



## **Search for Organic Material on Mars with the Thermochemolysis Derivatization Technique Onboard the MOMA Experiment**

M. Morisson, A. Buch, Cyril Szopa, D. Glavin, C. Freissinet, V. Pinnick, W. Goetz, M Stambouli, Imène Belmahdi, Patrice Coll, et al.

► **To cite this version:**

M. Morisson, A. Buch, Cyril Szopa, D. Glavin, C. Freissinet, et al.. Search for Organic Material on Mars with the Thermochemolysis Derivatization Technique Onboard the MOMA Experiment. 47th Lunar and Planetary Science Conference, Mar 2016, The Woodlands, TX, United States. LPSC 2016, pp.2159, Sess451: (Is There) Life on Mars? Martian Exobiology Tools, Analogs, and Environments. <insu-01285239>

**HAL Id: insu-01285239**

**<https://hal-insu.archives-ouvertes.fr/insu-01285239>**

Submitted on 9 Mar 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

### SEARCH FOR ORGANIC MATERIAL ON MARS WITH THE THERMOCHEMOLYSIS DERIVATIZATION TECHNIQUE ONBOARD THE MOMA EXPERIMENT.

M. Morisson<sup>1</sup>, A. Buch<sup>1</sup>, C. Szopa<sup>2</sup>, D. Glavin<sup>3</sup>, C. Freissinet<sup>3</sup>, V. Pinnick<sup>3</sup>, W. Goetz<sup>4</sup>, M. Stambouli<sup>1</sup>, I. Belmahdi<sup>1</sup>, P. Coll<sup>5</sup>, F. Stalport<sup>5</sup>, N. Grand<sup>5</sup>, W. B. Brinckerhoff<sup>3</sup>, I. Belmahdi<sup>1</sup>, F. Goesmann<sup>4</sup>, F. Raulin<sup>5</sup>, P. Mahaffy<sup>3</sup> and the MOMA Science Team.

<sup>1</sup>Ecole Centrale Paris, LGPM, Grande Voie des vignes, 92295 Châtenay-Malabry, France, <sup>2</sup>LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, <sup>3</sup>NASA Goddard Space Flight Center, 8800 Greenbelt Rd, Greenbelt, MD 20771, USA, <sup>4</sup>Max Planck Institut für Sonnensystemforschung (MPS), Lindau, Germany, <sup>5</sup>LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France.

**Introduction:** After the SAM experiment onboard the Curiosity rover, the Mars Organic Molecule Analyzer (MOMA) experiment onboard the future ExoMars mission will be the continuation of the search for the organic composition of the Mars surface. MOMA will have the advantage of extracting the sample from as deep as 2 meters below the martian surface to minimize effects of radiation and oxidation on organic materials. To analyse the wide range of organic compounds (volatile and non volatile compounds) potentially present in the martian soil MOMA includes two operational modes: UV laser desorption / ionization ion trap mass spectrometry (LDI-ITMS) and pyrolysis gas chromatography ion trap mass spectrometry (*pyr*-GC-ITMS). In order to analyse refractory organic compounds and chirality samples which undergo GC-ITMS analysis may be submitted to a derivatization process, consisting in the reaction of the sample components with specific reactants (MTBSTFA [1], DMF-DMA [2] or TMAH [3]).

To prove the feasibility of the derivatization within the MOMA conditions we have adapted our laboratory procedure to the space conditions (temperature, time, pressure and size) in order to decrease our detection limits and increase the range of the organic compounds that MOMA will be able to detect. Here, we only discuss the optimization of the thermochemolysis technique.

**Derivatization and Thermochemolysis:** Usual gas chromatography techniques dedicated to the analysis of non volatile and refractory organic compounds in space include derivatization (MTBSTFA and DMF-DMA) and pyrolysis. Derivatization allows to analyse volatile and non volatile compounds by protecting labile groups at low and intermediate temperatures (75-250°C). Pyrolysis (800-1000°C) allows to analyse

insoluble organic material such as macromolecules, but with a major drawback related to the difficulty of determination of the mother molecule because of the high molecular fragmentation. That is why several authors [4] have introduced thermochemolysis which allows to reach insoluble matter in complex matrix with a limited degradation of the organic material. Combining high temperature and derivatization (methylation), thermochemolysis with tetramethylammonium hydroxide (TMAH) (figure 1) allows to improve the pyrolysis technique which release polar functional group.

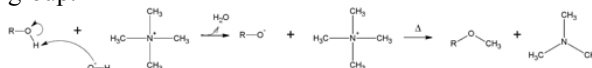


Figure 1 – Thermochemolysis reaction with an alcohol.

The methylation prevents secondary degradation of polar compounds and it also allows chromatographic separation of polar compounds with a standard apolar column. Moreover in the case of thermochemolysis, organic material is subjected to lower temperature than with pyrolysis (figure 2).

