

TRIMETHYLSULFONIUMHYDROXIDE (TMSH) AS A THERMOCHEMOLYSIS REAGENT FOR DETECTING FATTY ACIDS IN SCHWERTMANNITE AND SILICEOUS SINTER MARS-ANALOG ROCKS.

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Introduction: Detecting biosignatures in the form of organic matter is a promising path towards identifying life elsewhere in the universe [1]. Among the most prominent organic biomolecules used by terrestrial life are lipids, due to their importance as a building block in cellular structures in all known life and their relatively long preservation potential in the geologic record [2]. Fatty acids are bound in the phospholipids and glycolipids of both prokaryotic and eukaryotic cellular membranes. Abiotically and biotically produced fatty acids result in different gas chromatography--mass spectrometry (GC-MS) signatures – biotic fatty acids show an even-over-odd chain length preference, while abiotic fatty acids show no such preference and tend towards having shorter chain lengths [3]. For these reasons, they are fascinating potential biosignatures in current and future space missions.

The Mars Science Laboratory (MSL) mission has greatly enhanced our understanding of Mars and its potential past habitability. One of the major instruments aboard the mission is the Sample Analysis at Mars (SAM) instrument, which is the latest in a line of instruments using GC-MS to search for organic compounds in extraterrestrial environments [4]. GC-MS has been present on several Mars missions, including the Mars Viking and Phoenix landers [5]. The instrument detects and identifies different molecular species by separating the molecules in a column into a time sequence and analyzing the unique mass spectra of each species [4]. Samples may be directly heated to break apart the molecules in a process called pyrolysis, or subjected to a thermochemolysis procedure – a wet chemistry experiment that can improve the organic matter yield by liberating the organics from larger macromolecules [6]. Thermochemolysis involves the use of a reagent and is particularly important for the detection of polar organic molecules, which are turned by this process into volatile derivatives that are detectable by GC-MS [7]. Some of the main reagents used in Mars organics exploration are MTBSTFA (N,N-methyltert-butyl-dimethylsilyltrifluoroacetamide) and TMAH (tetramethylammonium hydroxide), both of which have flown on MSL. TMAH liberates fatty acids bound in macromolecules and methylates both FA and free fatty acids, greatly increasing FAME yield in Mars-analog samples in comparison to direct pyrolysis [3]. However, there are issues with both these reagents. MTBSTFA is not amenable to working with aqueous samples, and TMAH degrades the GC column at a rapid rate, producing molecules that

overwhelm the detector and make product identification difficult [8].

The goal of this work is to examine TMSH (trimethylsulfonium hydroxide) as a potential methylation reagent for detecting fatty acids by using it in GC-MS experiments on a set of rock samples from Mars-analog environments. TMSH works via a similar mechanism to TMAH, but can achieve methylation at lower temperatures [9] potentially resulting in less column degradation. Like TMAH, it performs well with aqueous samples. By assessing TMSH as a thermochemolysis reagent and optimizing its utility, we can potentially improve methods of GC-MS detection of biosignatures on other worlds.

Methods: The samples used in this work were opal-A and -CT siliceous sinter from a hydrothermal system in Iceland (IC9I and IC6S, respectively), and schwertmannite (sulfate-bearing hydrous ferric oxide) samples from Iron Mountain, California (SS2, SS6, SS10). They were collected in an organically clean manner [10] for previous FAME detection studies, including work testing TMAH as a reagent [3]. Samples were homogenized in an ashed (500°C for 8 hours) mortar and pestle. Frontier Multi-Shot (EGA/PY-303D) pyrolyzer and Agilent 7890B GC-5975C XL inert MSD GCMS were used for direct pyrolysis-GCMS analyses of analytes evolved from thermal pyrolysis and thermochemolysis. Samples were analyzed both with pyrolysis-only and TMSH thermochemolysis techniques. 3-5 mg of powdered sample was placed into sample cups with 1.5 µL of C₁₉ as an internal standard. Samples analyzed for alkanes were pyrolyzed at 600°C for 0.2 min. The oven program ramped from 50°C to 300°C at 20°C/min with a 10 minute hold. Samples analyzed for fatty acids were subject to TMSH thermochemolysis at a ratio of 1µL TMSH to 1mg sample, with the same pyrolyzer and oven programs as for alkanes. Molecules were identified using ChemStation software.

Previous work done using TMAH as a thermochemolysis agent on these same samples [3] was compared with the TMSH results.

Results & Interpretations: The TMSH and TMAH samples performed comparatively well on the Iceland samples, with both samples yielding C₁₄, C₁₆, and C₁₈. The TMSH run of sample IC9I (Figure 1) yielded C₉, while the TMAH run did not, however, it yielded C₁₀ instead. No alkanes (Table 2) were

identified in IC6S, although the IC9I sample yielded a multitude of alkanes and alkenes, including C₁₁, C_{11:1}, C₁₂, C_{12:1}, C₁₃, C₁₄, C_{14:1}, C₁₅, C₁₆, C_{16:1}, and C_{17:1}.

