

IMPACT OF THE SAMPLE PREPARATION ON THE ORGANIC COMPOUNDS DETECTED ON MARS AT JK AND CB

A. Buch¹, C. Szopa², C. Freissinet³, D. P. Glavin³, P. Coll⁴, M. Cabane², J. Eigenbrode³, K. Miller⁵, M. Martin³, R. E. Summons⁵, D. Archer⁶, A. Brunner³, P. Conrad³, S. Teinturier², D. Coscia², J. Dworkin³, J. Grotzinger⁷, P. Mahaffy³, C. McKay⁸, D. Ming⁹, R. Navarro-González¹⁰, and the MSL Science Team. ¹Ecole Centrale Paris, 92295 Chatenay-Malabry, France (arnaud.buch@ecp.fr), ²LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, France, ³NASA GSFC, Greenbelt, MD 20771, ⁴LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, France, ⁵Massachusetts Institute of Technology, Cambridge, MA 02139, ⁶Catholic University of America, Washington DC 20064, ⁷Caltech Institute of Technology, Pasadena, CA 91125, ⁸NASA Ames Research Center, Moffett Field, CA 94035, ⁹NASA Johnson Space Center, Houston TX 77058, ¹⁰Universidad Nacional Autónoma de México, Mexico.

Introduction: The wet chemistry experiment on the Sample Analysis at Mars (SAM) experiment in the Curiosity rover of the Mars Science Laboratory mission allows organic compounds to be extracted from solid samples in such a way to improve their detection either by increasing the release of chemical species from solid sample matrices, or by changing their chemical structure to make compounds analyzable by gas chromatography mass spectrometry (GCMS). The latter is of particular importance if polar compounds are present. SAM, includes two different wet chemistry experiments: MTBSTFA derivatization [1-2] and TMAH thermochemolysis [3-4]. Here we report on the nature of the MTBSTFA derivatization experiment on SAM, the detection of MTBSTFA products in the SAM evolved gas analysis and GCMS experiments, and the implications of this detection.

Sample Processing and SAM Protocol: The soil or powdered rock sample is heated up to ~1000°C in one of the two pyrolysis ovens in SAM. The gases released from the sample, within a predefined temperature range, are pre-concentrated in a SAM hydrocarbon trap and then transferred to a GC injection trap for a final injection into the GC. Adsorbants used in the SAM and GC hydrocarbon trap are Tenax® (TA) silica beads and Carbosieve G. The GC injection trap contains Tenax GR. Trapped volatiles are released from these traps by heating to ~300 °C. Special cells containing the derivatization reagent can be utilized if needed. The chemical extraction and derivatization of polar molecular compounds is achieved with the MTBSTFA (*N*-methyl-*N*-*tert*-butyldimethylsilyltrifluoroacetamide) and DMF (dimethylformamide) silylation reaction in order to transform refractory polar compounds into more volatile molecules that can be analyzed and detected by GCMS. 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 common derivatization 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 MTBSTFA are typically in the 90–100% range. Finally, MTBSTFA has the major advantage to react in the gaseous phase and is therefore compatible with laboratory pyrolysis systems like the one used in SAM to treat the solid samples.

SAM solid sample experiment results: Martian solid samples (Rocknest (RN), John Klein (JK), Cumberland (CB)) have been analyzed by evolved gas analysis (EGA) and GC using thermal conductivity (TCD) and MS detection [5-6]. The samples were heated up to approximately 840 °C at a rate of 35°C/min under He flow. For GC analyses, the majority of the gas released was trapped on a hydrocarbon trap over a specific temperature range. Adsorbed volatiles on the GC injection trap (IT) were then released into the GC column (CLP-MXT 30m x 0.25mm x 0.25µm) by rapidly heating the IT to 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 from Rocknest showed the presence of MTBSTFA by-products in the system. MTBSTFA was detected in the GC-TCD-QMS analysis blank 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, the detection of the hydrolysis products of MTBSTFA implies that some MTBSTFA reactions with all the labile compounds present in the Martian soil, in the sampling system, and/or inside the SAM instrument occurred during the experiment.

Several peaks have been identified by GCMS analysis of JK and CB as part of SAM background, some of them below the nmol level. Identification of these peaks reveal the presence of several aromatic, chlorinated hydrocarbons (Table 1) and silylated compounds such as water. The most interesting of these compounds are listed in Table 1. The question of the endogenous or exogenous origins of these compounds has to be asked. To answer it we have investigated several possibilities to produce these chlorinated hy-

drocarbons during the SAM experiment. They could come from : i) sample itself ii) MTBSTFA reaction iii) Tenax® degradation, and iv) Perchlorate oxidation.

