

FIRST RESULTS OF THE MARS ORGANIC MOLECULE ANALYZER (MOMA) GC-MS COUPLING

A. Buch¹, V. Pinnick², C. Szopa³, R. Danell⁴, N. Grand³, F. H. W. van Amerom², D. Glavin², C. Freissinet², I. Belmahdi¹, P. Coll⁵, F. Stalport³, B. Lustrement⁴, R. Arevalo², W. B. Brinckerhoff², H. Steininger⁵, F. Goesmann⁵, F. Raulin³, P. Mahaffy² and the MOMA Science Team.

¹Ecole Centrale Paris, LGPM, Grande voie des vignes, 92295 Châtenay-Malabry, France, ²NASA Goddard Space Flight Center, 8800 Greenbelt Rd, Greenbelt, MD 20771, USA, ³LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, ⁴Danell Consulting, Inc., Winterville, NC 28590, ⁵LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France

Introduction

Objectives : The goals of the joint ESA-Roscosmos ExoMars-2018 rover mission include the search for molecules relevant to life (large, non-volatile organic or biological molecules that suggest existing or prior biosynthetic activity) on the martian surface and near subsurface, and the discrimination of the endogenous from the exogenous sources of organics on Mars.

The Mars Organic Molecule Analyzer (MOMA) aboard the ExoMars rover will be a key analytical tool in providing chemical (molecular) information from the solid samples collected by the rover, with a particular focus on the characterization of the organic content. The core of the MOMA instrument is a gas chromatograph coupled with a mass spectrometer (GC-MS) which provides the unique capability to characterize a broad range of compounds, including both of volatile and non-volatile species.

Method : Core samples will be extracted as deep as 2 meters below the martian surface to minimize effects of radiation and oxidation on organic materials.

Samples will be crushed and deposited into sample cups seated in a rotating carousel.

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

Samples which undergo GC-MS analysis may be submitted to a derivatization process, consisting of the reaction of the sample components with specific reagents (MTBSTFA [1], DMF-DMA [2], TMAH [3]) which increase the volatility of complex organic species.

In order to optimize this instrumentation, and especially the GCMS coupling, a series of tests is currently being carried out with prototypes of MOMA instrumentation.

Instrumental Suite

The French GC brassboard was coupled to the US ion trap mass spectrometer brassboard in a flight-like configuration (fig 1) for several coupling campaigns. The MOMA GC setup is based on the Sample Analysis at Mars (SAM) heritage design with a He reservoir and 4 separate analytical modules including traps, columns

and Thermal Conductivity Detectors (fig. 1b). Solid samples are sealed and heated in this setup using a manual tapping station (fig. 1a), designed and built at MPS in Germany, for GC-MS analysis. The gaseous species eluting from the GC are then ionized by an electron impact ionization source in the MS chamber and analyzed by the linear ion trap mass spectrometer (fig. 1c).

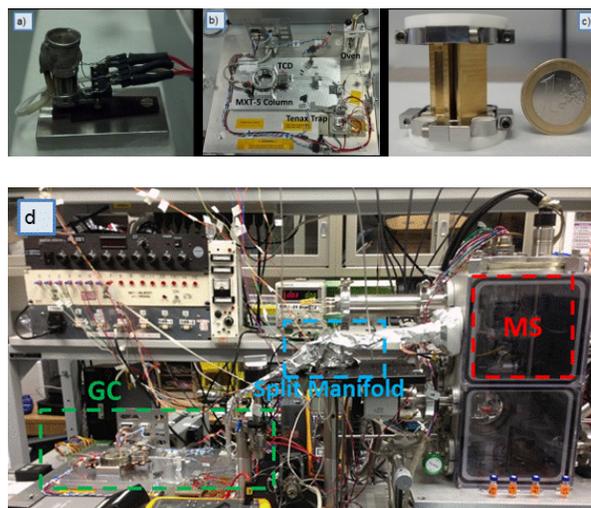


Figure 1: picture of the manual tapping station (a) where sample has been introduced before that it has been trapped, injected in the gas chromatograph (b) and detected in the MS ion trap (c).

