

MEASUREMENT PROTOCOLS FOR IN SITU ANALYSIS OF ORGANIC COMPOUNDS AT MARS

AND COMETS. P. R. Mahaffy¹, W. B. Brinckerhoff², A. Buch³, M. Cabane³, P. Coll⁴, J. Demick¹, D. P. Glavin¹, R. Navarro-Gonzalez.⁵ ¹NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, paul.r.mahaffy@nasa.gov, ²The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, ³Service d'Aéronomie, IPSL, Université Pierre et Marie Curie, Paris, ⁴LISA, Université de Paris VII et XII, Créteil, ⁵University of Mexico.

Introduction: The determination of the abundance and chemical and isotopic composition of organic molecules in comets and those that might be found in protected environments at Mars is a first step toward understanding prebiotic chemistries on these solar system bodies. While future sample return missions from Mars and comets will enable detailed chemical and isotopic analysis with a wide range of analytical techniques, precursor insitu investigations can complement these missions and facilitate the identification of optimal sites for sample return. Robust automated experiments that make efficient use of limited spacecraft power, mass, and data volume resources are required for use by insitu missions. Within these constraints we continue to explore a range of instrument techniques and measurement protocols that can maximize the return from such insitu investigations.

Mars: A significant step toward resolving the question of the habitability and potential for past or present life on Mars will be the detailed characterization of organic compounds that might be preserved in rocks, ices, or sedimentary layers such as those recently revealed by the Mars Exploration Rovers. The Scout Phoenix mission [1] will target an analysis of volatiles in ices and it is likely that the mobility of the planned Mars Science Laboratory (MSL) will enable it to locate and sample sedimentary layers. It is not yet clear how well near surface environments at Mars might preserve organic molecules produced in an earlier warmer and wetter epoch or delivered to Mars by meteoritic infall. These may be destroyed by oxidants such as hydrogen peroxide (produced photochemically

or by the chemistry of dust devil induced discharges) or by ultraviolet or particle radiation. For this reason, it is important not only to locate sites of high preservation potential, but to implement organic analysis experiments with the highest possible sensitivity and breadth of chemical analysis. We have explored the techniques of laser desorption mass spectrometry (LDMS) for analysis of insoluble refractory organics, chemical derivatization for analysis of soluble organics, and pyrolysis. The pyrolysis approach is to heat a few milligrams of sample from ambient temperature to approximately 1200°C using a linear temperature ramp. Gases are rapidly removed from the sample by an inert helium carrier gas. They are first analyzed directly by a mass spectrometer and then again after completion of the pyrolysis by rapid release of organic molecules trapped on a high surface area adsorbant into a GC column. The controlled sample heating also enables analysis of simple inorganic gases, such as CO₂, H₂O, SO₂ that provide information on mineral type and the degree of mineral alteration by weathering. The derivatization technique also employs the separation technique of multicolumn gas chromatograph mass spectrometer (GCMS) analysis for detection of a wide range of organic compounds. A subset of these techniques was recently selected for inclusion on the Mars Science Laboratory. Figure 1 illustrates a chemical derivatization reaction that enables detection of a wide range of molecules that are relevant to terrestrial life such as carboxylic acids, amino acids, and nucleobases to be analyzed by the GCMS technique. Such derivatization transforms polar organic molecules into highly volatile species that readily elute from the

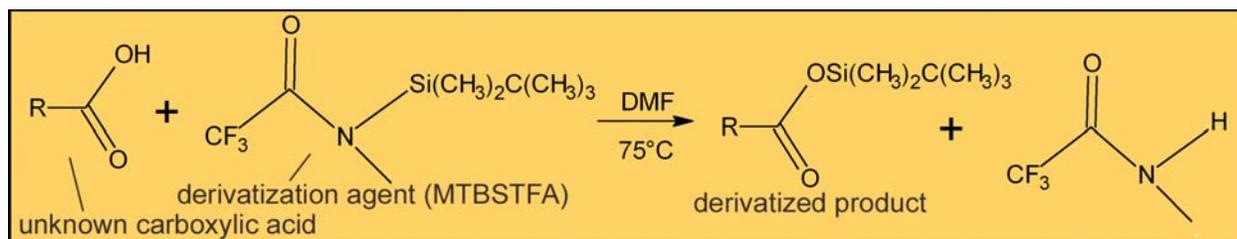


Figure 1. The chemical reaction that we have used on a wide variety of Mars analogue samples to transform polar molecules such as carboxylic acids and amino acids to volatile products that can readily be analyzed by the GCMS technique. The mass spectrometer, in this case, must have a mass range sufficient to reach the parent peak of the derivatized product. The derivatization agent is N,N-Methyl-tert.-butyl (dimethylsilyl) trifluoroacetamide (MTBSTFA) assisted by the solvent dimethylformamide (DMF). Lacking derivatization, the Viking GCMS would not have detected carboxylic acids.

GC columns. Mars analogues that we have examined include Atacama desert [2] samples, and weathered volcanic material that is often selected for remote sensing analogue studies.

