

Key Points:

- TMAH experiments with Murchison meteorite produces various aromatic acids, dicarboxylic acids, and amino acids
- SAM-like TMAH pyrolysis presents mixtures of methylated and non-methylated compounds due to decreased reaction yields at slower ramp rates
- All experiments with simulated MTBSTFA vapor produce byproducts that obscure the identification of Murchison-derived compounds

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Murchison Meteorite Analysis Using Tetramethylammonium Hydroxide (TMAH) Thermochemolysis Under Simulated Sample Analysis at Mars (SAM) Pyrolysis-Gas Chromatography-Mass Spectrometry Conditions

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Abstract The Sample Analysis at Mars (SAM) instrument aboard the Curiosity Rover at Gale crater can characterize organic molecules from scooped and drilled samples via pyrolysis of solid materials. In addition, SAM can conduct wet chemistry experiments which enhance the detection of organic molecules bound in macromolecules and convert polar organic compounds into volatile derivatives amenable to gas chromatography-mass spectrometry analyses. Specifically, N-tert-butyltrimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) is a silylation reagent whereas tetramethylammonium hydroxide (TMAH) is a thermochemolysis methylation reagent. Shortly after arriving at Mars, the SAM team discovered that at least one of the MTBSTFA cups was leaking, contributing to a continuous background inside SAM with the potential to interfere with future TMAH reactions. Therefore, here we characterized possible interactions between the two reagents to determine byproducts and implications for the detection of indigenous organics. SAM-like pyrolysis experiments supplemented with flash pyrolysis were accordingly conducted with fragments of the Murchison meteorite as a reference for exogenous organic matter delivered to Mars. Flash TMAH experiments yielded various aromatic acids, dicarboxylic acids, and amino acids while SAM-like pyrolysis presented mixtures of methylated and non-methylated compounds due to decreased reaction efficiency at slower ramp rates. All experiments in the presence of simulated MTBSTFA vapor produced pervasive silylated byproducts which co-elute and obscure the identification of Murchison-derived compounds. Despite challenges, a significant diversity of pyrolyzates and TMAH derivatives could still be identified in flash pyrolysis in presence of MTBSTFA. However SAM-like experiments with TMAH and MTBSTFA are hindered by both decreased methylation yields and additional co-eluting compounds.

Plain Language Summary The Sample Analysis at Mars (SAM) instrument aboard the Curiosity Rover on Mars can detect and analyze organic molecules that might be used by life as we know it. SAM does this by heating scooped soil or drill samples in order to vaporize and uncover any organic content that might be present. In addition, SAM can detect different types of organics that have more direct similarities to those used by modern organisms by adding one of two different kinds of chemical reagents prior to heating. However, shortly after arriving at Mars, it was discovered that one type of reagent, called MTBSTFA, was leaking inside of SAM with the potential to eventually interfere with the other, called TMAH, whenever it might be utilized. This study therefore reports on the chemical interactions between the two reagents and how they might impact the detection of indigenous organics on Mars. We determined heating samples in the presence of both reagents produces a series of byproducts which obscure the identification of organic compounds of interest. Still, despite analytical challenges, it is possible SAM may detect different types of organics which have yet to be detected on Mars with TMAH despite interference from leaking MTBSTFA.

1. Introduction

Since landing at Gale crater on 6th August 2012, the Mars Science Laboratory (MSL) Curiosity Rover has revolutionized our understanding of ancient Mars as a habitable planet. Sedimentary rocks analyzed at Yellowknife Bay,

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and along the drive toward Aeolis Mons (Mount Sharp), have revealed a long-lived fluvio-lacustrine environment once capable of hosting microbial life as we know it (Grotzinger et al., 2014). Results from Curiosity indicate circumneutral waters (Vaniman et al., 2014), a range of redox states (Hurowitz et al., 2017; Lanza et al., 2016; Ming et al., 2014), and an active sedimentary cycle (Grotzinger et al., 2015) which could have supported chemolithoautotrophy for tens of millions of years (Grotzinger et al., 2014).

In order to address Mars' potential to harbor life, the Curiosity rover has been equipped with a suite of instruments that can be utilized to investigate organics, mineralogy, textures, atmospheric composition, signs of water, and the surface radiation environment (Grotzinger et al., 2012). Researchers have thereby been able to evaluate the stratigraphic record of Gale crater and make inferences regarding habitability. In particular, the Sample Analysis at Mars (SAM) instrument suite is of special interest to the ongoing search for extraterrestrial life because it is capable of characterizing organic compounds within the Martian regolith and rock record (Mahaffy et al., 2012). In other words, SAM enables a broad understanding on the preservation and diversity of organic compounds that may have participated in prebiotic chemistry and possibly contributed to a hypothetical origin of life on Mars.

The SAM instrument suite is comprised of a sample manipulation system (SMS), pyrolysis oven, gas chromatograph (GC), tunable laser spectrometer (TLS), and a quadrupole mass spectrometer (QMS) not dissimilar in nature to benchtop gas chromatograph-mass spectrometers (GC-MS) found in laboratories (Mahaffy et al., 2012). When interfaced with a pyrolysis unit like on SAM, py-GC-MS can enable the direct analysis of solid materials via the thermal extraction of a sample's volatile organic fraction directly onto the GC column. SAM can detect organic compounds via the pyrolysis of drilled rock or scooped regolith samples to release volatiles that are either: (a) directed directly toward the QMS for evolved gas analysis (EGA), (b) directed toward the TLS for isotopic measurements, or (c) sent to a hydrocarbon trap which concentrates and later desorbs pyrolyzates onto one or several of the six capillary columns for GC-MS analysis (Mahaffy et al., 2012). Furthermore, SAM is capable of conducting wet chemistry experiments which enhance the thermal decomposition of macromolecules into discrete compounds and convert polar molecules into GC-amenable volatile derivatives via silylation or methylation (del Rio et al., 1996; Metcalffe & Wang, 1981). Specifically: N-tert-butyltrimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) in dimethylformamide (DMF) (4:1, v/v) is a derivatization reagent that adds a tert-butyltrimethylsilyl (t-BDMS) group to reactive polar groups (e.g., hydroxyl, carboxyl, amines, and amides) at low temperature (~75°C) resulting in volatile and thermally stable derivatives (Schummer et al., 2009); Tetramethylammonium hydroxide (TMAH) (25 wt. %) in methanol is a thermochemolysis reagent used to enhance the liberation of macromolecularly bound compounds at high temperature (>500°C) and simultaneously convert reactive polar groups into methyl ester and/or methyl ether derivatives (He et al., 2020a; Williams et al., 2019).

Soon after landing at Gale crater, it was discovered that at least one of the MTBSTFA-containing wet-chemistry cups inside SAM was leaking (Freissinet et al., 2015; Glavin et al., 2013). MTBSTFA vapor consequently became a persistent background element posing unique challenges to the interpretation of pyrolysis experiments conducted by SAM (Freissinet et al., 2015; Glavin et al., 2013). Still, analyses of Martian samples and the deliberate use of MTBSTFA has permitted the detection of indigenous assemblages of organic compounds including aromatic compounds, sulfur-containing compounds, chlorine-containing compounds, and silylated derivatives (Eigenbrode et al., 2018; Freissinet et al., 2015; Millan et al., 2022; Szopa et al., 2020). As the search for preserved organics on Mars continues, SAM conducted the first in situ TMAH thermochemolysis experiment at the Mary Anning drill site in the Glen Torridon region (Eigenbrode et al., 2011, 2020; Williams et al., 2021). This site was selected due to an abundance of clays that can adsorb and concentrate organics (Millan et al., 2022), minimal diagenetic alteration (Williams et al., 2021), and minimal iron oxide phases which are known to influence extraction efficiency (Williams et al., 2019). Fines from the Mary Anning drill sample were delivered into a freshly punctured TMAH wet chemistry cup then heated at a rate of 35°C min⁻¹ from 50 to 860°C. Volatiles were directed toward the QMS for EGA and toward the hydrocarbon trap to be concentrated and desorbed for GC-MS analysis (Eigenbrode et al., 2020; Williams et al., 2021). Preliminary assessments indicate that various methylated, oxygen-, sulfur-, and nitrogen-bearing aromatic organics not previously detected by SAM have been identified (Williams et al., 2021). However, because SAM contains only two TMAH wet chemistry cups, a blank thermochemolysis sample was not conducted to characterize background elements. The identification of some compounds consequently cannot preclude an origin from known SAM internal sources (e.g., hydrocarbon and injection traps). It also remains unknown how persisting MTBSTFA vapor can potentially interact with TMAH and influence the range of possible derivatives that are yet to be identified on Mars (Williams et al., 2019).

