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OPTIMIZATION OF THE SAMPLE ANALYSIS AT MARS WET CHEMISTRY EXPERIMENT FOR THE DETECTION OF ORGANICS IN GLEN TORRIDON. M. Millan^{1,2}, C. Pozarycki¹, A. McAdam¹, S. Andrejkovicova¹, P. Mahaffy¹, D. Glavin¹, A. Buch³, C. Szopa⁴, C. Freissinet⁴, A. Srivastava¹, S. Teinturier^{1,5}, C. Malespin¹, R. Williams¹, A. Williams⁶, J. Eigenbrode¹, R. Navarro-Gonzalez⁷, S. S. Johnson². ¹NASA Goddard Space Flight Center, Greenbelt, MD, 20771 maeva.millan@nasa.gov, ²Georgetown University, ³Laboratoire de Génie des Procédés et Matériaux, CentraleSupélec, France, ⁴Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), UVSQ, France, ⁵Goddard Earth Science Technology and Research, Universities Space Research Association, ⁶Dept. of Geological Sciences, University of Florida, ⁷Universidad Nacional Autónoma de México.

Introduction: As Curiosity ascends Mount Sharp, it is analyzing stratigraphic rock layers to find clues to Mars' environmental history and habitability [1]. The Sample Analysis at Mars (SAM) instrument suite onboard Curiosity includes a pyrolyzer coupled to a gas chromatograph-mass spectrometer (pyro-GCMS) mostly dedicated to the search for organic molecules on Mars. SAM is able to perform *in situ* molecular analysis of gases evolved from heating solid samples collected by Curiosity up to ~900°C. SAM can then detect, separate, and identify volatiles inorganic and organic compounds released from the gas phase of the solid samples.

SAM also carries nine sealed wet chemistry cups to allow for a new capability to be employed at Mars' surface, opening the possibility for a larger set of organics to be detected. Seven of the cups contain a 0.5 mL mixture of *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide and dimethylformamide (MTBSTFA:DMF 4:1) for derivatization and the two others contain tetramethylammonium hydroxide (TMAH), 25% in methanol mixture for thermochemolysis [2]. The cups also contain standards of organic molecules (36.2 nmol of 3-fluorovaline and 24.2 nmol of pyrene in the MTBSTFA cups) (Figure 1) for calibration and validation purposes.

The derivatization with MTBSTFA allows the detection and identification of complex, polar and/or refractory molecules. In this silylation method, the labile hydrogen of the targeted molecule is replaced by the MTBSTFA silyl group, transforming molecules into volatile derivatives easily amenable to GCMS analysis (Figure 1). Thus MTBSTFA reacts with organics of astrobiological interest—such as nucleobases, amino acids, carboxylic acids, and sugars—while preventing degradation of their chemical structure.

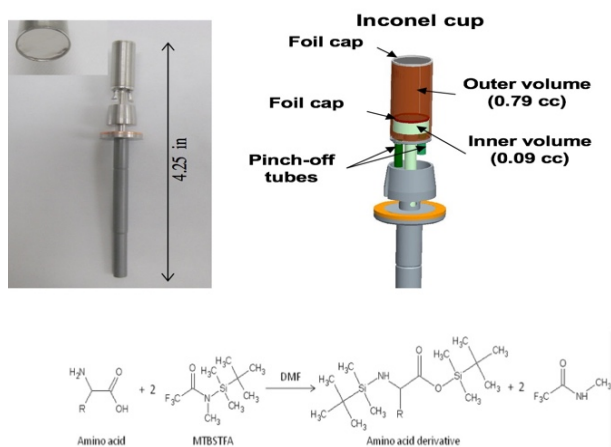


Figure 1. The MTBSTFA derivatization cup (top) and an example of the MTBSTFA reaction with an amino acid that displaces the labile hydrogens with a *tert*-butyldimethylsilyl group to produce a volatile amino acid derivative (bottom).

1st wet chemistry on Ogunquit Beach: EGA and GCMS of the Ogunquit Beach scooped sample have been analyzed and showed the detection of compounds of medium to high molecular masses, including derivatized molecules as well as varying amounts of various MTBSTFA by-products, such as *N*-methyl-2,2,2-trifluoroacetamide (TFMA) and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxanetetramethyldisiloxane (bi-silylated water), along with the whole MTBSTFA molecule. These results indicate that the derivatization reagent was in excess, as reactions clearly occurred and produced derivatized compounds. Derivatize benzoic acid and ammonia derivatized were also detected by both their mass spectra and retention times, above instrument background. However, no amino acids or fatty acids were detected.

