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Raman spectroscopic detection of phthalic and mellitic acids in evaporitic mineral matrices

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Raman spectroscopy is considered to be a powerful tool for the characterization of geological and biogeological materials in planetary exploration missions. The search and possible detection of life on Mars or on other promising Solar System bodies is a great challenge for the future space missions. 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. It is believed that several types of organic compounds could have been delivered to the surface of Mars via meteoritic bombardment. Naphthalene, phenanthrene and anthracene all convert to phthalic acid in the generic oxidation process, and higher polycyclic aromatic hydrocarbons and kerogen transform into benzenecarboxylic acid products (e.g., mellitic acid) during oxidation [1]. Phthalic and mellitic acids could therefore be very appropriate organic molecular targets for future detection of organic signatures on the Martian surface or near subsurface.
The primary goal of this research was the evaluation of Raman spectroscopy to detect key molecular features with high relevance to exobiological studies. The Raman microspectroscopic study of organic acids in experimentally prepared mixtures with halite and gypsum was performed in order to evaluate the potential of Raman spectroscopy to detect these biomarkers in relatively low concentrations. Gypsum and halite matrices were chosen as analogues of geological Martian minerals using 785 nm and 514 nm excitation wavelengths and with no sample preparation being effected. Samples consisting of each carboxylic acid mixed individually with the powdered minerals (gypsum and halite) were studied. To determine the detection limits of these biomarkers, various concentrations of carboxylic acids (25, 10, 5, 1wt %) in the mineral matrices were prepared. Carboxylic acids in 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 1wt% using both excitation wavelengths. A Raman signal of mellitic acid was obtained at a concentration as low as 1wt% in a halite matrix, and at a concentration of 5wt% when analyzed through a halite crystal. In the case of mellitic acid mixed with gypsum and analyzed through a gypsum crystal, the detection limit is 5wt% using both excitation wavelengths. This approach has also been evaluated using beta-carotene [2] and usnic acid [3] as biomarker molecules for Raman spectroscopic detection.

[1] Benner et al. (2000) PNAS 97, 2425-2430. [2] Vitek et al. (2009) PSS 57, 454. [3] Osterrothova and Jehlicka (2009) SAA 73, 576.