In the study presented here, we therefore conduct SAM-like pyrolysis experiments to characterize interactions between the MTBSTFA and TMAH wet chemistry reagents and the range of detectable organics from a Mars-like simulant. Specifically, the Murchison carbonaceous chondrite was utilized as a representative sample for exogenous organic matter that could have been delivered to the surface of Mars by meteorite or interstellar dust particle influx and subsequently detected by SAM (Chyba & Sagan, 1992; Sasselov et al., 2020). The goal of this study was to: (a) determine the range of TMAH thermochemolysis products/derivatives detectable under SAM-like pyrolysis conditions; and (b) identify interactions between MTBSTFA, TMAH, and Murchison-derived organics. Hydrocarbon traps normally used to concentrate volatiles on SAM were intentionally bypassed to exclude possible contributions from degradation products and replaced by an in-line cryogenic trap. Experiments were conducted by pyrolyzing Murchison under a SAM-like pyrolysis ramp ($35^{\circ}\text{C min}^{-1}$) and comparing results to flash pyrolysis ($10^{\circ}\text{C ms}^{-1}$) to corroborate analyte identification. We intend findings from this study will provide insight into the potential range of compounds expected to be detected or that have yet to be identified in the SAM data gathered at the Mary Anning drill site and future use of the remaining TMAH wet-chemistry cup on Mars.

2. Materials and Methods

2.1. Murchison Meteorite

Experiments were conducted on a subsampled portion from a 90 g fragment of the Murchison meteorite sample with intact fusion crust from Geoscience Australia (GA# 3943). Murchison was selected as an analog sample since it has been a well-studied organically rich primitive meteorite with a wide range of potentially prebiotically important molecules (Glavin et al., 2018 and references therein).

2.2. Sample Preparation

Samples for all pyrolysis experiments were prepared by loading ~ 0.5 – 1 mg of Murchison powder, obtained by gently abrading the surface of a subsampled portion with a five-times DCM-cleaned stainless-steel spatula, into combusted (16 hr at 550°C) quartz pyroprobe tubes containing a quartz rod and wool stage (CDS Analytical, Catalogue: 10A1-3015, 10A1-3016L, 1001-0345) (Miller et al., 2015).

2.3. TMAH Thermochemolysis

Samples for TMAH thermochemolysis were prepared inside a fume hood by adding $5\ \mu\text{L}$ of TMAH wt. 25% in methanol (Sigma-Aldrich, 334901) to Murchison-containing pyrolysis tubes and immediately transferred to the pyroprobe autosampler for pyrolysis.

2.4. TMAH Thermochemolysis With MTBSTFA

We conducted experiments simulating MTBSTFA vapor in SAM by adding $0.2\ \mu\text{L}$ of 4:1 v/v MTBSTFA (SigmaAldrich, 77626): DMF (Sigma-Adrich, 270547) to prepared pyrolysis tubes already containing $5\ \mu\text{L}$ of TMAH and sample immediately before analysis (Williams et al., 2019).

2.5. Pyrolysis Gas Chromatography-Mass Spectrometry

SAM is the most resource-intensive instrument aboard Curiosity (Grotzinger et al., 2012) Because of this, SAM operations are optimized to divert power between the various systems (e.g., sample manipulation system, manifold heaters, mass spectrometer) resulting in conservative pyrolysis ramps (Mahaffy et al., 2012). Experiments were conducted on a CDS Analytical 5250T pyroprobe with autosampler using both flash ($10^{\circ}\text{C ms}^{-1}$) and SAM-like ($35^{\circ}\text{C min}^{-1}$) pyrolysis ramps in the presence and absence of derivatization reagents (Figure 1). We then compared the diversity of pyrolyzates and reaction products released under flash and SAM-like pyrolysis conditions to assist in the characterization of volatile species. Neat samples (e.g., without reagents) and experiments with reagents were heated in the pyrolysis oven under a stream of ultra-high purity He ($35\ \text{mL min}^{-1}$) from 50 to 600°C while the pyroprobe housing and valves were held at 300°C . Volatiles released from the samples were transferred via a heated transfer line (300°C) directly into an Agilent 6890A gas chromatograph (GC) coupled to an Agilent 5975C (MS) Mass Selective Detector (MSD) system, bypassing a hydrocarbon or injection trap typically

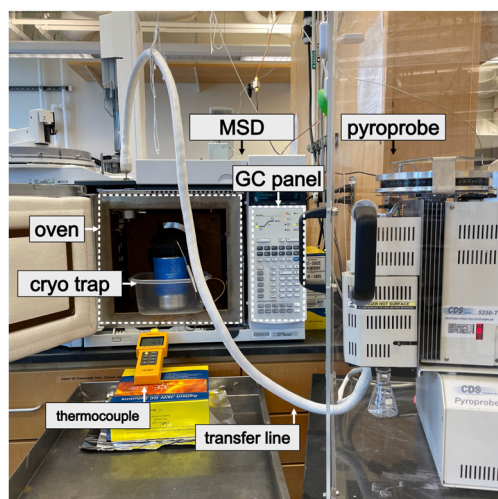


Figure 1. Pyrolysis-GC-MS setup. The pyroprobe with autosampler is operated inside a portable fume hood to prevent the possible release of reagent fumes into the laboratory space and the transfer line is interfaced with the Mass Selective Detector (MSD) GC-MS injector inlet. During cryogenic trapping, the GC oven remains open, and a portion of the column is submerged in a dry ice slurry of 40% ethylene glycol in ethanol. The temperature is kept between -55 and -60°C and monitored with a thermocouple. Once trapping is complete, the column is removed from the slurry, the oven door is closed, and the acquisition method is manually started using the GC control panel.

utilized on SAM (Figure 1) (Mahaffy et al., 2012). This was implemented to circumvent the introduction of potential trap contaminants and to recover all volatile material which may not be adsorbed or desorbed (either partially or totally). The inlet temperature was held at 300°C and operated with a 10:1 split. The GC was fitted with a J&W DB-5MS fused silica capillary column ($60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$), He carrier flow at 1.5 mL min^{-1} , and MS transfer line set to 280°C . Flash pyrolysis of samples occurred instantaneously and the GC was programmed with the following parameters previously utilized to simulate SAM (Miller et al., 2015): 35°C oven held for 5 min, followed by a $10^{\circ}\text{C min}^{-1}$ ramp to 300°C , then a final isothermal hold at 300°C for 8.5 min (40 min total). The MS was operated in electron impact (EI) mode at 70 eV scanning m/z 10–535 (Miller et al., 2015). SAM-like pyrolysis of samples occurred over ~ 16 min as the pyrolysis chamber is heated at $35^{\circ}\text{C min}^{-1}$ from 50 to 600°C . A portion of the GC column was accordingly submerged in a dry ice slurry containing 40% ethylene glycol in ethanol kept between -55 and -60°C to cryogenically trap volatiles prior to detection (Figure 1). The GC method and MS acquisition were manually initiated immediately after pyrolysis reached completion and the GC column was removed from the slurry. The MS was operated as above. Other than the lack of the traps, this configuration differs from SAM by utilizing a 60 m column and final 300°C GC temperature for better separation and detection of large molecular weight molecules (SAM limit ~ 180 – 280°C). Pyrolysis blanks preceded all samples to control the cleanliness of the analytical set-up and prevent potential cross-contamination. Blank pyrolysis tubes spiked with an internal standard containing C8–C40 n-alkanes (MilliporeSigma, 40147) were pyrolyzed after every four samples to diagnose potential leaks or significant changes in instrument sensitivity.

Results were analyzed using Agilent MassHunter Qualitative B.08.00 and Quantitative Analysis (for GC-MS) B.08.00 software. All reported compounds were identified using a combination of internal standards (e.g., amino acids standards), mass spectral libraries (NIST17), and interpretation of fragmentation patterns and comparison to reference literature (e.g., Gallois et al., 2007).

