

LASER DESORPTION MASS SPECTROMETRY ON TITAN. M. G. Trainer¹, W. B. Brinckerhoff^d, M. E. Castillo^{1,2}, R. Danell³, A. Grubisic^{1,2}, C. He⁴, S. Hörst⁴, X. Li^{1,5}, V. T. Pinnick¹ and F. van Amerom⁶, ¹NASA Goddard Space Flight Center, Code 699, Greenbelt MD 20771, melissa.trainer@nasa.gov, ²CRESST, University of Maryland, College Park, College Park, MD, ³Danell Consulting, Inc., Winterville, NC, ⁴Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD, ⁵CRESST, University of Maryland, Baltimore County, Baltimore, MD, ⁶Mini-Mass Consulting, Hyattsville, MD.

Introduction: The Mars Organic Molecule Analyzer (MOMA) investigation onboard the 2020 ExoMars rover mission will investigate Martian near-surface samples by laser desorption/ionization (LDI) coupled to a linear ion trap (LIT) mass spectrometer. This experimental technique uses UV laser impact to desorb molecules that shall be analyzed by mass spectrometry and is thus geared towards characterization of the organic inventory in Martian subsurface samples. The MOMA mass spectrometer represents the first implementation of a laser desorption/ionization mass spectrometer (LDMS) in space. LDMS provides significant advantages and complementarity to the analysis of semi-volatile organic molecules as compared with pyrolysis-gas chromatography/mass spectrometry (pyr-GCMS), a technique employed regularly on Mars by the Mars Science Laboratory Sample Analysis at Mars (SAM) instrument, and also carried for MOMA.

In addition to the analysis of mineral samples on Mars [1], LDMS is a powerful tool that could be used at other high value planetary targets for the analysis of complex surface materials, such as a salt-organic-ice mixture on an icy moon or the organic-rich surface of Titan. Here we present experiments that demonstrate the technical feasibility and scientific benefits of operating an LDMS instrument, such as MOMA, on the surface of Titan to determine the composition of complex organic samples.

LDMS Instrument: The general design of the MOMA ion trap and its performance has been described previously [2,3,4]. The flight model (FM) of the MS subsystem has been fully assembled and is undergoing a thermal vacuum campaign prior to rover integration. During an LDI experiment, molecules are desorbed and ionized directly from solid samples with a pulsed UV laser (266 nm, 1 ns duration) at Mars ambient pressures. Molecular cations, and their fragments, are injected into the MS through an inlet system employing a fast aperture valve that closes after ions are trapped, permitting the ion trap pressure to reduce to $<10^{-3}$ Torr, at which the detectors can be operated.

LDMS mode is designed to analyze compounds of moderate-to-low volatility (enthalpies of vaporization $\Delta H_v \geq 40 \text{ kJ mol}^{-1}$) such as heavier carboxylic acids, aromatic species, chain-like compounds, and macromolecular organics (Figure 1). The nature of

LDI permits some fraction of any large “parent” molecules to desorb intact without thermal degradation, simplifying analysis of nonvolatile organics [5].

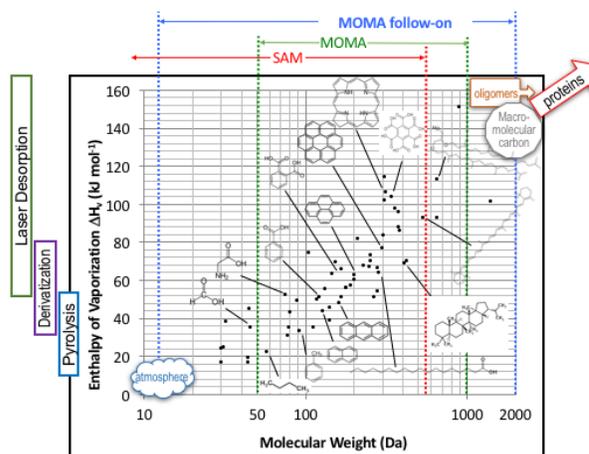


Figure 1. Laser desorption/ionization greatly expands the mass range and types of organic molecules that can be probed with mass spectrometry. LDI on the surface of Titan would enable the detection and characterization of a broad range of chemical signatures with implications for prebiotic chemistry.

During a mass scan, the linear ion trap mass spectrometer radially ejects ions based on mass-to-charge (m/z) ratios across a mass range of 50 to ≥ 1000 Da. The LIT can be operated in SWIFT mode (Stored Waveform Inverse Fourier Transform) in order to selectively enrich a sub-set of masses (within a narrower m/z range) out of the primary (broad) distribution of masses. This enables an isolation of key mass peaks of interest, as well as a secondary excitation/fragmentation step to perform tandem mass spectrometry (MS/MS) measurements for directed structural analysis.

LDMS at Titan: The ExoMars/MOMA investigation is well-suited to the characterization of a variety of Titan surface units, and would only require minor adaptations to operate on the surface of Titan as compared to Mars [6].