MOMA GCMS Results:

Qualitative Analysis : Volatile and non-volatile compounds were injected in the MOMA instrumental suite. Both of these compounds classes were detected by the TCD and by the MS. By using the TCD signal and the retention time we were able to identify each of these compounds. MS signal (total ion current) and single mass spectra by comparison with the NIST library, gave us an unambiguous confirmation of these identifications. Figure 2 shows the TCD trace (a) and the total ion chromatogram (TIC) from the MS (b) for a standard gas-phase mixture of 100 ppm butane, pentane, hexane and benzene in He. The mass spectra (c-e) arise from an average of 10 mass spectra averaged

around a given time point in the total ion chromatogram (i.e. averaged around a peak in total ion counts).

Repeatability of the measurement has been tested with the same hydrocarbons mixture. Results of the five successive injections show that the variability of the TCD and MS responses is under 10%.

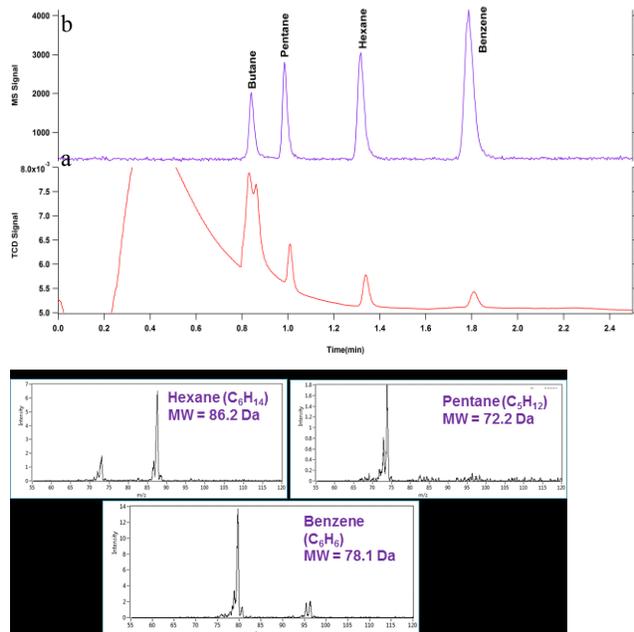


Figure 2: The TCD trace (b) and the total ion chromatogram (TIC) from the MS (a) for a standard gas-phase mixture of 100 ppm butane, pentane, hexane and benzene in He. The mass spectra arise from an average of 10 spectra averaged from the TIC peaks.

Quantitative Analysis: The sensitivity of the end-to-end test of the GC-MS interface depends heavily on the ionization efficiency of the analyte, the quality of the thermal control along the sample path, and the split manifold design. Based on commercial instrument, the MOMA requirement for sensitivity in the GC-MS mode for organic molecules is 1 pmol. In this test, sensitivity was determined for the GC TCD and MS response to a dilution series containing isopropanol, hexane and benzene deposited onto silica beads in the MOMA oven. For the MS, peak areas were integrated in the total ion chromatogram as well as in the resulting mass spectra. Isopropanol was not detected in the MS because the maximum characteristic mass (m/z) fell below the low mass cutoff ($m/z=50$) for the instrument. Generally, the MS was found to be 5 to 10 times more sensitive than the GC TCD for hexane and benzene respectively.

Table 1: TCD and MS sensitivity

Compounds	TCD Sensitivity	MS Sensitivity	
	LOD (pmol)	Peak integrated	LOD (pmol)
Isopropanol	14	ND	ND
Hexane	32	$m/z=57$	3
		$m/z=86$	22
		TIC	0.8
Benzene	24	$m/z=78$	5
		TIC	5

Conclusion: 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 end-to-end performance of the gas chromatography-mass spectrometry mode of operation. Both prototypes individually meet the performance requirements, but this work particularly demonstrates the capabilities of the critical GC-MS interface. Future work will focus on improving detection limits to provide margin to ensure the requirements will be met, as well as analyzing higher molecular weight compounds including derivitized amino acids and thermochemolized compounds.

References: [1] Buch, A. et al. (2009) J Chrom. A, 43, 143-151. [2] Freissinet et al. (2011) J Chrom A, 1306, 59-71. [3] Geffroy-Rodier, C. et al. (2009) JAAP, 85, 454-459.

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