3. Results and Discussion

3.1. Pyrolysis of Murchison Meteorite Without Reagents

Flash and SAM-like pyrolysis of Murchison to 600°C released an identical suite of compounds primarily comprised of aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and organosulfur compounds (Figure 2, Table 1). Aromatic molecules included benzene, naphthalene, anthracene, phenanthrene, pyrene, C1–C5 alkyl benzenes, and C1–C3 alkyl naphthalenes previously reported from meteorites (Derenne & Robert, 2010) (Table 1). Organosulfur compounds included C1–C3 alkyl thiophenes, benzothiophene, and thienothiophene (Table 1). Benzonitrile was the most abundant nitrogen-containing organic compound, phenol was the most abundant oxygen-containing organic compound, and dichlorobenzene was the only chlorinated compound detected (Table 1). These results are very similar to prior work characterizing the organic inventory of Murchison meteorite (e.g., Derenne & Robert, 2010; Komiya & Shimoyama, 1996; Levy et al., 1973; Remusat et al., 2005). SAM-like experiments indicated that, under identical GC conditions, differences in pyrolysis ramp rates does not alter pyrolyzate diversity (Table 1). Flash and SAM-like ($35^{\circ}\text{C min}^{-1}$) pyrolysis resulted in similar chromatograms with observable differences in relative abundances and a slight decrease in signal response as observed under SAM-like conditions (Figure 2).

3.2. TMAH Thermochemolysis of Murchison Meteorite

Flash pyrolysis of Murchison in the presence of TMAH revealed a distinct suite of methylated compounds (e.g., methyl ethers and methyl esters) previously undetectable by unassisted pyrolysis experiments (Figure 3, Table 2).

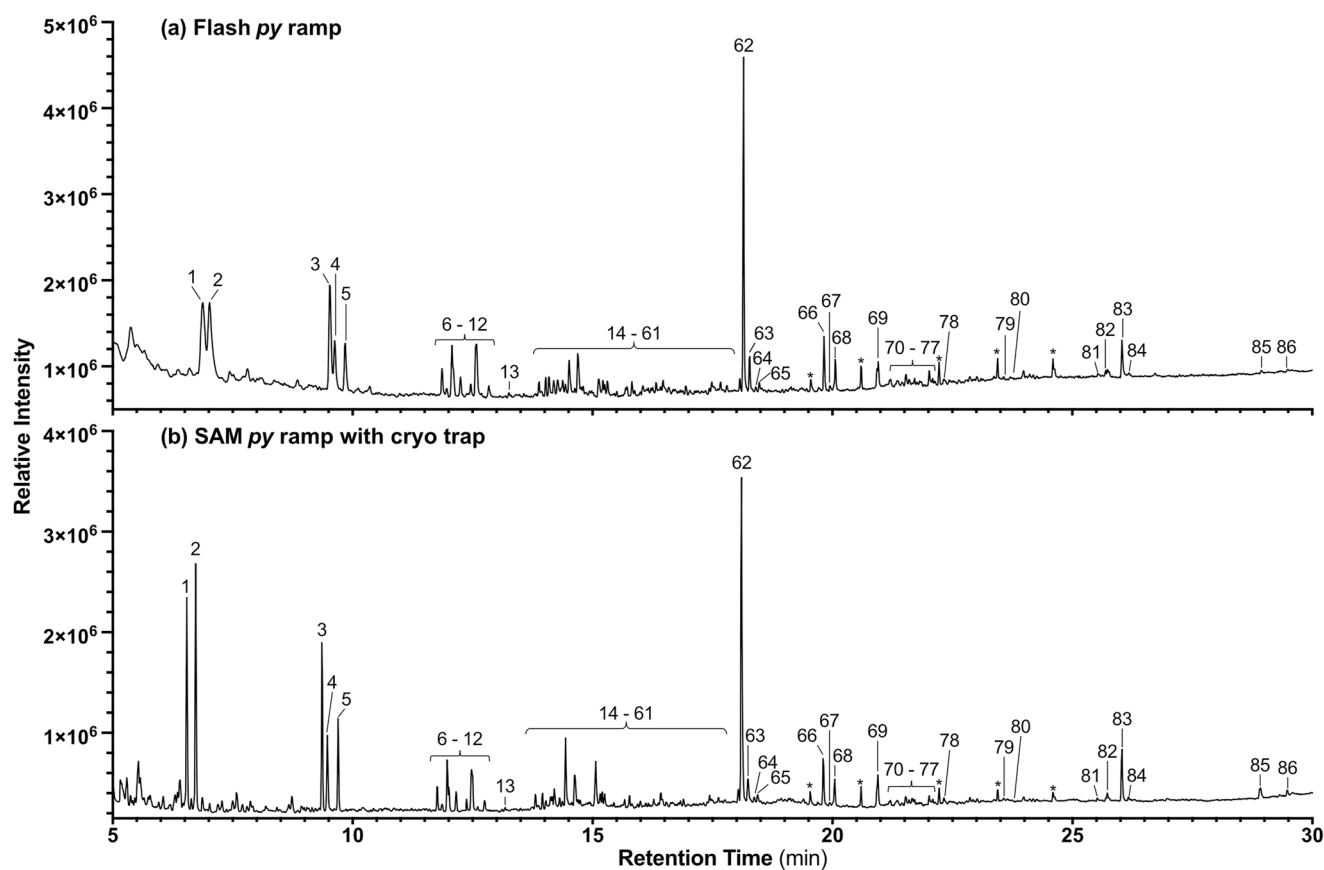


Figure 2. Murchison meteorite neat pyrolysis. Total ion chromatogram of pyrolyzed Murchison reveals pyrolyzates primarily characterized by aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and organosulfur compounds. (a) Flash and (b) SAM-like pyrolysis ramp with a cryogenic trap yielded an identical diversity of pyrolyzates listed in Table 1. (* = n-alkane contamination identified by Sephton et al. (2001)).

These include aromatic acids and dicarboxylic acids which are understood to be derived from cleaved ester and diester aliphatic linkages joining the insoluble organic matter (IOM) macromolecular framework (Remusat et al., 2005). The complete suite of compounds includes benzoic acid methyl esters, toluic acid methyl esters, methoxybenzoic acid methyl esters, naphthalene carboxylic acid methyl esters, methylnaphthalene carboxylic acid methyl esters, methoxynaphthalene carboxylic acid methyl esters, short-chain α , ω -dicarboxylic acid dimethyl esters, and amino acid methyl ester and dimethylamines (Figure 3, Table 2). Furthermore, phenol, some organosulfur compounds (e.g., thiophenes), and some alkylbenzenes along with alkylnaphthalenes are no longer detected (Table 1). This is because phenol is converted to anisole (i.e., methoxybenzene) while aromatic acids (e.g., benzoic acid, naphthalenecarboxylic acid) that might decarboxylate into alkylbenzenes or alkylnaphthalenes have now been methylated into volatile, thermally stable derivatives (Hatcher & Clifford, 1994; Martín et al., 1995; Saiz-Jimenez, 1995). Moreover, thiophenes, which may partly have originated from the cyclization of aliphatic sulfides, have now been detected as methyl sulfides (e.g., dimethyl sulfide) (Table 2) (Remusat et al., 2005). Similar to unassisted py-GC-MS experiments (e.g., absence of TMAH), results from TMAH experiments remain consistent with prior thermochemolysis work on the Murchison meteorite (Remusat et al., 2005; Watson et al., 2010).

