Reports

Gas Chromatographic Column for the Viking 1975 Molecular Analysis Experiment

Abstract. *A gas chromatographic column has been developed for use in the remote analysis of the martian surface. The column, which utilizes a liquid-modified organic adsorbent (Tenax) as the stationary phase, provides efficient transmission and resolution of nanogram quantities of organic materials in the presence of millionfold excesses of water and carbon dioxide.*

Each of the two Viking spacecraft to be launched toward Mars by the National Aeronautics and Space Administration during the summer of 1975 (*1*) will include a gas chromatograph–mass spectrometer system (*2*) among the instruments that are to be landed. The primary objective of this "molecular analysis experiment" is to determine the quantities and types of organic compounds in the martian soil. Although the mass spectrometer–computer system and the palladium gas chromatograph–mass spectrometer interface have been described earlier (*2, 3*), the development of an optimal gas chromatographic column remained a crucial problem, complicated by several unusual requirements:

1) Ideally, the column must exhibit good efficiency and minimum irreversible adsorption across the full range of possible soil pyrolysis products (*4*), including substances as diverse as amines, nitriles, aldehydes, alcohols, small heterocyclics, and various hydrocarbons.

2) Milligram quantities of water and carbon dioxide, which might be released during pyrolysis (*2, 5*), must be effectively separated from the organic compounds.

3) The column must have exceptional thermal stability (up to 200°C), absolutely minimizing "bleeding" into the mass spectrometer.

4) The column packing material must have mechanical strength sufficient to avoid deterioration during vibrations and shock of launch, space flight, and landing.

5) The operating conditions of the column should necessitate minimal power and carrier gas consumption.

Although these requirements could easily be met singly or in pairs, their simultaneous satisfaction is very difficult and appeared to require unusual materials. The unmodified adsorbents common in gas-solid chromatography suffer from irreversible adsorption and excessively long retention times. In gas-liquid chromatography, it is very difficult to make a compromise between thermal stability and the polar properties of liquid substrates. The recent development (*6, 7*) of polar surface-attached monolayers is attractive in many respects, as is the use of liquid-modified adsorbents, but the coating of liquid phases on highly adsorptive inorganic supports frequently causes appreciable tailing of large water peaks.

The incompletely explored but potentially useful materials appeared to be liquid-modified organic adsorbents. After some preliminary testing which strongly supported this hypothesis, we chose the following column materials for careful comparison: (i) a previously suggested Viking column consisting of 4.8 percent Dexsil 300 GC (a nonpolar carborane polymer) plus 0.2 percent Hi-Eff 8 (cyclohexanedimethanol succinate) on 80- to 100-mesh Chromosorb W-HP; (ii) a liquid-modified organic adsorbent consisting of 1.5 percent poly-metaphenoxylene (Poly MPE) (Applied Science Laboratories, State College, Pennsylvania) on 110- to 124-mesh graphitized carbon black (*8, 9*); (iii) a second liquid-modified organic adsorbent consisting of 60- to 80-mesh Tenax GC (2,6-diphenyl-para-phenylene oxide, a thermostable porous polymer) (Applied Science Laboratories) coated with Poly MPE by filtration methods after equilibration with a 2 percent solution of the liquid phase in ethyl acetate (the exact liquid loading was not determined); and (iv) a surface-bonded polyethylene glycol material consisting of Chromosorb W treated with Carbowax 20M according to the method of Aue *et al.* (*6*).

These materials were found to differ sig-

Table 1. Water transmission characteristics. All materials were tested in columns 2.0 m long by 0.75 mm in inside diameter with an H_2 flow rate of 2.0 ml/min and the temperature held isothermal at 50°C for 10 minutes and then programmed to 200°C at 8°C/min.

Column material	Water breakthrough time (sec)	Water peak width	t_1* (sec)	Secondary water peak	
				Width† (sec)	Maximum flux (ng/sec)
Dexsil–Hi-Eff 8–Chromosorb W-HP	42.8	0.6 sec/ng + 20 sec	130	>960	20
Poly MPE–carbon black	52.4	1.0 sec/ng + 20 sec	150	320	15
Poly MPE–Tenax	96	0.6 sec/ng + 20 sec	30	0	4

*The time required for the water flux to drop from saturation to less than 21 ng/sec (an instrumental threshold), and thus a measure of the extent of water peak tailing. †Time from the initiation of the temperature program, through the maximum of the secondary water peak, to a water flux of less than 10 ng/sec.

Table 2. Properties of column packing materials.

Column material	Bleed rate* (pg/sec)	Mechanical stability	Chromatographic transmission† of		Hydrocarbons
			Amines	Alcohols	
Dexsil–Hi-Eff 8–Chromosorb W-HP	>150	Friable	Poor, severe tailing	Poor, severe tailing	Good
Poly MPE–carbon black	~130	Extremely friable	Poor, severe tailing	Marginal, tailing	Excellent
Poly MPE–Tenax	<50	Compact, rugged	Good, slight tailing	Excellent	Good, broad symmetric peaks
Carbonwax 20M–treated Chromosorb W		Friable	Excellent	Good	Excellent

Measured at 200°C and expressed as equivalent *n*-butane flux on a calibrated flame ionization detector. Other conditions are as described in Table 1. †Tested with 100-ng amples, under conditions described in Table 1. See text.

