



***In situ* analysis of organic compounds on Mars by Gas Chromatography-Mass Spectrometry onboard ExoMars (MOMA).**

A. Buch (1), C. Freissinet (2), R. Sternberg (3), C. Szopa (4), P. Coll (3), V. Pinnick (5), S. Siljeström, F. Raulin (3) and the entire MOMA Team (7).
(1) LPGM, Ecole Centrale Paris, Chatenay-Malabry, France (arnaud.buch@ecp.fr), France (2) NASA GSFC, Greenbelt, MD, USA, (3) LISA, Univ. Paris-Est and Paris Diderot, Creteil, France, (4) LATMOS, Guyancourt, France, (5) School of Medicine, JHU, Baltimore, MD, USA, (6) SP Technical Research Institute of Sweden, Borås, Sweden, (7) Max Planck Institut für Sonnensystemforschung (MPS), Katlenburg-Lindau, Germany.

Abstract

With the aim to separate and detect organic compounds from Martian soil onboard ExoMars, we have developed three different space compatible sample preparation techniques able to extract and analyze a wide range of volatiles and refractory molecule with respect of their chirality by GC-MS.

1. Introduction

The search for signs of past or present life is one of the primary goals of the future Mars exploratory missions. With this aim, the Mars Organic Molecule Analyzer (MOMA) experiment of the ExoMars 2016-2018 upcoming joint ESA/NASA mission is designed to perform the *in situ* analysis of exobiological organic molecules in the Martian soil such as amino acids, carboxylic acids, nucleobases or polycyclic aromatic hydrocarbons (PAHs).

To search for "signs of life" molecules on the Martian surface and near subsurface, a GC-MS compatible sample processing system allowing the extraction and the chemical transformation of the organic compounds from the soil, within space compatible operating conditions, has been developed. The sample processing utilizing three derivatization/extraction reactions have been carried out. The first one is based on a silyl reagent N-Methyl-N-(Tert-Butyldimethylsilyl)trifluoroacetamide (MTBSTFA), the second one, N,N-Dimethylformamide Dimethylacetal (DMF-DMA) is dedicated to the chirality detection and the third one is a thermochemolysis based on the use of tetramethylammoniumhydroxide (TMAH).

2. Extraction/Derivatization

The Sample Processing System (SPS) is performed in an oven, dedicated to the MOMA experiment containing the solid sample (50-100mg). The internal temperature of which can be ranged from 20 to 900 °C. The extraction step is achieved by using thermodesorption in the range of 100 to 300°C for 5 to 20 min. Then, the chemical derivatization of the extracted compounds is performed directly on the soil by using a derivatization capsule which contains a mixture of MTBSTFA-DMF or DMF-DMA solution when enantiomeric separation is required. By decreasing the polarity of the target molecules, this step allows their volatilization at a temperature below 250°C without any chemical degradation. Once derivatized, the volatile target molecules are trapped in a cold and chemical trap and promptly desorbed into the gas chromatograph coupled with a mass spectrometer.

Preliminary tests, performed on garden soil and on a Martian analogue soils: Atacama soil. Atacama is an extreme, arid, temperate desert located in Chile that extends from 20°S to 30°S along the Pacific coast of South America. It has been suggested as Mars analogue [1], with the MOMA SPS-GC/MS experiment, allowed the detection of organic compounds such as amino and carboxylic acids below the ppm level [2]. When using DMF-DMA procedure with a chiral column, we are able to detect some amino acids with respect to their enantiomers [3] (figure 1).

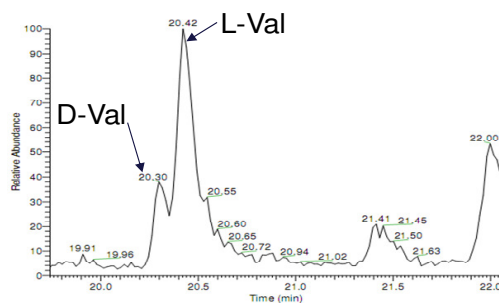


Figure 1: Example of extraction/derivatization of DL-valine by using DMF-DMA on a garden soil. Separation operated on a 30mx0.25mmx0.25µm β-Cyclodextrine column.

3. Thermochemolysis

Thermochemolysis is directly performed in the oven at 400°C during 5 min with a 25% (w/w) methanol solution of tetramethylammonium hydroxide (TMAH).

Pyrolysis in the presence of TMAH allows both an efficient cleavage of polar bonds and the subsequent methylation of COOH, OH and NH₂ groups, hence the release of less polar, GC-amenable compounds. It was successfully applied on two samples of one of the best Martian analogue soils: Atacama soil. The studied samples were pyrolysed in presence of TMAH and several families of biological molecules were detected. Indeed, fatty acids detected had a microbial origin. On the other hand, n-alkenes and n-alkanols were from preserved higher plants biopolymers [4].

4. Conclusion

By using extraction/derivatization and thermochemolysis procedures to perform in situ analysis of Martian soil, the MOMA experiment will be able to extract, separate and detect a wide range of organic compounds of astrobiological interest, including chirality when it exists.

References

[1] R. Navarro-Gonzalez, et al. The limitations on organic detection in Mars-like soils by thermal volatilization–gas chromatography–MS and their implications for the Viking sults PNAS 103,16089, (2006).

[2] A. Buch, R. Sternberg, C. Szopa, C. Freissinet, C. Garnier, C. Rodier, R. Navarro-González, F. Raulin, M. Cabane, D.P. Glavin and P.R. Mahaffy. Development of a gas chromatography compatible Sample Processing System (SPS) for the in-situ analysis of refractory organic matter in martian soil: preliminary result. *Advances in Space Research* 43, 143-151, 2009.

[3] C. Freissinet, A. Buch, R. Sternberg, C. Rodier and M. Stambouli. On the space analysis of life chiral's remnants: gas chromatography-mass spectrometry analysis of enantiomeric organic molecules as their N,N-dimethyl formamide dimethyle acetal (DMF-DMA) derivatives. *Journal of Chromatography A*.1217 (5), 731-740, 2010.

[4] C. Geffroy-Rodier, L. Grasset, R. Sternberg, A. Buch, A. Ambles, Thermochemolysis in search for organics in extraterrestrial environments, *Journal of Analytical and Applied Pyrolysis*, 85, 454-459, 2009.

