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► To cite this version:

Maeva Millan, Cyril Szopa, A. Buch, D. Glavin, C. Freissinet, et al.. In situ analysis of Mars soil and rocks samples with the SAM experiment: laboratory measurements supporting treatment and interpretation of the detection of organics. European Planetary Science Congress 2015, Sep 2015, Nantes, France. pp.EPSC2015-305. insu-01213124

HAL Id: insu-01213124

<https://hal-insu.archives-ouvertes.fr/insu-01213124>

Submitted on 7 Oct 2015

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***In situ* analysis of Mars soil and rocks samples with the SAM experiment: laboratory measurements supporting treatment and interpretation of the detection of organics**

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Abstract

The Sample Analysis at Mars (SAM) experiment onboard the Curiosity rover detected numerous organic compounds when analyzing the solid samples collected on the way to Mount Sharp. But MTBSTFA, the chemical reactant for the chemical treatment of the refractory molecules present in the solid samples and present in cups of SAM, was shown to be unfortunately present in the Sample Manipulation System (SMS). During the sample analysis, this chemical species reacts with the organic and inorganic molecules present in the samples. This reaction leads to the production and subsequent detection of numerous MTBSTFA derivatives which makes the treatment and the interpretation of the SAM data complex. Moreover, for the first time on Mars, the wet chemistry method was used on a Cumberland sample to help the GC separation and the MS identification of non volatile compounds. To ensure the identification of the organic molecules and try to discriminate organics generated internally to SAM from those present in the samples analyzed, it is mandatory to perform laboratory experimental calibrations under martian operating conditions.

1. Introduction

The rover Curiosity of the Mars Science Laboratory (MSL) mission, landed on Mars the August 6th of 2012 at Gale crater to provide clues of its past and/or present habitability. The SAM experiment is partly devoted to the in situ molecular analysis of gases evolving from solid samples collected by the rover on Mars surface/sub-surface. SAM is composed of a pyrolysis oven coupled to a gas-chromatograph mass spectrometer (GC-QMS) [1]. The GC-QMS is dedicated to the separation and the identification of organic and inorganic material evolved from the

samples by the derivatization method. The GC is especially devoted to the separation of organic molecules. A thermal conductivity detector (TCD) and a quadrupole mass spectrometer (QMS) allow the detection and identification of the molecules (Figure 1). The GC analytical channel which has been used to do almost all the measurements of the martian samples to date is composed of a MXT-CLP chromatographic column coupled with a Tenax GR thermal desorption trap.

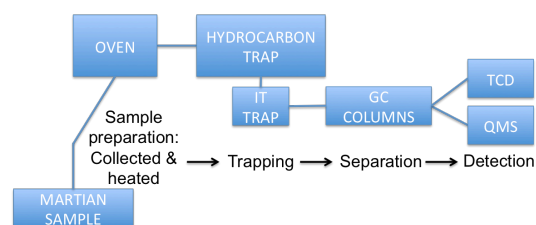


Figure 1: simplified analytical channel from samples collection to the detection and the identification of the organic molecules.

During the 900 first sols, Curiosity collected one sand sample at the Rocknest site, two rock samples at the Yellowknife Bay site (John Klein and Cumberland) and one rock sample at the Pahrump Hills site (Confidence Hills). They have been successfully analysed by the SAM experiment and provided an extended set of data. The chemical reactant carried within SAM and used for derivatization on the Cumberland sample is the *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA). It is present into seven of the SMS cups but is known to be leaking from cups, so its amount has been maximized to react with the molecules present in the Cumberland solid sample. To support the treatment and the interpretation of the data provided by the SAM instrument, it is of primary importance to perform laboratory experiments using SAM like apparatus and the same

sample wet chemistry treatment under simulated martian operating conditions.

2. SAM GCMS data treatment: comparison of organic molecules retention times between laboratory experiments and FM data

Organic compounds, mostly chlorinated, have been clearly detected by SAM [2]. Indeed, chlorobenzene and 3 chlorinated alkanes have been shown to be indigenous to Mars [6]. Thanks to laboratory experiments, it is known that chlorohydrocarbons are also produced by the reaction of perchlorates, globally distributed in Martian soil [2,4], with organic matter, during the pyrolysis. This organic matter can be present in the experiment and some chlorinated compounds have been identified as reaction products of the MTBSTFA and/or the Tenax TA porous polymer adsorbent used to concentrate organic molecules on the SAM hydrocarbon traps. The last GC-MS analysis: the opportunistic derivatization (OD) consisted in the application of the chemical reagent, the MTBSTFA, to the Cumberland solid sample. It reacts with polar organic molecules containing a labile hydrogen atom, to improve their volatilisation and their separation and detection by the SAM GCMS system. In the SAM chromatogram of the OD analysis, several chromatographic peaks were interpreted, thanks to the identification by the mass spectrometer, as long chains of alcohols and/or carboxylic acid derivatized. The aim of this work is to discuss the organic molecules detections done by SAM and to predict the relevant retention times. For laboratory experiments, a GC-MS apparatus including a SAM-like MXT CLP capillary column was used. A 20 cm capillary tube was coupled to the column to reproduce the carrier gas flow of the SAM experiment. A set of organic compounds, identified with MS or potentially present in SAM chromatograms, have been selected for this study.

3. Results

The laboratory studies using the GC5 spare column under martian operating conditions allowed to remove ambiguities on the identification of the organic components detected by SAM (Figure 2). It also allowed to disprove the presence of derivatized alcohols and carboxylic acids, suspected to be present in the OD analysis using the chemical

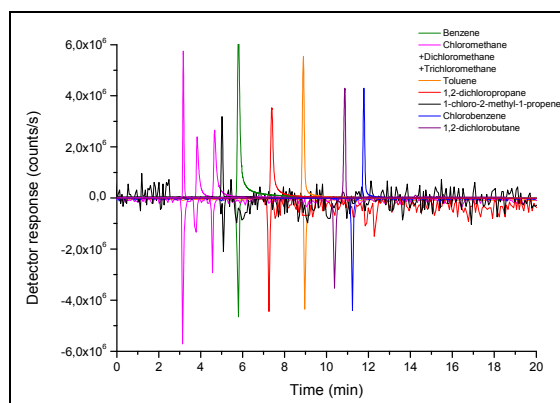


Figure 2: GC-MS analysis of organic compounds detected by SAM: comparison between the laboratory gas chromatogram and the reconstructed ion chromatogram.

<i>Column</i>	<i>Laboratory</i>	<i>SAM</i>
Suspected compounds	T_R (min)	T_R (min)
Carboxylic Acid	28	14.31
1-undecanol	26.7	17.15

Table 1: Example of suspected organic components disconfirmed by GC-MS laboratory analysis.

4. Summary and conclusions

The SAM experiment is a powerful tool to detect, separate and identify the organics on Mars. The retention times obtained in laboratory martian operating conditions, with those obtained in SAM chromatograms, is a strong method to strictly identify the molecules present in Mars surface/sub-surface solid samples, when the QMS signature is not sufficiently clear. This work is still under progress to identify the molecules present in the last OD analysis, essentially to identify the molecules such the retention times has not been confirmed by the laboratory measurements.

Acknowledgements

French Space Agency (CNES) support for SAM-GC development and exploitation.

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