From Background to Signal: Challenges of a Solid Sample Analysis Using SAM GC-MS

C. Freissinet[1], A. Buch[2], D. P. Glavin[1], M. Cabane[3], P. Coll[4], J. L. Eigenbrode[1], A. Steele[5], C. Szopa[3], P. R. Mahaffy[1] and the SAM science team

[1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, caroline.freissinet@nasa.gov, [2]Ecole Centrale Paris, 92295 Chatenay-Malabry, France, [3]LATMOS-UPMC, 75005 Paris, France, [4]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS 94010 Créteil, France, [5]Carnegie Institution of Washington, Washington, DC 20015.

Introduction

The Sample Analysis at Mars (SAM) experiment holds numerous capabilities. Amonst them, the GCMS mode (coupling of the Gas-Chromatograph and the quadrupole Mass-Spectrometer instruments) was designed for the separation and identification of the chemical components of the gases evolved from a solid sample, either processed by heat in pyrolysis or by chemical reactant in wet chemistry [1]. Prior to the three portioned samples already analyzed in pyrolysis GCMS, an internal SAM blank run was carried out with an empty quartz cup. This blank analysis was required to understand the background signal intrinsic to the GCMS response of the SAM experiment. The identification of the compounds present in the background and the understanding of their origin are necessary to perform quantitative analysis and to aid the interpretation of the solid sample results.

Methods

The GCMS blank was generated as the first Martian GCMS analysis, prior to the delivery of any solid sample into SAM.

The quartz cup underwent the same treatment than for the subsequent solid sample experiments, with a first preconditioning followed by an exposition towards SAM inlets, and was then sealed into the pyrolysis oven and heated to ~840ºC at a rate of 35ºC/min in 1 sccm He flow. A fraction of the evolved gases corresponding to a temperature cut of 146-532ºC (cup temperature) was sent to the hydrocarbon trap (containing glass beads, Tenax TA and Carbosieve G) for the subsequent analysis in GCMS. Compounds were separated on the MXT-CLP column (30 m x 0.25 mm I.D.) set at an initial temperature of 50°C followed by heating to 220°C at a 10°C/min rate.

Results and Discussion

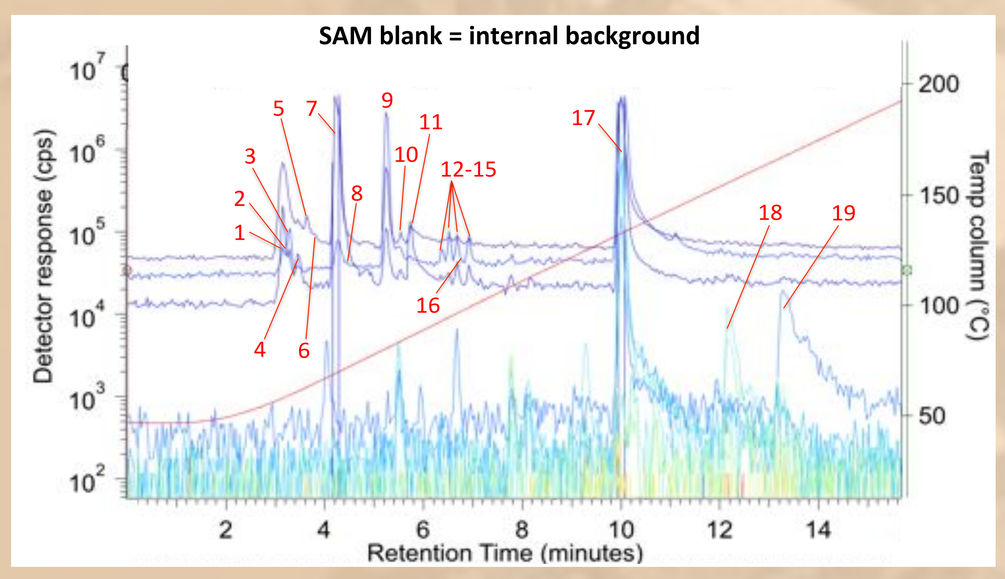

Fig 1. blank GCMS analysis. The chromatogram displays bands of masses (sum of specific range of m/z): the top ones are low molecular masses bands (m/z 45-86) and the bottom ones high molecular masses bands (m/z 87-535). The red line plots the GC column temperature.

