

MARS ORGANIC MOLECULE ANALYZER: PERFORMANCE OF A MINIATURE MASS SPECTROMETER FOR *IN SITU* DETECTION OF MARTIAN ORGANICS.



V. T. Pinnick¹, F. H. W. van Amerom², R. M. Danell³, A. Buch⁴, M. Atanassova¹, R. Arevalo¹, L. Hovmand¹, W. B. Brinckerhoff¹, P. R. Mahaffy¹, R. J. Cotter⁵, and the MOMA Team¹⁻⁸

(1) NASA Goddard Space Flight Center, USA (veronica.t.pinnick@nasa.gov), (2) SRI International, USA, (3) Danell Consulting, Inc., USA, (4) LPGM, Ecole Centrale Paris, Châtenay-Malabry, France, (5) Johns Hopkins University, School of Medicine, USA, (6) Max Planck Institut für Sonnensystemforschung, Germany, (7) LISA, LATMOS, Guyancourt, France, (8) Univ. Paris-Est, Créteil, France.

Objectives

To search for “signs of life” molecules (large, non-volatile organic or biological molecules that suggest existing or prior biosynthetic activity) on the Martian surface and near subsurface

To distinguish between the endogenous and exogenous sources of Martian organics



Instrument	Type of instrument	Measurement Objectives
1 Panoramic Camera System (PANCAM)	Two Wide-angle cameras and one high resolution camera. On the mast	To visually characterize the Rover's environment and its geology. Also very important for scientific target selection.
2 Water Ice and Subsurface Deposit Observations on Mars (WISDOM)	Ultra High Frequency (UHF) Ground penetrating Radar operating at 1–3 GHz	To establish the subsurface stratigraphy down to 3 meters depth. Also important to plan drilling strategy.
Mars Multispectral Imager for Subsurface Studies (inherited in Drill Integrated Science (Ma_MiSS))	Infrared Spectrometer for Subsurface Studies, imbedded in Drill Integrated package for Borehole Sciences	To characterize the geophysical environment and associated geophysical properties during drilling operations.
4 MicroOmega	IR microscope	To examine the collected sample looking for mineralogical variety.
5 Raman	Raman spectrometer	To determine the mineralogical and atomic composition of the collected sample.
Mars Organic Molecule Analyser (MOMA)	Gas-chromatograph – mass-spectrometer combined with atmospheric pressure matrix assisted laser desorption/ionization	To search for a broad range of organic molecules (ppb) and measure any enantiomeric excess (chirality). Also to conduct atmospheric analyses.
7 X-Ray Diffractometer (MARS-XRD)	X-ray diffractometer	To determine the true mineralogical composition of the sample.

Method

➤ Core soil samples will be extracted from as deep as 2 meters below Martian surface to minimize effects of radiation and oxidative damage.

➤ Samples will be crushed and deposited into 22-30 sample cups seated in a rotating carousel.

