MARS ORGANIC MOLECULE ANALYZER (MOMA) MASS SPECTROMETER STATUS AND SCIENCE OPERATIONS ON THE EXOMARS ROVER. William B. Brinckerhoff[1], Ryan M. Danell[2], Friso H. W. van Amerom[3], Veronica T. Pinnick[4], Ricardo D. Arevalo, Jr.[1], Lars Hovmand[5], Xiang Li[4], Zhiping Chu[1], Andrej Grubisic[4], Paul R. Mahaffy[1], Fred Goesmann[6], Harald Steininger[6], Walter Goetz[6], and the MOMA Team[1-9], [1]NASA Goddard Space Flight Center, 8800 Greenbelt Rd., Greenbelt, MD 20771 (william.b.brinckerhoff@nasa.gov); [2]Danell Consulting, Inc., Winterville, NC; [3]MiniMass Consulting, Hyattsville, MD; [4]Center for Research and Exploration in Space Science and Technology (CRESST), University of Maryland; [5]Linear Labs, LLC, Washington, DC; [6]Max Planck Institut für Sonnensystemforschung (MPS), Göttingen, Germany; [6]Laboratoire Interuniversitaire des Systèms Atmosphériques (LISA), Univ. Paris-Est, Créteil, France; [7]Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), Guyancourt, France; [8]Laboratoire de Génie des Procédés et Matériaux (LGPM), École Centrale Paris, Chatenay-Malabry, France; [9]Laser Zentrum Hannover e.V. (LZH), Hannover, Germany.

Introduction: The Mars Organic Molecule Analyzer (MOMA) investigation on the 2018 ExoMars rover will examine the chemical composition of samples acquired from depths of up to two meters below the martian surface, where organics may be protected from radiative and oxidative degradation [1,2]. MOMA incorporates both pyrolysis-gas chromatography/mass spectrometry (pyr-GCMS) and laser desorption mass spectrometry (LDMS) modes of operation, to detect and characterize a broad range of potential organic compounds in crushed drill samples. In concert with the other instruments in the rover's Pasteur Payload, MOMA will contribute substantially to understanding the distribution and structure of organics preserved in a variety of mineralogical environments, in support of the ExoMars goal to seek the signs of past or present life on Mars.

The MOMA investigation is led by the Max Planck Institute for Solar System Research (MPS) with PI Fred Goemann. MPS provides the pyrolysis ovens and the Rosetta-heritage tapping station that seals the ovens to the GC manifold, as well as the passively Q-switched 266 nm laser for LDMS, with the partnership of Laser Zentrum Hannover, e.V. The MSL/SAM-heritage GC subsystem is provided by a French team led by University of Paris/LISA. The mass spectrometer and electronics subsystem (MOMA-MS) is provided by NASA/GSFC. The complete MOMA flight instrument will be integrated at MPS in late 2015/early 2016 prior to delivery to the rover payload assembly, integration, and test (AIT) flow at Thales Alenia Space – Italy (TAS-I) in 2016.

Mass Spectrometer Modes: The design of the MOMA dual source linear ion trap has been described previously [3,4]. Briefly, the linear ion trap enables external electron ionization (EI), for GCMS, and Mars-ambient laser desorption/ionization (LDI), for LDMS, with ions injected through opposite ends of the miniature hyperbolic rod electrode array (Fig. 1).

In GCMS mode, the MS ingests a fraction of the GC effluent entrained in He, and produces full mass spectra at rates of several Hz, in order to track the narrow GC peaks from different compounds. An automatic gain control (AGC) algorithm is implemented to ensure the trap is optimally filled for each scan. GCMS mode is designed to analyze compounds of high-to-moderate volatility (enthalpies of vaporization $\Delta H_V \leq$ 50 kJ mol^{-1}) such as alkanes, amines, and lighter carboxylic and amino acids and aromatic species. Derivatization agent in some ovens enables detection of the higher ΔH_V species in this range, and leads to the requirement for a GCMS m/z range of 50-500 Da.

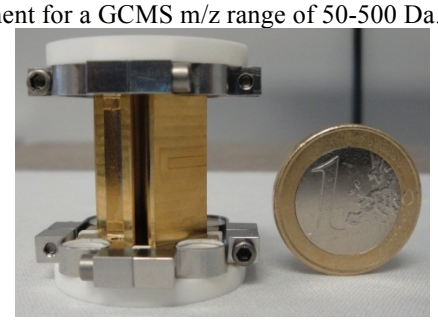

Fig. 1 Flight-scale MOMA linear ion trap. Four vertical rods and two end plates form the ion trapping volume.

In LDMS mode, the MS ingests ions from a burst of laser pulses focused onto a powdered sample, delivered on the rover carousel's refillable tray. Due to the requirement to close a valve and evacuate the MS following each burst, the duty cycle of LDMS is much slower: approximately one spectrum every 2 sec (depending on the number of pulses as well as the ambient Mars pressure). To ensure the trap is not over-filled with ions, unknown samples are subjected to a survey wherein the laser energy and pulse count are slowly increased during the run from minimal initial settings. LDMS mode is designed to analyze compounds of moderate-to-low volatility (enthalpies of vaporization $\Delta H_V \geq$ 40 kJ mol^{-1}) such as heavier carboxylic acids, aromatic species, chain-like compounds, and macromolecular organics. The nature of LDI permits some fraction of any large "parent" molecules to desorb intact, leading to the m/z range of 50-1000 Da. As previously demonstrated, the LDMS mode is immune to the

potentially oxidizing effects of heat-evolved perchlorates, simplifying analysis of nonvolatile organics [5].

