
1Ecole Centrale Paris, LCGM, Grande voie des vignes, 92295 Châtenay-Malabry, France, arnaud.buch@ecp.fr, 2NASA Goddard Space Flight Center, 8800 Greenbelt Rd, Greenbelt, MD 20771, 3LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, 4LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, 5Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico.

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 particular 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(dimethyl)silyl trifluoroacetamide) / DMF (Dimethylformamide) silylation reaction in order to transform refractory polar compounds into a more volatile form that can be analyzed and detected by GC/MS (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.

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 radially 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

![Figure 1. Scheme of the derivatization reaction of MTBSTFA/DMF with an amino acid.](image-url)
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.


**Acknowledgements:** SAM-GC team acknowledges support from the French Space Agency (CNES), French National Programme of Planetology (PNP), National French Council (CNRS), Pierre Simon Laplace Institute.