Optimization of the GCMS parameters: Following the wet chemistry experiment on the OG sample, laboratory experiments were conducted to improve the detection of derivatized organic molecules with SAM in future runs. Tests included the analysis of multiple organic mixtures (e.g. amino acids, carboxylic acids, etc.) under SAM-like operating conditions (e.g. temperature, helium flow) and varying the operating temperature of the GC columns. These runs showed that

by measuring the signal of compounds that elute while the column is cooling down, we can extend the effective range of heavy molecules that can be detected in comparison to previous SAM measurements (Figure 2). Laboratory experiments have also now shown that successive column cleanups after the sample GCMS experiment can release heavier compounds that may not have been released in the original experiment.

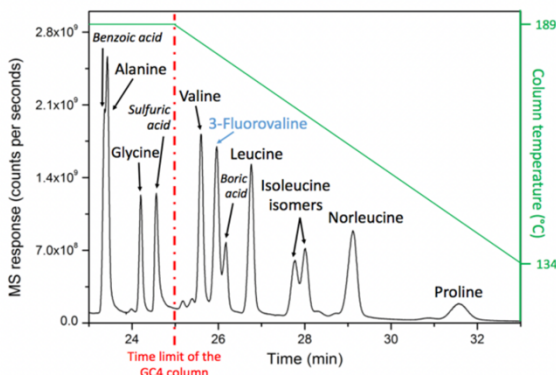
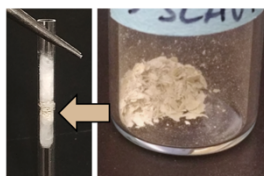


Figure 2. Gas chromatogram obtained with a sparse GC4 column of a 22 amino acids standards mixture analyzed in the laboratory. Only alanine and glycine would be detectable within the current SAM-flight operating conditions used for the GC4 column on the SAM flight model instrument. However, this laboratory experiments shows that recording the signal while the temperature is cooling down on Mars could allow the detection of heavier molecules such as the amino acids targeted for this study.

Wet chemistry on glycine-clays laced analogs: To prepare the next chemistry run in Glen Torridon and improve the detection of organics, laboratory experiments were performed on glycine-laced montmorillonite analogs (Figure 3). The goals were to evaluate the extraction and derivatization efficiency of amino acids, here glycine, present in the phyllosilicates interlayers and evaluate the limitations of the SAM-flight experiment in order to optimize it. Pyrolysis parameters were varied (oven, trap and transfer line temperatures) and the glycine abundance recovery was calculated. Results showed that glycine detection is limited in SAM-like pyrolysis but can be greatly improved by slightly increasing the transfer line and pyrolysis rate temperatures within the range allowed by SAM.

Figure 3. Ground Clay, packed between quartz wool in a quartz pyrolysis tube and spiked with MTBSTFA derivatization reagent before pyrolysis. **Pyrolysis & 2nd wet chemistry on Glen Etive (Glen**



Torridon): Both a pyrolysis only and wet chemistry experiments were performed on two separate Glen Etive drilled samples from the Clay-Bearing Unit (Glen Torridon). EGA and GCMS have been analyzed and showed the efficiency of the lessons learned from OG through a much less saturated chromatogram in chemistry reagents. High molecular weight compounds are still detected with some abundance higher than those present in the OG sample although less reagent was introduced. The highest abundance of Sulfur-bearing organics ever measured by the SAM instrument was detected in both the pyrolysis and wet chemistry runs. Pathways of formation of those sulfur compounds are under investigations through laboratory experiments to understand their potential source and origins.

References: [1] Grotzinger, J.P., et al. (2013) *Sci Express* 343, 1242771-1242714. [2] Mahaffy P.R. et al. (2012) *Space Sci Rev*, 401-478. [3] Freissinet, C. et al. (2017) LPSC meeting [#2687]. [4] Millan, M. et al. (2018) LPSC meeting [#1558]. [5] Williams, A. et al. (2019) *Astrobio*. 19, 522-546.

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