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Laboratory Detection And Analysis Of Organic Compounds in Rocks Using HPLC and XRD Methods D. Dragoi, I. Kanik, Y. Bar-Cohen, S. Sherrit, A. Tsapin, and J. Kulleck, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, ddragoi@cco.caltech.edu, kanik@pop.jpl.nasa.gov, yosi@jpl.nasa.gov, ssherrit@jpl.nasa.gov, tsapin@jpl.nasa.gov, jkulleck@mail2.jpl.nasa.gov

Introduction: In this work we describe an analytical method for determining the presence of organic compounds in rocks, limestone, and other composite materials. Our preliminary laboratory experiments on different rocks/limestone show that the organic component in mineralogical matrices is a minor phase on order of hundreds of ppm and can be better detected using high precision liquid chromatography (HPLC). The matrix, which is the major phase, plays an important role in embedding and protecting the organic molecules from the harsh Martian environment. Some rocks bear significant amounts of amino acids therefore, it is possible to identify these phases using powder x-ray diffraction (XRD) by crystallizing the organic. The method of detection/analysis of organics, in particular amino acids, that have been associated with life will be shown in the next section.

Sample preparation: The harsh Martian environment limits the chance to find organic materials on the surface/soil due to high level of UV radiation, Aeolian activity, CO atmosphere, Martian volcanic activity, etc. However, organic materials may be embedded and protected beneath the surface. In order to get subsurface material, an ultrasonic/sonic driller/corer (USDC) (see **Figure 1**), developed jointly by JPL and Cybersonics [1-2], was used to drill a hole into a vertical surface of a solid rock sample. The generated powder was collected from the surface to the final hole depth and analysed. The powdered cuttings are used for both, extraction of organic material using a Knudsen cell (KC) developed in our lab (see **Figure 2**) and structural analysis using XRD. The KC was loaded with powdered cutting specimen (about 1 cm³ in volume) and heated to 300 °C, in a 2 Torr air pressure environment. Approximately 50 µg of organic material was collected on a thin Al foil after an hour.

The Al foil was then introduced in a clean recipient and the organic deposit dissolved in 20 cm³ spectroscopic pure water. From previous experience with this type of material we assumed that the amino acids were present in the sample and the HPLC method was used as an appropriate method for amino acids analysis.

HPLC method: Amino acid analyses were carried out by HPLC separation of fluorescent diastereomeric derivatives [3-4]. Extracts were derivatized with o-phthalaldehyde/N-acetyl-L-cysteine, and the derivatives separated and identified by reverse-phase HPLC using a C18 column (Phenomenex) with 50 mM sodium acetate and methanol as the solvent system. Eluting amino acid derivatives were detected using a fluores-

cence detector, with lambda excitation at 340 nm and lambda emission at 450 nm.

Aspartic acid standards were used to calibrate retention times and detector response. In this way, we identified the organic component in the sample as: L-Aspartic, D-Glutamic, D-Serine, D-Alanine, L-Alanine, L-Valine, D-Valine, L-Leucine amino acids, three of them are shown in **Figure 3**.

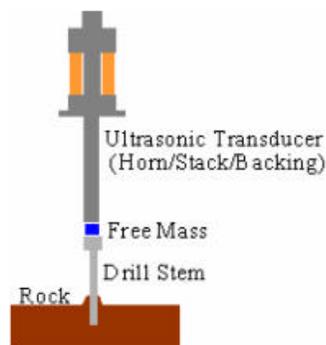


Figure 1: A schematic diagram of the USDC device. This device uses minimum axial force for coring in creating powdered cuttings.

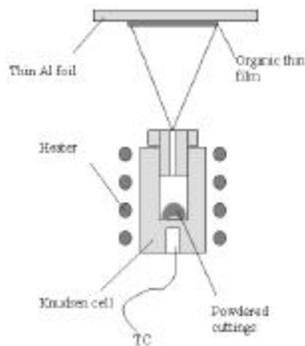


Figure 2: Knudsen cell and Al foil collector of organic material from powdered cuttings.

It is interesting to mention that the KC device can produce not only thin organic films, but also thin inorganic films, if operated on very fine powders and higher temperatures, where the film can be analyzed using XRD method.