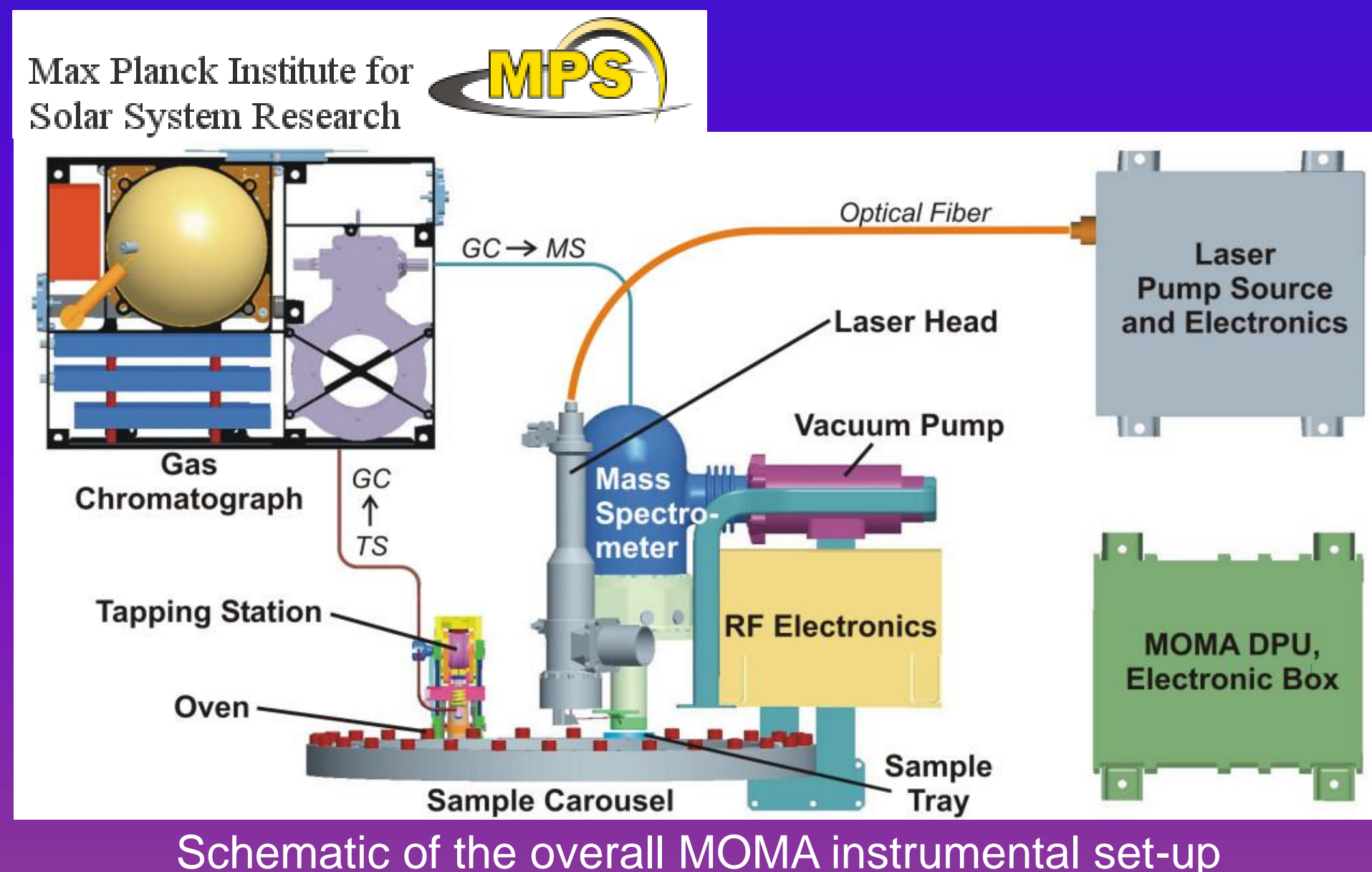
➤ Soil samples will be analyzed by UV laser desorption/ionization (LDI) and pyrolysis gas chromatography ion trap mass spectrometry (*pyr* GC-ITMS).

➤ LDI samples will be analyzed in ambient Mars atmospheric conditions : 4-9 Torr, composed mainly (95%) of CO₂.

➤ Samples which undergo GC-MS analysis may be exposed to derivatization compounds *in situ* to increase volatility.

Resource Limitations

The MOMA instrument operates under severely constrained resources which directly influence the ultimate instrument performance. The restrictions on mass, power and data volume limit the mass range, resolution and duty cycle of the mass spectrometer compared to a laboratory mass spectrometer.