The chromatogram displays whatever is present and volatilized in the sample manipulation system (SMS), transfer lines (heated to 135ºC), valves, hydrocarbon trap, injection trap and capillary column. GCMS signal can result from the volatilization of any molecule present in the path, or be a result of a reaction between internal components in SAM. The blank corresponds to the background level of the internal SAM gas flow path at a given time. It has to be taken as a reference, and a signal will be defined as any molecule above the background.

Table 1. Compounds forming SAM background, their correspondance on the chromatogram (Fig. 1) and their possible origin

Major species	#	Possible origin	Minor species	#	Possible origin
CO, CO_2, H_2O	1	Atmosphere/ trapped	Methylpropene, formaldehyde	2	MTBSTFA, DMF
SO_2	2	Trapped	Fluoromethylsilanes	1,3,6	MTBSTFA
Cyclopentene, pentadiene	4	Trap(s)	HCN	3	MTBSTFA/DMF
Acetone	5	MTBSTFA/DMF	Acetonitrile	6	MTBSTFA/DMF
Benzene	7	Tenax/Trap(s)	TBDMS-F	8	MTBSTFA
Toluene	9	Tenax/Trap(s)	Column bleeding	10	GC columns
Trifluoro-N-methylacetamide	10	MTBSTFA	TBDMS-phenol	16	MTBSTFA + Tenax
Monosilylated water	11	MTBSTFA	Trimethylsilylborate	18	MTBSTFA + glass beads
Ethylbenzene, xylene, phenylethyne, styrene	12-15	Tenax	Biphenyl	19	Tenax
Bisilylated water	17	MTBSTFA			

The presence of such a background has numerous implications for a solid sample analysis: making uncertain a Martian organic detection, quantification interferences, overlapping of background peaks with traces amount of organics, cross-reactions.

-> need to understand the origin of the internal background

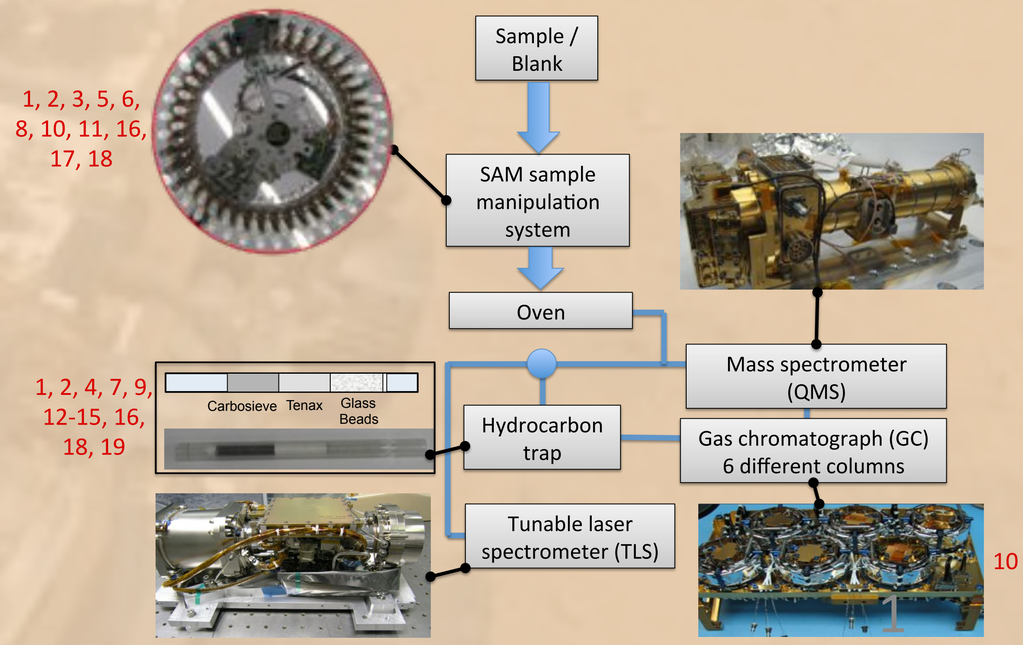

Fig 2. SAM suite of instruments; MS, GC, TLS. Possible sources of background compounds detected are displayed

