HOW TMAH THERMOCHEMOLYSIS CAN IMPROVE THE DETECTION OF TRACE ORGANIC MATTER ON MARS USING THE MOMA-PYR-GC-MS EXPERIMENT ABOARD THE EXOMARS-2020 ROVER.

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Introduction: The Mars Organic Molecule Analyzer (MOMA) experiment aboard the future ExoMars 2020 mission will be the continuation of the search for the organic composition of the Mars surface. The main advantage of Exomars is that the sample will be extracted as deep as 2 meters below the martian surface and is expected to be preserved from the effects of radiation and oxidation on organic materials. To analyze the wide range of potential organic composition (volatile and non volatile compounds) of the martian soil, the MOMA instrument utilizes both UV laser desorption / ionization (LDI) and pyrolysis gas chromatography ion trap mass spectrometry (*pyr*-GC-ITMS). In order to analyse refractory organic compounds, and charactize the enantiomeric ratio for the chiral species, the sample can be submitted to a derivatization process, consisting of the reaction of the sample components with specific reactants selected for MOMA.

Thermochemolyis vs Derivatization: The two derivatization reagents aboard the MOMA experiment wich will allow the chiral separation and the analysis of refractory compounds, making them more volatile and less polar by protecting the labile chemical groups are respectively MTBSTFA [1] and DMF-DMA [2] . In order to improve the Pyr-GC-MS analysis, TMAH (tetramethylammonium hydroxide) [3] will be used on MOMA to extract refractory compounds (macromolecules, kerogen, etc.) and protect polar compounds released from the mid-pyrolysis experiment. During conventional pyrolysis, macromolecule are generally cleaved into smaller compounds but secondary “reactions” can also occur (chemical reactions, condensation and (re)polymerization).The products released from the pyrolysis could be highly polar monomers and oligomers which are prone to poor chromatographic behavior. By using TMAH thermochemolysis, we first decrease the polarity of the released product (by methylation reaction) and we limit the secondary reactions which result in improved chromatographic performance. Moreover, it is then easier to determine the analyte’s parent molecular structure.

TMAH Optimization and Results: We performed pyrolysis and TMAH-thermochemolysis on a martian regolith simulant (JSC Mars-1) within conditions similar to those planned to be used for MOMA. But a range of values was explored for different analytical parameters in order to optimize the derivatization conditions, especially the thermochemolysis temperature.

We have proved that TMAH thermochemolysis allows the detection of numerous organic molecules complementary of those detected by using derivatization reaction (MTBSTFA and DMF-DMA) : carboxylic acids, hydrocarbons, alcohols, amines, amides, aromatic hydrocarbures, heterocycles and other more complex organic compounds. 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 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.

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.