Instrumental

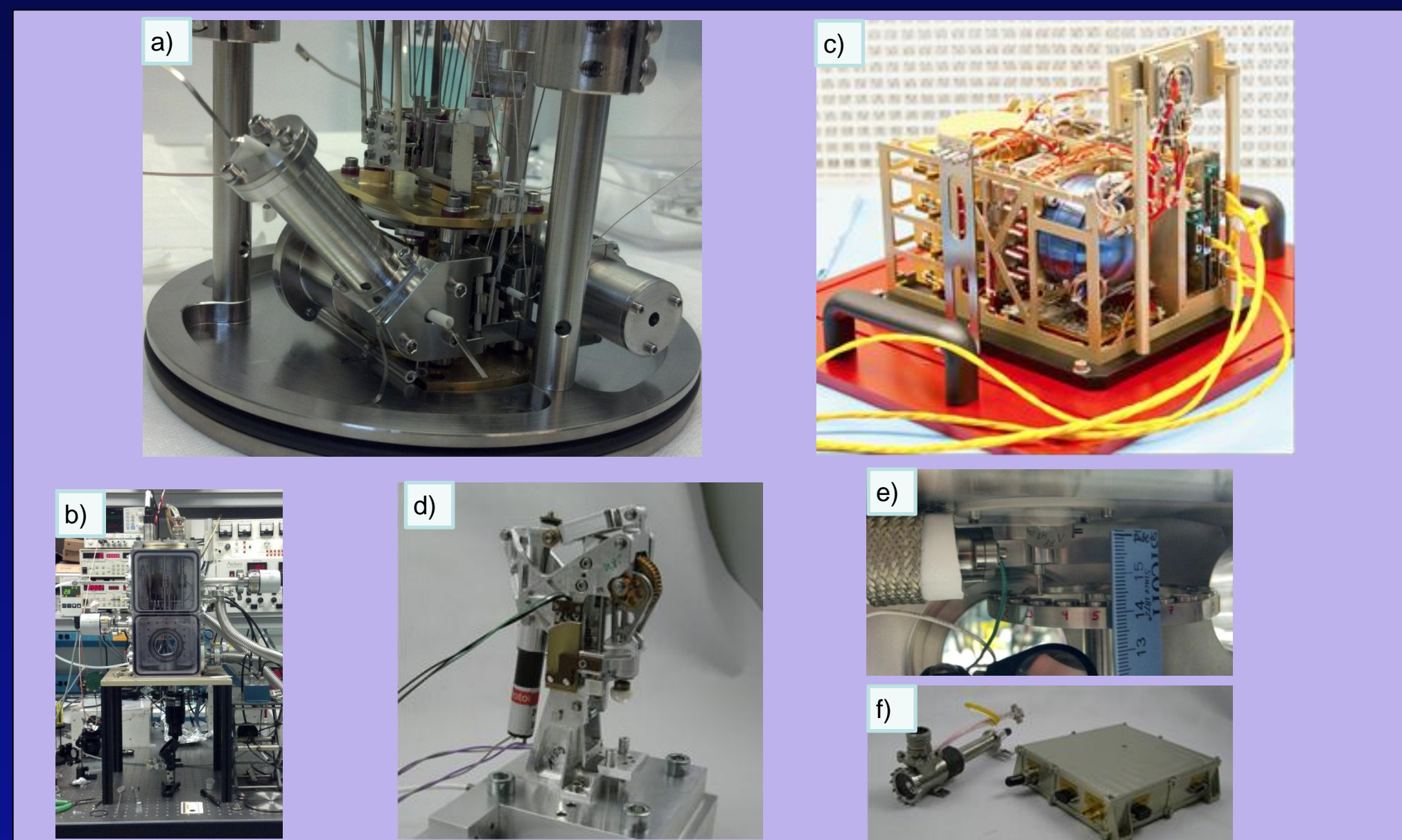


Figure 1. The flight-like laboratory prototype ion trap mass spectrometer instrument (a,b). The upper chamber (b) houses the custom-built linear ion trap (a) which accepts ions from two different ionization sources: EI (for GC-MS mode) and LDI from Mars ambient (bottom chamber). The brassboard gas chromatograph (c) design was based on the SAM heritage design with He reservoir and 4 separate columns including TCDs. Solid samples are sealed and heated by the tapping station (d) for GC-MS analysis. The LDI inlet system (e) allows ions to travel from Mars ambient pressure to vacuum through a fast-acting aperture valve. The laser (f) is a Nd-YAG laser with two doubling crystals (from 1064 nm to 266 nm) yielding a 1ns laser pulse with maximum energy of 250 uJ.

