

Searching for organic matter on Mars by immunological assays: Detection of mellitic acid in the surface and subsurface of the Atacama Desert terrestrial analog

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Abstract

The restrictions imposed by instrumentation and some methodological constraints make that only volatile organic compounds have been analyzed in situ by instruments in planetary exploration. The oxidation of the meteoritic organic matter on Mars might be in the form of non-volatile polycarboxylic acids. These compounds are difficult to detect by in situ remote gas chromatography-mass spectrometers (GC/MS) and, consequently, new methodologies and technologies have to be developed for future missions. We have developed a fluorescent inhibition microarray immunoassay (IMI) for the detection of mellitic acid (benzenehexacarboxylic acid), with a limit of detection of 5 ppb (ng mL^{-1}). We validated this method for searching mellitic acid in several drill core samples (down to 5 m depth) from the Atacama Desert (Chile).

1. Introduction

It has been suggested that the oxidation of the meteoritic organic matter on Mars might have produce and accumulate polycarboxylic acids, like mellitic acid, in the martian regolith [1]. Other works have been published indicating that at least the superficial polycarboxylic acids are further oxidized by UV radiation to simpler compounds like acetate [2], [3], although relatively high concentrations might have been accumulated in the subsurface. However, these compounds are difficult to detect by instruments aimed to the analysis of volatile compounds, like gas chromatography-mass spectrometers (GC/MS), because they are non-volatiles. Consequently, alternative methods to GC/MS have been developed like raman spectroscopy [4] microchip capillary electrophoresis [5] or immunological techniques as we report here.

2. Results

We have produced an antibody to mellitic acid (Fig. 1) and develop a fluorescent inhibition microarray immunoassay (IMI) for the detection of mellitic acid, with a detection limit of 5 ppb (ng mL^{-1}). Then, we applied this method for searching mellitic acid in several drill core samples (down to 5 m depth) from the Atacama Desert (Chile). Our results indicated a gradient of mellitic acid concentration, being higher at the top layers (1.17 to 1.57 ppm) and diminishing with depth to be undetectable at near 4 m deep (Fig. 2; [6]). In addition, the presence of mellitic acid was validated by conventional GC/MS analysis after an alkaline extraction [6].

3. Figures

Figure 1. Anti-mellitic acid antibody production. Mellitic acid was bound to BSA protein (Bovine Serum Albumin) to obtain an immunogenic conjugate for antibody production in rabbits.

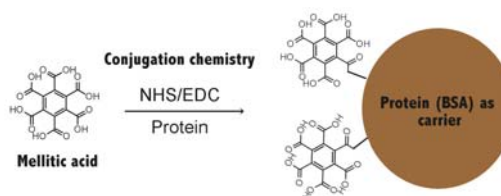
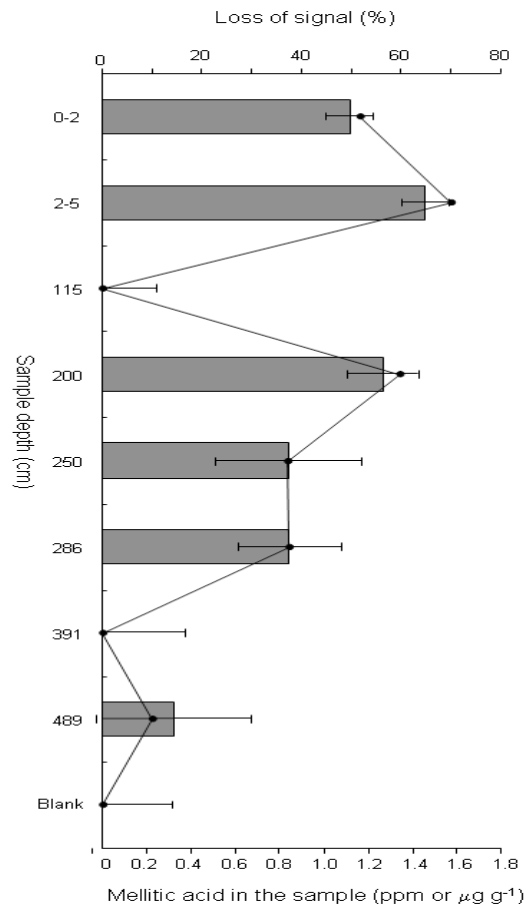


Figure 2. Results of IMI assay using the anti-mellitic antibody of several drill core samples from the Atacama Desert subsurface. *Loss of signal* indicates the % of the fluorescent signal lost in the IMI assays (*bars*). This signal was translated to mellitic acid

concentration (lines) by using the calibration curve (not shown).



4. Summary and Conclusions

Our results indicate that although the High UV radiation on Mars might completely oxidize polycarboxylic acids at the top surface, it is possible to be preserved in the subsurface, as it happens in Atacama. Our immunoassay can be easily implemented in instruments for *in situ* analysis like SOLID (Parro et al., 2005; 2011) and ESA's LMC (Sims et al., 2005), and coupled to drilling systems to collect samples from the subsurface.

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References

- [1] Benner, S.A., Devine, K.G., Matveeva, L.N., Powell, D.H.: The missing organic molecules on Mars. *Proc. Natl Acad Sci U S A*, Vol. 97, pp. 2425-2430, 2000.
- [2] Stalport, F., Coll, P., Szopa, C., Cottin, H., Raulin, F.: Investigating the photostability of carboxylic acids exposed to mars surface ultraviolet radiation conditions. *Astrobiology*, Vol. 9, pp. 543-549, 2009.
- [3] Stalport, F., Guan, Y.Y., Coll, P., Szopa, C., MacAri, F., Raulin, F., Chaput, D., and Cottin, H.: UVolution, a photochemistry experiment in low earth orbit: Investigation of the photostability of carboxylic acids exposed to mars surface uv radiation conditions, *Astrobiology* Vol. 10, pp. 449-461, 2010.
- [4] Jehlička, J., Vitek, P., and Edwards, H.G.M.: Raman spectra of organic acids obtained using a portable instrument at - 5°C in a mountain area at 2000 m above sea level, *J Raman Spectr*, Vol. 41, pp. 440-444, 2010.
- [5] Stockton, A.M., Tjin, C.C., Chiesl, T.N., and Mathies, R.A. Analysis of carbonaceous biomarkers with the Mars Organic Analyzer microchip capillary electrophoresis system: Carboxylic acids, *Astrobiology* Vol. 11, pp. 519-528, 2011.
- [6] Blanco, Y., Rivas, L.A., Ruiz-Bermejo, M., and Parro, V.: Immunological detection of mellitic acid in Atacama Desert: implication for organics detection on Mars, Icarus (In press), 2012

