

OPTIMIZATION OF THE TMAH THERMOCHEMOLYSIS TECHNIQUE FOR THE DETECTION OF TRACE ORGANIC MATTER ON MARS BY THE SAM AND MOMA-PYR-GC-MS EXPERIMENT.

A. Buch¹ arnaud.buch@ecp.fr, M. Morisson¹, C. Szopa², M. Millan^{3,4}, C. Freissinet², Y. He¹, D. Glavin³, J.Y. Bonnet², D. Coscia², A.J. Williams^{3,7}, F. Stalport⁵, F. Raulin⁵, M. Stambouli¹, S. Teinturier³, R. Navarro-González⁶, C. Malespin³, P. Mahaffy³, ¹CentraleSupélec, LGPM, Gif sur Yvette, France, ²LATMOS, Univ. P. et M. Curie, Univ. Versailles Saint-Quentin & CNRS, France. ³NASA-GSFC, Greenbelt, MD, USA, ⁴Georgetown University, Washington DC, LISA, ⁵UPEC-UPD/CNRS/IPSL, Paris-Créteil, France, ⁶Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, ⁷Towson University, Towson, MD.

Introduction: Both the Sample Analysis at Mars (SAM) and Mars Organic Molecule Analyzer (MOMA) instruments are able to identify organic material at the Martian surface and subsurface. Both experiments are equipped with pyrolysis-Gas Chromatography-Mass Spectrometry (Pyr-GC-MS) and derivatization reagents (MTBSTFA) that will allow the analyze refractory compounds, making them more volatile and protecting the labile chemical groups. In order to improve the Pyr-GC-MS analysis, TMAH (tetramethylammonium hydroxide) will be used on MOMA and SAM to extract refractory compounds (macromolecules, kerogen, etc.) and protect polar compounds released from the pyrolysis experiment.

We performed pyrolysis and TMAH-thermochemolysis of a Martian regolith simulant (JSC-Mars-1) to optimize analytical parameters, especially the thermochemolysis temperature, to ensure the success of the near future *in situ* thermochemolysis analyses on Mars.

Materials and Control Tests: The soil used in all of our experiments is a simulant of the Martian regolith named JSC Mars-1 [2,3], chosen for its high organic content [1]. Pyrolysis and thermochemolysis were performed using a Frontier Lab pyrolysis system coupled with a Thermo Scientific GC-MS (Trace GC Ultra-ISQ LT). The TMAH solution was 25% w/w in methanol, from Sigma-Aldrich.

The organic content of JSC Mars-1 was firstly characterized by classical solvent extraction assisted by ultrasonication, followed by MTBSTFA derivatization and GC-MS analysis. This showed that the soil is rich in carboxylic acids, amino acids, alcohols and linear hydrocarbons.

Thermal degradation of TMAH at different pyrolysis temperatures was carried out to discriminate between the molecules resulting from TMAH degradation and those stemming from the soil sample. Different volumes of TMAH were pyrolyzed at 400°C, 500°C, 600°C, 700°C, 800°C, and 950°C. The main products of thermal degradation of TMAH are given in Figure 1.

JSC Mars-1 was also pyrolyzed at 400°C, 500°C and 600°C (Fig. 2). At 400°C, the temperature is too low to desorb the main part of the organic matter linked to the mineral matrix. Numerous compounds are detected from 500°C pyrolysis temperature, and even more at 600°C. Most of them are polycyclic aromatic hydrocar-

bons (PAHs) and their alkylated, alkenylated and alkynylated derivatives. But many nitrogen-bearing and oxygen-bearing heterocycles are also identified. However, the major drawback of these results is determining the parent molecules from the thermally altered matter.

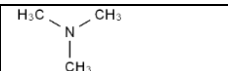

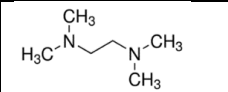
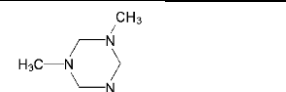
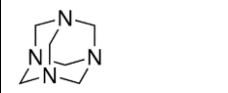
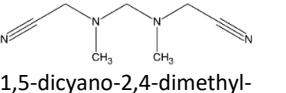
	
Trimethylamine	N,N-dimethylethylamine
	
N,N,N',N'-tetramethyl-ethylenediamine	Hexahydro-1,3,5-trimethyl-1,3,5-triazine
	
HMT	1,5-dicyano-2,4-dimethyl-2,4-diazapentane

Figure 1 - Main products of thermal degradation of TMAH.

Optimization of TMAH-Thermochemolysis on JSC Mars-1: Thermochemolysis with TMAH combines extraction and derivatization (methylation) by breaking the bonds between the organic matter and the mineral matrix, and by methylating polar functional groups (Fig. 3). The thermochemolysis was carried out with 10 mg of JSC-1 and 10 µl of TMAH solution. Figure 4 shows the chromatograms obtained after thermochemolyses performed at temperatures ranging from 400° to 700°C. From a qualitative point of view, a complexification of the chromatograms occurs when the pyrolysis temperature increases. Nevertheless, in the chemical families of carboxylic acids, alcohols, amines, amides and linear hydrocarbons, the same compounds were identified at each temperature. Due to the rearrangement and aromatization of the organic material, only the number of aromatics and hydrocarbons increases when the pyrolysis temperature increases.

As shown in Table 1, this increase is especially important during the transition from 400°C to 500°C where the thermal evolution of the organic matter starts, leading to the cyclisation and aromatization of the molecules [4][5]. Moreover, at 500°C, the chromatogram begins to be crowded in peaks – with more than 270 compounds detected. This leads to many coelutions and makes identification more difficult.