Miniaturized Linear Ion Trap MS

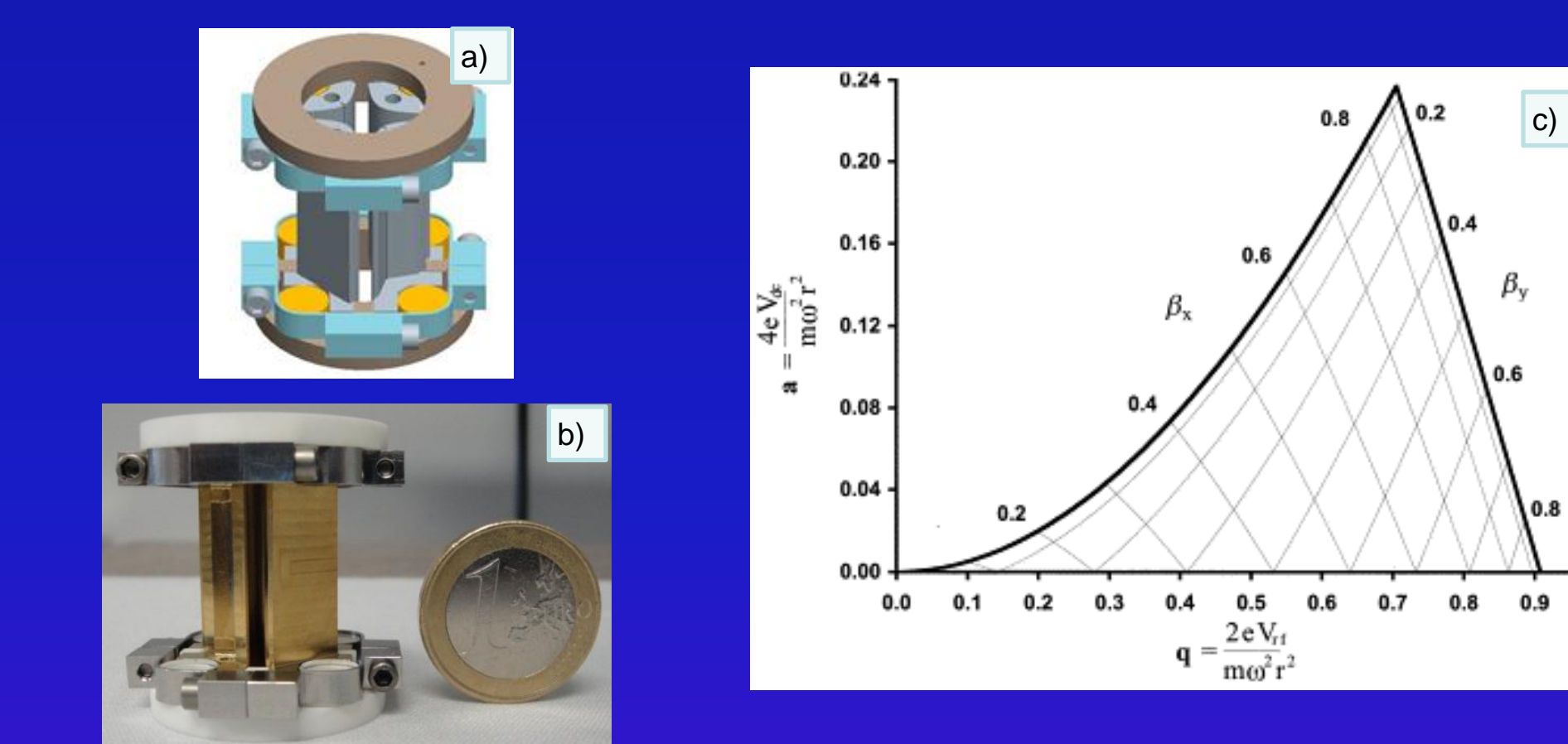


Figure 2. The CAD model (a) and the custom-built flight linear ion trap mass spectrometer (b). A typical analytical scan includes ionization, transfer into the MS, trapping and cooling of ions, and mass selected ejection of ions to a detector. The 2D design facilitates the ITMS serving as the detector for **both gas chromatography and laser desorption modes** since ion injection occurs orthogonally to ion ejection/detection. The plot (c) describes the trapping environment experienced by an ion in a linear quadrupole [1]. Ions are typically ejected at a constant q value. To reduce the RF voltage required to eject ions, the **radius of the ion trap was reduced** to 75% of the commercial design (Thermo LTQ). The MOMA ITMS trapping and ejection specifications are presented on the right.

Parameter	Definition	Value
r	internal radius	3 mm
V_{pp}	max RF amplitude	1.2 kV _{pp}
f	main RF frequency	700 kHz
V_{aux}	auxiliary RF amplitude	0-10 V_{pp}
f_{aux}	auxiliary RF frequency	15-350 kHz
V_{DC}	DC end plate bias	0-100 V
q_{eject}	trap ejection parameter	0.64, 0.784

Gas Chromatography

GC-MS provides the unique ability to characterize a broad range of compounds (volatiles or refractory compounds) evolved from solid samples. The key challenge with the analysis of refractory organic compounds contained in soils is their extraction and subsequent analysis by GC-MS. The MOMA experiment handles extraction of organic matter by thermodesorption followed by derivatization, the goal of which is to quickly extract the organic matter before degradation. Many refractory compounds can be analyzed (nucleobases, carboxylic acids, PAHs, etc.) however a key goal is to determine the chirality of amino acids, since on Earth, homochirality (especially the L-form) is an indicator for life.

Thermodesorption occurs over a range of temperatures from 150°C to 300°C over a span of 30 s to 10 min, depending on the chemical target. Under these conditions, amino acids have been shown to avoid degradation, and thus their chirality is preserved. Once extracted, refractory molecules with labile hydrogens (e.g. amino acids, nucleobases, carboxylic acids, etc.) are derivatized. General and sensitive derivatization occurs with dimethylformamide dimethylacetate derivatization (DMF-DMA). With DMF-DMA 11 of the 19 proteinic amino acids were separated on the Chirasil-β-dex (Varian) chiral column.

