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# The Sample Analysis at Mars (SAM) Wet Chemistry Experiment Introduction: The Sample Analysis at Mars (SAM)

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**The Sample Analysis at Mars (SAM) Wet Chemistry Experiment.** C. A. Malespin<sup>1</sup>, C. Freissinet<sup>1,2</sup>, P. R. Mahaffy<sup>1</sup>, S. Teinturier<sup>1,3</sup>, D. P. Glavin<sup>1</sup>, A. McAdam<sup>1</sup>, R. Williams<sup>1,4</sup>, A. Buch<sup>5</sup>, C. Szopa<sup>6,7</sup>, D. Cosca<sup>6</sup>, E. Raaen<sup>1</sup>, C. Johnson<sup>1</sup>, W. Brinckerhoff<sup>1</sup>, B. Prats<sup>1,8</sup>, and R. Gonzales<sup>9</sup> <sup>1</sup>NASA Goddard Space Flight Center, Greenbelt, MD, 20771 charles.a.malespin@nasa.gov, <sup>2</sup>Center for Research and Exploration in Space Science and Technology, UMBC, <sup>3</sup>GESTAR, Universities Space Research Association, Columbia, MD, <sup>4</sup>Department of Astronomy, University of Maryland, <sup>5</sup>Laboratoire de Genie des Procédés et Matériaux, CentraleSupélec, France, <sup>6</sup>LATMOS, UVSQ, France <sup>7</sup>Institut Universitaire de France, <sup>8</sup>eINFORMe, INC., <sup>9</sup>Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México

**Introduction:** The Sample Analysis at Mars (SAM) instrument suite is currently operating on 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 (MTBSTFA) and dimethylformamide (DMF) for derivatization and two that are filled with tetramethylammonium hydroxide (TMAH) and methanol for thermochemolysis [1]. Here we describe the testing and experimental procedure for the upcoming use of the MTBSTFA derivatization experiment on Mars.

Since MTBSTFA derivatization was not tested on the SAM flight instrument, the experiment needed to be optimized on Earth using the SAM testbed (TB). In preparation for the puncture of a wet chemistry cup on Mars, a high fidelity testing campaign using Mars analog samples from Lake Hoare, Antarctica was conducted using the TB, located at NASA GSFC. The TB is an identical copy of the flight instrument, and is described in detail elsewhere, [1, 2].

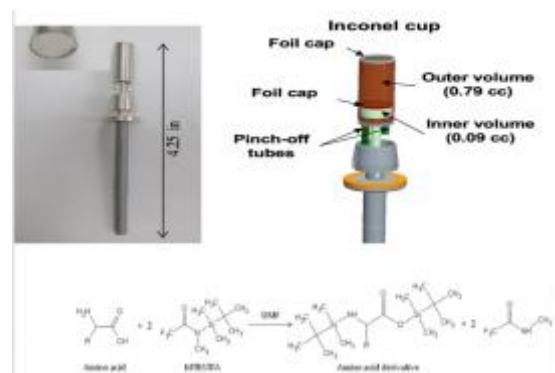
*Overview of wet chemistry.* One of the primary goals of the SAM investigation is the search for organic compounds on Mars. The wet chemistry cups onboard SAM are intended to transform complex organic molecules into more volatile derivatized products that can be readily analyzed by GCMS. The seven derivatization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

Three sealed MTBSTFA cups, identical to the flight cups, were loaded into the TB, which were used for the testing campaign. A more detailed description of SAM and the wet chemistry hardware can be found in Mahaffy et al [1]. Here we focus on the experimental procedure and parameters used.

**Experimental procedure:** The SAM wet chemistry experiment is based on the “standard” SAM EGA/GCMS sequence which nominally accepts ~120 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 before use by heating to 900°C under He flow in the pyrolysis oven.

Since the MTBSTFA would be pyrolyzed at 900°C and



**Figure 1.** The MTBSTFA cup (top) and reaction with an amino acid (bottom) that displaces the hydroxyl hydrogen with the methylated silica group to produce a volatile derivative.

since wet chemistry cups are sealed, this cleaning step is not necessary. 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. 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. In order to minimize the time the punctured cup was exposed to the open environment, the sample drop off from the rover was moved to the middle of the SAM experiment. Prior to receiving a sample, the wet chemistry cup is punctured onboard SAM using two puncture needles, one for each foil capping the solvent.

