FROM BACKGROUND TO SIGNAL: CHALLENGES OF A SOLID SAMPLE ANALYSIS USING SAM GC-MS

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Introduction: amongst the Sample Analysis at Mars (SAM) experiment capabilities, 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. With this aim, it was run using analytical conditions similar to those used for the Rocknest samples. 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.

SAM blank analysis: the GCMS blank was generated as the first Martian GCMS analysis, prior to the delivery of any solid sample into SAM (Fig. 1).

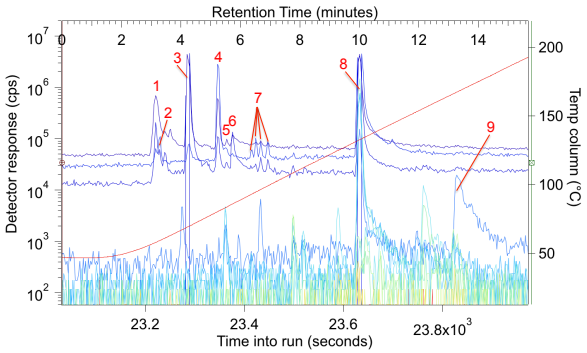

Figure 1: blank GCMS analysis. The chromatogram displays bands of masses (sum of specific range of m/z): the top ones correspond to low molecular masses bands (m/z 45-86) and the bottom ones high molecular masses bands (m/z 87-535). The red line plots the GC column temperature. Major peaks, 1: CO_2 H_2O, 2: SO_2, 3: benzene, 4: toluene, 5: trifluoro-N-methylacetamide, 6: monosilylated water, 7: branched aromatics, 9: bisilylated water, 9: methylsilylborate.

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.

Discussion:

Origin of background: 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. Thus, 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.

To track the origin of the background, it is necessary to determine first the nature of the compounds present on the chromatogram. An Igor tool [2] has been specifically developed to obtain the mass spectrum of an integrated peak. This mass spectrum can then be matched against the NIST library to identify potential candidates and determine the degree of confidence in the identification. The identification of the background is made easier on the chromatogram, as by its intrinsic purpose, the GC separates the complex mix of molecules into discrete ones. However, looking at the background signal in the Evolved Gas Analysis (EGA) mode (*i.e.* pyrolysis-QMS analysis) also helps assigning the origin of few molecules. Thus, aromatic compounds such as benzene and toluene, which are present in the GCMS blank signal but do not display a peak in the EGA, are likely to come from the traps and are suspected to be released from the Tenax TA. Aromatics such as ethylbenzene and xylene are suspected to be present in the blank signal, with no clear evidence about their origin. Other molecules present in the blank are H_2O, CO_2 and SO_2, internal to the system. Also, column bleeding products are observed, resulting from the thermal degradation of the internal polysiloxane phase of the column.

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) [3]. This molecule was sealed inside each of the seven derivatization cups present in the SMS. Although none of them have been punctured yet for the actual wet chemistry experiment, it is suspected that one or more may be releasing some of its reactant. Any MTBSTFA present inside the SMS would readily react with the water present to form monosilylated water, bisilylated water and a trifluoro-N-acetamide byproduct (Fig. 2). Those 3 compounds were identified in the GCMS blank by their mass spectra.

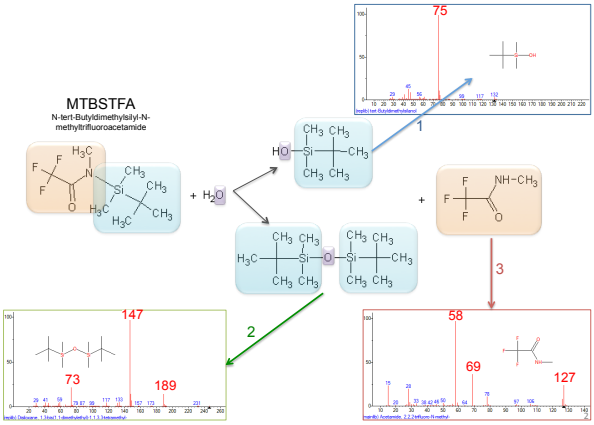

Figure 2: reactive pathways of the MTBSTFA with water to form products of monosilylated water (1), bisilylated water (2) and a trifluoro-N-methylacetamide byproduct (3), potentially at the origin of signals observed in the background.

Major peaks have been identified, however, work is still ongoing to characterize all the ~30 peaks observed in the GCMS background and understand their origin. 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.

Background quantification and signal limit of detection: the presence of such a background has numerous implications for the solid sample analysis: (1) It can make uncertain any detection of a compound also present in the background and make difficult to confirm a detection of a molecule present at a concentration lower than the background level. The quantification of these molecules is thus necessary to determine the limit of detection of organics in the solid samples above background. (2) It interferes with the analysis of trace levels of molecules, by overlapping peaks. Thus, 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 (cold sample drop off, He flush of the SMS, low temperature sample heating prior to higher temperature EGA analysis). (3) The presence of reactive species in the background can create newly formed products by interaction with suspected Martian molecules, for instance perchlorates. Before claiming detection of Martian molecules, it has to be ruled out that these compounds can not come from reaction with internal molecules. For this reason, laboratory experiments are performed under SAM-like conditions to understand the reaction products of molecules in the background with suspected molecules on Mars soil. The chlorinated hydrocarbons [4, 5] and nitrates [6, 7] 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. (4) Residual molecules in SAM can also contribute to combustion into CO_2 and have a role in the isotope ratio changes [8, 9, 10]. For all these reasons, the initial abundance of MTBSTFA has been extrapolated and its contribution to the total background is determined to be from 30 to 55 nmoles.

Moreover, another contributor to the background signal could be the scoop to CHIMRA sampling chain, which the Rocknest sample went through before being delivered to SAM (not used in the blank run). However, intensive cleaning and monitoring of sampling chain makes this possible source of organics to SAM for the first delivery unlikely [5, 11].

Conclusion: SAM background signal has been intensively studied from the first internal SAM blank. It led to the detection of ~30 peaks in the GCMS. 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. By quantifying the background and determining its precise origin, it helps finding ways to lower it to better extract the signal and identify the peaks of interest. A complete understanding of the GCMS background is thus an essential first step to investigate an endemic signal in a Martian solid samples.

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