds with diverse chemical structures without the application of a matrix, including CHNOPS compounds defined as relevant to the Dragonfly mission. Operating in both positive and negative polarity MS modes will be important in order to classify organic matter, as both polarities are together useful to characterize potential CHNOPS compounds. The complementary positive and negative spectra along with the large amount of complex data that can be produced on the current DraMS LDMS breadboard, are well-suited for the future development of machine learning models capable of characterizing CHNOPS compounds potentially present in samples analyzed in situ on Titan.

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