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<sup>-1</sup> 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. On Mars, the remainder of the gas is vented out an exhaust located on the side of the rover, but on the TB, the vented gas

is collected on an external cold trap for subsequent analysis using a lab GCMS. The fraction of gas captured below 250°C, where the majority of the MTBSTFA/DMF vapor exists, is lower than at higher temperatures. The fraction of evolved gas collected is a script parameter, allowing for a higher percentage of analytes to be targeted at mid and high temperatures, and allowing a quick change of those temperature cuts depending on the sample.

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, the trap is quickly cooled down to 0° C to help freeze out and collect any analytes, derivatized and non-derivatized.

The collected gas on the hydrocarbon trap is 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 MXT20 column without an adsorption injection trap (IT) and targeting light to medium molecular weight mid-polar organics. Column 4 is a ChirasilDex column with an IT used to focus and inject the analytes as quickly as possible into the column.

The SAM HC trap is heated to 320°C and the desorbed gases are split between columns 1 and 4. 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 still 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<sup>-1</sup>. Upon completion of GC1, the IT of GC 4 is flashed to inject gas into the column for GCMS. GC4 reaches a maximum temperature of 190°C using a similar 10°C.min<sup>-1</sup> ramp rate.

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

**Summary of SAM TB Lake Hoare results:** EGA and GCMS of Lake Hoare sediment cores have been performed on the SAM TB, without the introduction of any wet chemistry reagents. We use this sample as a control ‘blank’ under SAM-like conditions for comparison with the MTBSTFA experiment.

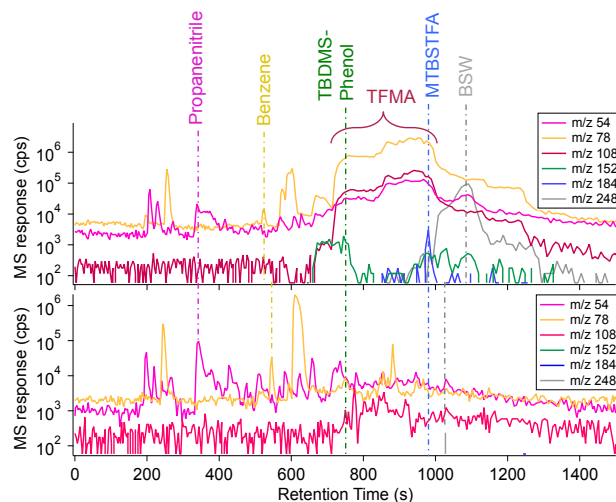
A detailed analysis of the Lake Hoare results, with and without MTBSTFA/DMF, will be discussed in a later paper, but we briefly note several compounds of interest in Figure 2. Propanenitrile, which is released from the sample, is seen in both data sets, albeit reduced by a factor of two in the

derivatization run. Benzene, found in almost all SAM runs because it is released from IT trap, is shown 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-tetramethyldisiloxanetetramethyldisiloxane, along with the whole MTBSTFA molecule since it has not yet been measured by SAM on Mars. This clearly shows there are sufficient reagents for reactions to occur and produce derivatized compounds, as seen by the *tert*-butyldimethylsilyl (TBDMS)-phenol peak in the upper plot.

**Path Forward:** The SAM TB wet chemistry campaign successfully demonstrated that using the proposed experimental procedure will produce sufficient reagent fluid/vapor to react with the sample, without saturating the HC trap or GC columns.

Development work to incorporate this procedure with the larger rover handoff plan is currently underway. 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.

Experience with derivatization on SAM is further being applied to optimize the protocols planned for the Mars Organic Molecule Analyzer(MOMA) investigation on the ExoMars rover.



**Figure 2.** Lake Hoare GCMS plot run using wet chemistry procedure(top) compared to Lake Hoare sample run without MTBSTFA (bottom). Select compounds of interest showing differences in signal intensity as a result of reactions with MTBSTFA reagent.

**References:** [1] Mahaffy, P.R. et al (2012) *Space Sci Rev.* 170, 401-478. [2] Malespin, C.A., et. al. (2015), LPSC, abst # 2558 [3] Bishop, J, et al. (1996), *Geochim Cosmochim.* 765-785

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