

MARS ORGANIC MOLECULE ANALYZER (MOMA) MASS SPECTROMETER FOR EXOMARS 2018

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Introduction: The Mars Organic Molecule Analyzer (MOMA), a dual-ion source mass spectrometer-based investigation capable of both pyrolysis-gas chromatography/mass spectrometry (pyr-GCMS) and laser desorption mass spectrometry (LDMS), is a key instrument on the Pasteur Payload of the 2018 ExoMars rover mission to seek the signs of past or present life on Mars. When combined with the rover's two-meter drill-depth sampling, MOMA affords a broad and powerful search for organics over a range of preservation environments, volatility, and molecular weight. This combination may prove critical, as complex organic compounds are highly susceptible to degradation by cosmic radiation, which is effective to at least one meter depth on Mars [1]. In addition to enabling mission science, MOMA critically informs strategies for both sampling and *in situ* analysis for Mars Sample Return (MSR), which remains a top goal of the international planetary science community [2]. The MOMA investigation is led by the Max Planck Institute for Solar System Research (MPS) with the mass spectrometer subsystem provided by NASA/GSFC.

Dual Source Mass Spectrometer: To achieve both GCMS and LDMS and remain within the limited mass, power, and volume resources available on ExoMars, a dual-ion source ion trap MS (ITMS) design was adopted. The 70 eV EI source ionizes compounds entrained in He gas that is split from the pyr-GC effluent and leaked into the MS. The pulsed UV laser source produces ions directly from the surface of samples, at Mars ambient pressure, positioned near the MS inlet by the rover's sample processing and delivery system (SPDS) on a refillable tray. This configuration necessitates a tolerance of higher pressures than typical in mass spectrometry, which was partly the basis for selecting an ion trap. The requirements on the ITMS in each of the operating modes are summarized in **Table 1**. These must be met across a range of Mars surface/rover ambient conditions (i.e., 4 to 8 Torr and -40°C to +20°C) to ensure the full science return over the 180 sol operational lifetime of the mission. The MS must record spectra quickly without long settling or

pumping times. Individual full m/z range scans must be taken at 10 Hz or faster in pyr-GC mode to capture the shapes of fast (~1 sec) peaks eluting from the columns.

Table 1. Summary of MOMA ITMS Requirements

Specification	pyr-GC mode	LDI mode
Mass range	50 – 500 Da	50 – 1,000 Da
Resolution (FWHM)	≤1 Da	≤2 Da from 500 to 1,000 Da
Sensitivity	≤1 pmol (SNR ≥ 10)	≤1 pmol mm ⁻² (SNR ≥ 3)
Accuracy	≤ 0.4 Da	
Drift	≤ 0.4 Da per experiment	

The MS assembly including ion trap, laser, pump, RF supply, and valved LDI inlet assembly is shown in **Fig. 1**. The assembly shown is only about 15 cm across the base. A linear ion trap geometry allows ions to be admitted from either end of the device.

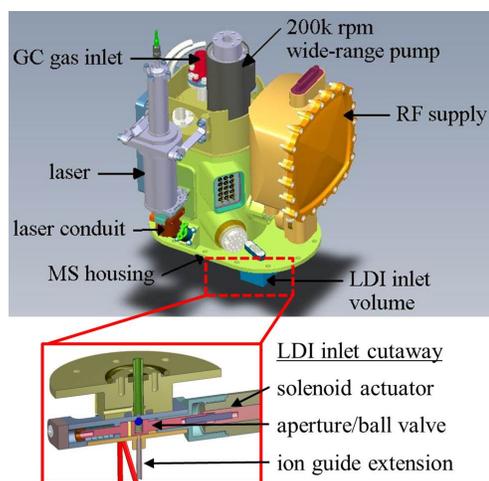


Fig. 1 Current design of the MOMA mass spectrometer. Laser ions from Mars ambient (4-8 Torr) enter the ion trap through the inlet while the valve is open (50-500 msec).

The core linear ion trap incorporates four parallel hyperbolic rods (similar to but significantly shorter

than quadrupole mass filters such as used in the Sample Analysis at Mars instrument) and two end-plate electrodes. This configuration is similar to Thermo Scientific's LTQ and LXQ ITMS systems. The Goddard-built miniature ITMS (**Fig. 2**) is 3-4 times smaller than the commercial analyzers, allowing lower voltages, weight, and power to be used to achieve the same m/z range, at the expense of ion trapping volume.

