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DETECTION OF ORGANICS AT MARS: HOW WET CHEMISTRY ONBOARD SAM HELPS.

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Introduction:

For the first time in the history of space exploration, a mission of interest to astrobiology could be able to analyze refractory organic compounds in the soil of Mars. Wet chemistry experiment allow organic components to be altered in such a way that improves their detection either by releasing the compounds from sample matrices or by changing the chemical structure to be amenable to analytical conditions. The latter is particularly important when polar compounds are present. Sample Analysis at Mars (SAM), on the Curiosity rover of the Mars Science Laboratory mission, has onboard two wet chemistry experiments: derivatization [1-2] and thermochemolysis [3-4]. Here we report on the nature of the MTBSTFA derivatization experiment on SAM, the detection of MTBSTFA in initial SAM results, and the implications of this detection.

MTBSTFA derivatization:

Chemical derivatization of polar molecular compounds is achieved by the MTBSTFA (N-Methyl-N-tert-butyl-dimethylsilyltrifluoroacetamide) / DMF (Dimethylformamide) silylation reaction in order to transform refractory polar compounds into a more volatile form that can be analyzed and detected by GCMS (Figure 1). The advantage of using MTBSTFA as the derivatization reagent is that it is a single-step reaction; it is less susceptible to hydrolysis compared with other reagents and it does not require separation of the derivatives prior to GC separation analysis. In addition, MTBSTFA is sensitive to a wide range of organic compounds with acidic hydrogen atoms. The reaction yields obtained using this derivatization reagent are typically in the 90–100% range. Finally, the MTBSTFA has also the major advantage to react in the gaseous phase, generally present in pyrolyzing system like the one used in SAM to treat the solid samples.



Figure 1. Scheme of the derivatization reaction of MTBSTFA/DMF with an amino acid.

First SAM Solid Sample Experiment Results:

The first scoops of the Martian soil (Rocknest, Gale crater) have been analyzed by evolved gas analysis (EGA) and via GC using thermal conductivity (TCD) and MS detection [5-6]. The samples have been heated up to approximately 840 °C with a heating rate of 35 °C/min under He flow. The evolved gas was analyzed directly by the QMS in EGA mode. For GC analyses, the majority of the gas released was trapped on a hydrocarbon trap (silica beads, Tenax TA, Carbosieve G) over a specific temperature range. Trapped volatiles were then released by heating to ~300 °C and sent to the GC under He flow. Then the content of the GC injection trap (IT) is released in the GC column (CLP-MXT 30 m x 0.25 mm x 0.25 µm) by rapidly heating the IT at 300 °C. Helium is used (0.9 bar inlet column pressure) as the carrier gas. The column temperature program started at 50 °C, and increased up to 220 °C with a ramp rate of 10 °C/min.

The first results obtained when running an analysis with an empty cup (no solid sample) showed the presence of MTBSTFA in the system. MTBSTFA was first detected in the EGA-QMS analysis blank then by GC-TCD-QMS analysis. Meaning that MTBSTFA is part of the background signal under its gaseous phase and is derived from at least one of the seven MTBSTFA/DMF derivatization cups in SAM [7]. Since MTBSTFA is able to react in the gaseous phase, its detection implies the possibility to have some MTBSTFA reactions with all the labile compounds possibly present in the Martian soil, in the sampling system and/or inside the SAM instrument.

The analysis of the different scooped samples confirmed the presence of MTBSTFA in the background. Indeed, on the EGA and GC-TCD-MS run we have detected the by-product acetamide-2,2,2-trifluoro-N-methyl that is characteristic of the presence of MTBSTFA. In addition, we also have observed the presence of compounds resulting from the derivatization reaction between MTBSTFA and water. Indeed, water has been detected by two ways: the EGA experiment and the GC-TCD-MS run. Due to the presence of mono- and bi-silylated water derivatives, several characteristic ions can be detected in the EGA mode (e.g. $m/z = 147, 73$), and two characteristic peaks in the GC-TCD-MS analysis are also observed (Figure 2).

