

IN SITU WET CHEMISTRY EXPERIMENT ON MARS USING THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT: “OPPORTUNISTIC DERIVATIZATION” TO INVESTIGATE ORGANICS IN A MARTIAN MUDSTONE. C. Freissinet^{1,2}, D. P. Glavin¹, A. Buch³, C. Szopa⁴, S. Kashyap⁵, H. B. Franz¹, J. L. Eigenbrode¹, W. B. Brinckerhoff¹, R. Navarro-González⁶, S. Teinturier¹, C. A. Malespin¹, B. D. Prats¹, P. R. Mahaffy¹ and the SAM and MSL science teams. ¹NASA Goddard Space Flight Center, Greenbelt, MD, caroline.freissinet@nasa.gov, ²NASA Postdoctoral Program, Oak Ridge Associated Universities, TN, ³Ecole Centrale Paris, Chatenay-Malabry, France, ⁴LATMOS-UPMC, Paris, France, ⁵University of Massachusetts Amherst, Amherst MA 01003, ⁶Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico.

Introduction: The wet chemistry experiments on the Sample Analysis at Mars (SAM) instrument were designed for the extraction and identification of refractory organic chemical components in solid samples using gas chromatography-mass spectrometry (GCMS) [1, 2]. One of the chemical agents used, *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA), was sealed inside seven Inconel metal cups present in the SAM Sample Manipulation System (SMS). Although none of these foil-capped derivatization cups have been punctured on Mars for a full-cup wet chemistry experiment as originally designed, data from SAM has shown that the MTBSTFA vapor that leaked into the SMS is available to react with volatiles in solid samples and is detected mostly as its reaction product with water [3, 4]. Despite the MTBSTFA background in SAM, several organic molecules indigenous to Mars have been identified by GCMS above background levels in a drilled mudstone sample called Cumberland (CB) collected at Yellowknife Bay [3]. Here we report preliminary results from an MTBSTFA “opportunistic derivatization” (OD) GCMS experiment that maximized the MTBSTFA deposition on a CB mudstone sample stored in SAM. The experiment was optimized for the detection of MTBSTFA residual vapor reaction products with refractory organic compounds and other molecules present in the CB mudstone sample.

MTBSTFA Opportunistic Derivatization: The CB sample used in the OD experiment was drilled in the Sheepbed mudstone on Sol 279, and a fresh triple portion aliquot of the mudstone sample (~ 135 ± 31 mg) was added on top of a previously pyrolyzed CB single portion sample. This “doggy bag” sample was left inside SAM for about 1280 sols and accumulated and reacted with MTBSTFA vapor present in the SMS during the traverse to the base of Mt. Sharp. The OD experiment was conducted as a multi-sol experiment as follows: 1) The first step (ODa) consisted of a medium temperature heating of the sample from ambient to ~560 °C at a rate of 35 °C/min under 1 standard cubic centimeters per min He flow, to remove most of the O₂ released from the decomposition of perchlorates, in order to limit the combustion of possible organic molecules and their MTBSTFA derivatives in the

second OD step. No GCMS was run during this first step, however, volatiles released from the sample during heating to 560 °C were analyzed directly using the quadrupole mass spectrometer (QMS) only. The cup was then removed from the pyrolysis oven and placed back into the SMS where the sample could re-adsorb and react with MTBSTFA vapor present in the SMS for 48 hours. 2) The second step (ODb) utilized a higher temperature heating, up to ~900 °C, to perform derivatization of molecules in the samples that evolve at elevated sample temperatures (either trapped inside minerals or resulting from the breakdown of more complex organics). During this ODb phase, four pyrolysis temperature cuts were sent to a hydrocarbon trap for GC analyses: ~40-115 °C, ~310-550 °C, ~590-670 °C and ~753 °C to the end of the run. The cuts were selected to target the release of compounds of interest, while also avoiding the saturation of the trap with MBSTFA byproducts or SO₂ from sulfate decomposition. The trap was set at a temperature of ~70 °C for the first cut, a temperature at which most the MTBSTFA reaction products with water would pass through, while derivatized compounds of interest would be retained. At a sample temperature of ~300 °C, the SAM trap was cooled down from 70 °C to 5 °C to trap smaller volatiles. MTBSTFA reaction products and other volatiles collected on the hydrocarbon trap were then analyzed by GC separation, on two GC columns (GC1-MXT-20 and GC4-Chirasil-Dex, each column is 30 m length, 0.25 mm ID, 0.25 μm film thickness) and QMS analysis after heating the trap to 310 °C [2]. After the ODa and ODb analyses of CB, a procedural control experiment is planned to be carried out using the identical SAM analytical conditions, on a quartz cup containing a triple portion CB sample that was heated previously to ~900 °C three times.

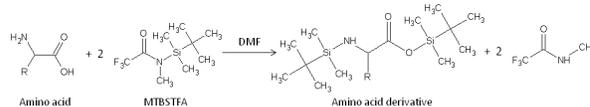


Figure 1: Example MTBSTFA reaction with an amino acid to form the volatile silyl ester derivative and a trifluoro-*N*-methylacetamide (TFMA) byproduct that are both detectable by the SAM GCMS.