SAM experiment lab: A first set of laboratory tests were done to evaluate the thermal stability of Tenax® GR and the possible products released. followed by tests with Tenax® that was exposed to MTBSTFA during the thermal test. The Tenax® sample was successively submitted to thermal treatments from 200°C to 600°C with 50°C steps. Each temperature was held for 5 minutes, then the liner was cooled down to 50°C during the rest of the run. Operating conditions are summarized in Figure 1.

GC-MS analytical conditons			
10 mg Tenax®	Injector Optic 4		0.5 µg perchlorate de calcium
	Temperature	200 to 600°C Held 5min - Steps 50°C	
	Helium flow	1ml/min	
10 mg Tenax® + 0.5 µL MTBSTFA	Mode	Splitless	0.5 µg perchlorate de calcium
	Split	20ml/min	
	Temperature	200 to 600°C Held 5min - Steps 50°C	
10 mg Tenax® + 0.5 µL MTBSTFA/DMF (3:1)	Gas chromatography Thermo Scientific Trace GC Ultra		0.5 µg perchlorate de calcium
	Column	Restek Rtx-20 (30m longueur; 0.25mm ID; 0.25µm df)	
	Oven temperature	35°C 5 min 10°C/min up to 300°C 300°C 5 min	

Figure 1. Operating conditions

Tenax® degradation results: Thermal degradation of Tenax® starts at 400°C. Detected compounds are mainly aromatic compounds such as benzene, biphenyl, or phenol (Figure 3 and Table 2). Indeed, Tenax® is an organic polymer and the detected compounds are coming from the thermal degradation of this polymer.

The structure of the Tenax® polymer (Figure 4) explains why aromatic compounds are detected during its thermal degradation. The main compound detected (fig. 4) is the terphenyl which is a part of the monomer of Tenax®. Other reactive compounds such as phenol or hydroxy-biphenyl are also directly generated from this monomer degradation.

Table 1.

Compounds generated by Tenax® degradation in lab experiment compared to compounds detected on Mars (J. Klein and Cumberland).

Compounds	Lab T (°C)	SAM blank	SAM sample (JK and CB)
H ₂ O	-	+	++
Benzene	300-600	+	++
Toluene	550-600	+	+
Ethylbenzene	550-600	+	+
Styrene	550-600	+	+
α-methylstyrene	600	-	-
Phenol	550-600	-	-
Naphtalène	550-600	+	+
Biphenyl	450-600	+	+
Diphenylmethane	500-600	-	-
p-methylbiphenyl	500-600	-	-
Hydroxybiphenyl	450-600	-	-
p-terphenyl	500-600	-	-
m-terphenyl-2'-ol	400-450	-	-
Quaterphenyl	600	-	-

Chlorobenzene	ND	+	++
---------------	----	---	----

At higher temperatures, the number of released compounds increases and the size of the released molecules decreases. The temperature range studied far exceeds the maximum temperature reached by the SAM trap which stays below 300°C Under these conditions only a few organic compounds should be released such as benzene. But the continuous use of the GC trap could generate a long term ageing of Tenax® resulting in the potential release of additional compounds. Among these compounds some of them could be reactive and give other by product when contacted with MTBSTFA or perchlorate.

Tenax® degradation results in presence of MTBSTFA: With MTBSTFA a part of the background signal, it could possibly interact either with martian organics or compounds produced by the thermal degradation of the trap. This is why we have studied the influence of the MTBSTFA on the compounds released from the Tenax®. During the thermal degradation of Tenax®, we have added a few microliters of MTBSTFA (0.5µL of MTBSTFA for 10 g of Tenax®). Results of adding MTBSTFA show that no derivatization reaction occurred on compounds with labile H. We have shown that phenol was one of the compounds released by Tenax® when temperature reached 550°C. But contrary to the results of the SAM experiment (table 1), after MTBSTFA addition, no TBDMS-phenol was detected at the retention time of 36 min against 16.7 min for phenol. The explanation is certainly the shorter time of contact since the laboratory derivatization reactions requires 15 min at 75°C.

Conclusion: We have confirm the presence of MTBSTFA by-products in the EGA and GC-TCD-MS background signals.

Major part of aromatic detected compounds on mars could be generate from the degradation of the Tenax® trap or from the MTBSTFA reaction.

the possible range of products that might be produced by the SAM background and the Tenax trap are being elucidated by laboratory studies and it will help clarify which of the compounds observed by SAM are indigenous.

References: [1] Buch, A. et al. (2009) J chrom. A, 43, 143-151. [2] Stalport, F. et al. (2012) Planet. Space Sci. 67: 1-13 [3] Geffroy-Rodier, C. et al. (2009) JAAP, 85, 454-459. [4] Eigenbrode et al. (2011) LPS LXXIII, abstract 1460. [5] Glavin, D., A. et al. (2013), LPSC. [6] Eigenbrode, J. et al. (2013), LPSC. [7] Freissinet, C. et al. (2013) LPPSC.[8] Navarro-Gonzalez, (2010), JGR, 115.

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