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## MOMA DERIVATIZATION CAPSULE FOR THE MARTIAN SAMPLE TREATMENT

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### Introduction

**Objectives :** The Mars Organic Molecule Analyzer (MOMA) experiment onboard the ExoMars 2020 rover (Rosalind Franklin) will analyze the content in organic molecules present in samples collected at the surface and subsurface (down to 2 meters) of Mars. MOMA has two complementary analytical modes: Laser Desorption/Ionization-Mass Spectrometry (LDI-MS) and Pyrolysis-Gas Chromatography-Mass Spectrometry (Pyr-GC-MS). In addition to the pyrolysis analysis, three types of derivatization reagents are present in twelve capsules and can be used to make possible the analysis of refractory and very polar compounds by increasing their volatility and protecting the labile chemical groups: N-methyl-N-tert-butyltrimethylsilyl-trifluoroacetamide – MTBSTFA [1]; dimethylformamide dimethyl-acetal - DMF-DMA [2]; and tetramethylammonium hydroxide TMAH [3]. MTBSTFA is the most versatile reagent. It is dedicated to analyze the labile compounds with a very high sensitivity. DMF-DMA preserves the chiral center of molecules and will allow their enantiomeric separation. TMAH will be used to extract and characterize the potential refractory compounds (macromolecules, kerogen, etc.) and protect polar compounds (alkylation) released from the pyrolysis experiment.

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 gas chromatograph coupled to mass spectrometer compared to a laboratory instrument but also it directly impacts the available options for sample treatment. This is why we have developed derivatization capsules dedicated to chemical extraction by derivatization (MTBSTFA, DMF-DMA, TMAH).

**Method :** To test the feasibility and the efficiency of the sample treatment using our derivatization capsules we have mimicked the MOMA procedure by coupling an test reactor reactor with a commercial GC-MS. We have filled six capsules with MTBSTFA, six with DMF-DMA, and six with TMAH. Then we have tested the opening temperature of each capsule and tested the efficiency of sample treatment with our derivatization capsule. For those tests we have used two different GC columns: a chirasil-Dex (30mx0.25mmx0.25µm) dedi-

cated to the separation of chiral compounds and a RTX5ms (30mx0.25mmx0.25µm) dedicated to both apolar and semi-polar compounds. Two similar columns are integrated in MOMA-GC flight model.

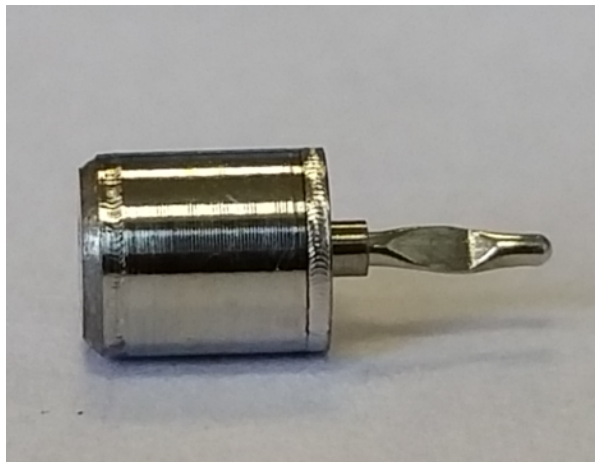
### Instrumentation suite :

**Derivatization Capsule :** The capsules have been designed to store different corrosive liquids dedicated to the derivatization and thermochemolysis processes. Moreover each liquid is released at a temperature corresponding to the melting temperature of specifically chosen eutectics and chosen to optimize the chemical reaction during the sample treatment. DMF-DMA is released at 145°C, MTBSTFA at 200°C and TMAH at 309°C.

The capsules are small “bullet like” containers constructed of stainless steel and have approximate dimensions of 3.6 x 3;2 mm. The body of the capsule is sealed by laser welding endcaps to each. One cap contains a tube used for filling that is then pinched off to complete the seal. The other cap contains the eutectic covering a pin-hole through which the reagent is released once the melting temperature is reached.

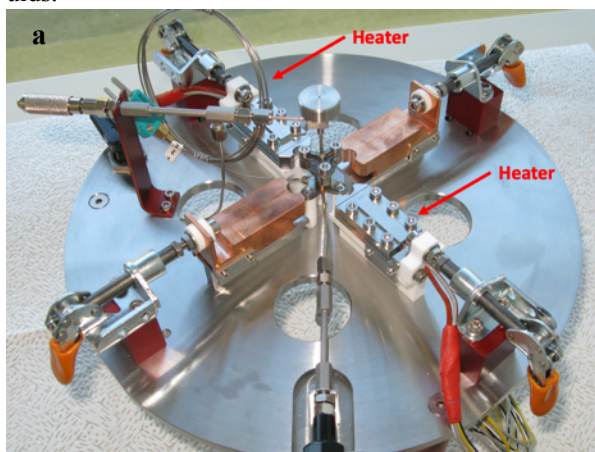
Each capsule is filled with 15µl of reagent. This is around 2/3<sup>rd</sup> of the total volume of the capsule. The empty volume is filled with argon to prevent the presence of oxygen which could oxidize the derivatization agent.

Before the eutectic melts, the temperature increase inside the capsule creates a significant back pressure. When the opening temperature is reached, the pressure inside the capsule should be high enough to eject the reagent into the oven.



**Figure 1:** picture of a derivatization capsule. We can see the body, a 3.6 x3.2mm cylinder where the reagent is contained, the pinched tube through which the reagent is introduced, and on the left, a thin layer of eutectic to close the pin-hole through which the reagent will be released at a given temperature.

**Reactor :** The reactor used in this study has been built to mimic the MOMA oven (tapping station). This reactor is composed of a stainless steel oven of about 1.5 mL volume with two heater plates and two cold traps. The two hot plates allow the oven to be heated up to 600°C, which is sufficient for our tests as derivatization reactions occur at lower temperatures. The two cold plates allow the oven to quickly cool down. The oven can be opened with three titanium screws and the capsules can be placed inside the oven. A septum is positioned over the oven so that it is not too hot. Through this septum, it is then possible to inject liquids.



**Figure 2:** Patented reactor and its oven. This reactor mimics the MOMA Oven volume and heating ramp.

### MOMA GCMS Results:

**Quantitative Analysis:** In order to test derivatization and thermochemolysis processes feasibility and efficiency, we have used standard solutions of several chiral amino acids and non chiral carboxylic acids. Each of these compounds was first treated via classical laboratory experiments and then via our MOMA patented reactor with the MOMA derivatization capsules. We have shown that the selected capsule eutectics allowed the derivatization and thermochemolysis reagents to be released at the right temperatures. Additionally we found that the efficiency of derivatization and thermochemolysis was identical both for laboratory experiments and MOMA like derivatization with capsules. This result verifies the method that will be used on Mars to analyze the soil and rock samples to be collected by the rover.

**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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