Results and Discussion: MTBSTFA was selected as one of the chemical reagents used in the SAM derivatization experiments since MTBSTFA can react

with a wide range of molecules that contain a labile hydrogen such as alcohols, primary and secondary amines, carboxylic acids and amino acids in the free form (Figure 1). The silyl ester products of these molecules are typically much more volatile than the original non-derivatized molecule, which enables the transfer of the MTBSTFA derivatives through the SAM gas processing system for GCMS analysis.

The initial abundance of MTBSTFA adsorbed on a cup and a sample was estimated from the abundances of the primary MTBSTFA byproducts formed from its reaction with water molecules including *tert*-butyldimethylsilanol, *N*-methyl-2,2,2-trifluoroacetamide, and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxane [3], and was expected to be at least 116 nmol or 0.03 mL, as estimated from the CB-Blank-1 EGA experiment [3]. In the ODb experiment, the abundances of MTBSTFA reaction products detected by GCMS and corresponding MTBSTFA abundances released from the Cumberland "doggy bag" triple portion were found to be ten times higher, in the μmol range. This result is not surprising since the OD experiments were optimized for the concentration and detection of MTBSTFA reaction products. However, only part of this was sent to the trap/GC columns, due to the temperature cuts and hot SAM trap combination.

The temperature cuts were chosen to target, among others, potential molecules trapped in the sulfate minerals of CB. S-containing molecules were previously observed at high temperature in the CB sample [5]. The two high-temperature SO_2 peaks evolving from CB are thought to be Fe-sulfate and Mg-sulfate [6]. Unfortunately, the temperature reached during the first OD step (ODa) started to decompose the Fe-sulfates, possibly releasing trapped organics. However, molecules trapped in the Mg-sulfates would be seen either as derivatized, or pristine, molecules in the OD experiment. The preliminary results show a tentative identification of thiophene, as expected, in GC4 (Fig. 2). Chlorobenzene was also tentatively identified, which has numerous implications. Unlike the previous detection of chlorobenzene in CB samples [3], this detection occurred at a higher temperature of the sample ($> 560^\circ\text{C}$ vs. $250\text{--}450^\circ\text{C}$ previously). This chlorobenzene, if indigenous to the martian sample, would originate from a different source than the $250\text{--}450^\circ\text{C}$ one. Several N-containing compounds were observed at higher abundances than previously seen, and 2-propenenitrile was observed for the first time in SAM. Lastly, the high abundance of chloromethane detected by GC in ODb (Fig. 2), combined with the

absence of chloromethylpropene, another usual MTBSTFA-perchlorate reaction product, suggests that a large fraction of the chloromethane may be indigenous to the sample. The OD data set is under investigation to identify more complex organic molecules on GC4, and also to decipher the chromatogram of the newly used GC1 column. This latter column not having an injection trap at the front end, leads to broader peaks and retention times that remain to be quantified with laboratory studies.

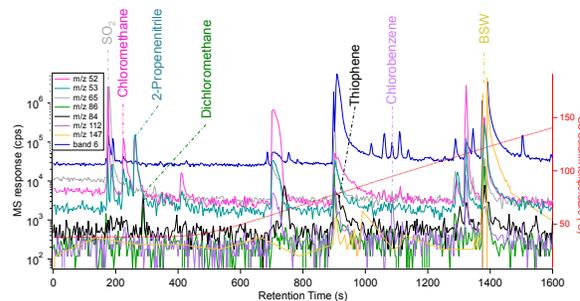


Figure 2: Chromatography from CB sample, ODb on GC4 after the sample has been cleaned out of part of its O_2 in ODa. Relevant m/z values are called out as well as a “band 6” that includes all m/z values between 87-150 Da. m/z 52 for chloromethane, m/z 53 for 2-methylpropene, m/z 65 for SO_2 , m/z 86 for dichloromethane, m/z 84 for thiophene, m/z 112 for chlorobenzene and m/z 147 for bisilylated water. GC column temperature is represented in red. All compounds represented, apart from BSW, are presumably martian.

Conclusion: This opportunistic derivatization experiment represents a successful demonstration of SAM capabilities. Newly optimized parameters, including a hot-trap to minimize MTBSTFA column overloading, multiple temperatures cuts, and a split column configuration, led to a successful derivatization on Mars using the residual MTBSTFA in the sample cup region of the instrument. Several MTBSTFA reaction products were generated during reactions with the Cumberland mudstone sample at elevated temperatures, as well as non-derivatized organic molecules, including chloromethane and 2-propenenitrile of likely martian origin. We are continuing the analysis of this interesting data set to identify derivatization products that could shed additional light on the chemical nature of the organic matter present in the Cumberland mudstone. This experiment is also a stepping stone for the future full-column derivatization, currently in preparation [2].

References: [1] Mahaffy, P. *et al.* (2012) *Space Sci Rev*, 170, 401-478. [2] Malespin, C. *et al.*, this conference. [3] Freissinet *et al.* (2015) *JGR Planets*. [4] Glavin, D. *et al.* (2013) *JGR Planets*, Vol. 118, 1-19. [5] Freissinet, C. *et al.*, LPSC 2015 abstract, [6] Sutter, B. *et al.*, this conference.