SAM-like pyrolysis with TMAH differed from flash experiments due to the absence of several methylated derivatives which were previously detected (Table 2). Derivatives which have been detected additionally display relative abundances that are approximately two orders of magnitude lower compared to flash conditions (Figure 3). Because of this, chromatograms from SAM-like TMAH thermochemolysis experiments are characterized by a mixture of peaks representing compounds detected in pyrolysis experiments with and without TMAH (Figure 3, Tables 1 and 2). Both phenol and anisole, alkylbenzenes and benzoic acids, alkylnaphthalenes and naphthalenecarboxylic acids, and thiophenes and dimethyl sulfide (among others) were detected within the same sample

Table 1
Flash and SAM Pyrolysis Products in the Absence and Presence of Derivatization Reagents

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	SAM ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	Notes
1	6.87	6.54	benzene	78	C ₆ H ₆	+	+	+	+	+	+	Tentatively detected from in situ TMAH experiment ^a
2	7.02	6.74	thiophene	84	C ₄ H ₄ S	+	+	+	+	+	+	
3	9.53	9.37	toluene	91	C ₇ H ₈	+	+	+	+	+	+	Tentatively detected from in situ TMAH experiment ^a
4	9.63	9.48	2-methylthiophene	97	C ₅ H ₆ S	+	+	co-elution	+	+	+	
5	9.85	9.70	3-methylthiophene	97	C ₅ H ₆ S	+	+	co-elution	+	+	+	
6	11.86	11.76	ethylbenzene	91, 106	C ₈ H ₁₀	+	+	+	+	+	+	
7	11.96	11.86	2-ethylthiophene	97, 112	C ₆ H ₈ S	+	+	–	+	+	co-elution	
8	12.07	11.97	p-xylene	91, 106	C ₈ H ₁₀	+	+	+	+	+	+	
9	12.25	12.15	2,4-dimethylthiophene	97, 111	C ₆ H ₈ S	+	+	–	+	+	co-elution	
10	12.47	12.39	3,4-dimethylthiophene	97, 111	C ₆ H ₈ S	+	+	–	+	+	co-elution	
11	12.57	12.48	styrene	104	C ₈ H ₈	+	+	+	+	+	+	
12	12.84	12.75	3,4-dimethylthiophene	111	C ₆ H ₈ S	+	+	–	+	+	co-elution	
13	13.26	13.18	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
14	13.89	13.81	propyl-benzene	91, 120	C ₉ H ₁₂	+	+	+	+	+	+	
15	13.94	13.87	2-propylthiophene	97, 126	C ₇ H ₁₀ S	+	–	–	+	+	–	
16	14.03	13.96	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
17	14.10	14.03	benzaldehyde	51, 77, 105	C ₇ H ₆ O	+	+	+	+	+	+	
18	14.19	14.12	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
19	14.22	14.16	2-(1-methylethyl)-thiophene	111, 126	C ₇ H ₁₀ S	+	–	–	+	+	–	
20	14.27	14.20	phenol	94	C ₆ H ₆ O	+	–	–	+	+	+	
21	14.30	14.25	1-(3-thienyl)-ethanone	111, 126	C ₆ H ₆ OS	+	–	–	+	+	–	
22	14.38	14.31	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
23	14.44	14.37	C ₁ -styrene	117, 118	C ₉ H ₁₀	+	+	–	+	+	+	
24	14.45	14.40	trimethylthiophene	111, 125, 126	C ₇ H ₁₀ S	+	–	–	+	+	co-elution	

Table 1
Continued

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	SAM ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	Notes
25	14.52	14.44	benzotrile	103	C ₈ H ₇ N	+	+	–	+	+	co-elution	
26	14.63	14.56	C ₁ -styrene	117, 118	C ₉ H ₁₀	+	+	–	+	+	co-elution	
27	14.69	14.63	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
28	14.76	14.69	benzofuran	118	C ₈ H ₆ O	+	+	–	+	+	+	
29	14.81	14.74	C ₁ -styrene	117, 118	C ₉ H ₁₀	+	+	–	+	+	+	
30	14.87	14.82	2-thiophenecarboxaldehyde	111	C ₅ H ₄ OS	+	–	–	+	+	–	
31	14.94	14.88	3-methyl-benzenethiol	91, 124	C ₇ H ₈ S	+	–	–	+	+	–	
32	14.98	14.93	α -methyl-benzeneacetaldehyde	105, 134	C ₉ H ₁₀ O	+	+	+	+	+	+	
33	15.02	14.96	trimethylthiophene	111, 125, 126	C ₇ H ₁₀ S	+	–	–	+	+	–	
34	15.14	15.07	dichlorobenzene	146	C ₆ H ₄ Cl ₂	+	+	+	+	+	+	
35	15.22	15.16	C ₃ -alkylbenzene	105, 120	C ₉ H ₁₂	+	+	co-elution	+	+	co-elution	Tentatively detected species from in situ TMAH experiment ^a
36	15.25	15.21	C ₄ -alkylbenzene	91, 119, 134	C ₁₀ H ₁₄	+	–	–	+	+	–	
37	15.31	15.25	C ₃ -alkylbenzene	117, 118	C ₉ H ₁₀	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
38	15.51	15.45	indane	117, 118	C ₉ H ₁₀	+	+	+	+	+	+	
39	15.66	15.62	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
40	15.69	15.66	C ₃ -alkylbenzene	116	C ₉ H ₈	+	+	–	+	+	–	Tentatively detected species from in situ TMAH experiment ^a
41	15.72	15.68	C ₄ -alkylbenzene	105, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
42	15.82	15.79	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
43	15.88	15.85	2-butyl-thiophene	97, 140	C ₈ H ₁₂ S	+	–	–	+	–	–	Tentatively detected from in situ TMAH experiment ^a

Table 1
Continued

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	SAM ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	Notes
44	16.00	15.96	C ₄ -alkylbenzene	105, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
45	16.05	16.02	2-methyl-benzonitrile	90, 117	C ₈ H ₇ N	+	+	+	+	+	+	
46	16.16	16.12	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
47	16.22	16.18	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
48	16.25	16.22	C ₄ -alkylbenzene	91, 117, 132	C ₁₀ H ₁₂	+	+	–	+	+	–	Tentatively detected species from in situ TMAH experiment ^a
49	16.32	16.29	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
50	16.43	16.39	C ₄ -alkylbenzene	91, 117, 132	C ₁₀ H ₁₂	+	+	–	+	+	–	Tentatively detected species from in situ TMAH experiment ^a
51	16.68	16.65	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	–	–	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
52	16.88	16.85	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	–	–	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
53	16.95	16.92	C ₄ -alkylbenzene	105, 119, 134	C ₁₀ H ₁₄	+	+	–	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
54	17.03	17.00	C ₄ -alkylbenzene	91, 117, 132	C ₁₀ H ₁₂	+	+	co-elution	+	+	co-elution	Tentatively detected species from in situ TMAH experiment ^a
55	17.13	17.09	C ₄ -alkylbenzene	91, 117, 132	C ₁₀ H ₁₂	+	+	co-elution	+	+	co-elution	Tentatively detected species from in situ TMAH experiment ^a
56	17.28	17.24	C ₄ -alkylbenzene	119, 133, 148	C ₁₁ H ₁₆	+	–	–	+	+	–	Tentatively detected species from in situ TMAH experiment ^a
57	17.32	17.29	C ₁ -indane	117, 131, 132	C ₁₀ H ₁₂	+	–	–	+	+	–	

