

The Molecular Analysis Team discusses the first atmospheric analysis. Seated at left: D. Howarth, T. Owen; at the blackboard: K. Biemann; seated at right (from back): L. Orgel, J. Oro, A. Nier, D. Rushneck, P. Simmonds, D. Flory & P. Toulmin.

In 1968 NASA began to plan for the “Viking” mission to explore the planet Mars from orbit and to study its surface. It was to consist of two identical Orbiter and Lander pairs (V-1 and V-2), both to be launched in 1973 about two months apart. The usual difficulties in funding, construction and testing forced a two-year delay of the launch. In addition to “life-detection” experiments, another important objective was to exam the chemistry of the Martian surface. Of particular interest was the search for organic compounds to learn about potential abiogenic, prebiogenic or biogenic processes occurring in the past or the present.

While there were hypotheses about synthetic processes that may possibly occur on Mars (or may have occurred during the past four billion years) one wanted to cast a very wide and sensitive net. Of all the possible chemical analysis schemes considered, a mass spectrometry-based experiment proposed by Klaus Biemann (MIT) was finally chosen. Its high sensitivity and wide applicability provided an approach independent of any preconceived notions about what to look for. To assure broad representation of the wide spectrum of investigations such an instrument could carry out, NASA assembled a team of scientists with expertise in fields ranging from permafrost, meteorites, and pre-biological chemistry to astronomy; the “Molecular Analysis Team”.

The constraints placed by the mission on the design of the experiment and the instrument were quite severe. Simple miniaturization of the way a soil sample is analyzed for organic compounds on Earth was out of the question. In addition to minimizing volume, weight and power requirements, the instrument had to operate in a fully automated, preprogrammed mode as well as by command from Earth. The lack of a repair service on Mars made it extremely important to design and construct the instrument to the highest reliability. NASA’s conservative policies required that only well proven concepts and technologies could be used. Because of volume and weight limitations, redundant components could not be incorporated.

## Experimental Results

To provide a baseline for the experiments to be carried out on Mars, a “blank” was run during the interplanetary cruise by heating one oven to 500 °C. This test not only demonstrated that the instrument was operating properly, but also that traces of the solvents, such as acetone, Freon, benzene and toluene, used for cleaning the instruments were still present. While this was unexpected, it provided very important post-launch performance data. Since the gas chromatographic peaks were very sharp, the compounds detected in this way must have been trapped in the oven and/or the tubing and valves ahead of the gas chromatographic column.

## Organic Analysis of Soil

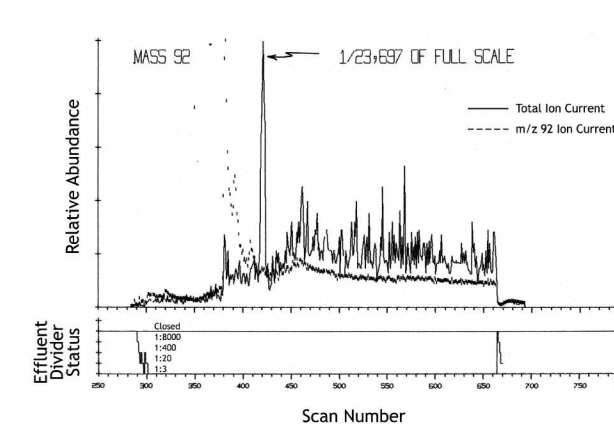
On Mars two soil samples each were analyzed on Viking-1 and –2 at various temperatures, totaling 14 complete GC/MS experiments. Surprisingly, no organic materials could be detected, other than the contaminating solvent traces already observed during the “cruise blank”! To improve the search, each mass chromatogram, from  $m/z$  12 to  $m/z$  215 was carefully examined for maxima but no coinciding set could be found (except for the solvent contaminants), indicating the absence of indigenous organic compounds at a sub-part per billion detection limit. Viking 1 landed July 20th, 1976 at 22°N 48°W in Chryse Planitia, while Viking 2 touched down September 3rd, 1976 at 44°N 226°W in Utopia Planitia. Although halfway around the planet, the results were exactly the same.