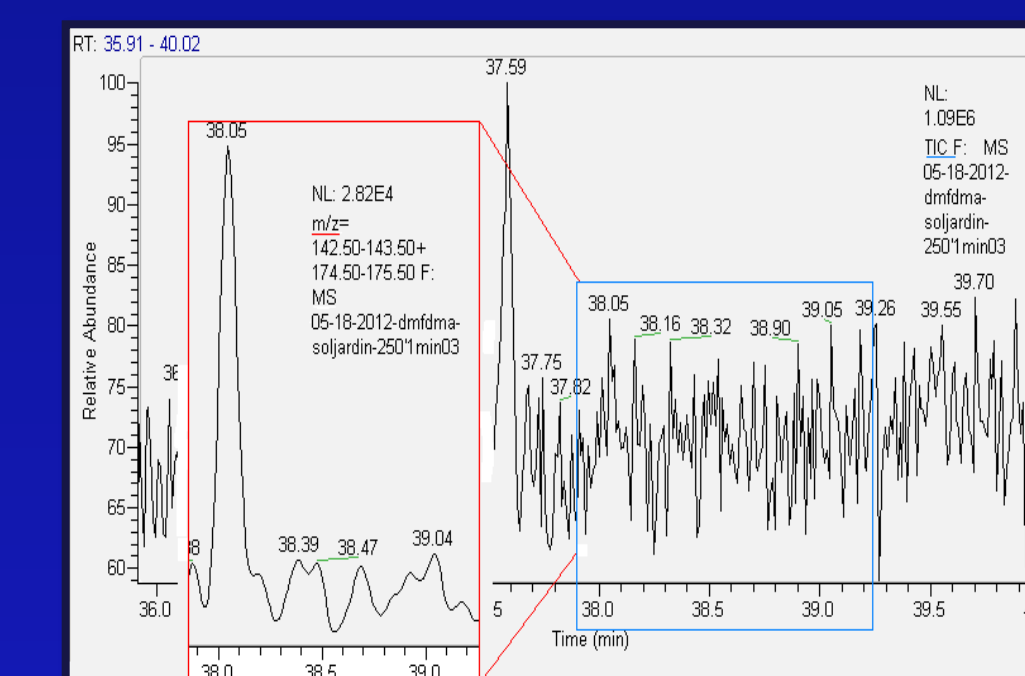


Figure 3. Chromatogram showing the detection of L-phenylalanine (SIM mode) on garden soil after 1 min. extraction at 250°C. No racemization is observed. Separation was performed on a (Chirasil-β-dex (eptakis-(2,3,6-tri-O-methyl)-β-cyclodextrine) column, WCOT Ultimatel type, 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness. Temperature program : Isotherm : 70°C – 5 min 70°C – 190°C ; 3 °C/min Isotherm : 190°C – 10 min

