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In situ analysis of martian regolith with the SAM experiment during the first mars year of the MSL mission: Identification of organic molecules by gas chromatography from laboratory measurements

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ABSTRACT

The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover, is specifically designed for *in situ* molecular and isotopic analyses of martian surface materials and atmosphere. It contributes to the Mars Science Laboratory (MSL) missions primary scientific goal to characterize the potential past, present or future habitability of Mars. In all of the analyses of solid samples delivered to SAM so far, chlorinated organic compounds have been detected above instrument background levels and identified by gas chromatography coupled to mass spectrometry (GC–MS) (Freissinet et al., 2015; Glavin et al., 2013). While some of these may originate from reactions between oxychlorines and terrestrial organic carbon present in the instrument background (Glavin et al., 2013), others have been demonstrated to originate from indigenous organic carbon present in samples (Freissinet et al., 2015).

We present here laboratory calibrations that focused on the analyses performed with the MXT-CLP GC column (SAM GC-5 channel) used for nearly all of the GC–MS analyses of the martian soil samples carried out with SAM to date. Complementary to the mass spectrometric data, gas chromatography allows us to separate and identify the species analyzable in a nominal SAM-GC run time of about 21 min. To characterize the analytical capabilities of this channel within the SAM Flight Model (FM) operating conditions on Mars, and their implications on the detection of organic matter, it is required to perform laboratory experimental tests and calibrations on spare model components. This work assesses the SAM flight GC-5 column efficiency, confirms the identification of the molecules based on their retention time, and enables a better understanding of the behavior of the SAM injection trap (IT) and its release of organic molecules. This work will enable further optimization of the SAM-GC runs for additional samples to be analyzed during the MSL mission.

1. Introduction

Current environmental conditions at the martian surface limits the presence of perennial liquid water. In the last 20 years of space exploration, there is growing evidence of past and/or contemporary liquid water activity, *e.g.* recurring slope lineae, flow

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tracks and hydrated minerals and salts (*e.g.* jarosite, perchlorate) which could have favored the emergence of life more than 4 billion years ago (Bibring et al., 2006; Carter et al., 2010; Klingelhofer et al., 2004; Ojha et al., 2015). Energy sources (radiation, internal heat) were also available in early martian history (Ehlmann et al., 2010; Werner, 2009). However, life as we know it requires another ingredient: organic molecules. Finding organic compounds will provide key information to help us understand martian habitability.

1.1. *Organic molecules on mars*

Sources of organic molecules at the martian surface can be of two main origins:

1. Organic compounds, constantly delivered by exogenous sources, such as meteorites, interplanetary dust particles (IDPs), comets and micrometeorites with an estimated flux of $\sim 2.4 \times 10^9$ g yr^{-1} (Flynn, 1996).
2. Organics formed through endogenous abiotic chemical processes such as ancient hydrothermal activity or atmospheric chemistry (Chyba and Sagan, 1992; Konn et al., 2009; Steele et al., 2012). Finally, organics on Mars could be produced by biological processes.

The Mars Exploration Program Analysis Group (Mars Exploration Program Analysis Group, 2015) is partly driven by the search for evidence of past life, through the presence of habitable environments and biosignatures. Since organic molecules play a key role for habitability, they are among the priority targets of Mars exploration. During the first *in situ* exploration of martian surface soil by the Viking landers in 1976, chlorohydrocarbons were detected with the GC–MS experiment. However, their presence was originally attributed to terrestrial contaminants in the Viking instruments (Biemann and Lavoie, 1979; Biemann et al., 1977). In 2008, the Phoenix lander showed that perchlorates (ClO_4^-) were present in the near surface in the martian polar region (Hecht et al., 2009). When perchlorates salts are rapidly heated (typically > 500 °C), they decompose into molecular oxygen and volatile chlorine bearing molecules such as HCl and Cl_2 (Navarro-Gonzalez et al., 2010). Thus, these decomposition products may oxidize and chlorinate organic chemical species and make their detection and identification more complex (Glavin et al., 2013; Steininger et al., 2012).

The first detection of martian organic molecules was reported after analyses of a drilled sample from a mudstone, called Cumberland, in Yellowknife Bay, done with the SAM experiment onboard the Curiosity rover. These analyses revealed the presence of chlorobenzene and dichloroalkanes (from C_2 to C_4 (Freissinet et al., 2015)) produced from the reaction of organic matter with oxichlorines both present in the Sheepbed mudstone.

