

A laboratory pilot for in situ analysis of refractory organic matter in Martian soil by gas chromatography–mass spectrometry

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Received 21 December 2004; received in revised form 14 April 2005; accepted 5 May 2005

Abstract

The “Sample Analysis at Mars” project (SAM) is a multi purpose space experiment devoted to the in situ analysis of the Martian environment. It is designed to run multiple analyses on gas or solid samples, and eventually liquids, and is proposed to be part of the scientific payload of the future NASA Mars Science Laboratory 2009 (MSL 2009). One of its main objectives is to discover traces of a past or present life on the planet. Here is presented the laboratory pilot system for automated analysis of possibly refractory organic matter in Martian soil samples, which corresponds to a part of the Chemical Separation and Processing Laboratory of SAM experiment. It is a one-pot process performing, in a row, extraction, derivatization and transfer of the organic molecules to a gas chromatography–mass spectrometer for analysis. We have shown that such a system is able to detect 10 pmol of refractive material from a 100 mg sample of Atacama desert, which is a good Martian analogue for organics analysis. This pilot can handle and allow the analysis of a wide range of molecules, including carboxylic and amino acids, which are of utmost interest for the goal which is aimed. Further on, such a system is universal, and could be taken as a good start for any future in situ exploratory space mission.

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Keywords: Mars; In situ exploration; Exobiology; Extraction; Derivatization; GC–MS; On-line analysis; Micro-reactor; Sample analysis at Mars; MSL 2009

1. Introduction

The emergence of life, on Earth, or on other celestial bodies, is a question of a tremendous complexity (Davies, 1998; Horneck, 1995). On Earth, the first occurrence of solid minerals is 4.2 Gyr old (Froude et al., 1983), and of living system of 3.5 Gyr old for sure and maybe 3.8 Gyr (Schopf, 1993; Mojzsis et al., 1996). McKay (1996) hypothesis that life should have begun somewhere between those two points, maybe before. About 4.5–3.5 Gyr is finally suggested. But, from now,

we have no evidence of the origin of the prebiotic/biotic organic material on Earth; it could have been endogenous, exogenous or both (Chyba and Sagan, 1992). Too many events occurred on Earth since its formation and shielded the first organics traces and their evolution. To conclude, we still need more information to answer the great question of the origin of life.

One way to get through would be to look outside our planet. Could we find traces of organics on a comet, a meteorite or an other planet, as they are probably less altered from their original state than Earth is, it would give us information on the prebiotic/biotic material and on the occurrences that life is possible once the specific conditions of life emergence are gathered (Brack, 1996, 1997; McKay and Stoker, 1989). One of the best

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targets in solar system is Mars. Earth and Mars should have had a similar evolution during their first billion years. If so, Mars is a good candidate for having once developed life or a prebiotic state, since life on Earth could have started during this very period of time (McKay, 1996). So far, the only information on living presence on Mars which have been retrieved in situ came from the Viking life experiments in 1978. The results were ambiguous as they could be interpreted as possible living systems presence, but no organic signature with the GC–MS analysis was detected (Biemann et al., 1977). Knowing better the Martian environment now, it is most improbable that any life could survive on the surface of Mars. An explanation of these results is the detection limit of the GC–MS. Glavin et al. (2001) showed that pyrolysis of several millions cells in the Viking Martian sample would not have been detected by the GC–MS. An other one is the presence of strong oxidizing agents in the upper layer of the crust (hydrogen peroxide, superoxide, or other). Those agents degrade organics. So they should have been once on Mars, and might be still there, in oxidized state (Benner et al., 2000). And such molecules could not have been analyzed by Viking probes.

Today, Spatial Agencies are planning on new missions, taking into account that analysing techniques have tremendously evolved since 25 years. One of the next NASA Martian mission, scheduled in 2009, will be dedicated mostly to the research of life indicators. It will send a rover with the Mars Science Laboratory (MSL) package. The “Sample Analysis at Mars experiment” (SAM) is especially designed in that direction to gather a wide range of signatures, organic and inorganic, in order to identify a present or extinct life on Mars. This experiment might be launched as a part of scientific payload onboard the MSL 2009 mission. The whole system is described elsewhere (Cabane et al., 2004).

In this article, we present the work achieved on a laboratory breadboard to demonstrate the viability of the analytical method developed to analyze the organics possibly present in the Martian soil. As it turns out, any molecules to be found is interesting. It would have been too long to study every possibility. To make a first choice, we relied on workshops on one part (Westall et al., 2000), and on Benner’s hypothesis on Martian organics evolution on the other part (Benner et al., 2000). Therefore, we have focused our work on amino acids and carboxylic acids, which are both semi-volatile compounds.

To analyze such molecules within the spatial constraints (miniaturization, automation, low energy consumption) by gas chromatography (GC), derivatization techniques must be used. Derivatization is a chemical reaction that slightly modifies the target, keeping its structure so that one can deduce it from the derivative mass spectrum and increases the volatility (Rodier

et al., 2001a). Most of the time, it should be carried on in liquid phase, using multi-steps approach. So far, no derivatization has been used in space, even if some experiments have been designed to, like for the COmetary Sampling And Composition (COSAC) experiment of the Rosetta space mission launched in February 2004 (Rosenbauer et al., 1999). A single step derivatization process, which could provide ready-to-analyze products by gas chromatography (Rodier et al., 2001b) has been achieved. Using the *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) as silylation reagent, this process is space compatible and highly sensitive (sub-pb detection limit for some amino acids).

But before any derivatization, the target molecules must first be extracted from the Martian soil sample. Studies have been made on this topic, and permitted to select isopropanol as the best solvent for the extraction of amino and carboxylic acids together (Buch et al., 2003). Nevertheless, isopropanol does react with MTBSTFA. A complete evaporation of the extracting solvent has to be performed.

The objective of the work described in this paper is to develop a pilot which could perform in a single crucible (reactor), extraction, evaporation, derivatization and transfer of organic material included in a soil sample to a GC–MS within the in situ operating conditions.

2. Experimental

2.1. Instrumentation

2.1.1. Reactor

The reactor was designed with the following specifications: it should have an internal volume of 1.5 ml, an inlet and an outlet for gas, an inlet for liquid, tightly closed so that no gas exchange with the exterior could occur, and be heated and regulated in temperature. The pressure inside could be measured.

The resulting reactor is in two parts. The upper part includes all the connections (liquid, gas, pressure, heating cartridge). The lower one includes the crucible and the O-ring (see Fig. 1). It is convenient with preparative operation (sample filling and cleaning). Both pieces were realised in stainless steel and coated with Silcosteel by Restek Inc. (Restek Inc., Bellefonte, PA, USA) to lower the risks of interactions of derivatized molecules with the metallic surfaces, equipped with Valco 1/16” fitting (VICI AG, Shenkon, Switzerland) for in- and outlet port. The pressure gauge is a XTL-190M from Kulite (Kulite, Leonia, NJ, USA) and the heating system is composed of a heating cartridge (230VAC 75 W), controlled by a STATOP 4860 temperature regulator (Pyro-Contrôle, Vaulx-en-Velin, France), linked to a K-type thermocouple as temperature gauge for monitoring.

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