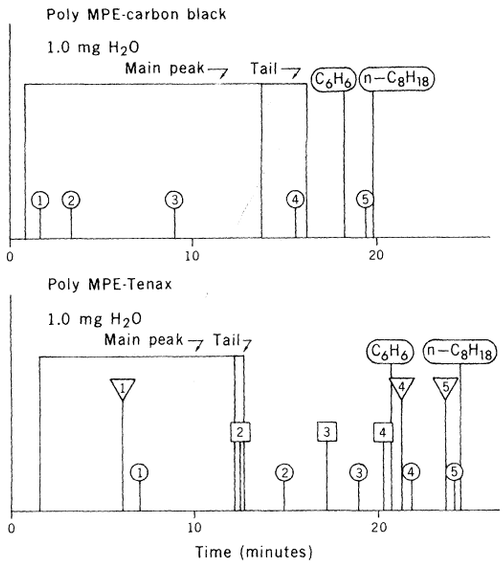

Fig. 1. Plots of retention time illustrating the superior resolution of organic species from water on the Poly MPE–Tenax column. Circled numerals indicate carbon numbers in the homologous series of alcohols, squares represent aldehydes, and triangles represent amines. The Poly MPE–carbon black column does not provide well-defined peaks for amines and aldehydes. Conditions are as specified in Table 1.

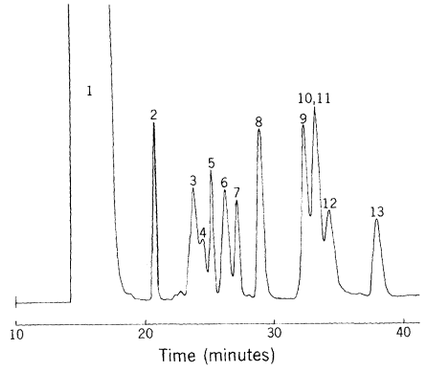

Fig. 2. Chromatogram illustrating the resolution of 12 representative compounds on a Poly MPE–Tenax column. Conditions are as specified in Table 1. Key: *1*, isopropanol (solvent); *2*, benzene; *3*, dimethyl furan; *4*, octane; *5*, isopentyl alcohol; *6*, nonane; *7*, furfuryl alcohol; *8*, mesitylene; *9*, *p*-cresol; *10* and *11*, tridecane and dimethylaniline; *12*, phenethyl amine; and *13*, benzyl cyanide.

nificantly in their water-transmission characteristics. The results of gas chromatographic–mass spectrometric observations are summarized in Table 1. In every case, water amounts greater than 50 μg appeared as flat-topped peaks with widths directly proportional to the quantity of water. The sharpness of the trailing edge of the peak varied substantially, however, and the carbon black and Dexsil materials were characterized by sizable secondary water peaks which were separated from the main zone and appeared only after the temperature program had been initiated. These secondary peaks apparently represented water so strongly adsorbed by the column that it was released only when the column temperature was increased. The Poly MPE–Tenax column provided a bulk water peak as narrow as the Dexsil column, exhibited by far the least water peak tailing, and had almost no secondary water peak.

Other important characteristics of these packing materials are summarized in Table 2. When bleed rates were determined mass spectroscopically, the major part of the total ion current increase was due to water and carbon dioxide. The flame ionization detector measurements appear to furnish the best estimate of relative organic bleed rates. The particularly low bleed of the Poly MPE–Tenax column can presumably be ascribed to the close chemical similarity between the adsorbent and its liquid modifier, both of which are polyphenyl ethers. All of the data, including bleed rates, were obtained under identical chromatographic conditions. For the relative measurements described here, the only variable has been the column packing material, although it must be emphasized that chromatograph performance can depend strongly on other variables. Better or worse overall performance might be obtained on other instruments, but the relative differences between columns should be maintained. The entries in Table 2 describing chromatographic transmission refer to observations made on homologous series of monofunctional compounds throughout the range of column operating conditions. The terms "excellent," "good," and "poor" refer to the apparent level of quantitative transmission observed for 100-ng test samples. A compound type marked "excellent" should be detectable at the 1-ng level; "good," at the 10-ng level; and "poor," perhaps not even at the 100-ng level. In addition, both the Poly MPE–Tenax and Poly MPE–carbon black columns exhibited poor performance with carboxylic acids. The Poly MPE–Tenax column exhibited good performance with aldehydes; the Poly MPE–carbon black column, poor.

As noted in requirement (ii) above, the effective separation of water and carbon dioxide from organic materials is of great importance. Figure 1 compares the Poly MPE–Tenax and Poly MPE–carbon black columns in this regard. The superiority of the Tenax column is particularly evident here, and is confirmed in Tables 1 and 2. On this basis, the Tenax column has been chosen for use during the Viking mission. The flight column will have the dimensions and will be operated under the conditions specified in Table 1, and, according to the common chromatographic terminology (*9*, *10*), can be classified as a "micropacked column" incorporating a liquid-modified porous polymer adsorbent.

A further demonstration of the efficient chromatography of a Poly MPE–Tenax column is provided by the chromatogram in Fig. 2, which incorporates 12 representative standard compounds of widely varying chromatographic properties. Most of these compounds are detectable as symmetrical peaks even at concentrations as low as 1 to 5 ng. Several prototype columns are now being tested at different sites as a part of the Viking lander assembly. After an 11-month exposure to different environmental conditions, no changes in the performance of these columns have been noted.

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