The difficulty to detect indigenous organic molecules in the martian soil can be attributed to: (1) analytical capabilities of the instruments used for their analysis and instrument background, (2) the specific samples chosen for analysis, (3) unfavorable environmental conditions at the martian surface such as UV and ionizing radiation, or even oxidizing properties of the soil (Benner et al., 2000; Navarro-Gonzalez et al., 2006; Pavlov et al., 2012; Poch et al., 2013). This knowledge was taken into consideration for the MSL mission. It was partly developed to seek martian organic molecules in near surface and atmosphere.

The Curiosity rover landed on Mars in Gale Crater on 6 August 2012. The site was selected for its evidence of layered materials rich in clays and sulfates, signs of aqueous transformation in an ancient lake environment (Grotzinger et al., 2012, 2014). Curiosity has a robotic arm including a scoop and a drill to sample martian soil and rocks respectively, down to a few centimeters deep. Below the surface, the rocks may have been preserved from the harmful martian environmental conditions (alteration and oxidation), increasing the probability of finding organic molecules not altered by the surface environment.

One major objective of the SAM investigation is to search for organic compounds in the rocks and soils.

1.2. *The SAM GC–MS experiment and analyses at mars*

SAM is an analytical laboratory composed of a pyrolysis oven coupled to a gas-chromatograph quadrupole mass-spectrometer (GC–MS) and a tunable laser spectrometer (Mahaffy et al., 2012). Here we focus only on the GC–MS instrument which is devoted to the molecular analysis of organic and inorganic volatile chemical species either evolved from solid samples after their thermal (sample pyrolysis up to 850 °C) and/or chemical processing, or coming from the atmosphere. The GC is dedicated to separate and identify the organics after their detection by a thermal conductivity detector (TCD) and the MS.

The GC subsystem includes 6 different analytical channels, each one dedicated to analyze a specific range of volatile molecules, depending on their physical and chemical properties. To date, most of the GC measurements were implemented with the analytical channel GC-5, which includes an injection trap, a TCD, and an MXT-CLP© chromatographic column used to separate organic molecules containing 5 to 15 carbon atoms.

Before proceeding to a GC–MS analysis, the volatiles released

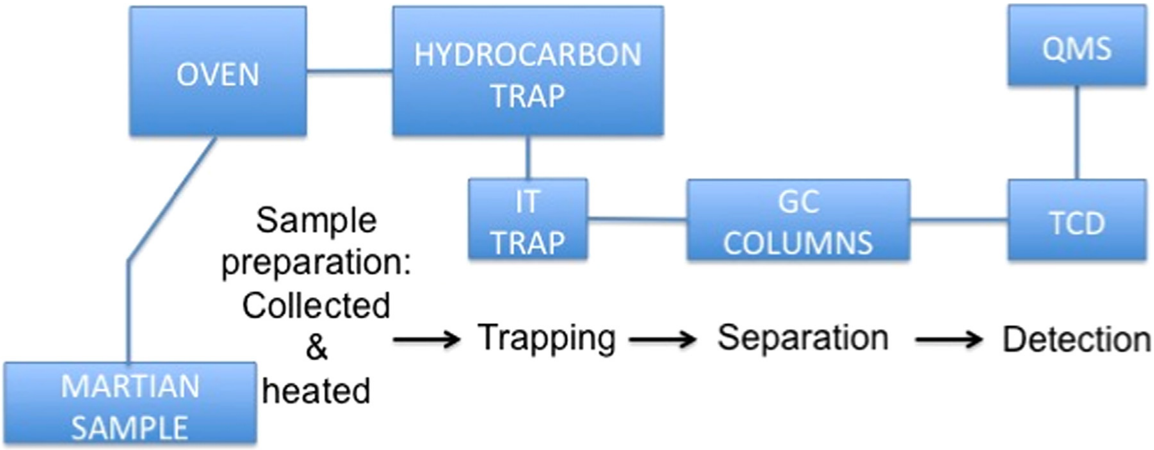

Fig. 1. Simplified analytical pathway of a volatile analyzed with the SAM GC–MS experiment on Mars. IT=Injection Trap, QMS=Quadrupole Mass Spectrometer.