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PREPARING FOR THE FINAL THERMOCHEMOLYSIS EXPERIMENT ON THE MARS SCIENCE LABORATORY MISSION USING THE SAMPLE ANALYSIS AT MARS TESTBED. L. Chou¹, S. Teinturier^{1,2}, J. Eigenbrode¹, A. Williams³, A. McAdam¹, M. Millan^{4,12}, P. D. Archer, Jr.⁵, J. Lewis^{1,6}, C. Freissinet⁴, C. Szopa⁴, A. Buch⁷, D. Boulesteix⁷, B. Prats⁸, M. Johnson⁹, H. Rider¹⁰, A. Siguelnitzky¹¹, W. Brinckerhoff¹, D. P. Glavin¹, S. S. Johnson¹², P. Mahaffy¹, C. Malespin¹. ¹NASA Goddard Space Flight Center, Planetary Environments Lab (luoth.chou@nasa.gov; 8800 Greenbelt Rd, Greenbelt, MD 20771), ²Catholic University of America, ³University of Florida, ⁴LATMOS/CNRS, ⁵Jacobs, NASA JSC, ⁶Howard University, ⁷University Paris-Saclay, ⁸eINFORMe, Inc, ⁹Microtell LLC, ¹⁰Honeybee Robotics, ¹¹Sig Engineering, ¹²Georgetown University.

Introduction: On board NASA's Mars Science Laboratory (MSL) *Curiosity* Rover, the Sample Analysis at Mars (SAM) instrument suite has been characterizing the surface of Mars for the past decade in search of environments that may support past or present life. The SAM instrument includes evolved gas analysis (EGA) and pyrolysis-gas chromatography (pyro-GC) coupled with mass spectrometry (MS), which are used to analyze thermally volatilized gases and organic molecules from Mars drill fines [1]. A unique capability of SAM is the ability to perform thermochemolysis (thermally assisted hydrolysis and methylation) experiments using a chemical reagent, tetramethylammonium hydroxide (TMAH) in 25% w/w methanol. Thermochemolysis combines the process of pyrolysis and derivatization into a single step, in which (1) heat is used to cleave bonds in refractory carbonaceous macromolecules and (2) methylation is used to reduce the polarity of the resulting organic fragments, as well as unbound polar molecules to enhance their stability and volatility and, thus, detectability by GC-MS. Two cups containing 500 μ L TMAH reagent and recovery standards, nonanoic acid, pyrene, and 1-fluoronaphthalene, were included in the SAM instrument suite to aid in the search for organic matter on Mars, including chains of carboxylic acids of possible prebiotic or biotic significance (*e.g.*, fatty acids, *etc.*).

The First TMAH Experiment on Mars. On Sol 2879 of the mission, the first thermochemolysis experiment was performed on the Mary Anning drill sample, a phyllosilicate-rich sandstone collected in the Glen Torridon Region within the rover's study site in Gale Crater. Preliminary results indicated that the TMAH experiment proceeded as expected, resulting in the detection of a variety of methylated compounds as well as oxygen-, sulfur-, and nitrogen-bearing aromatics [2, 3, 4]. Some of these compounds, confirmed not to derive from the SAM instrument background, could represent a suite of molecular fragments liberated from the thermo-chemical cleavage of Mars macromolecular organic matter [2,4]. However, the experiment did not detect any carboxylic acids such as fatty acids. While this could suggest that the Mary Anning sample did not contain carboxylic acids, it was also noted that SAM did not conclusively observe one of the TMAH recovery

standards, nonanoic acid. This could be due to SAM's flight operating conditions that did not allow for the methylated nonanoic acid and potentially other high molecular weight compounds in the samples to be sufficiently transferred to (or eluted from) the GC column(s) [5].

Motivation. In order to fully understand these non-detections and to best prepare for the last thermochemolysis experiment on MSL, we use the SAM Testbed (TB) at NASA GSFC to optimize the TMAH experimental procedures prior to implementing it on the flight model (FM) on Mars.

Experimental Design: The goals of this study are to (1) design an end-to-end analytical procedure that aid in the detection of trace polar analytes in a large background ("noise") of TMAH solvent, (2) optimize the GC-MS heating program to allow for the most comprehensive separation of molecules with a wide range of molecular weights, and (3) establish the optimal sequences for the Gas Processing System (GPS) including valve configurations and venting cadences to ensure that the most critical analytes are subsampled by GC-MS without overwhelming the system with the wet chemistry reagent. To achieve these goals, the experiment was re-designed as two separate steps that can be conducted in two sols:

Step 1. This preparation step serves to pre-heat the sample in the SAM oven and "boil off" methanol and other TMAH volatile byproducts (*e.g.*, trimethylamine, dimethyl ether, *etc.*) at low temperatures (~ 150 °C) under helium carrier gas flow. This helps to reduce the overwhelming TMAH background signal in the subsequent thermochemolysis step. Fortunately, methanol can also be used as a solvating agent to possibly mobilize materials from the oven and those that may have been previously stuck in the GPS. During this boil-off step, any volatiles that are generated will be sent towards the GC through the GPS and SAM hydrocarbon (HC) trap, which is kept at an optimal temperature (~ 70 °C) to allow light volatiles (*e.g.*, methanol) to pass but heavier volatiles to be retained. After that, the HC trap is heated to ~ 300 °C, and any released analytes are separated via the GC and detected via the MS. This configuration ensures that no valuable compounds are vented and lost during boil-off and provides an

