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RESULTS OF THE MOMA GC-MS COUPLING CAMPAIGN WITH THE ENGINEERING TEST UNIT (ETU)

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Introduction

Objectives : The goals of the joint ESA-Roscosmos ExoMars-2020 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 Rosalind Franklin 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-mass spectrometer (GC-MS), with on-board derivatization capabilities, which provides the unique capability to characterize a broad range of compounds, including a range of volatile, non-volatile species, and chiral analysis.

Method : Core samples will be extracted as deep as 2 meters below the martian surface to minimize the effects of radiation and oxidation on organic materials. Samples will be crushed and deposited into sample cups seated in a rotating carousel. The cups are sealed with a tapping station and gas processing system prior to pyrolysis.

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

In a subset of GC-MS analyses, select samples are subjected to in situ derivatization, consisting of the reaction of the sample components with specific reactants (MTBSTFA [1], DMF-DMA [2], TMAH [3]), which increase the volatility of complex organic species.

In order to test our MOMA instrumentation suite, and especially the GCMS coupling, a series of tests have been carried out with our Engineering Test Unit (ETU).

ETU Suite

The French GC ETU was coupled to the US ion trap mass spectrometer ETU in a configuration (Figure

1) for the coupling campaign. The MOMA GC setup is based on the Sample Analysis at Mars (SAM) heritage design with a He tank and four separate analytical modules, including thermal desorption injection traps (IT) made of Tenax® TA, columns and Thermal Conductivity Detectors. Solid samples are sealed and heated in this setup using a patented reactor, designed and built at LGPM and LATMOS. This reactor has been designed to mimic the MOMA oven. After being released from the ITs, the gaseous species are separated in the GC and from where they elute to be ionized by an electron impact ionization source in the MS chamber, and then ions are analyzed by the linear ion trap mass spectrometer (Figure 1). Derivatizing reagent (MTBSTFA, DMF-DMA or TMAH) is either delivered in this configuration in the same way it is on the MOMA flight unit, using eutectic based capsules or by direct injection.

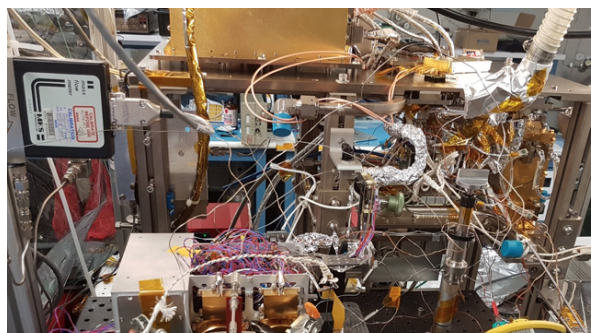


Figure 1: picture of the ETU gas chromatograph and the ETU MS ion trap.

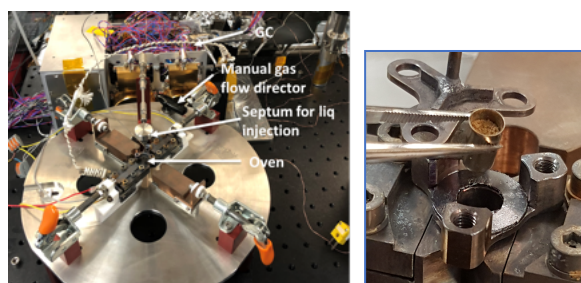


Figure 2: picture of patented oven (close-up at the right) used for GC-MS ETU coupling

MOMA GCMS ETU Results:

Chiral Separation : Volatile and non-volatile chiral analog standard compounds were injected through the oven septum or deposited in the MOMA ETU instrument suite. Amino acids and carboxylic acids were detected by the mass spectrometer after derivatization and GC separation. Chiral compounds were derivatized with DMF-DMA (15µL stocked in MOMA capsule) in order to volatilize them and to achieve a chiral separation with the Chirasil-Dex column (Figure 3).

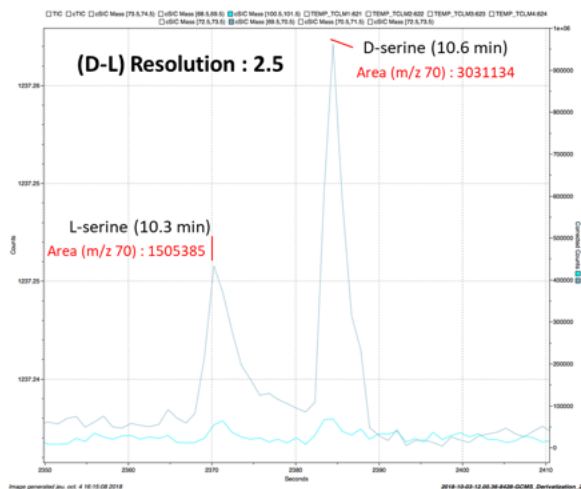


Figure 3: Total ion chromatogram (TIC) from the MS for L,D-serine after online DMF-DMA derivatization of standard serine.

Analogue Sample: Mars analogue (JSC-Mars1) sample and Murchison meteorite (Figure 4) have been successfully analyzed by direct pyrolysis GCMS and after DMF-DMA derivatization, and TMAH thermochemolysis. These two techniques are complementary to the additional MOMA MTBSTFA derivatization capability (not shown here).

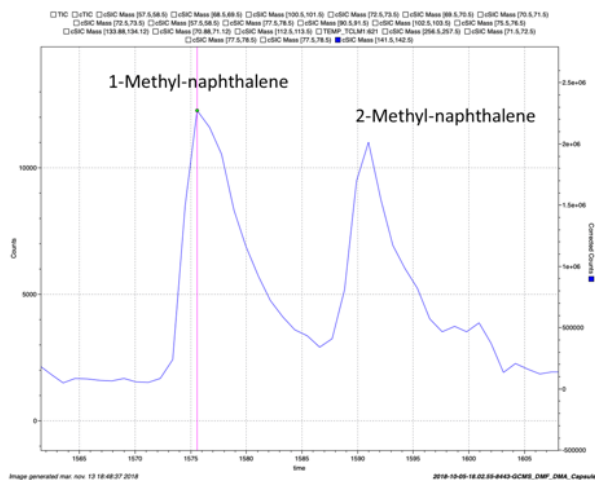


Figure 4: Isomeric separation of methyl-naphthalene found in Murchison meteorite after online DMF-DMA derivatization.

Conclusion: The results described here demonstrate the current status of the end-to-end performance of the gas chromatography-mass spectrometry mode of operation. We show that from a technical point of view the MOMA instrument is working as expected. From a chemical point of view we have shown that three of the four MOMA sample preparation methods tested here (DMF-DMA, thermochemolysis with TMAH, and Pyrolysis) work efficiently under MOMA-like operational conditions. Additionally, we have demonstrated chiral and isomeric separation with both a standard sample and organics extracted from the Mars analogue samples.

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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