Laser Desorption Ionization

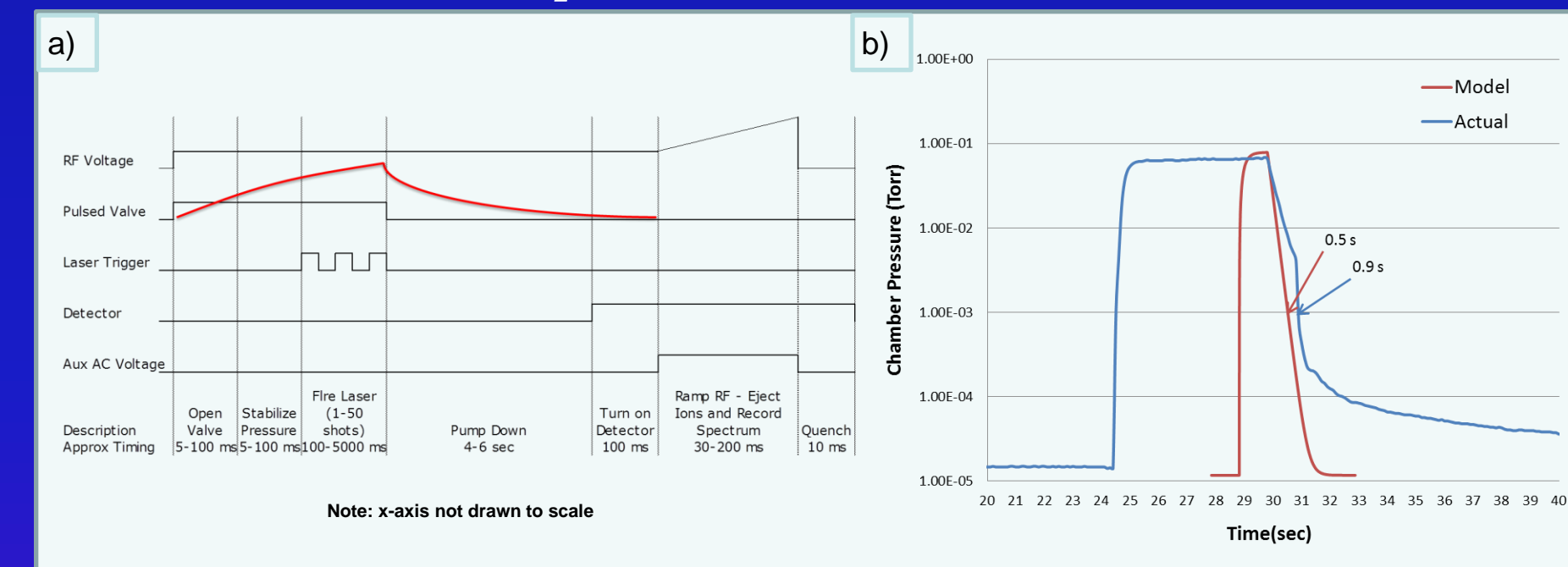


Figure 4. LDI is performed at Mars atmospheric pressure (4-9 Torr, predominately CO₂). MOMA-MS will utilize an aperture valve to allow ions to transfer directly into the ion trap according to the general timing diagram (a). Ions produced from laser pulses are transferred into vacuum by a combination of electric field and the flow produced by the pressure drop across a capillary inlet. The maximum safe operational pressure before HV electronics can be switched on for ejection/detection is 1 mTorr, which requires ~1 sec pumpdown time (b) after closing the aperture valve using the miniaturized flight turbopump (~4 L/s).

