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A J Williams, J Eigenbrode, Maëva Millan, R H Williams, A Buch, et al.. Organic Molecules Detected with the First TMAH Wet Chemistry Experiment, Gale Crater, Mars. 52nd Lunar and Planetary Science Conference, Mar 2021, Online, Unknown Region. pp.LPI Contribution No. 2548, id.1763. insu-04469561

HAL Id: insu-04469561

<https://insu.hal.science/insu-04469561>

Submitted on 20 Feb 2024

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ORGANIC MOLECULES DETECTED WITH THE FIRST TMAH WET CHEMISTRY EXPERIMENT, GALE CRATER, MARS

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Introduction: The Curiosity rover is ascending Mt. Sharp, in Gale crater, exploring stratigraphic packages of rocks for evidence of habitability [1] and searching for organic compounds using the Sample Analysis at Mars (SAM) instrument suite. SAM performs sample analysis via pyrolysis and gas chromatography mass spectrometry (GC-MS). SAM additionally performs wet chemistry experiments, either by *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) derivatization or tetramethylammonium hydroxide (TMAH) thermochemolysis. Coupled with wet chemistry, the GC-MS can detect non- to semi-volatile organics that could derive from martian macromolecules, as occurs on Earth. The SAM TMAH experiment hydrolyzes molecules in drill samples, releasing them from their host macromolecules, and then through methylation renders them sufficiently volatile for detection by GC-MS [2]. This work reports on the results from the first in situ TMAH wet chemistry experiment conducted by SAM on Mars. Ongoing analyses indicate that the TMAH experiment was successful, and that a variety of aromatic molecules were generated. Some of these molecules *may* be indigenous to Mars whereas others are internal to SAM. Laboratory experiments are underway to confirm identification by retention time comparison using SAM flight spare GC columns.

Background: Two of the nine wet chemistry cups on SAM contain the TMAH reagent; the other seven contain MTBSTFA [2]. Each TMAH cup contains an outer reservoir filled with ~ 500 μ L of TMAH in methanol (1:3v) with pyrene and 1-fluoronaphthalene in solution used as internal standards. Inside is a second sealed reservoir filled with nonanoic acid that will react with TMAH when the reservoir is punctured and serves as an additional internal calibration standard.

The first TMAH wet chemistry experiment on Mars was performed in September 2020 at the Mary Anning (MA) drill site in the Glen Torridon region. The drill site was selected based on anticipated mineralogic similarity to the Glen Etive drill site, which would prioritize abundant clay minerals and minimal iron oxide phases. A location that was substantially stratigraphically below the diagenetically altered material near the contact with the Greenheugh pediment was also desired to limit the impact of alteration on the sample site.

Methods: Six sample portions were delivered to a punctured SAM TMAH cup. The sample was saturated with TMAH in the cup and raised into the pyrolysis oven. A split of the volatiles released from pyrolysis was monitored by the quadrupole mass spectrometer (QMS) for the entire temperature ramp for evolved gas analysis (EGA). For GC-MS, the volatiles released during pyrolysis were diverted through the SAM hydrocarbon trap under He flow as cuts at selected temperature intervals. The cut from >560°C was sent only to the QMS for EGA. Volatiles trapped on the SAM hydrocarbon trap were released by heating the trap to ~300°C and then split between GC1 (MXT-20) and GC2 (MXT-5) chromatographic channels for their separation.

Results:

A Successful TMAH Experiment. Engineering data indicate the TMAH cup was punctured and powdered sample from the MA drill hole delivered. Trimethylamine byproduct masses from the TMAH reaction were detected. The 1-fluoronaphthalene recovery standard was also identified, but not the nonanoic acid and pyrene standards.

High molecular weight molecules. ‘Bands’ of masses grouped together and having mass-to-charge (m/z) 190 to 485, represent high molecular weight molecules detected by the SAM QMS. These data may indicate that large, complex molecules were present.

Aromatic organics. A variety of methylated, oxygen-, sulfur-, or nitrogen-bearing aromatic organics were detected in GC-MS and/or EGA data. The origin of these molecules is discussed below.

Discussion: The successful first *in situ* TMAH experiment demonstrates that a variety of organic molecules can be liberated by the SAM TMAH experiment.

A) Organics detected in EGA and GC-MS. Some of the molecules that were identified in both the EGA and GC-MS data *may* be indigenous to the sample, as opposed to being SAM-internal byproducts. This interpretation is still assessed. Examples of molecules identified in both EGA and GC-MS include benzene, toluene, trimethyl- and tetramethyl-benzene, naphthalene, and methyl-naphthalene (Fig. 1). TMAH has a basic pH and is a methylating agent that enhances the cleavage of polar bonds and methylates pyrolysis products *in situ*. The presence of methylated single and double ring aromatics

suggests that these organics might derive from a macromolecular source that was cleaved and methylated by TMAH thermochemolysis. We note that with limited TMAH reagent, no TMAH blank was conducted, so we cannot rule out carry over from previous analyses.