Comets: The role of the exogenous delivery of organic material to the terrestrial planets in the origin of life motivates the detailed exploration of the organic chemistry of comets. Simple organic molecules CH_4 , C_2H_6 , C_2H_2 , CH_3OH , H_2CO and others have been observed by remote sensing in comets, but the fast flyby of Comet Halley by the Giotto and Vega spacecraft did not yield a detailed understanding of the composition of more complex organic molecules present in the coma. Since the cold ices of the cometary nucleus may never have reached liquid water temperatures, it is appropriate to interrogate these samples with a variety of techniques such as the direct ionization (LDMS), the dry pyrolysis processing, as well as the liquid based derivatization methods. As in the case of the Mars exploration, our primitive knowledge of the organic composition of comets suggests that these samples are best explored with a broad chemical analysis. For missions that flyby the nucleus or rendezvous with a comet without touching the surface, both the gases of the coma and the collected dust particles can be analyzed by the protocols described. The best cometary analogues to evaluate the measurement protocols may be the chemically complex residues produced by laboratory irradiation of ices formed from simple combinations of gases such as H_2O , CH_4 , and NH_3 . Primary goals of the analysis of cometary organics will be to

measure the mixing ratios in homologous carbon chain series such as CH_4 , C_2H_6 , C_3H_8 , ... $\text{C}_n\text{H}_{2N+2}$ and similar series for the more oxidized alcohols, aldehydes, or carboxylic acids. Other parameters of interest include the degree of branching of organic chains, the fraction of aliphatic vs aromatic molecules, and the isotopic composition of C and H as a function of chemical complexity. These measurements may distinguish thermodynamically driven abundance distributions from those that are kinetically controlled and heterogeneous catalytic formation mechanisms from homogeneous processes.

In situ Laboratories: The analytic power of the individual techniques described is greatly enhanced when several of these techniques can be combined to interrogate the same sample. The organic composition should be analyzed in the context of the host mineralogy and highly complementary elemental and mineralogical techniques are those that resolve fine scale spatial variations.

References: (1) Smith, P. "The Phoenix Scout Mission", 34th Annual Lunar and Planetary Science Conference, 1855 (2003). (2) Navarro-González, R., Rainey, F.A., Molina, P., Bagaley, D.R., Hollen, B.J., Rosa, J., Small, A.M., Quinn, R.C., Grunthaler, F.J., Cáceres, L., Gomez-Silva, B., and McKay, C.P., "Mars-Like Soils in the Atacama Desert, Chile, and the Dry Limit of Microbial Life", *Science* 7, 1018-1021 (2003).

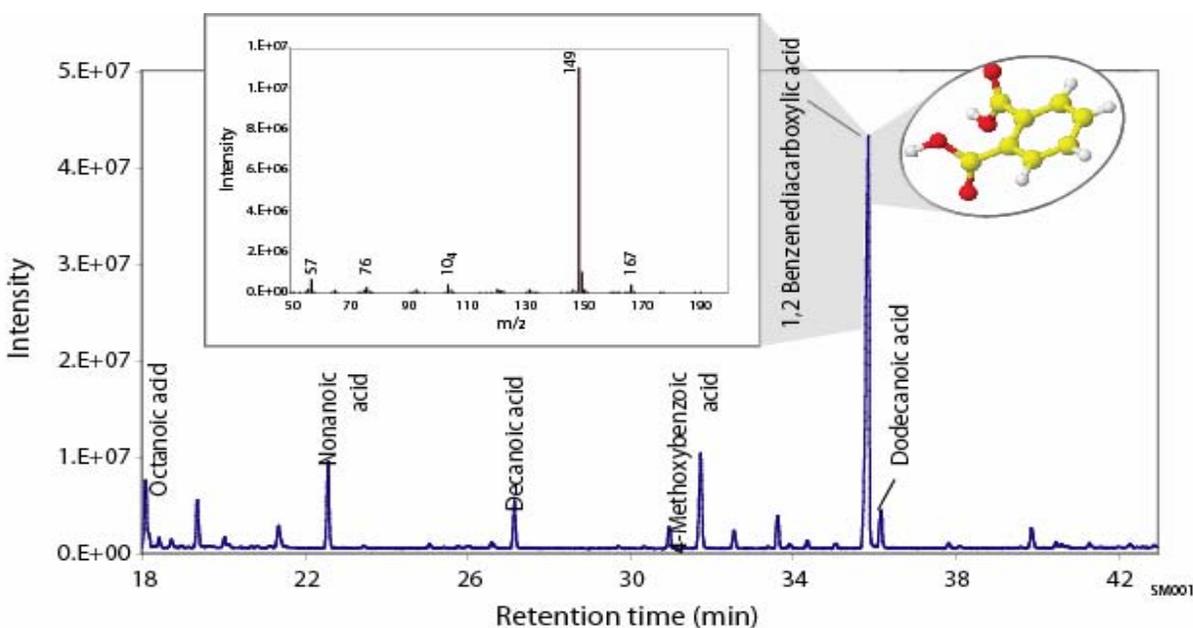


Figure 2. The derivatization agent MTBSTFA allows a variety of polar molecules that are not seen in pyrolysis GCMS to be identified. This sample is from a dry region of the Atacama desert where there are few organic molecules produced by dry extraction techniques.