Table 1. FAMES detected in schwertmannite and siliceous sinter samples using TMSH and TMAH. o = detected, ? = potentially detected

		C6:0	C9:0	C10:0	C12:0	C13:0	C14:0	C15:0	C16:0	C16:1	C17:0	C18:0	C18:1
Iron Mountain Samples	SS2	TMSH	o						o				
		TMAH			o				o				
	SS6	TMSH				o		o	?			o	
		TMAH			o			o	o	o	o	o	o
	SS10	TMSH							N/A				
		TMAH			o	o	o		o	o		o	o
Iceland Samples	IC6S	TMSH					o	o	o		o	o	o
		TMAH					o	o	o		o	o	o
	IC9I	TMSH	o				o	o	o	o		o	o
		TMAH		o			o	o	o	o		o	o

The schwertmannite samples did not produce quality spectra in the pyrolysis-only analyses, possibly due to the pyrolysis of the sulfate minerals overwhelming the detector, and in some cases completely obscuring the C₁₉ peak. The TMAH experiments with these samples yielded multiple FAMES, including C₁₀, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C_{16:1}, C₁₇, C₁₈, and C_{18:1}, but the TMSH analyses were less prolific. The analysis of SS6 with TMSH yielded three FAMES, versus seven when TMAH was used with the same sample. C₆ was detected in the SS2 sample using TMSH, but was not present with any other experimental method. A possible reason for the discrepancy in FAME yield in the schwertmannite samples is that a thermal desorption method was used for the TMAH analyses, as the TMAH experiments were conducted during a previous study [3]. This may have caused the mineralogy to interfere with the detector, similarly to the problem encountered in the pyrolysis-only runs of the schwertmannite.

Table 2. Alkanes detected in schwertmannite and siliceous sinter samples using pyrolysis-only o = detected, ? = potentially detected

	C11:1	C11:0	C12:1	C12:0	C13:0	C14:1	C14:0	C15:0	C16:1	C16:0	C17:1
SS2								N/A			
SS6			?							?	
SS10								N/A			
IC6S								N/A			
IC9I	o	o	o	o	o	o	o	o	o	o	o

Conclusions: Initial results on a limited set of Mars-analog samples show that TMSH may be an adequate replacement for TMAH for certain mineralogies. On siliceous sinter samples, TMSH yielded the same amount of FAMES as TMAH, and yielded more small-carbon chain FAMES on both the siliceous sinter, and the schwertmannite deposits. Future work will involve using TMSH in the analysis of a broader range of Mars-analog samples and on samples that are analogs for other planetary bodies, such as Ceres and Europa. This work will help determine whether TMSH could be a useful thermochemistry reagent in future planetary missions.

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References: [1] Des Marais, D. J., et al (2008) *Astrobiology* 8, 715–730. [2] Engel, M. H. & Macko, (1993) *S. Organic Geochemistry: Principles and Applications*. [3] Williams, A. J., et al (2019) *Astrobiology*, 19(4), 522–. [4] Mahaffy P.R., et al (2012) *Space Sci Rev*, 401-478. [5] Boynton, W. V., et al (2001) *J. Geophys. Res. Planets* 106, 17683–17698. [6] Grasset, L., et al (2002) *Org. Geochem.* 33, 181–188. [7] del Rio, J. C., et al (1996) *Trends Anal. Chem.* 15, 70–79. [8] Ishida, Y., et al (1999) *J. Anal. Appl. Pyrolysis* 49, 267–276. [9] Akoto L. et al (2005) *J Anal App Pyrol* 73, 69-75. [10] Wilhelm, M.B., et al (2017) *Org. Geochem.* 103, 97–104. [11] Williams, A. J., et al (2015) *Lunar and Planetary Science Conference* (Vol. 46, p. 1814).

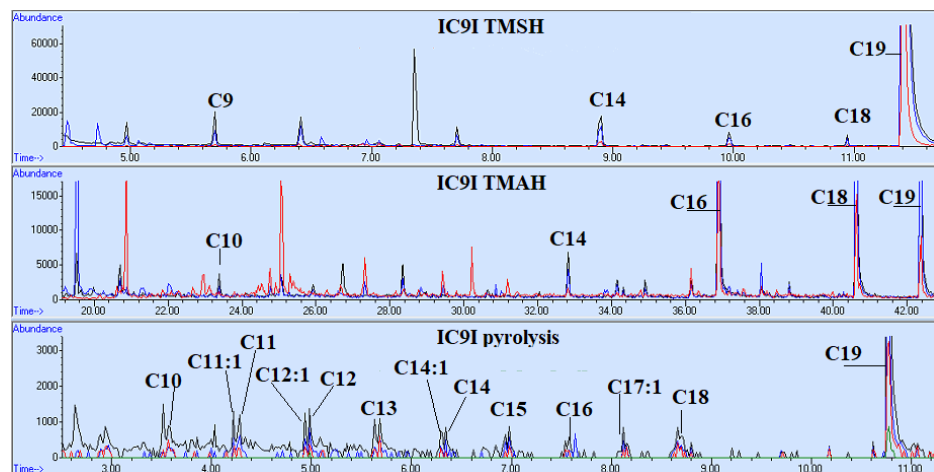


Figure 1: Retention time (x) vs relative abundance (y) of gas chromatographs of sample IC9I with TMSH, TMAH, and direct pyrolysis methods. Peaks of FAMES can be seen in the TMSH and TMAH plots, while alkanes are apparent in the pyrolysis-only method.