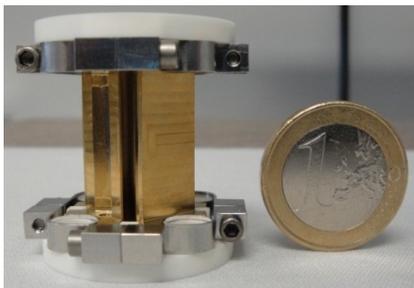


Fig. 2 Flight-scale MOMA linear ion trap. Four vertical rods and two end plates form the ion trapping volume.

The GCMS operation of MOMA follows a closed neutral gas EI source approach, well known from quadrupole instruments such as SAM and the Huygens GCMS, analyzing more volatile organics. The LDMS approach, which detects key classes of nonvolatile organics, has comprised a largely new development, although it is based on the discontinuous atmospheric pressure ionization (DAPI) scheme of Gao *et al.* [3]. Cations desorbed from the sample with a burst of focused UV laser pulses are guided toward the inlet by a DC electric field and carried into the trap by the ambient flow established with the aperture valve (**Fig. 1**) briefly open. Ions are trapped during the transient high pressure in the ITMS. Following valve closure, the ITMS then pumps down to the sub-mtorr range within a few seconds, permitting ion detection. A typical laser sample "spot" analysis involves a sequence of several such burst/valve-actuation/scan cycles, each producing one mass spectrum.

Instrument Testing: The MOMA ITMS flight-like breadboard has been tested against performance specifications within mission resource and schedule constraints. The technical requirements on the ITMS (**Table 1**) have been met and the subsystem has passed its NASA preliminary design review (PDR) in Dec. 2012.

The mass resolution and limit of detection specifications have been established with reference compounds providing reproducible conditions (**Fig. 3**). The mass range has been checked with known high-molecular weight species such as the peptide Angiotensin II (m/z 1047) and with cluster-forming sources such as NaI (**Fig. 4**), which demonstrates sensitivity to organics exceeding 2000 Da. High molecular weight

peaks in complex samples such as Mars analogs are now being systematically studied in a round robin campaign using both MOMA and commercial instrumentation. Initial assessment of MOMA-like, as well as SAM, protocols applied to organic-bearing Antarctic sediments was described by Bishop *et al.* [4].

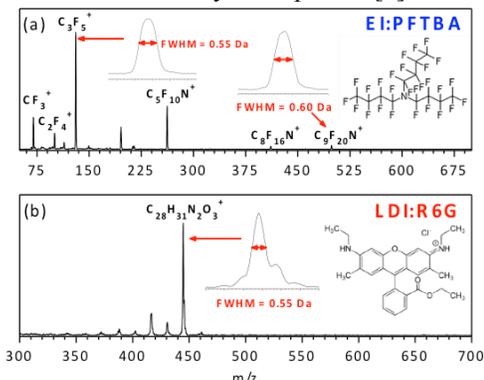


Fig. 3 MOMA-MS performance in both the GCMS (a) and LDMS (b) ion modes meets flight specifications including unit mass resolution and detection limits. PFTBA: perfluoro-tributyl-amine ($\text{CF}_3(\text{CF}_2)_3\text{N}$); R6G: Rhodamine 6G $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$, 1 pmol mm^{-2} loaded on sample plate.

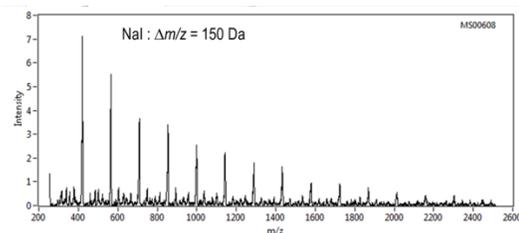


Fig. 4 Mass range of cluster-producing NaI in LDMS mode. Spectrum compares favorably with data from a high-performance commercial (Thermo LTQ) ion trap analysis.

The ion trap has further demonstrated flight performance in tandem mass spectrometry (MS/MS), in which trapped ions are selected and fragmented in isolation, allowing their structure to be elucidated.

In 2013, a complete engineering test unit (ETU) of the MOMA mass spectrometer will be built and tested with flight prototypes of the MOMA GC, pyrolysis, and laser subsystems, to verify the preliminary design and support a critical design review (CDR) in 2014. Intensive Mars analog work with breadboards and ETU will continue, guided by ongoing Mars science results.

References: 1. Pavlov, A.A. *et al.* (2012) *GRL* **39**, L13202. 2. NRC Planetary Science Decadal Survey (2011). 3. Gao, L. *et al.* (2008) *Analyt. Chem.* **80**, 4026. 4. Bishop, J. L. *et al.* (2012) *Icarus* doi:10.1016/j.icarus.2012.05.014.

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