• Ions can survive well beyond the required CO₂ pumpdown time of 1-2 seconds.

TRL 6 Demonstration

Prototype MOMA ITMS represents the flight model in form and function and meets performance metrics under relevant environment

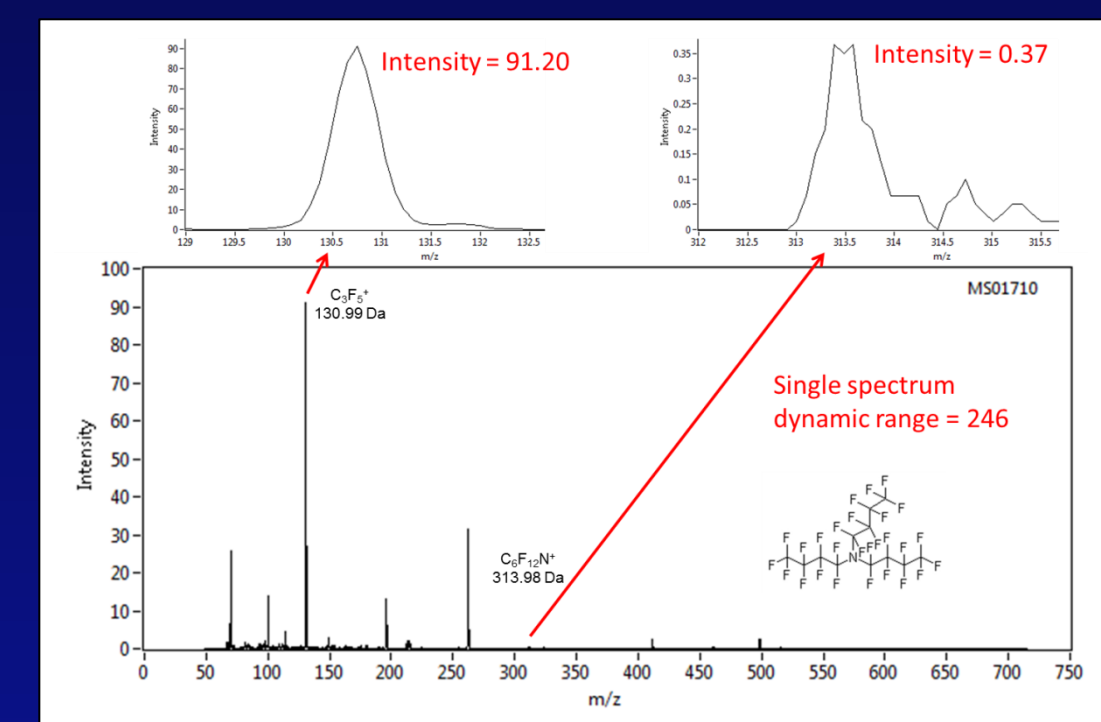


Figure 5. Dynamic range of MOMA ITMS for PFTBA in electron impact ionization mode (for GC-MS mode). Intensity = 91.20, Intensity = 0.37, Single spectrum dynamic range = 246.

Figure 6. Sensitivity

requirement of 1 pmol is demonstrated in LDI mode with Rhodamine 6G (top) and in EI mode with PFTBA (bottom). Also, the **resolution** requirement of 1 Da width at m/z 500 is demonstrated with both compounds.