The trap(s) composites are a major part of SAM internal background. Other major contributors to the background signal are the reaction products of one of the chemicals used for SAM wet chemistry experiment: N-methyl-N-tert-butyldimethylsilyl-trifluoroacetamide (MTBSTFA) [2]. This molecule was sealed inside each of the seven derivatization cups present in the SMS. Any MTBSTFA would readily react with the water present to form byproducts (Fig. 3), which were identified in the GCMS blank by their mass spectra.

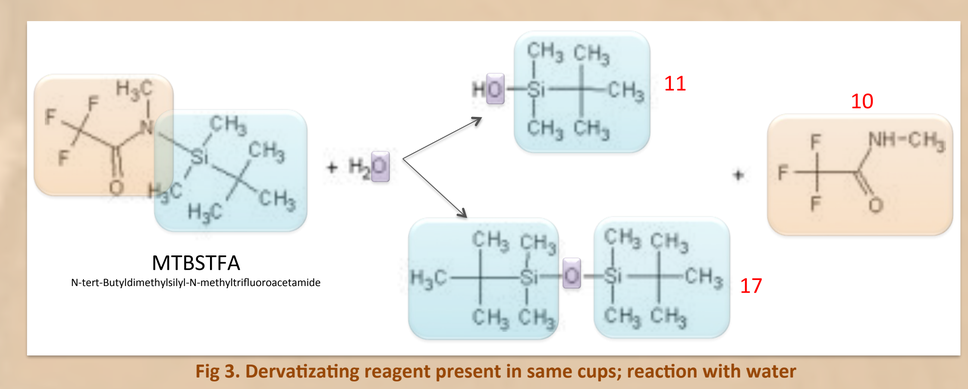

Fig 3. Dervatizating reagent present in same cups; reaction with water

The abundance of MTBSTFA has been quantified and its contribution to the background is determined to be in the nmoles level. Lowering the effect of background in general, and MTBSTFA in particular, would significantly improve the signal to noise ratio, and strategies are under investigation in this purpose.

The presence of reactive species in the background can create newly formed products by interaction with suspected Martian molecules, for instance perchlorates. The chlorinated hydrocarbons [3, 4] and nitrates [5, 6] detected on the portioned samples from Rocknest scoop#5 are thus under deep investigation to identify any possible pathway of formation from MTBSTFA and perchlorates.

Before claiming detection of Martian molecules, it has to be ruled out that these compounds can not come from reaction with internal molecules. Laboratory experiments are performed under SAM-like conditions to understand the reaction products of molecules in the background with suspected molecules on Mars soil.

Conclusion

SAM internal background signal has been intensively studied from the first internal SAM blank. It led to the identification of ~20 molecules in the GCMS, and their origin are now well understood. This is an important process for the subsequent investigation of the organic molecules detected in the pyrolysis of the solid samples, to attest if they are from Martian origin or come from terrestrial carbon present in the system.

The compounds with the highest GCMS response come from SAM internal sources, such as thermal degradation from the traps and reaction products from MTBSTFA. This latter molecule might interact with molecules released from solid samples, which could complicate the interpretation of their origin. A complete understanding of the GCMS background is thus an essential first step to investigate an endemic signal in a Martian solid samples.

References

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Acknowledgements

Thanks to the SAM and MSL teams.
Thanks to the NASA Postdoctoral Program (NPP) for the financial support of my work and travel.

LPSC 2013 – The Woodlands, TX – Poster 1249