Table 1
Continued

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	SAM ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	Notes
58	17.51	17.48	C ₁ -indene	115, 130	C ₁₀ H ₁₀	+	+	–	+	+	+	
59	17.58	17.55	C ₁ -indene	115, 130	C ₁₀ H ₁₀	+	+	–	+	+	+	
60	17.62	17.58	C ₁ -indene	115, 130	C ₁₀ H ₁₀	+	+	–	+	+	+	
61	17.67	17.64	C ₁ -indene	105, 128	C ₁₀ H ₈	+	+	+	+	+	+	
62	18.15	18.15	naphthalene	128	C ₁₀ H ₈	+	+	+	+	+	+	Tentatively detected from in situ TMAH experiment ^a
63	18.28	18.28	benzo[c]thiophene	134	C ₈ H ₆ S	+	–	–	+	+	+	Tentatively detected from in situ TMAH experiment ^a
64	18.41	18.41	thieno[2,2-b]thiophene	140	C ₆ H ₄ S ₂	+	–	–	+	+	–	
65	18.48	18.48	thieno[3,2-b]thiophene	140	C ₆ H ₄ S ₂	+	–	–	+	+	–	
66	19.83	19.83	C ₁ -alkylnaphthalene	115, 141, 142	C ₁₁ H ₁₀	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
67	19.96	19.96	2-methyl-benzo[b]thiophene	147	C ₉ H ₈ S	+	+	–	+	+	–	
68	20.06	20.06	C ₁ -alkylnaphthalene	115, 141, 142	C ₁₁ H ₁₀	+	+	+	+	+	+	Tentatively detected species from in situ TMAH experiment ^a
69	20.96	20.96	biphenyl	154	C ₁₂ H ₁₀	+	+	+	+	+	+	
70	21.15	21.15	methylbiphenyl	152, 167	C ₁₃ H ₁₂	+	–	–	+	+	–	
71	21.19	21.19	C ₂ -alkylnaphthalene	141, 156	C ₁₂ H ₁₂	+	+	+	+	+	+	
72	21.38	21.38	C ₂ -alkylnaphthalene	141, 156	C ₁₂ H ₁₂	+	+	+	+	+	+	
73	21.54	21.54	C ₂ -alkylnaphthalene	141, 156	C ₁₂ H ₁₂	+	+	+	+	+	+	
74	21.60	21.60	C ₂ -alkylnaphthalene	141, 156	C ₁₂ H ₁₂	+	+	+	+	+	+	
75	21.63	21.63	methylbiphenyl	152, 167	C ₁₃ H ₁₂	+	+	+	+	+	+	
76	21.82	21.82	C ₂ -alkylnaphthalene	141, 156	C ₁₂ H ₁₂	+	+	+	+	+	+	
77	22.03	22.03	acenaphthylene	152	C ₁₂ H ₈	+	+	+	+	+	+	
78	22.33	22.33	diphenylmethane	167, 168	C ₁₃ H ₁₂	+	+	+	+	+	+	
79	23.48	23.48	phenalene	165, 166	C ₁₃ H ₁₀	+	+	+	+	+	+	

Table 1
Continued

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	SAM ramp	+5 μ L TMAH	+0.2 μ L MTBSTFA	Notes
80	23.70	23.70	fluorene	165, 166	C ₁₃ H ₁₀	+	+	+	+	+	+	
81	25.53	25.53	H-fluoren-9-on	152, 180	C ₁₃ H ₈ O	+	+	+	+	+	+	
82	25.73	25.73	dibenzothiophene	184	C ₁₂ H ₈ S	+	+	+	+	+	+	
83	26.03	26.03	anthracene	178	C ₁₄ H ₁₀	+	+	+	+	+	+	
84	26.18	26.18	phenanthrene	178	C ₁₄ H ₁₀	+	+	+	+	+	+	
85	28.94	28.94	fluoranthene	202	C ₁₆ H ₁₀	+	+	+	+	+	+	
86	29.49	29.49	pyrene	202	C ₁₆ H ₁₀	+	+	+	+	+	+	

^aWilliams et al. (2021).

(Tables 1 and 2). The co-occurrence of both methylated and non-methylated species suggests partial methylation of compounds from decreased TMAH thermochemolysis reaction rates at slow pyrolysis ramps (Lievens et al., 2013; Onay & Kockar, 2003). Specifically, OH⁻ formation resulting in the release of methyl radicals and trimethylamine from TMAH is pressure dependent (Onel et al., 2013). During TMAH flash thermochemolysis,

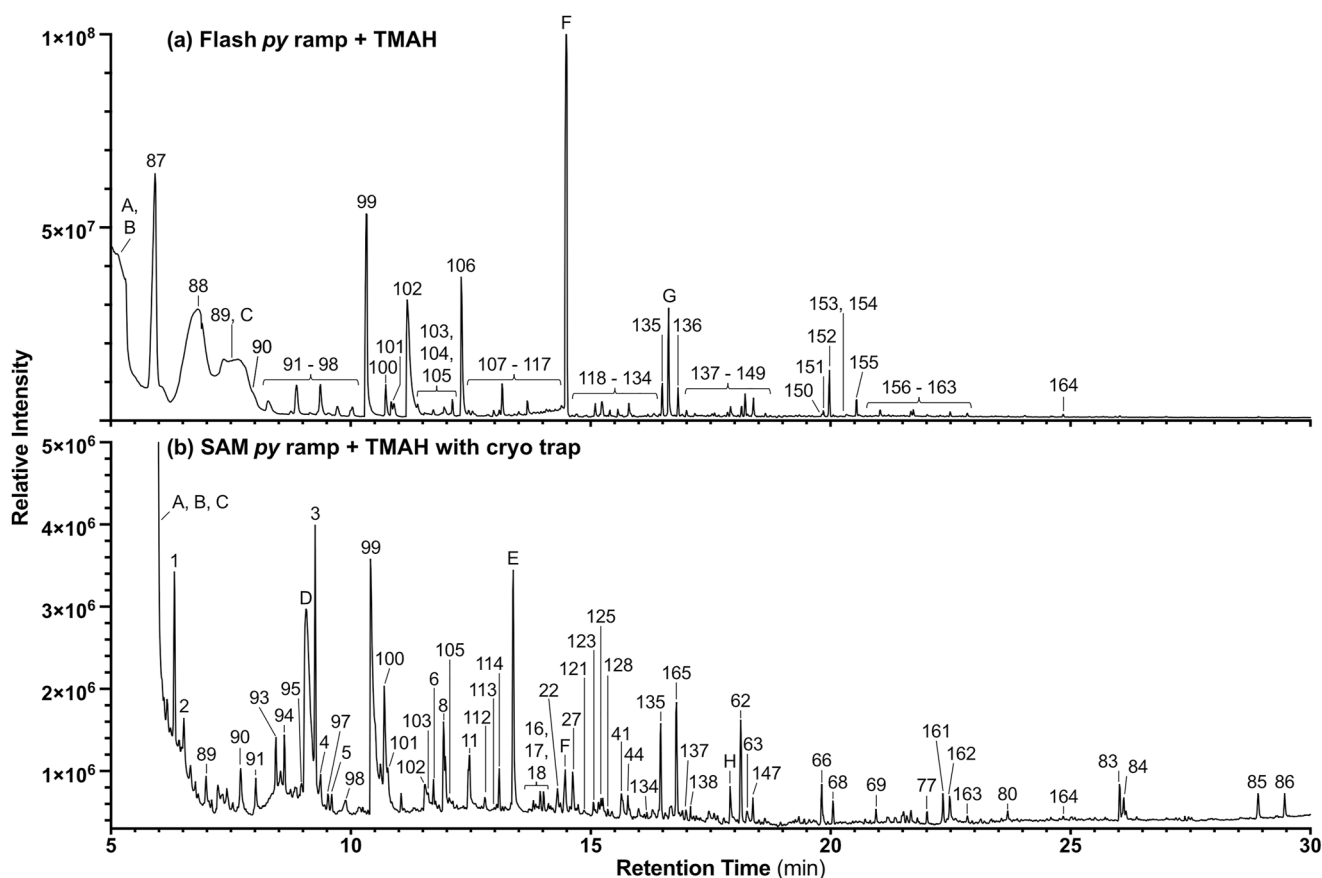


Figure 3. TMAH thermochemolysis of Murchison meteorite. Total ion chromatogram of pyrolyzed Murchison with 5 μ L of TMAH reveals a new suite of methylated compounds (e.g., methyl esters and ethers) previously undetectable. Derivatized compounds included aromatic acids, carboxylic acids, dicarboxylic acids, and amino acids. (a) Flash and (b) SAM-like pyrolysis ramps with a cryogenic trap produced a diversity of methylated derivatives listed in Table 2.

