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TMAH THERMOCHEMOLYSIS OF A MARTIAN REGOLITH SIMULANT: OPTIMIZATION OF AN ANALYTICAL METHOD FOR THE DETECTION OF TRACE ORGANIC MATTER BY THE MOMA-PYR-GC-MS EXPERIMENT ONBOARD THE EXOMARS-2020 ROVER

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Introduction: The Mars Organic Molecule Analyzer (MOMA) experiment onboard the ExoMars 2020 rover is mainly dedicated to the search for organic material in the Martian surface and subsurface (down to 2 meters). MOMA has two operational modes: Laser Desorption/Ionization-Mass Spectrometry (LDI-MS) and Pyrolysis-Gas Chromatography-Mass Spectrometry (Pyr-GC-MS). Two derivatization reagents onboard the MOMA experiment will allow the chiral separation (DMF-DMA) and the analysis of refractory compounds (MTBSTFA), 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 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 within operating conditions similar to the MOMA ones with the aim of optimizing the analytical parameters, especially the thermochemolysis temperature, and ensuring the success of the future *in situ* molecular analysis on Mars.

Materials and control tests: The analogue used in all of our experiments was a simulant of the regolith of Mars 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. 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. In the range of the pyrolysis temperature, a study of thermal degradation of TMAH was carried out to discriminate between the molecules resulting from the degradation of TMAH and those stemming from the soil sample. Different volumes of TMAH were then 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. The chromatograms are shown on Figure 2. At 400°C, the temperature is too low to desorb the main part of the organic matter linked to the mineral matrix.

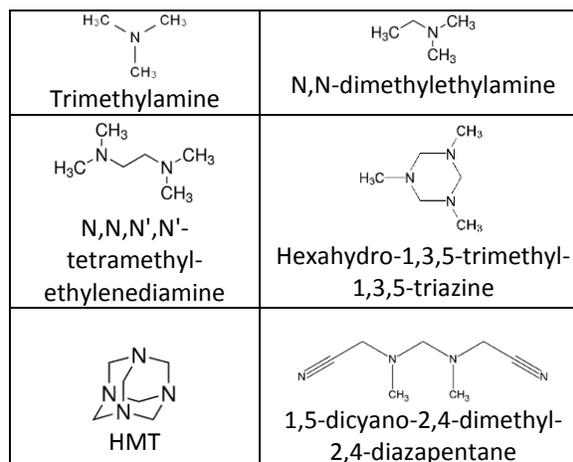


Figure 1 - Main products of thermal degradation of TMAH.

Numerous compounds are detected after the 500°C pyrolysis and more after 600°C. Most of them are polycyclic aromatic hydrocarbons (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 to trace back to the parent molecule from such a thermally altered matter.

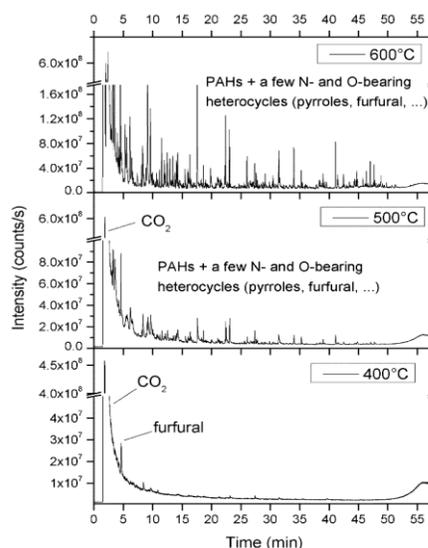


Figure 2 - Chromatograms obtained after a 400°C (bottom), 500°C (middle) and 600°C (top) pyrolyses of 20mg of JSC Mars-1.

TMAH-Thermochemolysis of JSC Mars-1: Thermochemolysis with TMAH combines extraction and derivatization by breaking the bonds between the organic matter and the mineral matrix, and by methylating polar functional groups as shown on Figure 3 in the case of an alcohol.

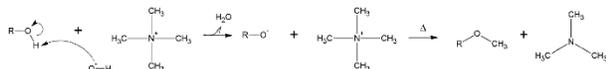


Figure 3 – Reaction mechanism of an alcohol with TMAH.

The thermochemolysis was carried out with 10mg of JSC-1 and 10 μ L of TMAH solution. Figure 4 shows the chromatograms obtained after thermochemolyses performed at temperatures ranging from 400°C to 700°C. A complexification of the chromatograms occurs when the 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.

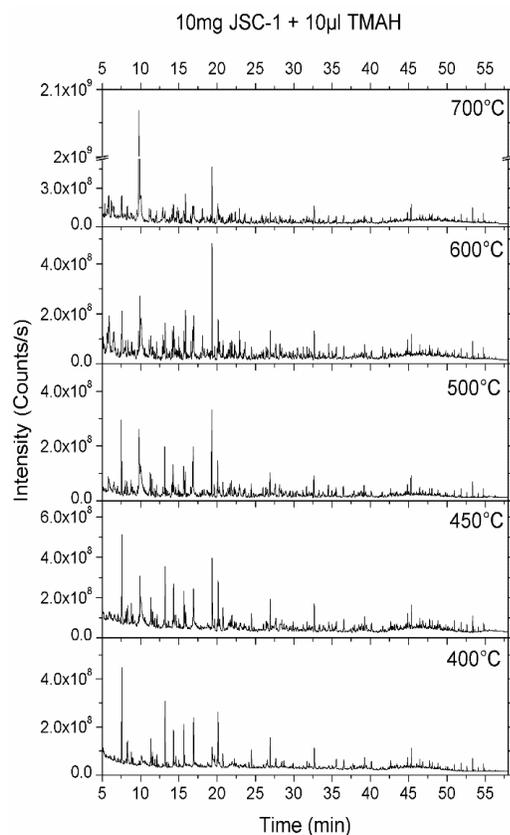


Figure 4 – Chromatograms obtained after thermochemolyses of 10mg of JSC Mars-1 between 400°C and 700°C.

As shown in Table 1, this increase is especially important during the transition between 400°C and 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 overcrowded in peaks – with more than 270 compounds detected. This leads to many co-elutions and makes identification more difficult.

	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.

Conclusions: The results of the pyrolysis experiments show that the pyr-GC-MS technique alone is suitable for the extraction of the organic matter at high temperatures. However, it does not allow a clear identification of the compounds originally present in the sample because of the thermal evolution of the matter at high temperatures.

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 from 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 provide more information about heavy refractory compounds. This is why – depending on the organic content – 500°C and 600°C may be suitable as well.

During this study, the quantities of compounds released at each temperature cannot be determined because a quantitative study (i.e. with an internal standard) is too difficult to implement for now in pyrolysis experiments.

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.