

The Past, Present and Future for the Linear Ion Trap Mass Spectrometer (LITMS) and Related Ion Trap Instrumentation. W. Brinckerhoff¹, A. Grubisic², R. Danell³, F. van Amerom⁴, V. Pinnick⁵, X. Li⁵, R. Arevalo¹, S. Getty¹, M. Trainer¹, P. Mahaffy¹, P. Chu⁶, K. Zacny⁶, S. Rogacki⁷, ¹NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771) william.b.brinckerhoff@nasa.gov; ²CRESST, University of Maryland at College Park, College Park, MD ; ³Danell Consulting, Inc., Winterville, NC; ⁴Mini-Mass Consulting, Hyattsville, MD; ⁵Center for Research and Exploration in Space Science and Technology (CRESST), University of Maryland, Baltimore County, Baltimore, MD; ⁶Honeybee Robotics Spacecraft Mechanisms Corp., New York, NY; ⁷Space Physics Research Laboratory (SPRL), University of Michigan, Ann Arbor, MI.

Introduction: Over the next decade, the in situ investigation and chemical characterization of high-priority planetary bodies will require progressively more compact and analytically capable payloads. From the Pioneer Venus Program in the 1970's up through the ongoing MSL and MAVEN missions, quadrupole mass spectrometer (QMS) systems have served as low-risk, cost-efficient means to explore the inner and outer reaches of the solar system. However, spaceflight QMS instruments are inherently limited, as they are designed for the analysis of volatile phases only, require high vacuum, and offer only a limited mass range (≤ 550 Da). Moreover, QMS sensors do not provide any detailed information regarding molecular structure. In contrast, ion traps enable the measurement of both volatile (via electron ionization, EI) and non-volatile (via laser desorption/ionization, LDI) compounds, operate under relaxed vacuum conditions (reducing pumping requirements) and can disambiguate molecular structures via tandem mass spectrometry and/or high mass resolving power.

Although traditional 3D ion traps have been operated on the International Space Station [1] and Rosetta's Philae Lander [2], the Mars Organic Molecule Analyzer (MOMA) on the ExoMars rover represents the first planetary application of a 2D (or linear-type) ion trap. The workhorse MOMA breadboard instruments have demonstrated the detection of ppmw-levels of nonvolatile organics embedded in geological materials, even in the presence of perchlorate salts, via LDI techniques [3]. The MOMA Engineering Test Unit (ETU), which simulates the form, fit and function of the flight model, has been shown to detect $< \text{pmol}/\text{mm}^2$ levels of analyte [4]. In order to further advance these capabilities of MOMA and its fundamental 2D ion trap architecture, a next-generation Linear Ion Trap Mass Spectrometer (LITMS) has been under development at NASA GSFC with support from the ROSES MatISSE Program.

The LITMS investigation is focused on the ability to conduct fine-scale organic and inorganic analyses of short (5 – 10 cm) rock cores, such as those that could be acquired by a drill-enabled robotic arm on a planetary lander or rover. Like MOMA, the LITMS investi-

gation supports both pyrolysis/gas chromatograph mass spectrometry (GCMS) and laser desorption/ionization mass spectrometry (LDI-MS). However, unlike MOMA the LITMS instrument enables the compositional analysis of subsampled core fines. Further, LITMS offers an extended mass range (up to 2000 Da), high-temperature (up to 1300°C) evolved gas analysis and dual-polarity ion detection.

Current Status: The complete LITMS brassboard, including the sensor and mechanical housing (Fig. 1), pulsed laser system and RF power supply, is scheduled for integration in the late summer of 2016. Following the functional checkout of the system, the brassboard will be interfaced to the Precision Core Sampler (PCS) at Honeybee Robotics in Pasadena, CA, and the performance of the combined instrument will be verified under Mars relevant atmospheric conditions over the course of several dedicated integration and test campaigns. Following these campaigns, the brassboard will be returned to NASA GSFC and undergo vibration qualification (GEVS-levels) to reach TRL 6 maturity.

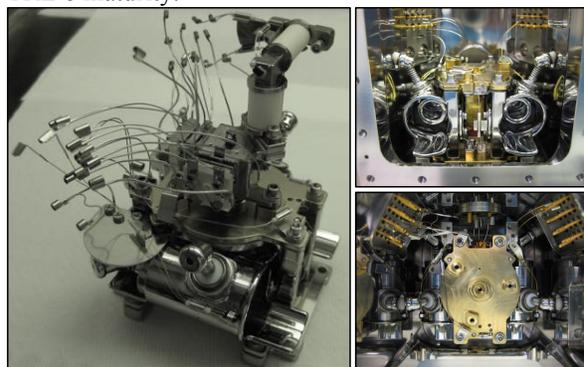


Fig. 1. (Left) LITMS ion trap subassembly, including electron ionization (EI) source with flying leads, shielded conversion dynodes, hyperbolic rods, and gas inlet. (Top right) Front view and (bottom right) overhead view of the ion trap subassembly (EI source removed for easier visual access) integrated into the LITMS mechanical housing.