Table 2
Methylated Products From Flash and SAM Pyrolysis With TMAH in the Absence and Presence of MTBSTFA

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash		SAM		Notes
						ramp + 5 μ L TMAH	+0.2 μ L MTBSTFA	ramp + 5 μ L TMAH	+0.2 μ L MTBSTFA	
A	4.25	3.35	N,N-dimethyl-methylamine	58	C ₃ H ₉ N	+	+	+	+	TMAH byproduct ^a
B	4.75	3.41	N,N-dimethyl-ethanamine	58, 73	C ₄ H ₁₁ N	+	+	+	+	TMAH byproduct ^a
87	5.93	5.31	carbonic acid	29, 31, 45, 59	C ₃ H ₆ O ₃	+	+	+	+	
C	6.82	5.48	N,N,N',N'-tetramethyl-methanediamine	58, 102	C ₃ H ₁₄ N ₂	+	+	+	+	TMAH byproduct ^a
88	6.90	5.59	saturated C ₃ -fatty acid	57, 88	—	+	+	+	+	
89	7.37	6.99	branched saturated C ₄ -fatty acid	43, 71, 87	—	+	+	+	+	
90	8.02	7.68	branched unsaturated C ₄ -fatty acid	41, 69, 100	—	+	co-elution	+	co-elution	
91	8.28	8.02	saturated C ₄ -fatty acid	74	—	+	+	+	+	
92	8.63	—	unsaturated C ₄ -fatty acid	41, 69, 100	—	+	+	—	—	
93	8.75	8.44	C ₁ -pyrrole	81	—	+	+	+	+	
94	8.87	8.62	dimethyl(disulfide	45, 79, 94	C ₂ H ₆ S ₂	+	+	+	+	
D	—	9.07	(dimethylamino)acetonitrile	42, 58, 83, 84	C ₄ H ₈ N ₂	—	—	+	+	TMAH byproduct ^a
95	9.15	8.99	pyridine	52, 79	C ₅ H ₅ N	+	+	+	+	
96	9.37	—	hydroxy saturated C ₂ -fatty acid	29, 45, 74	—	+	+	+	+	
97	9.72	9.53	branched saturated C ₅ -fatty acid	57, 88	—	+	co-elution	+	+	
98	10	9.90	hydroxy saturated C ₃ -fatty acid	59	—	+	+	+	co-elution	
99	10.33	10.42	N(2)-methyl-glycinamide	42, 44, 73	C ₃ H ₈ N ₂ O	+	+	+	co-elution	
100	10.73	10.70	methyl dimethylcarbamate	72, 88, 103	C ₄ H ₉ NO ₂	+	+	+	co-elution	
101	10.90	10.78	saturated C ₅ -fatty acid	74	—	+	+	+	co-elution	
102	11.21	11.55	N,N-dimethyl-glycine	42, 58, 117	C ₅ H ₁₁ NO ₂	+	+	+	co-elution	Likely amino acid contamination
103	11.72	11.62	branched saturated C ₆ -fatty acid	87, 102	—	+	+	+	+	
104	11.95	—	methylpyridine	93	C ₆ H ₇ N	+	+	—	—	
105	12.12	12.05	saturated oxo C ₄ -fatty acid	57	—	+	+	+	+	
106	12.32	—	N,N-dimethyl-alanine	42, 44, 56, 72, 131	C ₅ H ₉ NO ₃	+	+	+	co-elution	Likely amino acid contamination
107	12.54	—	2,4-dithiapentane	61, 108	C ₃ H ₈ S ₂	+	+	—	—	
108	12.74	—	branched saturated oxo C ₆ -fatty acid	57, 85	—	+	+	—	—	
109	12.81	—	methyl acetoxyacetate	43, 73, 102	C ₅ H ₈ O ₄	+	—	—	—	
110	12.88	—	methyl 2-(methylthio)acetate	61, 74, 120	C ₄ H ₈ O ₂ S	+	+	—	—	
111	12.98	—	hydroxybutanone methyl ester	43, 85, 100	—	+	+	—	—	
112	13.10	13.00	anisole	65, 78, 108	C ₇ H ₈ O	+	+	+	+	
113	13.10	13.04	saturated dicarboxylic acid	115	—	+	+	+	+	
114	13.16	13.10	saturated C ₆ -fatty acid	74	—	+	+	+	+	
115	13.51	13.42	2,3-dimethyl-2-cyclopenten-1-one	67, 95, 110	C ₇ H ₁₀ O	+	+	+	+	
116	13.62	—	hydroxy saturated C ₄ -fatty acid	45, 59, 74, 132	—	+	+	—	—	

Table 2
Continued

Number	Flash RT (min)	SAMS RT (min)	Compound	m/z	Formula	Flash ramp + 5 μ L		SAMS ramp + 5 μ L		Notes
						TMAH	+0.2 μ L MTBSTFA	TMAH	+0.2 μ L MTBSTFA	
E	13.68	13.54	N,N,2-trimethyl-2-propanamine	86	$C_6H_{15}N$	+	+	+	+	TMAH byproduct ^a
117	14.36	-	glyceraldehyde dimethyl ether	45, 59, 89	$C_3H_{10}O_3$	+	co-elution	-	-	Likely amino acid contamination
118	14.40	14.39	dimethylpyridine	79, 92, 106, 107	C_7H_9N	+	+	+	+	
F	14.48	14.47	hexahydro-1,3,5-trimethyl-1,3,5-triazine	86, 128	$C_8H_{15}N_3$	+	+	+	+	TMAH byproduct ^a
119	14.54	-	(methoxymethyl)-benzene	91, 122	$C_8H_{10}O$	+	+	-	-	
120	14.72	-	2,5-dihydro-2,5-dimethoxy-furan	41, 71, 99	$C_6H_{10}O_3$	+	+	-	-	
121	14.91	14.86	methoxy C_1 -alkylbenzene	77, 91, 107, 122	-	+	+	+	+	
122	15.09	15.05	dimethyl fumarate	59, 85, 113, 144	$C_6H_8O_4$	+	+	+	+	
123	15.10	15.07	saturated C_6 -fatty acid	74	-	+	+	+	+	
124	15.15	-	methoxy C_1 -alkylbenzene	77, 91, 107, 122	-	+	+	-	-	
125	15.24	15.22	saturated C_x -dicarboxylic acid	55, 59, 97, 115	-	+	+	+	+	
126	15.25	-	branched saturated C_4 -dicarboxylic acid	59, 115	-	+	+	-	-	
127	15.38	-	m-ethylaniline	106, 121	$C_8H_{11}N$	+	+	-	-	
128	15.40	15.36	branched saturated C_8 -dicarboxylic acid	87, 102	-	+	+	+	+	
129	15.57	-	N,N-dimethyl-benzenemethanamine	58, 91, 135	$C_9H_{13}N$	+	+	-	-	
130	15.62	-	1-methyl-2-pyrrolidinone	45, 99	C_5H_9NO	+	+	-	-	
131	15.78	-	N,N,O-trimethyl-serine methyl ester	102, 116	$C_7H_{15}NO_3$	+	+	-	-	Likely amino acid contamination
132	15.80	-	branched saturated C_5 -dicarboxylic acid	59, 101, 129	-	+	+	-	-	
133	15.89	-	methoxy C_2 -alkylbenzene	91, 121, 136	-	+	+	-	-	
134	16.19	16.16	branched C_6 -dicarboxylic acid	73	-	+	+	+	+	
135	16.50	16.45	benzoic acid	51, 77, 105, 136	$C_8H_8O_2$	+	+	+	+	Tentatively detected from in situ TMAH experiment ^a
G	16.64	-	N,N,N',N'-tetramethyl-1,2-ethanediamine	58, 116	$C_6H_{16}N_2$	+	+	+	+	TMAH byproduct ^a
165	-	16.79	N-methylglycine	42, 44, 89	$C_3H_7NO_2$	-	-	+	+	Likely amino acid contamination
136	16.82	-	saturated C_8 -fatty acid	74	-	+	co-elution	-	-	Likely fatty acid contamination
137	17.00	16.97	dicarboxylic acid	59, 100, 129	-	+	+	+	co-elution	
138	17.17	17.15	branched dicarboxylic acid	59, 69, 101, 114, 143	-	+	+	+	co-elution	
139	17.25	-	N-methoxycarbonyl-sarcosine	42, 58, 102, 161	$C_6H_{11}NO_4$	+	+	-	-	Likely amino acid contamination
140	17.44	-	branched dicarboxylic acid	112	-	+	+	-	-	
141	17.53	-	dicarboxylic acid	59, 99, 127	-	+	+	-	-	

