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ISOTOPE RATIO MONITORING GAS CHROMATOGRAPHY
MASS SPECTROMETRY
(IRM-GCMS)

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On Earth, the ^{13}C content of organic compounds is depleted by roughly 13 to 23 permil from atmospheric carbon dioxide. This difference is largely due to isotope effects associated with the fixation of inorganic carbon by photosynthetic organisms. If life once existed on Mars (and it utilized similar enzymatic and metabolic processes as does life on Earth), then it is reasonable to expect to observe a similar fractionation. Although the strongly oxidizing conditions on the surface of Mars make preservation of ancient organic material unlikely, carbon-isotope evidence for the existence of life on Mars may still be preserved. Carbon depleted in ^{13}C could be preserved either in organic compounds within buried sediments, or in carbonate minerals produced by the oxidation of organic material.

A technique is introduced for rapid and precise measurement of the ^{13}C contents (at natural abundances) of individual organic compounds. A gas chromatograph is coupled to an isotope-ratio mass spectrometer through a combustion interface, enabling "on-line" isotopic analysis of isolated compounds. The effluent of an open tube capillary column is split between a flame ionization detector (in order to yield a conventional chromatogram) and a micro-volume combustion system. Hydrogen is used as the carrier gas, and, downstream from the splitter, is removed completely by use of a palladium-tube separator and is replaced by a small flow of helium (0.25 mL/min). Removal of carrier gas allows use of columns with flow rates as high as 20 mL/min. If the bore of the chromatographic column is small enough that the optimum carrier-gas flow-rate is 1 mL/min or less, then the palladium-tube separator can be bypassed with the following modifications: an inert gas (e.g., helium) replaces the carrier gas in the chromatographic column and the split ratio between the combustion interface and the FID must be decreased so that 0-0.5 mL/min (or less) of carrier is delivered to the combustion system. Water produced by combustion is removed by diffusion through a permeable membrane, and peaks of CO_2 are carried directly into the ion-source of the mass spectrometer. Manipulation of small pressure gradients allows systematic control of gas flow, enabling solvent diversion, admission of standards and maintenance of O_2 in the combustion reactor without disturbance of flow to the mass spectrometer. Ion-source characteristics are adjusted to yield maximum sensitivity and linearity; masses 44, 45, and 46 are continuously collected by triple Faraday cups connected to high-speed amplifiers. The isotope ratios are determined by integration of ion currents over the course of each chromatographic peak. Software incorporates automatic peak determination, corrections for background, and deconvolution of overlapped peaks. Because input of chromatographic effluent to the combustion system is continuous, all peaks in a chromatogram can be isotopically analyzed from a single injection.

Isotopic ratios of 0.67 nanomole samples of CO_2 introduced upstream from the palladium separator are measured with a standard deviation of better than 0.2 permil. The standard deviation of ratio measurement for samples between 5 and 30 nanomoles is 0.06 permil. In the absence of any correction, observed isotopic composition of the CO_2 peaks decreased by 0.05 permil per nanomole due to ion-source non-linearities. Overall performance of the instrument was evaluated by the

analysis of a mixture of high purity n-alkanes (19–25) of known isotopic composition. Isotopic values measured via IRM-GCMS averaged within 0.55 permil of their conventionally measured values. Repeated measurements (n=5, average sample size = 12 nmol C delivered to ion source) yield an average standard deviation of 0.65 permil for each compound. At present, performance is limited by the accuracy of background corrections and by the method of standardization. Two-nanomole aliquots of standard CO₂ are introduced between sample peaks. Background corrections are determined for each peak.

There are several possible roles IRM-GCMS might play in the Mars missions, most notable is post-flight analysis of organic samples. In addition, the technology of on-line isotopic determination can be adapted for the analysis of inorganic carbon, for example, in carbonate minerals. Instrumentation for either application could be included for on-board experiments.