The First Complete SAM Wet Chemistry Experiment on Mars. C. A. Malespin[1], C. Freissinet[2], D. P. Glavin[1], P. R. Mahaffy[1], M. Millan[1,3], A. Buch[4], C. Szopa[4,5], S. Teinturier[1,6], A. McAdam[1], R. Williams[1,7], J. Eigenbrode[1], E. Raaen[1], J. P. Dworkin[1], and R. Navarro-Gonzalez[8] [1]NASA Goddard Space Flight Center, Greenbelt, MD, 20771 charles.a.malespin@nasa.gov, [2]LATMOS, UVSQ, France, [3]Georgetown University, [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, Columbia, MD, [7]Department of Astronomy, University of Maryland, [8]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico

Introduction: The Sample Analysis at Mars (SAM) instrument suite is currently operating in the Curiosity rover in Gale Crater, Mars. SAM carries nine sealed wet chemistry cups, seven which contain a mixture of *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide and dimethylformamide (MTBSTFA:DMF 4:1) for derivatization and two that are filled with tetramethylammonium hydroxide (TMAH) and methanol for thermochemolysis [1]. Here we describe the first derivatization experiment performed on Mars with SAM that includes the puncture of one of the MTBSTFA cup.

Overview of wet chemistry. One of the primary goals of the SAM investigation is the search for organic compounds on Mars. The wet chemistry cups onboard SAM are intended to make complex organic molecules more volatile derivatized products that can be readily analyzed by GCMS. An example of the MTBSTFA derivatization reaction with an amino acid is shown in Figure 1. The seven derivatization cups contain 0.5 mL of a mixture of MTBSTFA and DMF in a 4:1 ratio. These cups also contain trace standards (36.2 nmol of 3-fluorovaline and 24.2 nmol of pyrene) (Figure 1) for calibration and verification purposes.

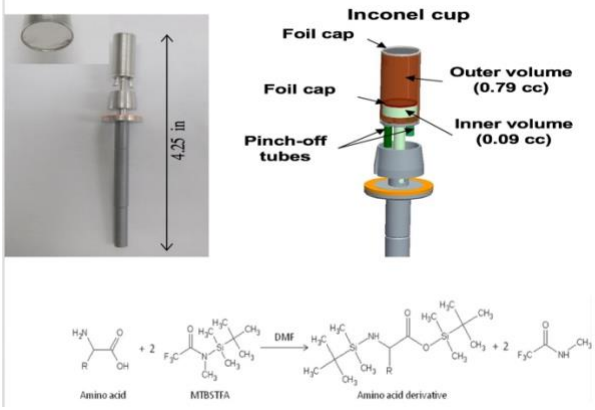

Figure 1. An example of the MTBSTFA reaction with an amino acid that displaces the labile hydrogens with *tert*butyldimethylsilyl groups to produce a volatile derivative.

Although at least one of the MTBSTFA cups is leaking into SAM and the leak had been used to perform opportunistic derivatization [2], none of the cups had been punctured to perform a full-cup derivatization, until December 2017 when the first full-cup wet chemistry experiment was run.

Experiment 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 the MTBSTFA would be pyrolyzed at 900°C and since wet chemistry cups are sealed, this cleaning step is not feasible. Instead, the 'prep' script heats and conditions the manifolds and pipes, pumping out and cleaning SAM. The quadrupole mass spectrometer (QMS) takes backgrounds 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 was 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 since MTBSTFA will slowly evaporate from the cups after puncture at Mars pressure at temperatures above 9 °C. Typically the SAM SMS is at -10 ° C during puncture. 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 sample from the rover arm. After sample delivery, the cup is put into the SAM oven under helium flow in preparation for analysis.

Part 3- Pyrolysis EGA and GCMS of sample. Part 3 begins minutes after part 2 ends with the cup in the oven. The sample is heated using the standard SAM 35°C/min pyrolysis ramp, up to ~900 °C. 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 remainder of the gas is vented out an exhaust located on the side of the rover. The fraction of gas captured below 250 °C,

where the majority of the MTBSTFA/DMF vapor exists, is lower than at higher temperatures. From ambient to 100 °C, the sample is collected for 5 seconds every 200 seconds. From 100 °C to 250 °C, the sample is collected 5 seconds every 70 seconds. Above 250 °C to the maximum sample temperature of ~900 °C, the sample is collected for 20 seconds every 40 seconds.

To help further mitigate clogging the SAM hydrocarbon trap and GC columns, during the low temperature (< 250 °C) portion of the pyrolysis ramp the SAM hydrocarbon trap is kept at 80°C. Laboratory studies have shown that at this temperature MTBSTFA is not efficiently trapped, while still allowing any complex derivatized organics to be collected (such as derivatized amino acids). Once the sample temperature reaches 250 °C and most of the derivatizating agent has evaporated , the trap is quickly cooled down to 0 °C to help freeze out and collect any analytes, derivatized and non-derivatized.

The SAM HC trap is heated to 320 °C and the collected gases will desorb and be used for a split column GCMS analysis. SAM has 6 GC columns, the wet chemistry experiment utilizes columns 1 and 4 for GCMS. Column 1 is an 30 meters long MXT-20 column and does not have an injection trap (IT) nor a thermal conductivity detector (TCD), and targets light to medium molecular weight mid-polar organics. Column 4 is a 30 meters long Chirasil-Dex column with an IT used to focus and perform a sharp injection of the analytes into the column for a better peak separation. The fragility of the chiral phase of the column, coupled to the presence of the TCD downstream the GC column, limits the column temperature to 190 °C.

GCMS analysis of column 1 begins immediately at the end of the EGA since it has no injection trap to retain released gas. However, organics are trapped at the front-end of this column due to a combination between He flow and temperature. The column is ramped up from ambient to 250 °C at a rate of 10 °C min^{-1}. Upon completion of GC1, the IT of GC4 is flashed to inject gas into the column. GC4 reaches a maximum temperature of 190°C using a similar 10°C.min^{-1} ramp rate.

The entire three part procedure was validated, both for science and engineering purposes, using filled MTBSTFA:DMF cups on the SAM TB [3]. Lake Hoare samples were used as an analog for the wet chemistry TB campaign, due to it being a well characterized organic rich sample [3,4].

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

A detailed analysis of the results will be discussed in a later paper, but we briefly note several compounds of interest represented by medium to high molecular masses. Benzene, found in almost all SAM runs because it is released from IT trap, is used as a standard compound for comparison. We also detected various MTBSTFA by-products such as *N*-methyl-2,2,2-trifluoroacetamide (TFMA) and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyl-disiloxanetetramethyldisiloxane, along with the whole MTBSTFA molecule. This clearly shows the derivatization reagent is in excess for reactions to occur and produce derivatized compounds. More analyses is needed on this newly and exciting set of data to decipher the organics content of OG under a MTBSTFA derivatization experiment.

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.

References: [1] Mahaffy, P.R. et al. (2012) *Space Sci Rev. 170*, 401-478. [2] Freissinet, C. et al. (2017) LPSC meeting [#2687]. [3] Malespin, C. A. et al. (2017) LPSC meeting [#2369]. [4] Bishop, J, et al. (1996), *Geochim Cosmochim*, 765-785

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