The absence of even the polycyclic aromatic hydrocarbons so relatively abundant in meteorites, which must fall on Mars as on Earth, was at first a puzzle. However, one of the three “active biology” instruments, the “Gas Exchange Experiment” headed by V. Oyama of NASA Ames Research Center revealed the evolution of oxygen when a Martian soil sample was brought into contact with an aqueous solution of organic nutrients. This finding suggested that the Martian surface material had a highly oxidizing character, probably from ferric oxide; which also causes the red color of the planet. In addition, the strong seasonal sandstorms known to occur on Mars disperse the dust particles high into the atmosphere where they are exposed to intense UV radiation for long periods of time. All these factors combined can destroy any organic material produced on or reaching the surface, at least in the first 10 cm of the soil surface; the depth reached by the Viking Surface Sampler.

Fortunately, the other explanation for the apparent absence of organics, that the instrument did not work, can be eliminated based on the abundant and consistent performance data. The proper functioning of the system from soil sampling to the mass spectrometer is demonstrated by the sharp GC peaks, as mass chromatograms, for the solvent traces as shown in the data. The evolution of considerable quantities of water at 500 °C shows that there was Martian soil, probably containing hydrated minerals, in the oven. This caused the effluent divider to cycle

properly as indicated by the valve signals and the ion pump current. The latter also shows that the hydrogen-separator functioned efficiently. The performance of the mass spectrometer is demonstrated by the mass spectra and mass chromatograms of the solvent traces as well as the analyses of the atmosphere discussed below. The latter also provided a continuous sensitivity check for the mass spectrometer, based on the known atmospheric pressure of CO<sub>2</sub> and the conductance of the leak to the ion source.

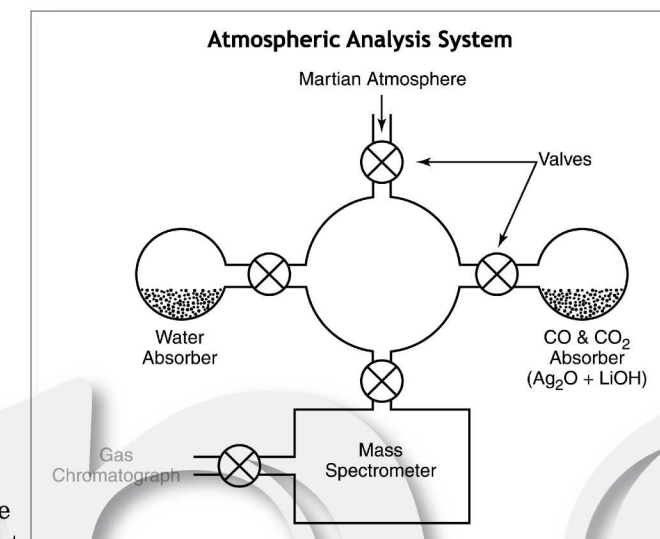
Chromatogram and Extracted Ion Current Profile of Soil Analysis from Mars Viking Lander GC/MS



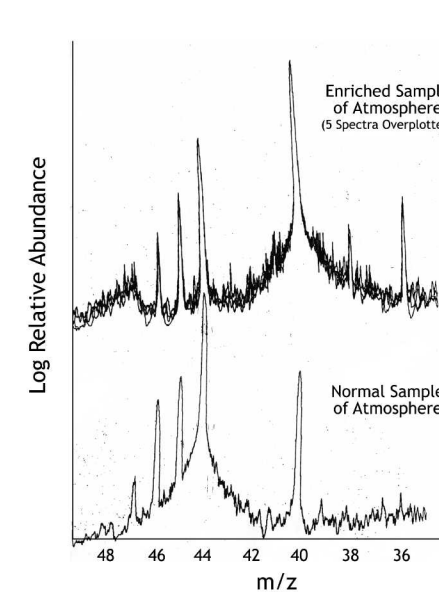
## Atmospheric Analysis at the Martian Surface

Having a mass spectrometer operating on the surface of the planet provided an opportunity to also measure the composition of the atmosphere. Such measurements were carried out during the entry into the atmosphere and brief descent of the Viking Lander by another mass spectrometer designed by Al Nier of the University of Minnesota. This instrument was mounted on the aeroshell and discarded with it before touch-down. A stationary system could make additional measurements, back up the data from the descent mass spectrometer, or replace them in case of the latter’s failure. One such measurement concerned the abundance of nitrogen in the atmosphere at the surface, which, according to some models, could be very low. Because terrestrial biological systems are unthinkable without an atmosphere containing nitrogen, biologists wanted a detection limit of 100 ppm or better for this gas. The “entry” mass spectrometer used two Faraday cups for the measurement of ion currents rather than an electron multiplier, so it could not achieve the desired sensitivity. Of course, there was another problem: the Martian atmosphere was known (from earth-based IR measurements) to consist chiefly of CO<sub>2</sub> and some CO. Both contribute to  $m/z$  28 and 14 and thus interfere with a direct measurement of nitrogen at low levels.