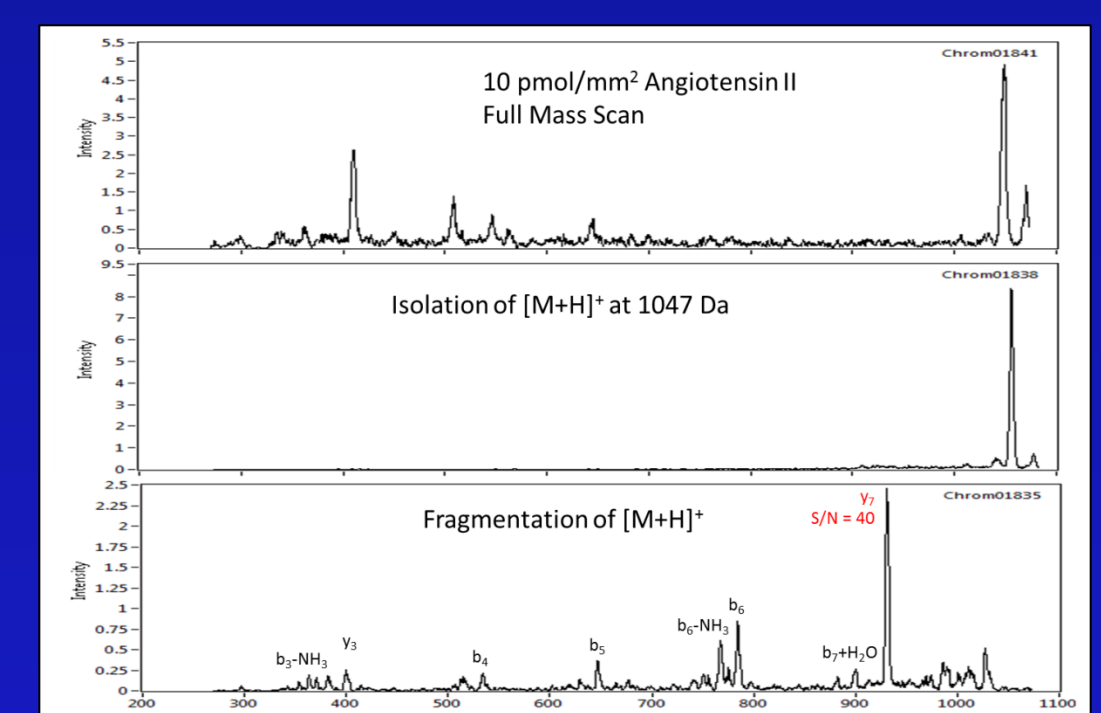


Figure 7. MS/MS performance using small linear peptide Angiotensin II. In this case, CO₂ from the Mars chamber is used as the collision and cooling gas.

Conclusions

The Mars Organic Molecule Analyzer is a key analytical instrument aboard the ExoMars Rover set to launch in 2018. The results described here demonstrate the current status of the methodology development for GC-MS and the performance parameters of the flight miniaturized ion trap. The ITMS, which serves as a detector for both GC and LDI modes, has met all of the performance requirements designated in the MOMA-MS TRL 6 review plan.

References

[1] Tanner, S.D.; Baranov, V.I. *JASMS*, 1999 10(11), 1083-1094.

Acknowledgements

Funding provided by the Mars Exploration Program (point of contact, George Tahu, NASA/HQ). MOMA is a collaboration between NASA and ESA (PI F. Goesmann, MPS).

USA	Germany	France
•NASA-GSFC	•MPS	•CNES
•Johns Hopkins School of Medicine	•Laser Zentrum-School of Medicine Hannover	•LISA
•University of Michigan	•Universität Bremen	•LATMOS
		•École Centrale Paris
		•Université Nice
Sweden	Netherlands	
•SP Technical Research Institute	•Universiteit Leiden	