

Thermochemolysis – A new sample preparation approach for the detection of organic components of complex macromolecules in Mars rocks via gas chromatography mass spectrometry in SAM on MSL J. Eigenbrode¹, D. Glavin¹, J. Dworkin², P. Conrad¹, and P. Mahaffy¹, ¹NASA Goddard Space Flight Center, Planetary Environments Laboratory, Code 699, Greenbelt, MD 20771, USA ²NASA Goddard Space Flight Center, Code 691, Greenbelt, MD 20771, USA.

Introduction: Organic chemicals, when present in extraterrestrial samples, afford precious insight into past and modern conditions elsewhere in the Solar System. No single technology identifies all molecular components because naturally occurring molecules have different chemistries (e.g., polar vs. non-polar, low to high molecular weight) and interface with the ambient sample chemistry in a variety of modes (i.e., organics may be bonded, absorbed or trapped by minerals, liquids, gases, or other organics). More than 90% of organic matter in most natural samples on Earth and in meteorites is composed of complex macromolecules (e.g. biopolymers, complex biomolecules, humic substances, kerogen) because the processes that tend to break down organic molecules also tend towards complexation of the more recalcitrant components. Thus, methodologies that tap the molecular information contained within macromolecules may be critical to detecting extraterrestrial organic matter and assessing the sources and processes influencing its nature.

Inert-pyrolysis (under He) as a front-end, sample preparation technique thermally desorbs low-molecular-weight organics (i.e. <700 Da) and degrades organics via rather non-selective, thermal fragmentation, thus introducing a volatile sample for gas chromatographic separation and mass spectral identification. It also has the potential of accessing organics trapped within minerals. For this reason, pyrolysis-GCMS is one of the most commonly used techniques for initial survey of organics in terrestrial sediments and is well suited for the search for organics on Mars (i.e., Science Analysis at Mars instrument suite, SAM, of NASA's 2011 Mars Science Laboratory, MSL); however, the capability of detecting organic carbon in a broad range of sample chemistries sacrifices information on the original chemical nature (functionality and polarity) of many organic materials expected of extraterrestrial organics [1,2]. The lost molecular information will likely be critical for pinpointing organic sources (biotic or abiotic), (bio)geochemical processing, and preservation mechanisms of extraterrestrial organics

as they do in terrestrial materials [cf. 3]. Alternative sample preparation techniques target free molecules such as amino acids and carboxylic acids (e.g. one-pot derivatization experiments: MTBSTFA-DMF in SAM and DMF-DMA in the Mars Organic Molecule Analyzer (MOMA being built for ESA/NASA's 2016 ExoMars mission) [4,5]), which may be prominent in recently deposited organic matter, but are less likely to persist in rocks and sediment over geological time scales.

In this study, the effectiveness of tetramethylammonium hydroxide (TMAH) thermochemolysis was investigated as a sample preparation approach for GCMS analysis of Martian samples of varying mineral and chemical matrices. Thermochemolysis involves concurrent mild thermal bond cleavage and selective base-catalyzed cleavage (hydrolysis) of ester, amide, and ether bonds that hold high-molecular-weight, complex organics. The free lower molecular-weight carboxylic acid, alcohol, and amine hydrolysis products are subsequently derivatized (in this case, methylated) to form highly volatile products amenable to GCMS analysis.

Methods: TMAH thermochemolysis GCMS was applied to both chemical standards that represent potential molecules expected on Mars due to meteorite delivery (PAHs, organic acids, carboxylates, etc.) [1, 2] and natural terrestrial analog samples that represent some feature analogous to Mars materials (e.g. Fe-oxide, smectite, and sulfate rich sediments, presence of perchlorates or ancient kerogen). Results of thermochemolysis at 600° C was compared to inert-pyrolysis at 600° C.

Results: Inert-pyrolysis produced low yields of organic molecules both in abundance and diversity. The products were often difficult to interpret based on either poorly resolved mass spectra or lack of reference spectra to confirm identification. In some cases, the internal standard (pyrene) was not detected. In comparison, thermochemolysis using 25% TMAH in methanol most often produced significantly greater yields (1.5 to >100x), more easily interpretable (i.e., matches to

reference spectra because of the predictable nature of hydrolysis and methylation). Multiple molecular biosignatures were detected in some samples using thermochemolysis. TMAH thermochemolysis was successful in yielding molecules from samples with challenging mineral matrices or chemistries, including those with oxides, hydroxides, salts, and water. Carboxylates, organic acids, and PAHs are readily detectable using thermochemolysis, though halogenated, alkylated, and other complex free molecules often produced multiple products.

Study Conclusions: TMAH thermochemolysis is a promising sample preparation approach for the detection of diverse organic components in rock and sediment samples, including those bound in macromolecules. Successful yields of abundant and meaningful molecular signatures from natural samples and organic standards in samples with a wide range of mineral and chemical composition suggest it is well suited for the diversity of Martian samples anticipated in forthcoming missions and may overcome problematic issues of other approaches (particularly with water, hydrated mineral phases, and oxidizers).

Integration into SAM on MSL: The two-year delay in the original launch date of MSL (now set to launch in Nov 2011), presented the opportunity for integrating a thermochemolysis experiment into SAM. Hardware design for the liquid chemical extraction cells already in the SAM were adaptable to TMAH in methanol without hardware modification. Materials compatibility, temperature and radiation exposure tests showed no compromise in materials or significant loss in TMAH performance. Of the nine wet-chemistry extraction cells in the sample processing system on SAM, two are dedicated to TMAH thermochemolysis.

Closing remarks: The detection of organic matter on Mars will be associated with many unknowns about its potential formation, concentration, and preservation [6]. Detection and molecular characterization of organic matter imposes a separate challenge because we have very few constraints to predict its chemistry or its host materials. All of the organic detection experiments included in SAM provide different observations that have the potential to yield critical insight into the presence and nature of organic matter or the key sample conditions needed for optimizing fol-

low-up experiments. The breadth of experimental capabilities of SAM maximize the potential of successful detection and characterization should organic matter be encountered by MSL. Once further constraints can be placed on the nature of organic matter and its host sediments, the evolution of sample preparation and detection techniques will be even further optimized, reducing the risk being compromised by unforeseen factors.

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