Engineering Test Unit (ETU): The MOMA-MS ETU successfully completed a battery of tests to verify all performance requirements in support of the critical design review (CDR) in Sep. 2014 and the ongoing flight AIT. The ETU is a form, fit, and functional equivalent to the flight model (FM), developed and operated under flight protocols including contamination control, while permitting flexible interchange of gas and solid samples for analysis campaigns. The instrument is mounted on a "pseudo ultra-clean zone" (pUCZ) that mimics the sample carousel interface. The ETU has been integrated with advanced prototypes of the oven/tapping station/GC and pulsed laser subsystems to assure the highest available fidelity of end-to-end testing, script development, and troubleshooting.

The mass resolution and limit of detection specifications for direct mass spectra in each mode have been established and confirmed on the MS ETU with reference compounds. In LDMS mode, MOMA-MS has the additional capability to perform tandem mass spectrometry, or MS/MS, wherein a compound is isolated and subsequently fragmented in the ion trap, permitting molecular structural analysis. MS/MS performance depends on pressure, timing, stability, and intrinsic sensitivity, which are particular to each instrument model. Recent testing of the MS ETU has confirmed that MOMA-MS meets its MS/MS limit-of-detection (LOD) requirement of 10 pmol mm^{-2} of an appropriate complex organic, such as the peptide Angiotensin II at m/z 1047 (Fig. 2).

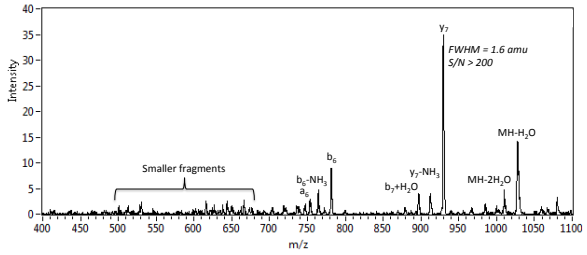

Fig. 2 MS/MS isolation and fragmentation of the selected analyte (Angiotensin II peptide) following laser desorption and ionization, demonstrated on the ETU, enables higher-confidence assignment of molecular structure through matching of known fragment ions. The 'b' and 'y' ions characterize the particular amino acid sequence of Angiotensin II.

MOMA Mars Operations: Planning for ExoMars and MOMA operations is based on the 218-sol rover Reference Surface Mission sols comprising 38 sols of startup, egress, and commissioning, followed by 180 sols of science operations. Drill samples are acquired during 6 Experiment Cycles (2 samples each) and 2 Vertical Surveys (5 samples each), yielding a minimum of 22 total samples. The rover carousel holds at least 30 MOMA ovens, while the refillable tray by design supports an unlimited number of samples. The short length of the baseline mission necessitates a fairly structured science operations cycle. Once delivered to the carousel via crusher and dosing station, each powdered sample is analyzed sequentially by MicrOmega, Raman, and MOMA (nominally LDMS then GCMS). MOMA is allocated three dedicated sols for experimental sequences on a given sample:

(1) LDMS Survey: 200 spectra at each of 3 or more sample points. Each run covers a small range of laser pulse energies, burst counts, and ion trap parameters.

(2) LDMS Targeted: Focused and MS/MS analysis of points identified by Survey and/or MicrOmega.

(3) GCMS: Each pyrolysis run selects single injection trap + column to elute to MS, sampling at 1-5 Hz.

A short series of calibration spectra is collected before each sequence. For GCMS a small internal valved tank of perfluorotributylamine (PFTBA) is used. For LDMS MOMA includes an inorganic, cluster-producing calibration target in the carousel.

Each sequence is nominally run with fixed initial parameters to enable inter-run and inter-sample comparisons. However, MOMA supports several types of adjustable parameters for tailoring follow-up scripts to be responsive to science results from any instrument (see table). Based on MSL/SAM experience, we can anticipate a preference to spend more than the nominal time allocation to extract maximal science from a given sample. The full ExoMars team will be involved in any decisions regarding such follow-up scripts (including analysis of replicate samples).

Parameter	Available Range	Nominal / Initial	Notes
Sample Points	1-20 points along arc	3 pts (e.g. 5, 10, 15)	spot size ~ 0.5 mm diameter
Laser Energy	15 μJ – 250 μJ	ramp 15-50 μJ	affects intensity, fragmentation
Laser Burst	1 – 50 pulses/burst	1, 3, & 10 pulses	higher → more ions in trap
Laser Rep Rate	1 – 100 Hz	100 Hz	affects valve open time
MS/MS	Isolate any m/z in range 50-1000 Da	Manually selected list ~3-5 masses	Can be automated e.g. with high-m/z peak detections
Oven Type	Pyrolysis, Derivatization	Pyrolysis	Deriv. agents: MTBSTFA, DMF-DMA, and TMAH
Temp. Cut	~30 – 1000 °C	~250 °C	Used to isolate organics
Injection Trap	Tenax-GR, Carbosieve	Tenax-GR	Use in conjunction w/column
Column	MXT-5, MXT-CLP, MXT-Q-BOND, Chirasil-Dex	MXT-5	cover range of organics
EI Parameters	20, 100 μA; 50-200 ms	20 μA, 100 ms	higher → more ions in trap

References: 1. Pavlov, A.A. et al. (2012) *GRL* **39**, L13202. 2. Quinn, R.C. et al. (2013) *Astro* **13**, 515 – 520. 3. Brinckerhoff, W. et al. (2013) *IEEE Aerospace Conf.* doi: 10.1109/AERO.2013. 4. Arevalo, R. et al. (2014) *LPS* **45**, 2894. 5. Li, X. et al. (2014) *Astrobiology*, in press.

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