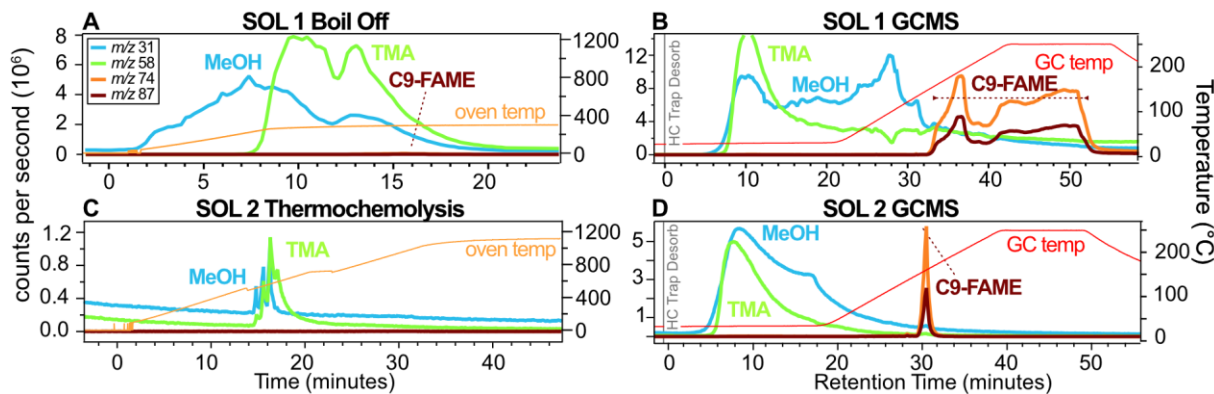


Fig 1. SAM Testbed ion pyrograms (A, C) and ion chromatograms (B, D) of 75 μL of TMAH and 5.079 μmol of nonanoic acid-methyl ester (C9-FAME) using the optimized TMAH script. **(A)** EGA during boil off on Sol 1 showing the evolution of methanol (MeOH), trimethylamine (TMA), and C9-FAME. **(B)** GC chromatogram of volatiles from 'A' showing that C9-FAME was overloaded in the column. **(C)** EGA during thermochemolysis on Sol 2 of the same sample, and **(D)** GC chromatogram of volatiles from 'C' showing a clear elution of C9-FAME. Note: the SAM oven temperature is estimated to be $\sim 100^{\circ}\text{C}$ - 150°C higher than the true sample temperature.

opportunity to detect any compounds that may have been previously stuck within SAM.

Step 2. The second thermochemolysis step is conducted as in the Mary Anning TMAH experiment [2]. The same sample is heated from $\sim 25^{\circ}\text{C}$ to $\sim 950^{\circ}\text{C}$ at $35^{\circ}\text{C min}^{-1}$ while portions of the evolved gases are subsampled and sent to the HC trap, which is once again kept at $\sim 70^{\circ}\text{C}$. After pyrolysis, the trap is heated to $\sim 300^{\circ}\text{C}$, and the trapped analytes are released to one of the six GC channels for analysis.

Leveraging the SAM Testbed. The SAM TB is a high-fidelity replica of the FM and is used by science and engineering team members to test and validate new protocols prior to implementing them in flight. Several experiments were conducted on the SAM TB using Ni cups that were filled with samples prior to loading into one of SAM's TB quartz cups. The samples contained $\sim 75 \mu\text{L}$ of the TMAH reagent (the maximum that can be loaded into the Ni cup) and calibrants such as C9-FA, nonanoic acid-methyl ester (C9-FAME), and pyrene. The GC channel used was the MXT[®] 5 (GC2) column comprising polydimethylsiloxane with 5% phenyl.

Results and Discussions: Our team worked to revise the original TMAH script in order to determine whether the lack of detection of C9-FAME was due to specific SAM operating conditions (*e.g.*, valve configuration) or rather was related to the thermochemolysis reaction (*e.g.*, inefficient reaction temperature, ramp rate *etc.*). After preparing a new script which included a boil-off step, we analyzed a TMAH sample with 5.079 μmol C9-FAME (Figure 1). Preliminary results suggest that with the new experimental design, the SAM TB can detect and separate C9-FAME. Following this experiment, we will analyze a TMAH sample with the same amount of C9-

FA to determine if the thermochemolysis reaction remains effective after the boil off step.

Conclusions: The SAM Testbed is an extremely valuable tool used to develop and validate methods prior to implementing them on the FM on Mars. Our goal is to establish a robust procedure that could be implemented on the flight model to detect organic matter, including the nonanoic acid standard, during the next (and final) TMAH experiment on the MSL mission. Further details on the SAM TB experiments and how they were used to support SAM flight operations will be reported in a future manuscript.

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