Results: Initial testing of a LITMS prototype instrument was completed with both 700 kHz and 1.6 MHz RF supplies. Using these two frequencies, an m/z

range down to 18 Da in EI mode and up to >2000 Da in LDI mode as well as sub-unit mass resolution up to at least 500 Da has been demonstrated (Fig. 2). Recently the flight-like dual frequency RF supply that will be used for final brassboard instrument testing has become available, and initial performance testing has been completed.

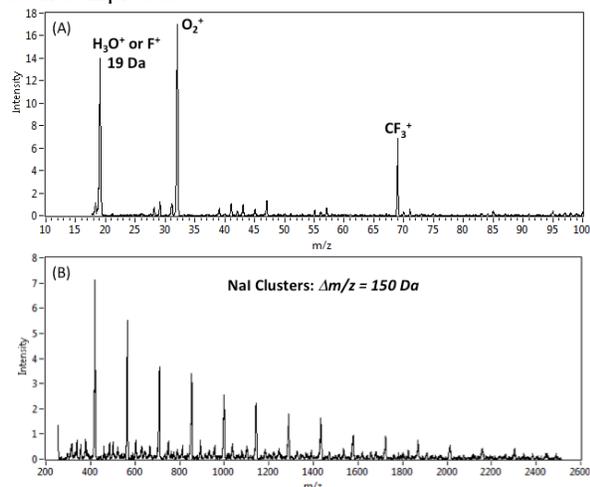


Fig. 2. (A) Low mass range GCMS spectrum of PFTBA with 1.6 MHz RF supply. (B) High mass range LDMS spectrum of NaI clusters with 700 kHz RF supply.

The detection of negative ions, particularly in LDMS mode, can provide complementary information and improve identification of electronegative species, containing elements such as S and Cl, as well as classes of organics (including several carboxylic and amino acids) that favor anion formation. This results in one ion polarity providing a significantly clearer mass spectrum than the other polarity, depending on the physicochemical properties of the compound under study (Fig. 3). Negative ion mode also allows the detection of the strong oxidant perchlorate (ClO₄⁻), which has been measured at high levels (up to 0.7 wt.%) in the Martian soil by the Phoenix Mars Lander [5,6] and could have presented analytical challenges to the pyrolysis experiments on Viking and Phoenix [7], and may also do so on MSL.

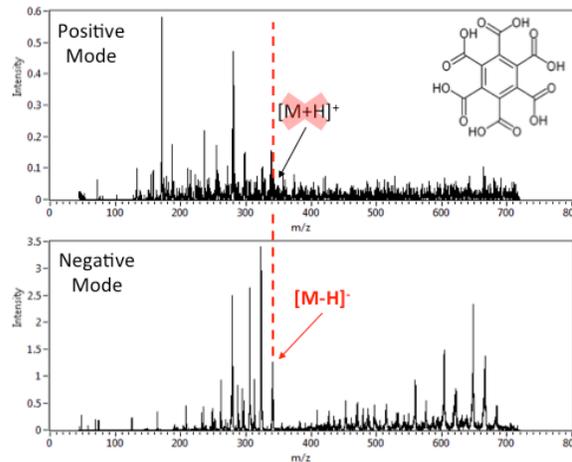


Fig. 3. Positive and negative mode spectra of mellitic acid demonstrating the clear detection and higher signal-to-noise in negative mode vs. positive mode.

Future Plans: Because mobile exploration of the surface and subsurface of the red planet is critical to address current and future astrobiology goals, the LITMS instrument will join the rest of the payload instruments on the Atacama Rover Astrobiology Drilling Studies (ARADS; PI: Brian Glass) project and be tested in the field in early 2017. This analog Mars mission, which is supported by the ROSES PSTAR Program, seeks to integrate and test progressively an innovative rover-drill system with a small collection of highly capable and technically mature scientific instruments. The scientific objective of the project is to understand the mobility and distribution of soluble salts, organic compounds, organic biomarkers, and life in extremely arid environments.

However, the application of the LITMS is not limited to Mars or remote terrestrial destinations. Rather, simple modifications to the gas processing subsystem and laser desorption ion inlet interface can adapt the LITMS instrument to the exploration of higher or lower pressure environments, including ultrahigh vacuum conditions found at Europa and Enceladus.

References: [1] Chutjian, A. et al. (2007) *SAE Tech Paper Series, 37th ICES*; [2] March, R. E. and Todd, J. F. J. (2005) *John Wiley & Sons, Inc.*; [3] Li, X. et al. (2015) *Astrobiology*; [4] Arevalo Jr., R. et al. (2015) *IEEE Aerospace*; [5] Hecht M. et al. (2009) *Science* 325: 64-67. [6] Kounaves S. et al. (2009) *J. Geophys. Res.* 115: E00E10 doi: 10.1029/2009JE003424. [7] Navarro-González R. et al. (2010) *J. Geophys. Res.*, 115: E12010, doi:10.1029/2010JE003599.