MOD: AN ORGANIC DETECTOR FOR THE FUTURE ROBOTIC EXPLORATION OF MARS

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MOD (Mars organic detector) is capable of detecting amino acids and amines (the degradation products of amino acids) and polycyclic aromatic hydrocarbons (PAHs) at sub-picomole ($<10^{-12}$ mole) levels. In addition to detecting organic compounds, MOD will be capable of determining the carbonate content of the samples--thus providing information about the type of minerals associated with any detected organic compounds. An important aspect of MOD is that, with the CO_2 detection capability, information about the mineralogy of the Martian samples will be generated even if no organic compounds are detected.

MOD directly detects amino acids (or their amine decomposition products) and PAHs in a 0.1 to 1.0 gram powder sample of soils or fines collected from coring in rocks. The organic compounds are separated from the sample using sublimation, thus avoiding the need for wet chemistry. This isolation method is based on the fact that amino acids, amines and PAHs have appreciable vapor pressures at temperatures greater than 150°C.

In the MOD breadboard design, organic compounds are directly sublimed from the sample--thereby eliminating the need for complex wet chemical extraction. Because amino acids and PAHs have appreciable vapor pressures at elevated temperatures, they can be isolated by heating a sample under partial vacuum (readily obtained on Mars where the surface pressure is only 4-6 torr) in a closed chamber. This chamber is interfaced with the sample acquisition component of the analytical system maintained at the Mars ambient temperature. This procedure requires no extensive sample manipulation procedures or reagents.

To demonstrate the MOD concept, several experiments have been conducted (1). A mixture of dry amino acids was placed in a quartz glass sublimation apparatus (SA) with an interior cold finger (cooled @-195°C with liquid N_2). The SA was evacuated to 5-6 torr to approximate Martian atmospheric pressure and the sample end then inserted into a tube furnace and heated to 450°C for 5 minutes. The sublimed material was then scraped off the tip of the cold finger and analyzed using the same HPLC method recently used for the analyses of amino acids in Martian meteorites. We found that we could recover ~100 % of the starting pure amino acids using this simple approach. No decomposition into products such as amines was observed with the pure amino acid mixtures. Other experiments with PAHs demonstrated that the sublimation method also can be used to obtain excellent recovery of these compounds under the same conditions used for the amino acids.

The behavior of amino acids in a fossil mollusk shell during sublimation was found to be more complex than pure amino acid mixtures. We found that matrix bound amino acids were not readily sublimed at 450°C, and instead, will almost completely decompose into the amines. Virtually all of the amino acids were decomposed into amines produced by amino acid decarboxylation. Methylamine, which is produced from glycine, production at 450°C was increased after a second heating at 700°C. Nearly 100% of the glycine and alanine present in the original sample was recovered in the form of amines. Even though extensive decomposition of the original amino acids took place with the natural samples, the resulting amine products can be readily detected using the same methodologies used for amino acid detection. Thus, even when amino acid decomposition is significant, MOD will be able to detect the amine decomposition products, so the presence of amino acids in the original sample can still be inferred.

An important aspect of our sublimation approach is that the target compounds can be detected with high sensitivity directly on the tip of the cold finger using fluorescence-based methods. The detection of sublimed PAHs can be carried out directly on the cold finger, because these compounds are extremely fluorescent when irradiated with near UV light. Detection limits with this approach are in the sub-femtomole (10^{-15} mole) range. The detection of amino acids and amines has been achieved in our experiments by coating the cold finger surface with fluorescamine. While several other immobilized reagents can also be used, fluorescamine and its hydrolysis products, are non-fluorescent, while the amino acid derivatives (fluorophores) are highly fluorescent in the UV (380 nm). Moreover, fluorescamine has been shown to be an extremely sensitive reagent for the detection of primary amines at sub picomole levels ($<10^{-12}$ moles). Using a low pressure Hg mineral light for excitation and the naked eye as a detector, we could readily detect 10^{-7} moles of sublimed amino acids. Sublimed PAHs could also be directly detected based on their intense fluorescence when irradiated with light from the mineral lamp. If the concentrations of amino acids in a Martian sample are in the ppb range, the sublimation of one gram of sample would yield amounts of amino acids and/or amines in the picomole range, well within the detection limit of fluorescamine.

MOD will includes a CO_2 and H_2O detector based on the Tunable Diode Laser (TDL) spectrometers developed for the Mars '98 MVACS experiment and the New Millennium Mars Microprobe DS-2 mission. This CO_2 and H_2O detection capability will allow for the determination of the amounts of CO_2 and H_2O evolved during the sublimation heating used for organic isolation. This will provide information about the type of sample in which the detected organic compounds are found. For example, measurement of CO_2 pressure evolved as a function of sample temperature will help identify the carbonate mineral phase; carbonate (siderite) decomposes at 350°C, while magnesium carbonate decomposes at 450°C and calcium carbonate (calcite) breaks down at 890°C. Analyses of the Martian meteorite ALH84001 have found that it contains 40% Siderite, 40% magnesium carbonate, and 20% calcium carbonate. This kind of carbonate mineral composition will be readily detected by MOD.

MOD could be used point the way to samples that contain organic material on Mars. By targeting amino acids and PAHs, MOD can also begin to answer key questions about the occurrence and sources of organic material on Mars, as well as the type of mineral matrix in which the organics are contained.

References Cited

1. D. P. Glavin and J. L. Bada, *Anal. Chem.* **70**, 3119-3122 (1998).