XRD method: The powder-cutting specimen (not processed using KC) was placed on an X-ray holder and tested by a Siemens D500 at JPL.

The present investigation was conducted by using an updated version of Siemens D500 with Cu-K_α radiation, a Kevex semiconductor x-ray detector, and a rotating

holder for the specimen to remove the preferred orientation effect. The instrument is automated using Materials Data, Inc. (MDI) software. A standard laboratory x-ray analysis was conducted and is shown in **Figure 4**

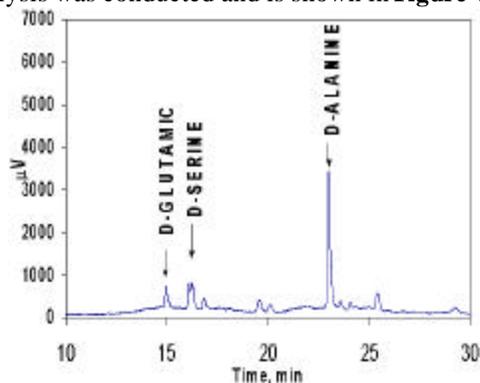


Figure 3: HPLC analysis of Santa Barbara rock, organics extracted from a solid sample, 1 cm depth from surface using the USDC and KC device.

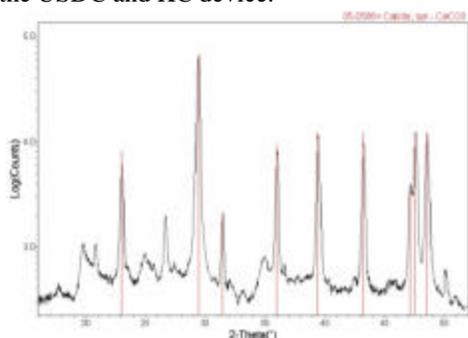


Figure 4: XRD pattern of a powdered cut specimen (Santa Barbara rock).

The XRD pattern shows Calcite as the main phase, and the other phases remain to be identified. A miniature x-ray diffractometer, called CHEMIN, under development at NASA Ames [5] can produce the same characteristic spectrum as shown in **Figure 4**.

If the KC is loaded with alanine amino acid only (no inorganic component), the organic thin film can be obtained as a thin film deposit on Al foil, which is better analyzed using XRD. **Figure 5** shows the XRD pattern of the deposit as crystalline alanine phase and Aluminum from the substrate. It suggests that if an appropriate concentrator is used to enhance the sample concentration then XRD analysis can be performed on the organic films to identify the main organic component which reduces the need for the HPLC test.

Concluding remarks: The feasibility of determining the presence of organic materials in rocks was shown in this preliminary laboratory study. The method is based on Ultrasonic/Sonic (USDC) sampling of subsurface rock, heat extraction of the organic phase from the powder cuttings using a Knudsen cell, and HPLC analysis of the extract.

Our experiments show that the chirality of alanine amino acid is preserved in the extraction process which is a fact that has important implications for life detection.

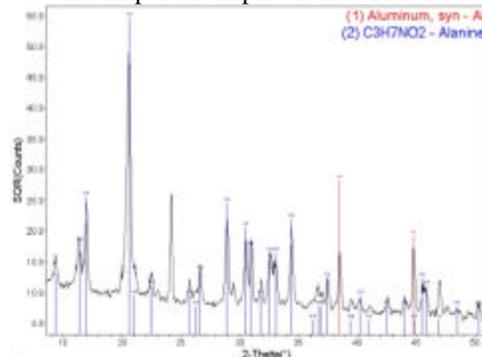


Figure 5: XRD pattern of alanine evaporated and deposited on Al foil using the KC device.

It is suggested that if the organic phase is greater in the matrix or a concentrator is used, then it can be crystallized and detected in principle with a miniaturized XRD instrument such as (CHEMIN), instead of a dedicated HPLC instrument which is a costly and limited with respect to the Martian environment.

Future work which integrates the sampling of the USDC and the analysis of the CHEMIN instrument will allow for the automation of the sampling and measuring process of subsurface organics in Martian type rocks. The in-situ instrumentation that is required to perform the tests can be further miniaturized allowing for the development of a low mass, low volume, low power system.

References:

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