Quantitative experiments have also been performed by using a specific internal standard which is able to resist to TMAH and high temperatures.

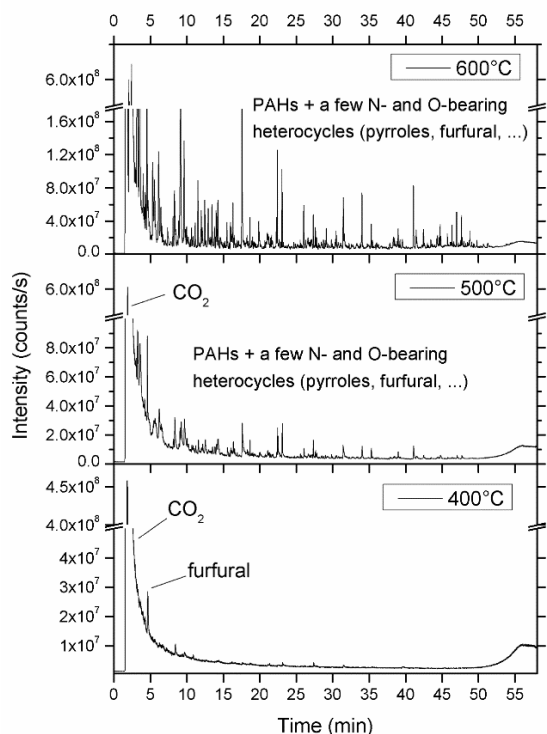


Figure 2 - Chromatograms obtained after a 400°C, 500°C, and 600°C pyrolyses of 20mg of JSC Mars-1.

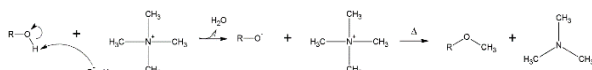


Figure 3 – Reaction mechanism of an alcohol with TMAH.

Conclusions: The results of the pyrolysis experiments show that the pyr-GC-MS technique alone is very destructive because of the thermal evolution of organic matter at high temperatures and identification of the organic molecules originally present in the sample is difficult.

TMAH thermochemolysis allows the detection of numerous organic molecules. The compounds are detected from 400°C and are sufficiently protected from thermal degradation to still be identified up to 600°C. Since the number of aromatics and heterocycles increases dramatically at 500°C, and since these compounds are thought to be thermally evolved molecules, 400°C seems to be the most suitable thermochemolysis temperature. However, higher temperatures give us more information about heavy refractory compounds. This is why – depending of the organic content – 500°C and 600°C may be suitable as well.

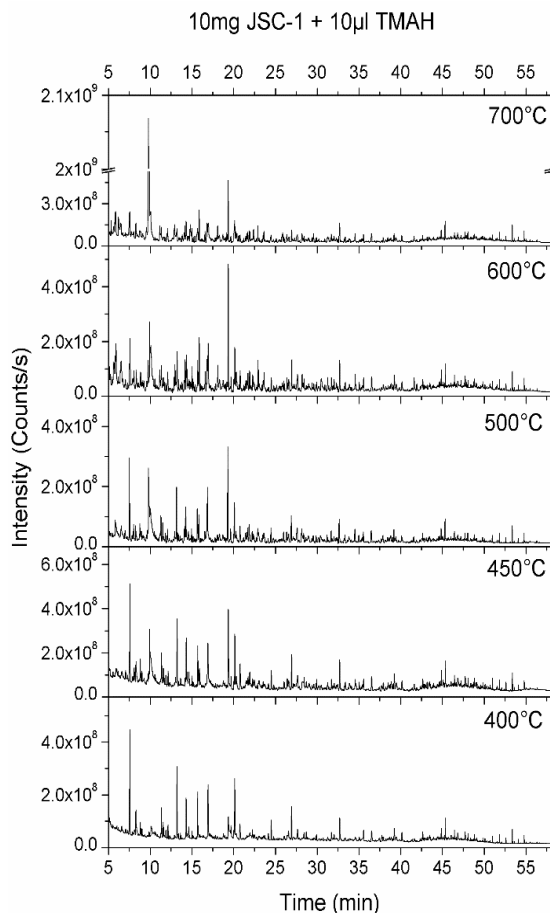


Figure 4 – Chromatograms obtained after thermochemolyses of 10mg of JSC Mars-1 between 400°C and 700°C.

	400°C	500°C	600°C
Carboxylic acids	33	32	32
Linear hydrocarbons	13	13	13
Alcohols	11	11	11
Amines/amides	5	5	5
Aromatic hydrocarbons	30	83	87
Heterocycles	17	30	30
Others	7	7	7
TOTAL identified	116	181	185

Table 1 Compounds identified by thermochemolysis of 10 mg of JSC Mars-1.

References: [1] Allen et al., *Lunar Planet. Sci. Conf. XXXI*, p. 1287, 2000. [2] Allen et al., *Lunar Planet. Sci. Conf. XXIX*, no. Table 2, p. 1690, 1998. [3] Morris et al., *Geochim. Cosmochim. Acta*, vol. 57, no. 19, pp. 4597–4609, 1993. [4] Bergman, *Acc. Chem. Res.*, vol. 6, no. 1, pp. 25–31, Jan. 1973. [5] Lockhart et al., *J. Am. Chem. Soc.*, vol. 103, no. 14, pp. 4082–4090, Jul. 1981.