



Raman spectroscopic identification of phthalic and mellitic acids in mineral matrices

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ABSTRACT

Raman spectroscopy has many advantages for planetary exploration, and the Raman technique is currently being developed for future space missions. The Raman microspectroscopic study of organic acids (phthalic and mellitic acids) in experimentally prepared mixtures with halite and gypsum was performed using near infrared 785 nm and visible 514 nm excitation wavelengths. Gypsum and halite matrices were chosen as analogues of Martian minerals. Carboxylic acids mixed with mineral powders were also investigated through a UV-transparent crystal of gypsum and halite (approximately 2 mm, resp. 5 mm thick), thereby creating a type of artificial inclusion that could potentially be present in Martian minerals. The detection limit of phthalic acid mixed in mineral matrices and analyzed through crystals was 1 wt% using both excitation wavelengths. A Raman mellitic acid signal was obtained at a concentration as low as 1 wt% in halite matrix, and at a concentration of 5 wt% when analyzed through halite crystal. In the case of mellitic acid mixed with gypsum and for analyses through a gypsum crystal, the detection limit is 5 wt% using both excitation wavelengths.

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1. Introduction

Raman spectroscopy is considered to be a powerful tool for characterization of geological and biogeological materials in planetary exploration missions. The main benefits offered by Raman spectroscopy are that it can identify water, ice, and organic and inorganic molecules, not to mention that it requires no sample preparation. The miniaturized Raman spectrometer is considered to be a candidate instrument for the Pasteur payload planned for the ExoMars rover, the ESA-NASA mission, to be launched in 2018. ExoMars will, for the first time, combine mobility and access to subsurface locations (down to a depth of 2 m) where organic molecules may be well preserved. It will be essential, however, to choose a landing spot where there are ample minerals suitable for the long-term preservation of biomarkers (e.g., clays, sulphates).

Previous investigations have proven that Raman spectroscopy is a useful method to characterize key biomarkers that are produced by extremophiles as part of their survival strategy [1–3], to identify organic minerals [4,5] and to detect organic molecules (betacarotene, usnic acid, urea) present in extremely small concentrations and mixed in with minerals [6–9].

For centuries, the possibility of life on Mars has fascinated mankind. The 1976 Viking missions failed to detect organic

molecules on the Martian surface, even those expected from meteoritic bombardment. Since then, it is believed that the Martian regolith is highly oxidative and would convert all organic molecules to metastable intermediates, which might be embedded in soils and rocks. These results suggest that, in order to detect organic molecules that may have arisen from life on Mars or may have been delivered to Mars via meteorites, it is necessary to dig deep below the Martian surface. Several types of organic compounds are known to have come to Mars via meteorites (alkanes, alkylbenzenes, naphthalene and higher polycyclic aromatic hydrocarbons, kerogen, amino acids, hydroxyacids) [10]. It has been proven that naphthalene, phenanthrene and anthracene all convert to phthalic acid in the generic oxidation process [11–13], and higher polycyclic aromatic hydrocarbons and kerogen transform into benzenecarboxylic acid products (e.g., mellitic acid) during oxidation [14]. Phthalic and mellitic acids could therefore be very appropriate organic molecular targets for future detection of signatures on the Martian surface or near subsurface.

In 2000, Benner concluded that 2 kg of meteoric-derived mellitic acid may have been generated per square meter of the Martian surface over 3 billion years and that if mixed in the regolith to a depth of 1 m, we can expect 500 ppm by weight. In addition, if gardening mixes the material to a depth of 1 km, benzenecarboxylates will be present at concentration of 500 ppb [15].

This work has been carried out to evaluate the potential of Raman spectroscopy to detect key molecular features with high relevance to exobiological studies and also to compare data from

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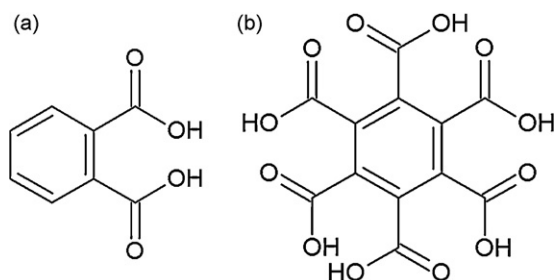


Fig. 1. (a) Structure of phthalic acid. (b) Structure of mellitic acid.

785 and 514 nm excitation wavelengths of Raman spectroscopy. The choice of Raman excitation wavelength is a key issue for exobiological studies on Mars and potentially elsewhere. A major weakness of Raman spectroscopy when analyzing organics is fluorescence, which can be avoided by selecting the appropriate wavelength. It has recently been proposed that the ExoMars mission operate with a visible 532 nm laser; however, at this wavelength, the Raman spectroscopy could be subject to fluorescence, which can mask the results.