Adapting to the Titan Atmosphere. The difference in atmospheric surface pressure between Mars (~ 7 -10 mbar) and Titan (1500 mbar) would require a change in the interface between the laser desorption region and the LIT. On Mars, the LDI occurs in the ambient CO_2 atmosphere, and the ion optics are optimized to transmit

ions into the mass spectrometer with a fast aperture valve. The use of LDI in CO_2 has been well characterized for MOMA. At Titan, the pressure and the atmospheric composition ($\sim 95\% \text{N}_2/\sim 5\% \text{CH}_4$) need to be accommodated. We present tests exploring the effect of pressure and gas composition on the abundance and fragmentation of desorbed ions on the MOMA breadboard instrument at NASA Goddard Space Flight Center. Preliminary results on CsI (calibrant compound for MOMA) indicate that performance in the N_2 atmosphere is similar to that of CO_2 , but the pressure at the sample will need to be optimized for preservation of molecular ions (Figure 2). This could be accomplished with differentially pumped sample chamber. The effects of trace CH_4 will also be evaluated.

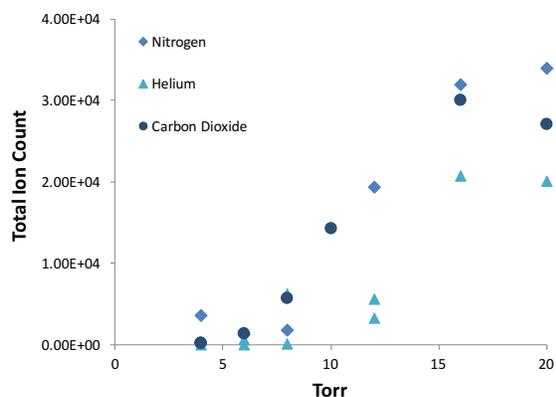


Figure 2. Preliminary tests on CsI across as a function of pressure show that N_2 is as efficient of a buffer gas as CO_2 for ion formation through LDI.

Titan surface analogs. Two-step LDMS has been used in previous studies of Titan-like organic materials [7,8]. Recent studies by our group using a commercial LIT instrument run at MOMA-like conditions were used to compare the formation of fused-ring vs. polyphenyl compounds in Titan aerosol analogs formed with aromatic compounds (Figure 3) [9].

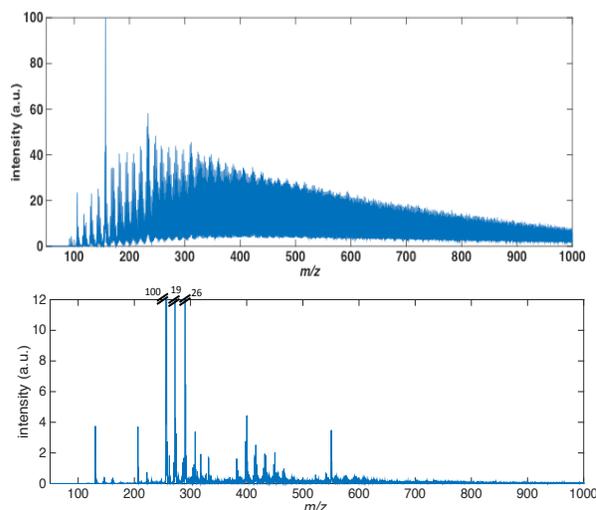


Figure 3. Recent MOMA-like analyses of Titan-like aerosols formed from benzene/ N_2 (top) and naphthalene/ N_2 (bottom) show a clear difference in structure for single- vs. double-ring synthesis [9].

The MS/MS capability afforded by the LDMS was essential in the determination of the molecular structure, and would be invaluable to the analysis of complex mixtures one would find on Titan. Various surface analogs for Titan organics will be tested, including analogs for the organic aerosol as it would be directly deposited on the surface, including those formed with CO [10], and the hydrolysis products of aerosol reacted in water and water/ammonia mixtures, meant to simulate long-term reaction in cryolavas on the surface [11,12,13]. The latter offers prime locations for searching for biologically-relevant molecules and assessing the habitability of Titan [14].

References: [1] Goetz W. et al. (2016) LPSC, #2614. [2] Pinnick V. T. et al. (2016) LPSC, #2770. [3] Brinckerhoff W. B. et al. (2013) *IEEE Aerospace Conf.* doi: 10.1109/AERO.2013. [4] Arevalo Jr. R. et al. (2015) *IEEE Aerospace Conf.* doi: 10.1109/AERO.2015.7119073. [5] Li X. et al. (2014) *Astrobiology* **15**, 104-110. [6] Castillo J. C. et al. (2016) *Low Temp. Mat. and Mech.*, CRC Press, ed. Bar-Cohen, pp. 229-269. [7] Imanaka H. et al. (2004) *Icarus* **168**: 344-366. [8] Mahjoub A. et al. (2016) *PSS* **131**: 131 1-13. doi:10.1016/j.pss.2016.05.003. [9] Gautier T. J. (2016) *PSS*, in review. [10] Hörst et al (2012) *Astrobiology* **12**, doi:10.1089/ast.2011.0623. [11] Neish C. D. et al. (2008) *Astrobiology*, **8**, 273-287. [12] Neish C. D. et al. (2009) *Icarus*, **201**, 412-421. [13] Neish C. D. et al. (2010) *Astrobiology*, **10**, 337-347. [14] Neish C. D. et al. (2017) LPSC, #1457.