**MARS ORGANIC MOLECULE ANALYZER: PERFORMANCE OF LASER DESORPTION IONIZATION LINEAR ION TRAP MASS SPECTROMETER.** A. Grubisic[1], F. H. W. van Amerom[2], R. M. Danell[3], V. T. Pinnick[1], R. D. Arevalo[1], X. Li[1], L. Hovmand[1], A. E. Southard[1], W. B. Brinckerhoff[1], P. R. Mahaffy[1], and the MOMA Team[1-7], [1]NASA Goddard Space Flight Center (Mail Stop: 699 B33-E214, Greenbelt MD 20770, USA; Andrej.grubisic@nasa.gov), [2]Mini Mass Consulting, USA, [3]Danell Consulting, USA, [4]LPGM, Ecole Centrale Paris, Châtenay-Malabry, France, [5]Max Planck Institut für Sonnensystemforschung, Germany, [6]LISA, LATMOS, Guyancourt, France, [7]Univ. Paris-Est, Créteil, France.

**Introduction:** Mars Organic Molecule Analyzer (MOMA) is a key analytical tool on the joint ESA-Roscosmos ExoMars-2018 rover mission, whose primary goal is to seek for evidence of extinct or extant life on Mars by acquiring subsurface samples up to 2 meters deep.[1] With its ability to provide chemical (molecular) information on organic content in solid samples, MOMA is central to the mission's overall objective. The instrument consists of a linear ion trap mass spectrometer (LIT-MS) with two fundamentally different modes of operation: 1) pyrolysis gas chromatography-mass spectrometry (GC-MS) and 2) Mars atmospheric pressure laser desorption ionization-mass spectrometry (LDI-MS). The combination of these analytical techniques provides a unique capability to characterize a broad range of compounds allowing chemical analyses on volatile and non-volatile species in geological samples. Here we report on the latest performance and characterization measurements of the MOMA-MS engineering test unit (ETU; Figure 1), specifically in the laser desorption ionization mode, in which we duplicate/validate the performance metrics of the prototype LIT-MS and demonstrate it meeting the critical specification requirements.

**MOMA Mass Spectrometer:** The MOMA LIT-MS consists of four l = 28 mm long hyperbolic rods with $2 \cdot r_0$ = 6 mm separation between opposing rods. During analysis, chemical compounds are ionized and injected into the trap through one, mode-dependent endplate of the LIT. During trapping and cooling, ions oscillate in the fixed RF field of the rods and are trapped axially by a positive DC bias to the endplates relative to the rods. For ion ejection, an auxiliary waveform applied to one pair of opposing rods creates a mass-selective instability that excites ions of a specific mass-to-charge (m/z) ratio and ejects them. These ions are guided through a narrow slit in the rods, where they are detected via a conversion dynode-channel electron multiplier detector combination.

The symmetric nature of the LIT allows it i) to accept ions from either end of the ion trap, thus coupling to, both, an electron impact (EI) source (GC-MS) and the LDI source (LDI-MS), as well as ii) to employ two detectors for redundancy and/or increased sensitivity. Through compatibility with moderate vacuum pressures (~$10^{-3}$ torr) and a unique fast-acting aperture valve, MOMA can directly sample at Mars ambient conditions, as well as utilize Martian atmosphere for ion cooling and thus improved ion trapping. It can furthermore exploit ambient gases to perform MS/MS measurements for detailed structural characterization of molecular ions of interest.

The three critical performance requirements of MOMA-MS in the LDI-MS mode are the mass range (*m/z: 50* – 1000), mass resolution (full width half maximum peak widths of 1 Da below *m/z* 500 and 2 Da between *m/z* 500-1000), and detection limit (1 pmol/mm$^2$ Angiotensin II in MALDI matrix).

