Potential Sources of Artifacts and Backgrounds Generated by the Sample Preparation of SAM

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POTENTIAL SOURCES OF ARTIFACTS AND BACKGROUNDS GENERATED BY THE SAMPLE PREPARATION OF SAM. A. Buch[1], I. Belmahdi[1], C. Szopa[2], C. Freissinet[4], D. Glavin[4], P. Coll[3], M. Cabane[2], M. Millan[2], J. Eigenbrode[4], R. Navarro-Gonzalez[5], J.C. Stern[4], V. Pinnick[4], D. Coscia[2], S. Teinturier[2], M. Morisson[1], M. Stambouli[1], T. Dequaire[3], P. Mahaffy[4] and the MSL Science Team. [1]Ecole Centrale Paris, LGPM, Grande voie des vignes, 92295 Châtenay-Malabry, France, [3]LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, [4]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, [2]NASA Goddard Space Flight Center, 8800 Greenbelt Rd, Greenbelt, MD 20771, [5]Universidad Nacional Autónoma de México, México, D.F. 04510.

Introduction: *Sample Analysis at Mars (SAM)* is one of the instruments of the MSL mission. Three analytical devices are onboard SAM: the Tunable Laser Spectrometer (TLS), the Gas Chromatography (GC) and the Mass Spectrometer (MS). To adapt the nature of a sample to the analytical devices used, a sample preparation and gas processing system implemented with (a) a pyrolysis system, (b) wet chemistry: MTBSTFA and TMAH (c) the hydrocarbon trap (silica beads, Tenax® TA and Carbosieve G) and the injection trap (Tenax® GR composed of Tenax® TA and 30% of graphite) are employed to concentrate volatiles released from the sample prior to GC-MS analysis [1].

This study investigates several propositions for chlorinated hydrocarbon formation detected in the SAM background by looking for: (a) all products coming from the interaction of Tenax® and perchlorates, (b) also between some soil sample and perchlorates and (c) sources of chlorinated hydrocarbon precursors. Here we report on the detection of chlorohydrocarbon compounds and their potential origin.

SAM Results: Volatile compounds and abundant chlorinated hydrocarbons have been detected with SAM when analyzing samples collected in several sites explored by Curiosity rover [2–4]. Majority of the volatile compound come from the degradation of the MTBSTFA under hight temperature. Some of the chlorohydrocarbon compounds are produced during pyrolysis by the reaction of Martian oxychlorine compounds (perchlorate (ClO_4^-) or chlorate (ClO_3^-)) in the samples with terrestrial carbon from a derivatization agent (MTBSTFA) used in SAM [2].

Chlorobenzene cannot be formed by the reaction of MTBSTFA and perchlorates [2] and two other reaction pathways for chlorobenzene were therefore proposed : *(1)* reactions between the volatile thermal degradation products of perchlorates (e.g. O_2, Cl_2 and HCl) and Tenax® (see figure 1) and *(2)* the interaction of permingchlorates (T>200°C) with OM from Mars's soil such as benzenecarboxylates [5]. The oxychlorine compound in Sheepbed starts releasing O_2 at temperatures around 200°C, the same temperature where we also see evidence of masses (e.g. 78, 112) in EGA consistent with aromatic hydrocarbons being released from the samples.

By Product From Thermal Degradation of Tenax®: Tenax® GR has been heated at different temperature from 200°C to 600°C. Released organic compounds has been monitored by GC-MS by using a Restek column RTX5SilMS (30mX0.25mmX0.25µm). At 300°C and under, no aromatic compounds have been formed by the thermal degradation of Tenax.

At 350°C a large range of aromatic compounds produced by Tenax® GR (benzene, phenyl, biphenyl, terphenyl derivatives and others) have been identified. After 400°C, among the other compounds already detected, phenylethyne is identified.

However in SAM experiment, trap is heated at 300°C [1] and released some by-products at this temperature. Indeed, benzene, toluene, phenylethyne, styrene, biphenyl and chlorobenzene have been detected by SAM GC-MS [2]. Presence of perchlorate in the martian soil has to be taken in account to explain that production.

Influence of the Martian Perchlorate: To simulate the SAM experiment, perchlorate ($Ca(ClO_4)_2 \rightarrow HCl$, Cl_2 , O_2) [2] have been heated, in our laboratory built reactor, separately from the Tenax® GR, which is located in the injector. Results show that perchlorates have an impact on the degradation of Tenax® GR. We have detected a large range of aromatic compounds: thermal degradation products, chlorinated and oxidized compounds *(Figure 1)*. Benzene and chlorobenzene have been formed by the thermal degradation of Tenax® at 300°C in presence of perchlorate. At 400°C, in addition of benzene and chlorobenzene, toluene, phenylethyne, styrene and biphenyl are formed by the interaction of Tenax® GR and perchlorate.

Whatever the temperature, the addition of $Ca(ClO_4)_2$ raise the quantity of hydrocarbon products until 18mg ($CaClO_4$). Then, the amount of hydrocarbon products decrease as they are degraded, chlorinated or oxidized.

We have also proved that the increase of the amount of chlorobenzene CBZ formed is related to the increase of the temperature.

Quantity of CBZ released is directly correlated with the quantity of $Ca(ClO_4)_2$. More we have perchlorate more the quantity of CBZ is importante.

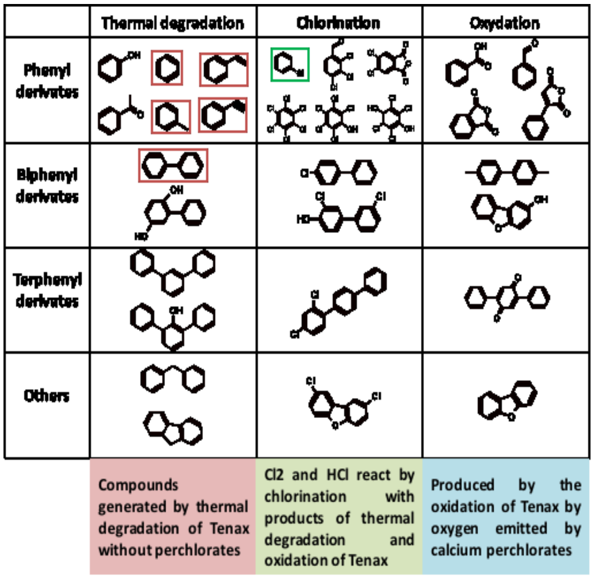

Figure 1 –summary of the species detected in lab in SAM condition in presence or in absence of perchlorate.

Nevertheless it is important to note that on SAM the quantity of CBZ produced by Tenax is still inferior at the quantity detected on Mars.

Conclusions: From Tenax® GR thermal degradation, we observe a production of benzene, toluene, styrene and biphenyl below 350°C and phenylethyne below 450°C. Within the range of temperature studied we have observed no impact of the derivatization agents (MTBSTFA/DMF) on the Tenax® GR by thermal degradation. But in the presence of calcium perchlorates production of benzene and chlorobenzene have been detected at 300°C after interaction with Tenax® GR. Chlorobenzene produced by this way take part of the SAM backround but does not explain the presence of CBZ detected on the Martian soil. Other process which imply oxychlorine and indigenous compounds can explain the CBZ formation [6].

The absence of detection of other aromatic compounds detected in SAM background at 300°C could be explained by the presence of other minerals (such as iron oxides) in Martian soil which are able to facilitate the release O_2 (e.g. hematite).

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