Table 2
Continued

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp + 5 μ L		SAM ramp + 5 μ L		Notes
						TMAH	+0.2 μ L MTBSTFA	TMAH	+0.2 μ L MTBSTFA	
142	17.55	-	ethyltetramethylcyclopentadiene	135, 150	$C_{11}H_{18}$	+	+	-	-	
143	17.56	-	methoxy C_3 -alkylbenzene	91, 135, 150	-	+	+	-	-	
144	17.58	-	branched dicarboxylic acid	114	-	+	+	-	-	
H	17.92	17.91	tributylamine	142	$C_{12}H_{27}N$	+	+	+	+	TMAH byproduct ^a
145	17.96	-	N,N,4 trimethyl-benzenamine	91, 119, 134, 135	$C_9H_{13}N$	+	+	-	-	TMAH byproduct ^a
146	18.28	-	C_1 -benzoic acid methyl ester	91, 119, 150	-	+	+	-	-	
147	18.40	18.38	saturated C_9 -fatty acid	74	-	+	+	+	+	Likely fatty acid contamination
148	18.57	-	N,N,S-trimethyl-L-cysteine	56, 71, 116, 117, 177	$C_7H_{15}NO_2S$	+	+	-	-	Likely amino acid contamination
149	18.64	-	dicarboxylic acid	74	-	+	+	-	-	
150	19.70	-	1,2,3-trimethoxybenzene	110, 153, 168	$C_9H_{12}O_3$	+	+	-	-	
151	19.85	19.85	saturated C_{10} -fatty acid	74	-	+	+	+	+	Likely fatty acid contamination
152	19.98	-	N,N,O-trimethyl-L-threonine	84, 56, 116	$C_8H_{17}NO_3$	+	+	-	-	Likely amino acid contamination
153	20.21	20.21	3-methoxy-benzoic acid	135, 166	$C_9H_{10}O_3$	+	+	+	+	
154	20.39	-	C_2 -benzoic acid	133, 164	-	+	+	-	-	
155	20.55	-	N,N-dimethyl-aspartic acid	42, 88, 98, 116, 130, 189	$C_8H_{15}NO_4$	+	+	-	-	Likely amino acid contamination
156	20.72	20.72	C_2 -indole	144	-	+	+	+	+	
157	20.74	20.74	4-methoxy-benzoic acid	135, 166	$C_8H_8O_3$	+	+	+	+	
158	21.40	21.40	methyl 4-methoxy-3-methylbenzoate	91, 149, 180	$C_{10}H_{12}O_3$	+	+	+	+	
159	21.73	-	N-(methoxycarbonyl)-proline	128	$C_8H_{13}NO_4$	+	+	-	-	Likely amino acid contamination
160	21.86	-	1-methoxy-naphthalene	115, 143, 158	$C_{11}H_{10}O$	+	+	-	-	
161	22.35	22.34	dicarboxylic aromatic acid	135, 163, 194	-	+	+	+	+	
162	22.52	22.48	dicarboxylic aromatic acid	135, 163, 194	-	+	+	+	+	
163	22.85	22.85	trimethylindole	144, 158	$C_{12}H_{12}$	+	+	+	+	
164	24.05	24.05	tetramethylindole	158, 172	$C_{12}H_{15}N$	+	+	+	-	

Note. Letters indicate TMAH pyrolysis byproducts.
He et al. (2020b).

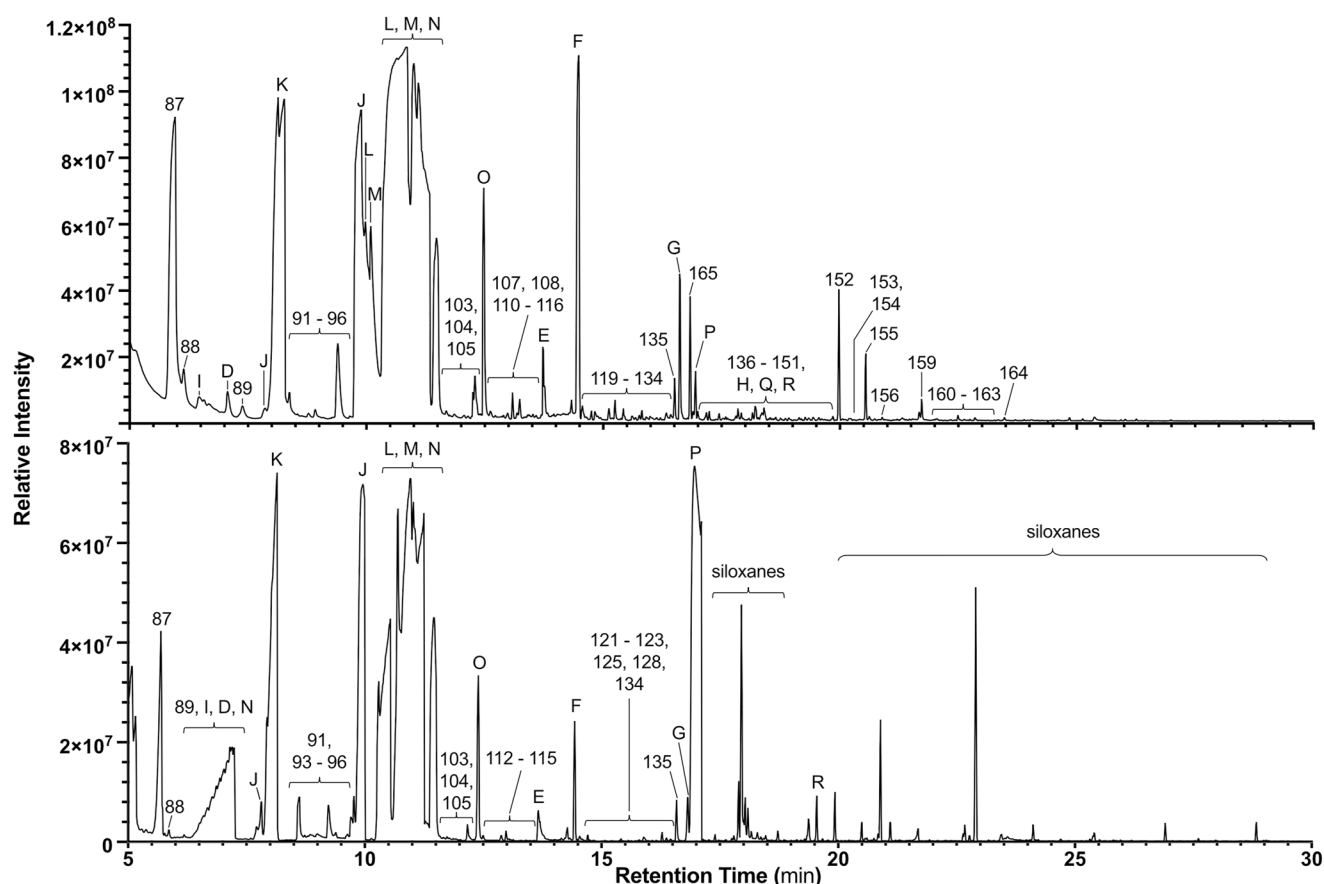


Figure 4. TMAH thermochemolysis of Murchison meteorite with simulated MTBSTFA background. Total ion chromatogram of pyrolyzed Murchison with 5 μ L of TMAH and 0.2 μ L of MTBSTFA produces a massive detection of t-BMDS derivatives listed in Table 3. (a) Flash pyrolysis yielded an identical diversity of derivatives as TMAH without MTBSTFA, however, analyte co-elution with silylated compounds posed challenges toward compound identification. (b) SAM-like pyrolysis ramp primarily yielded silylated products which greatly obscured the identification of analytes.

samples experienced an immediate and significant pressure increase which enhances the yield of methylated products (He et al., 2020b). During SAM-like thermochemolysis, a constant He flow may sweep away volatiles (including TMAH) and replace warming helium gas within the pyrolysis chamber throughout the temperature ramp, precluding comparable pressures and limiting TMAH exposure (He et al., 2020b). Pyrolyzate methylation is consequently lower under SAM-like conditions resulting in the observed decrease in response and co-occurrence of methylated and non-methylated end members (Figure 3, Tables 1 and 2).