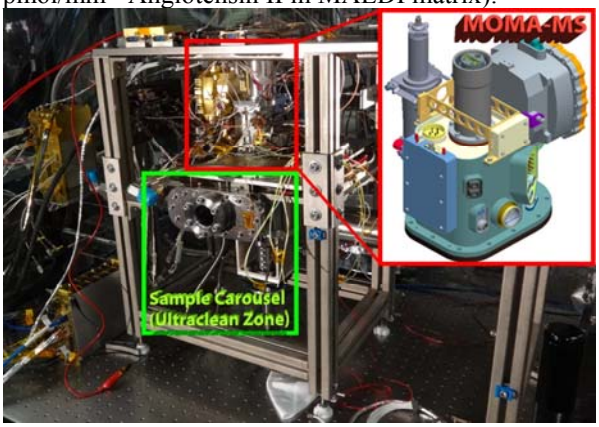


**Figure 1.** Engineering Test Unit at NASA GSFC, with inset illustrating MOMA-MS.

**Laser Desorption Ionization:** In this mode of operation, a nanosecond pulsed laser desorbs and ionizes molecules directly from powdered samples presented to the inlet of the mass spectrometer at Mars ambient conditions (4-8 Torr Mars atmosphere, primarily $CO_2$). Rapid sample heating during LDI readily desorbs and ionizes complex organic molecules from geological samples with minimal fragmentation, as shown in Figure 2.[2] Additionally, intact organic species can be obtained even in 1 % perchlorate-containing mineral matrices, characteristic of the Martian surface, which often proves difficult for the GC-MS mode alone. For demonstrations presented herein, an early prototype UV (266 nm) laser system (LZH e.V.) is employed, capable of delivering 100 Hz bursts of < 1 ns pulses with a maximum pulse energy of $E_P$ = 240 μJ under

flight-like illumination conditions (45º incidence angle, 0.6 mm x 0.4 mm beam size). In this configuration, maximum peak intensities $I_P$ > 40 MW/cm$^2$ can be attained at the sample, with $I_P$ = 3 - 5 MW/cm$^2$ typically employed in these studies.

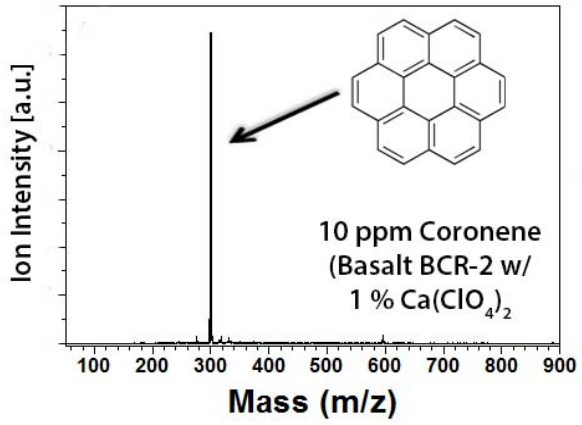


**Figure 2**. LDI mass spectrum of coronene (m/z = 300 Da) doped at 10 ppm level in a Mars-relevant geological matrix (Columbia River Basalt - BCR-2) containing 1% perchlorate.

During LDI, a specially designed fast-acting ball-sealed aperture valve momentarily exposes (~100 ms duration) the mass spectrometer to the Martian atmosphere, with a 30 mm long capillary inlet tube acting as a conductance-limiting aperture. Generated ions are guided toward (and through) the ion inlet tube located ~ 3 mm away from the sample by a combined action of i) an electrostatic potential gradient between the sample plate and biased inlet tube, and ii) hydrodynamic gas flow between the high pressure sample (4-8 torr) and low pressure mass spectrometer (~$10^{-4}$ torr) regions. For the selected inlet capillary geometry, we show that the gas molecular flow is viscous-like at Mars ambient conditions, and yields maximized ion transmission at P > 3 torr of Martian atmosphere, with ion transport predominantly determined by hydrodynamic gas flow.

To operate the ion detectors at typical operating voltages (up to 5 kV), the mass spectrometer region is evacuated after LDI to ~$10^{-4}$ torr in several seconds by a miniature wide range pump. We have previously shown that ions can survive > 20 sec at various gas flow levels MOMA-MS is likely to experience at Mars ambient conditions.

We have furthermore explored how the LDI process depends on the excitation laser intensity. With Rhodamine 6G (R6G) as a proxy for a complex molecular ion, we observe a dramatic onset for ion generation at a laser intensity that is analyte specific (~3 MW/cm$^2$ for R6G). Furthermore, upon continued illumination of the sample, a shift in the threshold value is observed, indicating a potential presence of two analyte subpopulations, with one more easily desorbed than the other.

By focusing on 1 pmol/mm$^2$ Angiotensin-II peptide as a test case, we have additionally demonstrated the required high mass range and limit of detection of MOMA-MS in the LDI mode (Figure 3).

