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

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

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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 volatils compounds) pententially 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 adapated 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 thermochemiolysis 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 labil 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 wich allows to reach insoluble matteri in complexe 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 wich release polar functional group.

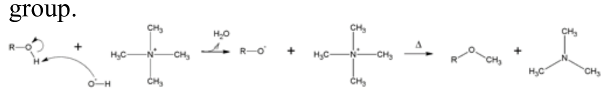

Figure 1 –Thermochemysis reaction with an alcohol.

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

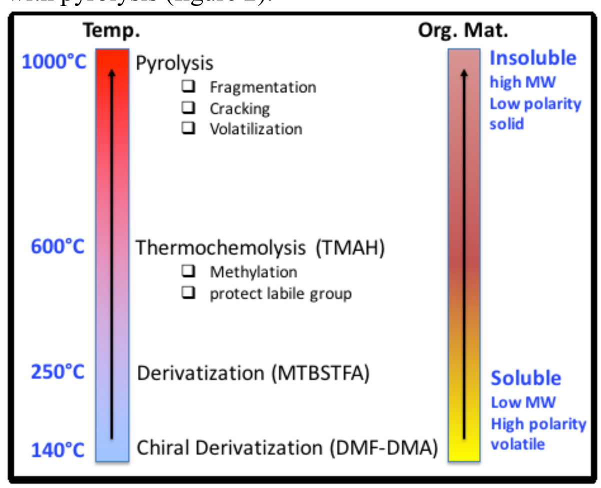

Figure 2 –. Overview of the space compatible sample treatment for the in situ GCMS analysis.

Optimization of the thermochemolysis parameters for the MOMA experiment: Optimization experiments have been carried out with JSC-1 soil, a martian analogue wich 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).

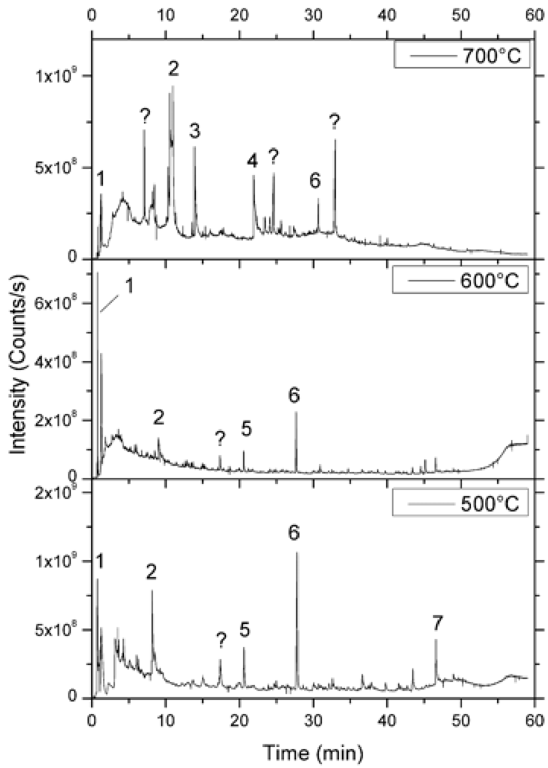

Figure 3 –. Chromatograms obtained after thermochemolysis of JSC-1 at different temperatures (700°C, 600°C and 500°C). 1 : trimethylamine ; 2 : 1,3,5-trimethyl-1,3,5-triazine ; 3 : N,N'-dibutyl-1,2-ethanediamine ; 4 : HMTA ; 5 : pentamethyl-benzene ; 6 : hexamethyl-benzene ; 7 : 6-methoxy-2-(1-buten-3-yl)-naphthalene..

TMAH thermochemolysis library: Chromatograms obtained after thermochemolysis may be complexe because of the degradation of organic compouds 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 complexe spectra obtained from unknown samples. It will also help to interpret the SAM results when TMAH experiments start on Mars.

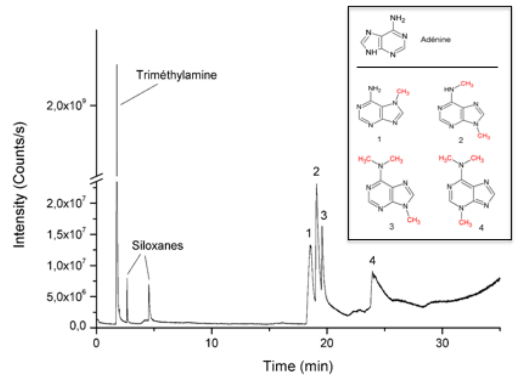

Figure 4 –. Chromatograms obtained after thermochemolysis of adenine at 650°C.

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.

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