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

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Introduction

The Sample Analysis at Mars (SAM) experiment holds numerous capabilities. Amongst 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 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 chemical components of the gases evolved from a solid sample, either processed by heat in pyrolysis or by chemical reactant in wet chemistry \([1]\).

The chromatogram displays whatever is present and volatilized in the sample manipulation system (SMS), transfer lines (heated to 135°C), 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.

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 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

Results and Discussion

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 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-butyl(dimethyl)silyl trifluoroacetamide (MTBSTFA) \([2]\). This molecule was sealed inside each of the seven derivatization cups present in the SAM. 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.

The abundance of MTBSTFA has been quantified and its contribution to the background is determined to be in the nMolale 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\(\#3\) 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.

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

<table>
<thead>
<tr>
<th>Major species</th>
<th>Possible origin</th>
<th>Minor species</th>
<th>Possible origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, CO(_2), H(_2)</td>
<td>Atmosphere/ trapped</td>
<td>Methylpropane, formicdehyde</td>
<td>MTBSTFA, DMF</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>Trapped</td>
<td>Methyltrimethylsilane</td>
<td>MTBSTFA</td>
</tr>
<tr>
<td>Cyclopentene, pentadiene</td>
<td>Traps(s)</td>
<td>SCN</td>
<td>MTBSTFA, DMF</td>
</tr>
<tr>
<td>Acetone</td>
<td>MTBSTFA, DMF</td>
<td>Acetonitrile</td>
<td>MTBSTFA, DMF</td>
</tr>
<tr>
<td>Benzene</td>
<td>Tenax/Traps(s)</td>
<td>EDTA-F</td>
<td>MTBSTFA</td>
</tr>
<tr>
<td>Toluene</td>
<td>Tenax/Traps(s)</td>
<td>Column bleeding</td>
<td>GC columns</td>
</tr>
<tr>
<td>Trifluoro-6-methylacetamide</td>
<td>MTBSTFA</td>
<td>FTMSA-phenol</td>
<td>MTBSTFA + Tenax</td>
</tr>
<tr>
<td>Monosilylated water</td>
<td>MTBSTFA</td>
<td>Tetramethyssilicate</td>
<td>MTBSTFA + glass beads</td>
</tr>
<tr>
<td>Dibutyranes, xylene, phenylethynyl, xylene</td>
<td>12-15 C</td>
<td>Diphenyl</td>
<td>Tenax</td>
</tr>
<tr>
<td>Bisilylated water</td>
<td>MTBSTFA</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

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Conclusion

SAM internal background signal has been intensively studied from the first internal SAM blank. It led to the identification of \(\approx 20\) 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 complicates the interpretation of their origin. A complete understanding of the GCMS background is thus an essential first step to investigate an endemnic signal in a Martian solid samples.

References

\([2]\) Buch, A. et al. (2013) this meeting.
\([3]\) Glavín, D. et al. (2013), this meeting. \([4]\) Eigenbrode, J. et al. (2013), this meeting.
\([5]\) Wray, J. et al. (2013), this meeting. \([6]\) Navarro-Gonzales, R. et al. (2013), this meeting.

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