For this reason, an inlet system was designed and incorporated into the GC/MS allowing the measurement of the atmospheric composition before and after removal of CO<sub>2</sub> and CO. In the latter mode, the air sample contained in the reservoir was exposed first to silver oxide (to convert CO to CO<sub>2</sub>) and lithium hydroxide (to absorb all CO<sub>2</sub>) and then to magnesium perchlorate, to absorb the resulting water. As it turned out, Nier’s “entry” mass spectrometer already showed that there was quite a bit of N<sub>2</sub> in the atmosphere, enough to be measured in the presence of CO<sub>2</sub> and CO by simply subtracting their contributions to  $m/z$  28 based on the ion currents at  $m/z$  44 and 12.



Mass Spectrum of the Argon Isotopic Region of Martian Surface Atmosphere After Ten Enrichment Cycles (top) Compared to Single Cycle (bottom)



Luckily, the CO/CO<sub>2</sub> removal system could be used for another purpose; the detection and measurement of minor atmospheric components. The removal of the CO<sub>2</sub> created an under-pressure in the sample volume, which thus could be refilled with more Martian air. The number of such cycles could be controlled by ground command, producing an “enrichment” of the residual gas which made it possible to first determine the abundance of the argon isotopes, and then to detect the other noble gases.

The higher abundance of <sup>15</sup>N, when compared with the terrestrial value, is due to the preferential loss of the lighter isotope during the depletion of nitrogen from the primordial Martian atmosphere. The kinetic energy of N<sup>+</sup> ions during the UV induced photo-ionization and photo-dissociation of N<sub>2</sub> in the upper atmosphere is sufficient to overcome the gravity field of the smaller planet and thus can escape. On the other hand, the lower abundance of <sup>40</sup>Ar must be due to a depletion of <sup>40</sup>K.

## Postlude

After the successful Viking mission the question was often asked: “Why was this concept not used to build a portable GCMS?” The answer is simple: Most of the design efforts and \$\$\$ spent were directed towards solving problems unique to the Martian environment and special requirements for a long space flight. Most importantly, the power, volume and reliability limitations would be much less severe for earth-based instruments, allowing the use of a conventional vacuum system, helium as a carrier gas and capillary columns. One also would use a quadrupole mass spectrometer. The latter had been considered in 1972 as an alternative to the magnetic sector instrument, but was shown in a subcontract to the Bendix Corporation to be heavier and require more power. Finally, it should be noted that the Viking GC/MS was built by Litton Industries, with the mass spectrometer supplied by the Aerospace Division of the Perkin-Elmer Corp.

Composition of the Surface Atmosphere of Mars

Gas		Concentration
Carbon Dioxide	CO <sub>2</sub>	95.3%
Nitrogen	N <sub>2</sub>	2.7%
Argon	Ar	1.6%
Carbon Monoxide	CO	(0.2)%
Oxygen	O <sub>2</sub>	0.15%
Water Vapor	H <sub>2</sub> O	0.03%
Neon	Ne	0.55 ppm
Krypton	Kr	0.3 ppm
Xenon	Xe	0.08 ppm
Ozone	O <sub>3</sub>	0.03 ppm

Comparison of the Isotope Ratios of Some Elements on Earth and Mars

Ratio of Element	Earth	Mars*
<sup>12</sup> C/ <sup>13</sup> C	89	90
<sup>16</sup> O/ <sup>18</sup> O	499	500
<sup>14</sup> N/ <sup>15</sup> N	277	165
<sup>40</sup> Ar/ <sup>36</sup> Ar	292	3000
<sup>129</sup> Xe/ <sup>132</sup> Xe	0.97	2.5

\* Uncertainties in these values are presently +/-10% except for Ar and Xe.

## Leading References:

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