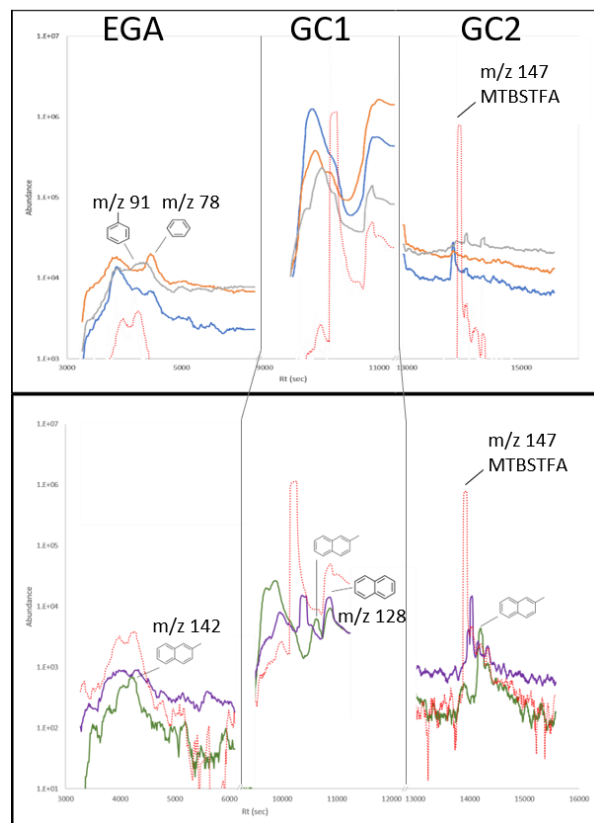


Figure 1. Single ion EGA and chromatograms from the SAM TMAH experiment. Single-ring benzene and toluene are at top, and double-ring (methyl)naphthalene are at bottom.

B) Organics detected with GC-MS only. Molecules detected only with GC-MS may be either indigenous to the sample or be formed from reactions with TMAH within the SAM gas processing system (e.g., reactions with Tenax in the hydrocarbon trap or with the column stationary phase). Examples of the organics detected in GC-MS only include pentamethyl-benzene, benzoic acid methyl ester, dimethyl-, trimethyl-, and tetramethyl-benzenamine, dihydronaphthalene, 2-butyl-thiophene, and benzothiophene. Pentamethylbenzene may be part of a multi-methylated benzene suite. Benzoic acid has been detected with SAM from both Mars-indigenous [3-5] and SAM-internal [5,6] sources. The benzoic acid methyl ester therefore reflects the reaction of TMAH methylating benzoic acid of indeterminate source. The multi-methylated benzenamine suite is also currently of indeterminate source. The benzenamine may be Mars-indigenous or a byproduct of benzene reacting with the N in TMAH. Ongoing benchtop experiments will elucidate these sources. Regardless, the methylation of the benzenamine reflects an expected reaction with TMAH.

The thiophene-bearing molecules have been previously detected on Mars with SAM [6] and are likely Mars-indigenous. These molecules were not methylated but may have been liberated from a macromolecular source by the TMAH reaction.

C) SAM-internal organics. Several known SAM-internal molecules were identified in the EGA and GC data, including mono- and bisilylated water from reactions with water and MTBSTFA, and derivatized boric acid from the reaction of MTBSTFA with the hydrocarbon trap. Aromatic byproducts detected here and associated with the reaction of MTBSTFA with the hydrocarbon trap Tenax include benzene, toluene, 1-ethynyl-3-methyl-benzene, benzoic acid, naphthalene, and diphenylmethane [6]. Detection of benzene, toluene, and naphthalene here as SAM-internal byproducts does not confirm the source of these molecules in the EGA data.

Sources of organics. Meteoritic input is one possible source of organics on the martian surface. Several organics identified with the TMAH experiment are also liberated from the Murchison meteorite with SAM-like TMAH thermochemolysis benchtop experiments, including toluene, trimethylbenzene, methylnaphthalene, 2-butyl-thiophene, and benzothiophene. During TMAH thermochemolysis, the Murchison insoluble organic matter is degraded into its constituent parts, some of which are detectable with GC-MS [7]. Molecules detected with neat pyrolysis of Murchison include benzene and naphthalene [8].

Amines and amides are not prevalent in Murchison pyrolysate [9] and benzenamines are also not generated during TMAH thermochemolysis of Murchison. However, UV irradiation experiments of benzene and naphthalene in the presence of water and NH_3 -containing ices can generate benzenamine and dihydronaphthalene [10]. It is therefore possible that UV irradiation has contributed to radiation processing of meteoritic organics.

TMAH methylates carboxylic acids with high efficiency. Carboxylic acid methyl esters (CAMEs) have been generated from TMAH thermochemolysis of Murchison [11]. The lack of CAMEs in these data suggest that 1) CAMEs are not present in amounts detectable with SAM as run or 2) flight operating conditions require optimization before they can be detected clearly.

Conclusions: Multiple aromatic molecules were detected with the first TMAH experiment on SAM and may be a mix of SAM-internal and radiation processed macromolecular organic matter of either exogenous or martian origin.

References: [1] Grotzinger, J. et al (2013) *Sci Express* 343, 1242771-1242714 [2] Mahaffy, P. et al (2012) *Space Sci Rev*, 401-478 [3] Freissinet, C. et al (2015) *JGR*, 120, 495-514 [4] Freissinet, C. et al (2020) *Planet Sci J* 1, 41-52 [5] Millan, M. et al. (in review) *Nat Astron* [6] Buch, A. et al (2019) *JGR* 124, 2819-2951 [7] Eigenbrode, J. et al (2018) *Science* 360, 1096-1101 [8] Sephton, M. et al (2015) *Astrobio*, 15, 779-786 [9] Derenne, S. & Robert, F. (2010) *Met & Plan Sci* 45, 1461-1475 [10] Materese, C. et al (2015) *Astrophys J* 800, 116-124 [11] Williams, A. et al (2019) *Astrobio*, 19, 522-546