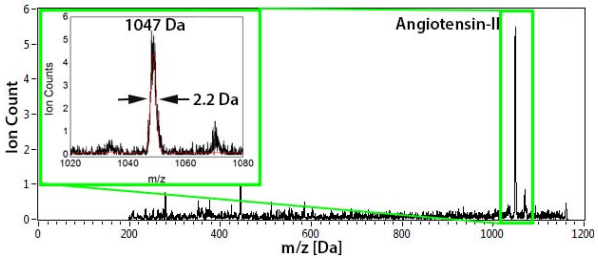


**Figure 3.** LDI mode mass spectrum of 1pmol/mm$^2$ Angiotensin-II (m/z $[M+H]^+$ = 1047 Da) in DHB matrix. MOMA-MS ETU Measurement.

**MS/MS**: This powerful feature in MOMA-MS is a widely used analytical approach for identification of complex organic and bioorganic compounds, and represents the first space-flight implementation of it. It builds on the fact that structure-specific fragmentation patterns result when molecular ions collide with neutral gas molecules introduced into the ion trap. Through detection of fragment ions in the resulting mass spectrum, the original structure of the parent ion can be reconstructed.

In MOMA-MS, a Stored Waveform Inverse Fourier Transform (SWIFT) approach is employed for MS/MS analysis of trapped ions.[3] Here, an auxillary signal containing frequencies that efficiently couple to the secular motion of undesired ions is applied in a dipolar fashion to two of the rods making up the LIT, resulting in isolation of ions within a relatively narrow mass range. After isolation, the ion of interest is selectively excited causing it to collide with background gas molecules present within the instrument. After sufficient ion-neutral collisions, the ion breaks apart into fragments, which are trapped and subsequently mass analyzed, thus yielding a fragment mass spectrum.

We successfully demonstrated MS/MS operation on 10 pmol/mm$^2$ Angiotensin-II (m/z = 1047 Da) peptide, as shown in Figure 4, where the protonated parent ion $[M+H]^+$ is first isolated (middle) and subsequently fragmented (bottom), yielding a fragmentation spectrum demonstrating a set of characteristic peptide backbone fragments labeled with the standard b and y nomenclature. In this case, these fragment ion masses can be used to sequence the peptide, demonstrating the utility of MS/MS operation.

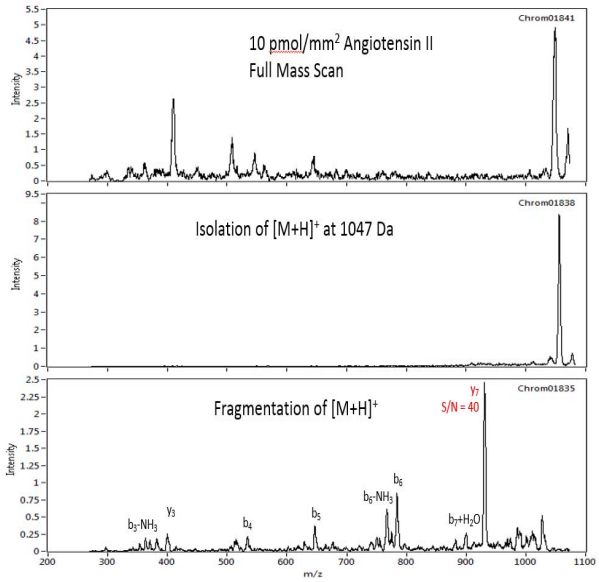


**Figure 4.** MS/MS operation demonstrated on 10 pmol/mm$^2$ Angiotensin-II (m/z $[M+H]^+$ = 1047 Da) in DHB matrix: (top) LDI-MS spectrum; (middle) Isolation of 1047 Da peak via SWIFT; (bottom) Fragmentation spectrum of the 1047 Da ion. MOMA-MS early prototype measurement.

**References:** [1] Brinckerhoff W.B. et al (2013) IEEE Aerospace Conference. [2] Li X. et al, Danell R. M., Brinckerhoff W. B., Pinnick V. T., van Amerom F. H. W., Arevalo R. D., Getty S. A., Mahaffy P. R., Steininger H. and Goesmann F. (2014) Astrobiology, submitted. [3] Guan, S. and Marshall A. G. (1993) Anal. Chem. 65, 1288.

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