LESSONS LEARNED FROM THE FIRST FULL CUP WET CHEMISTRY EXPERIMENT PERFORMED ON MARS WITH THE SAMPLE ANALYSIS AT MARS INSTRUMENT. M. Millan[1,2], C. A. Malespin[1], C. Freissinet[3], D. P. Glavin[1], P. R. Mahaffy[1], A. Buch[4], C. Szopa[3,5], A. Srivastava[1], S. Teinturier[1,6], R. Williams[1,7], A. Williams[8,1], A. McAdam[1], D. Coscia[3], J. Eigenbrode[1], E. Raaen[1], J. Dworkin[1], R. Navarro-Gonzalez[9] and S. S. Johnson[2]. [1]NASA Goddard Space Flight Center, Greenbelt, MD, 20771 maeva.millan@nasa.gov, [2]Georgetown University, [3]Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), UVSQ, France, [4]Laboratoire de Genie des Procedes et Materiaux, CentraleSupelec, France, [5]Institut Universitaire de France, [6]Goddard Earth Science Technology and Research, Universities Space Research Association, [7]Department of Astronomy, University of Maryland, , [8]Dept. of Geological Sciences, University of Florida, [9]Universidad Nacional Autónoma de México

Introduction: The Curiosity Rover is currently ascending Mount Sharp, analyzing stratigraphic rock layers to find clues to Mars' environmental history and habitability [1]. One of its key instruments, the Sample Analysis at Mars (SAM) instrument suite, contains a pyrolyzer coupled to a gas chromatograph-mass spectrometer (pyro-GCMS). This pyro-GCMS is largely 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 in inorganic and organic compounds released from the solid samples.

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

MTBSTFA allows the separation, detection, and identification of complex, polar and/or refractory molecules. The derivatization method is a silylation method where 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). MTBSTFA is then able to react with organics of astrobiological interest—such as nucleobases, amino acids, carboxylic acids, and sugars—while preserving their chemical structure from degradation.

Although one of the MTBSTFA cups inadvertently leaked into SAM, and that leak was used to perform an opportunistic derivatization experiment [3], none of the seven cups were punctured to perform a full-cup derivatization until December 2017, when the first full-cup wet chemistry experiment was run.

Here we describe the first derivatization experiment performed on Mars with SAM that includes the puncture of one of the MTBSTFA cup. We detail what we learned from the results as well as the optimization experiments that were performed in the laboratory to improve the future runs on Mars using this derivatization technique.

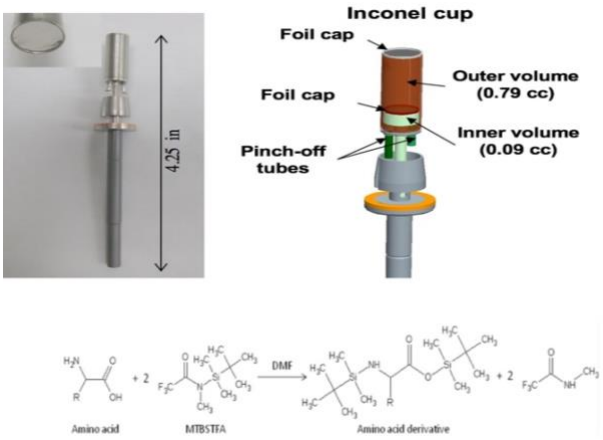

Figure 1. The MTBSTFA derivatization cup (top) and an example of the MTBSTFA reaction with an amino acid that displaces the labile hydrogens with a *tert*butyldimethylsilyl group to produce a volatile amino acid derivative (bottom).

Experimental procedure: The SAM wet chemistry experiment is based on the "standard" SAM EGA/GCMS sequence which nominally accepts ~45 mg of sample for analysis. For the wet chemistry experiment, the sequence is divided into three sequential parts, which all occur on the same Sol.

Part 1. Prep and background. In a nominal SAM EGA sequence (i.e. without derivatization), the cup being used to accept sample is preconditioned and cleaned before use by heating to 900°C under He flow in the pyrolysis oven.

Since MTBSTFA pyrolyzes at 900°C and wet chemistry cups are sealed, this cleaning step is non tenable. Instead, a 'prep' script heats and conditions the manifolds and pipes, pumping out and cleaning SAM. The quadrupole mass spectrometer (QMS) then takes background readings of both the MS alone and of the manifolds prior to the introduction of MTBSTFA fluid/vapor and sample volatiles.