In our study, samples consisting of carboxylic acid (phthalic and mellitic acids) mixed one by one with powdered minerals (gypsum and halite) were examined. Various concentrations of carboxylic

acids (25, 10, 5, and 1 wt%) in the mineral matrices were prepared to determine the detection limits of Raman spectroscopy for the detection of these biomarkers. Carboxylic acids mixed with mineral powders were then covered by a UV-transparent crystal of the same minerals, because it is possible that organic materials can be trapped inside such minerals.

2. Experimental

2.1. Samples

Samples were prepared by mixing a weighed amount of phthalic acid (Sigma–Aldrich, 99.5%) and mellitic acid (Sigma–Aldrich, 99%) with commercially obtained crystalline powders of two mineral matrices: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Sigma–Aldrich, min. 99%) and halite (NaCl) (Merck, 99%). The mixtures were pulverized and homogenized in an agate mortar. 25, 10, 5, and 1 wt% concentrations of carboxylic acids in the matrices were prepared to determine the detection limits of these biomarkers. The gypsum and halite crystals in this study were natural crystals, approximately 2 mm, resp. 5 mm thick (Table 1).

2.2. Raman microspectroscopy

Raman microspectrometric analyses of powders and powders through crystal were performed on a multichannel Renishaw *InVia*

Table 1

Detection of key features of phthalic and mellitic acids by 785 and 514 nm laser excitation wavelengths.

Carboxylic acid	Approximate carboxylic acid content (wt%)	Halite		Gypsum	
		In a matrix alone	Both in a matrix and through a crystal	In a matrix alone	Both in a matrix and through a crystal
Mellitic Acid	25	●○	●○	●○	●○
	10	●○	●○	●○	●○
	5	●○	●○	●○	●○
	1	●○	--	--	--
Phthalic Acid	25	●○	●○	●○	●○
	10	●○	●○	●○	●○
	5	●○	●○	●○	●○
	1	●○	●○	●○	●○

–, not found; ●, found by 785 nm laser excitation wavelengths; ○, found by 514 nm laser excitation wavelengths.

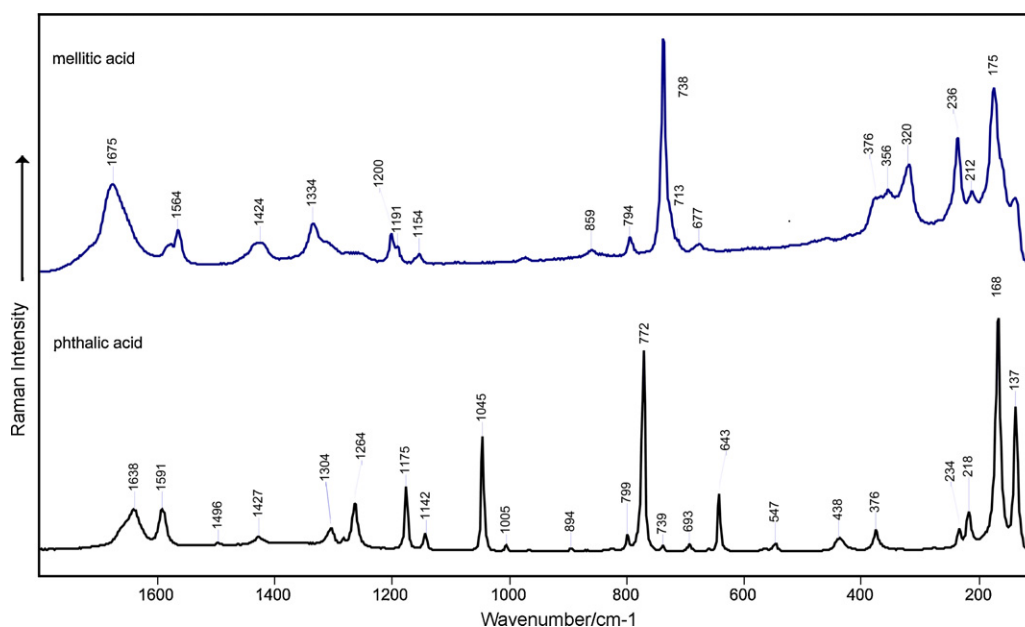


Fig. 2. Raman spectra for pure compounds used as biomarker analogues (phthalic and mellitic acids).

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