3.3. TMAH Thermochemolysis of Murchison Meteorite With Simulated MTBSTFA Background

Flash and SAM-like pyrolysis of Murchison meteorite in the presence of TMAH and a simulated MTBSTFA background produces various silylated byproducts which co-elute and hinder the identification of methylated derivatives (Figure 4, Table 3). These include: tert-butyl dimethyl fluorosilane; N,N-dimethyl-formamide (DMF); 2,2,2-trifluoro-N-methyl-acetamide; N,N-dimethyl trifluoroacetamide; tert-butyl(methoxy)dimethylsilane (silylated methanol); tert-butyl dimethylsilanol (commonly designated monosilylated water - MSW); and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyl-disiloxane (commonly designated bi-silylated water—BSW), 1,1,3,3,5,5-hexamethyl-1,5-di(tert-butyl)-1,3,5-trisiloxane, and bis(tert-butyl dimethylsilyl)amine (Table 3). Despite challenges posed by undesired products, nearly all TMAH derivatives were identified via diagnostic mass spectra and retention times to rule out overprinting signals (Table 2). Prior results from unassisted and TMAH experiments (without MTBSTFA) (Figures 2 and 3) were critical for guiding identifications. Our experiments with simulated vapor therefore suggest that while producing suboptimal results, persisting MTBSTFA vapor should not have considerably altered results from the first TMAH experiment on Mars. However, coelutions from

Table 3
Silylated Products From Flash and SAM Pyrolysis With MTBSTFA

Number	Flash RT (min)	SAM RT (min)	Compound	m/z	Formula	Flash ramp	SAM ramp	Notes
I	6.48	6.4–7.2	tert-butyl dimethylfluorosilane	77	C ₆ H ₁₅ FSi	+	+	MTBSTFA/DMF byproduct ^a
J	7.87	7.81	2,2,2-trifluoro-N-methyl-acetamide	58, 69, 127	C ₃ H ₄ F ₃ NO	+	+	MTBSTFA/DMF byproduct ^a
K	8.13	8.13	N,N-dimethyltrifluoroacetamide	72, 141	C ₄ H ₆ F ₃ NO	+	+	MTBSTFA/DMF byproduct ^a
J ^b	9.84	9.93	2,2,2-trifluoro-N-methyl-acetamide	58, 69, 127	C ₄ H ₆ F ₃ NO	+	+	MTBSTFA/DMF byproduct ^a
L	9.98	10.3–11.5	tert-butyl(methoxy)dimethylsilane	59, 89	C ₇ H ₁₈ OSi	+	+	MTBSTFA/DMF + TMAH/MeOH byproduct
M	10.11	10.3–11.5	N,N-dimethyl-formamide	44, 73	C ₃ H ₈ N ₂ O	+	+	MTBSTFA/DMF byproduct ^a
N	10.80	10.3–11.5	tert-butyl dimethylsilanol	75	C ₆ H ₁₆ OSi	+	+	MTBSTFA/DMF + TMAH/MeOH byproduct
O	12.40	12.40	[2-(N,N-Dimethyl)]-1,2-propanediamine	42, 44, 56, 72, 102	C ₅ H ₁₄ N ₂	–	+	MTBSTFA/DMF + TMAH/MeOH byproduct
165	16.84	–	unknown compound	71, 98, 99, 127	–	+	–	
P	16.95	16.95	1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyl-disiloxane	147, 189	C ₁₂ H ₃₀ OSi ₂	+	+	MTBSTFA/DMF + TMAH/MeOH byproduct
Q	18.34	18.34	bis(tert-butyl dimethylsilyl)amine	146, 188	C ₁₂ H ₃₁ NSi ₂	+	+	MTBSTFA/DMF + TMAH/MeOH byproduct
R	19.62	19.61	1,1,3,3,5,5-hexamethyl-1,5-di(tert.butyl)-1,3,5-trisiloxane	221	C ₁₄ H ₃₆ O ₂ Si ₃	+	+	MTBSTFA/DMF + TMAH/MeOH byproduct

Note. Letters indicate MTBSTFA/DMF and MTBSTFA + TMAH pyrolysis byproducts.

^aHe et al. (2021). ^bIdentical mass spectrum to J.

MTBSTFA byproducts may impose additional challenges in the absence of analytical blanks. This is because the one remaining TMAH cup on SAM represents an indispensable opportunity for the ongoing search of organics on Mars.

3.4. Results From the First TMAH Experiment on Mars

Preliminary analyses of the SAM TMAH thermochemolysis experiment have indicated TMAH and MTBSTFA reaction byproducts including trimethylamine, MSW, BSW, and the 1-fluoronaphthalene internal standard in the TMAH cup have been detected. However, the C9 straight-chain saturated fatty acid standard expected to be derivatized by TMAH into a fatty acid methyl ester, and the pyrene standard, have yet to be identified (Williams et al., 2021). Still, the detection of bands of high molecular weight mass-to-charge ratios (m/z) of 190–485 representing a complex suite of compounds which tentatively include methylated oxygen-, sulfur-, and nitrogen-bearing aromatic organics indicate a successful first TMAH experiment on Mars (Williams et al., 2021). Combined analysis of EGA and GC-MS data corroborate the detection of benzene, toluene, C3–C4 alkylbenzenes, naphthalene, and C1 alkylnaphthalenes. In addition, a C5 alkylbenzene, benzoic acid methyl ester, C2–C4 alkylbenzenamines, dihydronaphthalene, 2-butyl-thiophene, and benzothiophene were independently detected from GC-MS data (Williams et al., 2021). Preliminary identifications are consistent with result from laboratory pyrolysis experiments presented here (Tables 1–3), indicating compounds detected on Mars may represent liberated molecules from a macromolecular source characteristic of meteoritic input (e.g., Derenne & Robert, 2010; Remusat et al., 2005; Sephton, 2002, 2012). Nevertheless, compounds identified from EGA and GC-MS data may additionally represent known internal SAM organics sources including MTBSTFA reaction with the hydrocarbon trap known to produce, amongst others, benzene, toluene, C3 alkylbenzenes, benzoic acid, naphthalene, and diphenylmethane (Buch et al., 2019; Eigenbrode et al., 2018; Freissinet et al., 2015; Glavin et al., 2013; He et al., 2021; Leshin et al., 2013; Miller et al., 2015, 2016).

4. Conclusions

We present results from pyrolysis and thermochemolysis experiments on samples of Murchison meteorite as an analog for organics that might be detectable by the SAM instrument suite on Mars. Murchison meteorite was

selected because its organic composition has been well-characterized (e.g., Derenne & Robert, 2010; Komiya & Shimoyama, 1996; Levy et al., 1973; Remusat et al., 2005; Sephton, 2002), it contains compounds previously detected on Mars (Eigenbrode et al., 2018), and because carbonaceous matter from chondrites and interplanetary dust may represent a significant source of organics present in Mars regolith (Chyba & Sagan, 1992; Flynn, 1996; Frantseva et al., 2018). In the presence of TMAH, comparable distributions of aromatic acids, dicarboxylic acids, and amino acids are observed under flash and SAM-like pyrolysis ramps. However, TMAH thermochemolysis experiments demonstrate lower methylation efficiency under SAM-like conditions resulting in the co-occurrence of methylated derivatives at low relative abundances along with non-methylated compounds. This decrease in yield is inferred to result from thermodynamically controlled reactions at slow pyrolysis ramps (Lievens et al., 2013; Onay & Kockar, 2003). Specifically, OH⁻ formation resulting in the release of methyl radicals and trimethylamine (TMA) from TMAH is pressure dependent (Onel et al., 2013). Flash pyrolysis exposes samples to an immediate and significant pressure increase and enhanced production of methylation products while pyrolysis at low ramp rates diminishes the potential for comparable yields (He et al., 2020b). Experiments simulating the co-occurrence of MTBTFA vapor produce various silylated products which obscure the identification of analytes detectable with TMAH alone. These are primarily silylated methanol, MSW, and BSW. Despite challenges posed by co-eluting compounds, most methylated-derivatives could still be identified in flash pyrolysis by comparing retention times and mass spectral fragmentation patterns to reference experiments. In contrast, SAM-like experiments with TMAH and simulated MTBSTFA “vapor” are hindered by both decreased methylation yields and TMAH/MTBSTFA byproducts. Our results indicate that a significant diversity of pyrolyzates and derivatives may be potentially identified from SAM GC-MS data. However, without the availability of analytical blanks, the outcome of TMAH pyrolysis experiments on Mars remains uncertain.

Data Availability Statement

Data from pyrolysis experiments presented in this study are publicly available in the Figshare data repository Mojarro (2023).

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