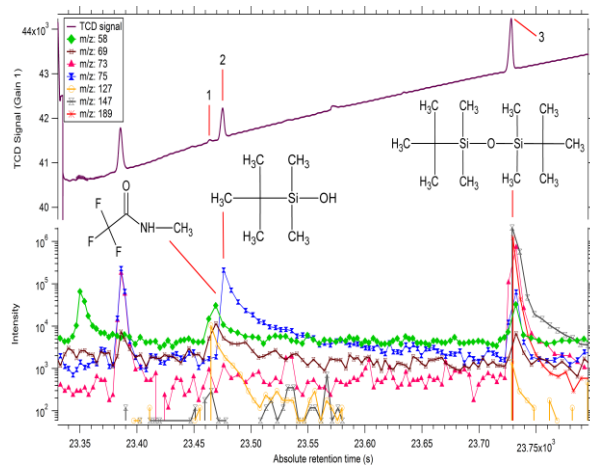


Figure 2. GC-TCD (top) and GC-MS (bottom) analysis of the first portion at Rocknest. Only The MTBSTFA characteristic m/z values have been plotted on this figure.

In addition to water, a silylated chloride compound has been detected after pyrolysis of the Rocknest soil. This compound is the simplest chloride derivative compound: chloro(1,1-dimethylethyl)dimethyl-silane (Figure 3), and it co-elutes with the mono-silylated water derivative.

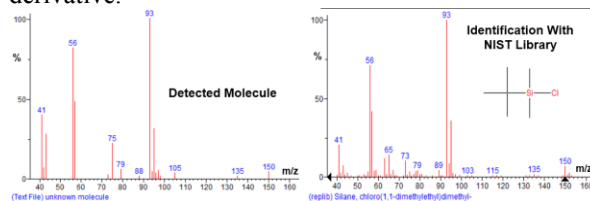


Figure 3: Mass spectrum of the silylated chloride compound identified in the Rocknest portion #3 GC-MS data by using NIST library.

Discussion:

The presence of MTBSTFA in the EGA and GC-TCD-MS background allows us to confirm the first results obtained in EGA and TLS experiments meaning the presence of water in the Martian atmosphere and/or soil. In contrast to the TLS measurement, the detection of water after derivatization is dependent on the concentration of MTBSTFA in the background. Indeed if the MTBSTFA is the limiting species then the water could not be totally derivatized and detected as well. Moreover, the presence of two chromatographic peaks associated with water derivatives increases the difficulty of quantification of water. Indeed the presence of the mono-silylated water can come from: (1) an incomplete MTBSTFA reaction, (2) from the degradation of the bi-silylated water under high temperature, (3) or a combination of (1) and (2). For all of these cases, the sum of the two peak will allow us to estimate the water quantity. We have compared the GC-MS peaks area related with water (mono and bi-silylated) of the different Rocknest portions as a function of the temperature

cut. If we assume that the same quantity of sample is injected in the GC then, the main conclusion could be that for the same temperature cut there is a higher water concentration in the first portion compared to the blank. That could mean that like the Martian atmosphere, the Rocknest sample contains water as well. This hypothesis is confirmed by the GC-MS analysis of the second portion where the temperature cut is lower and the water concentration higher. The opposite is true when the temperature cut is between 533 to 822°C where water concentration drastically decreases because it has been eliminated at lower temperature.

Sample	Temperature	GC-MS Area (cps.sec)	
		Mono-silylated water (m/z : 75)	Bi-silylated water (m/z : 147)
Blank	144-533°C	0.64E+06	2.25E+06
Portion #1	144-533°C	2.25E+06	3.56E+07
Portion#2	98-425°C	1.39E+07	4.07E+07
Portion #3	533-822°C	0.03 E+06	1.43E+06

Table 1: Peak area calculated after Gaussian fitting by using the "SAM" Igor tool. For the mono and bi silylated water we have used the base peak, respectively m/z : 75 and m/z : 147.

The chloride compounds detected in the GC run could come from three different sources: (1) HCl compounds which is able to react with MTBSTFA to lead silylated chloride. Since HCl derivative has not been detected in the blank, it could be originated from soil or it could be generated as a secondary reaction occurred during the pyrolysis. (2) the reaction of MTBSTFA with the perchlorate, if it is present in the soil sample [8]. Indeed the MTBSTFA is a highly reactive compound able to react with labile compounds but it also could be oxidized at high temperature by oxidizing compounds such as perchlorate. (3) At high temperature, perchlorate degradation could lead to HCl formation.

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