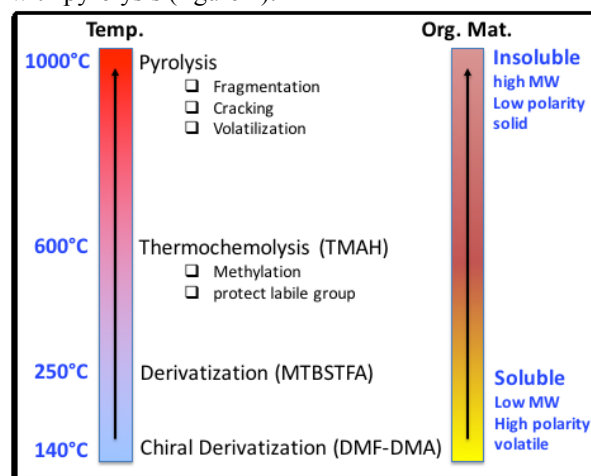


Figure 2 – Overview of the space compatible sample treatment for the in situ GCMS analysis.

**Optimization of the thermochemolysis parameters for the MOMA experiment:** Optimization experiments have been carried out with JSC-1 soil, a martian analogue which contains high organic concentrations (hydrocarbons, alcohols, amines, amino acids, carboxylic acids,...). JSC-1 has been first characterized by using classical solvent extraction assisted by ultrasonication. Thermochemolysis has been performed by using a Frontier Lab pyrolyser coupled with a ThermoFisher GC-MS (Trace-ISQ).

Several parameters have been tested: volume of TMAH, impact of solvent (MeOH) using for TMAH dilution, temperature of reaction and time of reaction before the injection. Best results are generally obtained with a TMAH solution 25% w/w in methanol during

15 sec at a temperature ranging between 650°C and 700°C (figure 3).

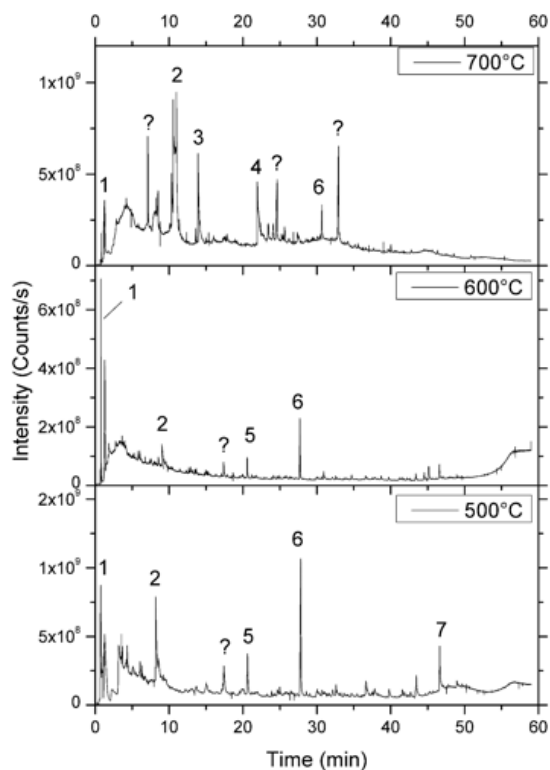


Figure 3 – Chromatograms obtained after thermochemolysis of JSC-1 at different temperatures (700°C, 600°C and 500°C). 1 : trimethylamine ; 2 : 1,3,5-trimethyl-1,3,5-triazine ; 3 : N,N'-dibutyl-1,2-ethanediamine ; 4 : HMTA ; 5 : pentamethyl-benzene ; 6 : hexamethyl-benzene ; 7 : 6-methoxy-2-(1-buten-3-yl)-naphthalene..

**TMAH thermochemolysis library:** Chromatograms obtained after thermochemolysis may be complex because of the degradation of organic compounds prior their TMAH derivatization. Moreover methylation can occur in different ways if the molecule contains several labile groups (figure 4). That is why we have investigated molecules of astrobiological interest which are difficult to reach with other derivatization techniques. For instance, it is the case of purines and pyrimidines bases. This work will facilitate the interpretation of complex spectra obtained from unknown samples. It will also help to interpret the SAM results when TMAH experiments start on Mars.

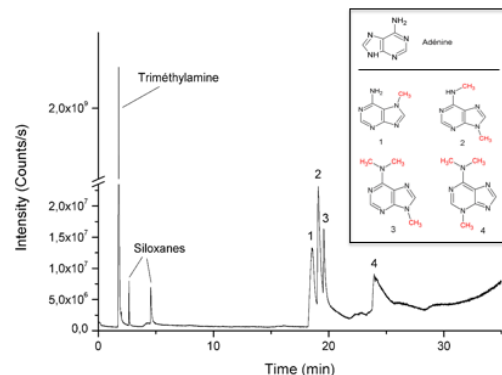


Figure 4 – Chromatograms obtained after thermochemolysis of adenine at 650°C.

**Conclusions:** Among the space compatible derivatization techniques, thermochemolysis is the most promising one. It requires one step reaction at medium temperature compared to pyrolysis and allows to reach a wide range of organic compounds which are difficult to reach with pyrolysis or even with MTBSTFA derivatization.

**References:** [1] Buch, A. et al. (2009) J Chrom. A, 43, 143-151. [2] Freissinet, C. et al. (2013) J Chrom. A, 1306, 731-740. [3] Geffroy-Rodier, C. et al. (2009) JAAP, 85, 454-459. [4] Challinor J. (2001) JAAP, 61, 3-34.