Part 2. Cup puncture and sample dropoff. The timing and order of events is critical in the development of the procedure since it is important to begin heating the sample as quickly as possible after the rover drops off portions into the punctured wet chemistry cup. This is because MTBSTFA will slowly evaporate from the cup after puncture at Mars pressure at all temperatures above 9°C. Prior to receiving a sample, the wet chemistry cup is punctured onboard SAM using two puncture needles, one for each foil capping the solvent (Figure 1). The cup is then moved to the inlet to accept a sample from the rover arm. After sample delivery, the cup is placed into the SAM oven under helium flow for analysis.

Part 3. Pyrolysis EGA and GCMS of sample. The sample is pyrolyzed up to ~900°C at 35°C/min. In order to avoid saturating the SAM hydrocarbon trap with MTBSTFA:DMF fluid, only a portion of the evolved gas is captured for analysis. The remaining gas is vented out an exhaust located on the side of the rover. The sample is collected for 5 seconds every 200 seconds during the ramp from ambient to 100°C. Then 5 seconds every 70 seconds from 100°C to 250°C. From 250°C to the maximum sample temperature of ~900°C, the sample is collected for 20 seconds every 40 seconds.

To further help mitigate clogging the SAM hydrocarbon trap and GC columns, during the low temperature (< 250°C) portion of the pyrolysis ramp, the SAM hydrocarbon (HC) trap is kept at 80°C. Previous laboratory experiments have showed that at this temperature MTBSTFA is not efficiently trapped, while still allowing complex derivatized organics to be collected (such as derivatized amino acids).

Once the sample temperature reaches 250°C and most of the MTBSTFA has evaporated, the trap is cooled down to 0°C to freeze out and collect derivatized and non-derivatized molecules. Once the SAM HC trap is heated to 320°C, the collected gases can desorb and be used for a split column GCMS analysis. SAM has six GC columns. Columns 1 and 4, a MXT-20 and Chirasil-Dex respectively, are used in for GCMS.

The entire three part procedure has now been validated, both for science and engineering purposes, using filled MTBSTFA:DMF cups on the SAM Testbed [3].

Summary of SAM results: EGA and GCMS of a single portion, ~45 mg, of Ogunquit Beach (OG) scooped sample have now been analyzed SAM for the first cup puncture MTBSTFA experiment.

A detailed investigation of the results will be discussed in a forthcoming paper, but we briefly note several compounds of interest represented by medium to high molecular masses. Using benzene, found in almost all SAM runs because it is released from IT trap, as a standard compound for comparison, we detected 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, along with the whole MTBSTFA molecule (Figure 2).

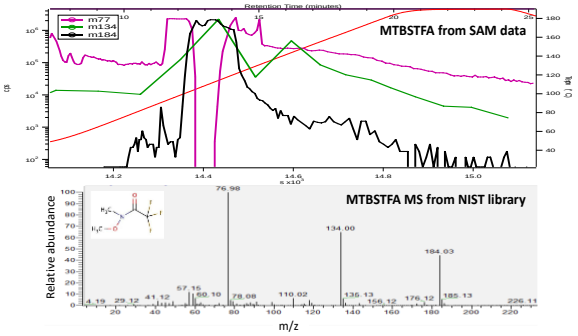

Figure 2. Chromatogram from SAM showing the saturated detection of MTBSTFA (top) compared to the laboratory MS from the NIST library (bottom).

These results show the derivatization reagent is in excess for reactions to occur and produce derivatized compounds. Data processing and laboratory experiments on martian analog samples are still ongoing to identify organics that have mass spectra missing from common MTBSTFA libraries and to further understand the type of environments where they can be found.

Optimization of the future runs: Following the first wet chemistry experiment on Mars and the results obtained, a series of laboratory experiments are being conducted to improve the detection of derivatized organic molecules with SAM in future runs. Tests include the analysis of multiple organic mixtures under SAM-like operating conditions (temperature, helium flow) and varying the operating temperature of the GC column.

So far, these tests have shown that by measuring compounds that continue to 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.

Further testing on the SAM testbed will confirm if this new approach will allow SAM to detect molecules that continue to elute, even after the column heating has finished. 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.

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]

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