Separation of Light Hydrocarbons on Micropacked Bidentate Alkylsilane Silica Columns by Gas Chromatography

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Abstract

Micropacked bidentate alkylsilane silica columns are prepared and characterized for the separation of light hydrocarbons by gas chromatography. The chromatographic and kinetic properties of the phases are examined, and the results are reported. The results show that a column packing chemically modified with 1,1,4,4-tetramethyl-1,4-dichlorodisilylethylene exhibits better separation performance probably due to effective dispersive interactions between the solutes and the stationary liquid phase. A 3.0-m column of this packing material provides a good, rapid separation of a mixture of 10 hydrocarbons at a lower column head pressure under isothermal conditions.

Introduction

Part of the ongoing research efforts at NASA–Ames on gas chromatographic (GC) instrumentation for future exobiology experiments in the solar system is the development of stable and efficient micropacked GC columns. This is because future space missions will involve the determination of light hydrocarbons, nitriles, dinitriles, CO, H_2, and CO_2. These compounds, which are present in small concentrations, are to be determined in the presence of large amounts of N_2 and Ar, the main constituents of the target atmospheres. Therefore, large volumes of samples must be introduced into the GC column to satisfy the detector sensitivity (1). Although porous-layer open-tubular (PLOT) and conventional GC columns provide efficient analysis of light hydrocarbons, the large volume requirement limits the usefulness of these columns in future space missions due to their poor mechanical strength and low sample capacity (1–4). For these reasons, micropacked columns are considered to be suitable alternatives because of their high sample capacity, low flow rate, low bleeding of the liquid stationary phase, and small resistance to mass transfer (5–8).

The chromatographic properties of micropacked alkyl bonded silica columns for the GC analysis of light hydrocarbons has been recently reported (9). The packings described in that work allowed fast analysis of the test solutes at low linear carrier gas velocities when compared with the literature data (10). However, work continued on other column packings in order to improve performance and achieve the desired separations at operating conditions that are compatible with GC experiments aboard spacecrafts (11).

This report presents the GC properties of micropacked silicas chemically modified with bidentate silanes that have the general formula $X(R)_2SiYSi(R)_2X$, where X is a reactive functional group (e.g., Cl), R is an alkyl group, and Y is a connecting bridge such as –O– or a number of $-CH_2-$ groups. Although information on their chromatographic behavior as GC packings is not available in the literature, these phases have been found to exhibit better stability compared with alkyl bonded phases in liquid chromatography, probably due to the formation of multiple bonds on the silica surface (12,13). Such packings could be of special benefit for gas chromatographic–mass spectrometric experiments in future space missions because they accommodate the rigors of flight environments and minimize column or stationary phase bleed.

Experimental

Materials and chemicals

Porasil C silica (particle size, 149–177 μm; surface area, 100 m^2/g; pore diameter, 300 Å) was purchased from Waters Associates (Millipore Corp.; Milford, MA). The silanizing reagents (see Table I), hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS), were obtained from United Chemical Technologies (Bristol, PA) and used as received. Analytical-reagent-grade toluene, tetrahydrofuran (THF), methylene chloride, and methanol were obtained from general sources.

Synthesis of stationary phases

Prior to the preparation of the stationary phases, about 20 g silica was refluxed with 3N HCl at 100°C for 2 h, rinsed thoroughly with deionized water, and dried overnight at approximately 150°C in an oven. The phases were prepared under anhydrous conditions as follows. About 3 g silica was added to a

warm solution of 30 mL dry toluene and 10 mL of the appropriate silane (for 1,1,4,4-tetramethyl-1,4-dichlorosilylethylene, 5.0 g was used) in a 100-mL two-neck round bottom flask. The slurry was refluxed for 24 h at 110°C under a gentle helium flow (99.999% UHP He) to provide mild agitation of the reaction mixture and to expel HCl produced by the silane reaction. Subsequently, the silylated silica was cooled, transferred to a sintered glass crucible, and washed successively with three 50 mL portions of dry toluene, methylene chloride, methanol, methanol–water (50:50, v/v), and methanol under suction. To remove any unreacted molecular chlorine, each phase was refluxed with 50% THF–H_2O for 1 h at 80°C and washed with THF and methanol under suction. The cleaned particles were then end-capped by refluxing for 2 h in a mixture of 30 mL toluene and 8 mL HMDS–TMCS (1:1 molar ratio) at 100°C. The final product was again washed as described previously, dried under vacuum in a desiccator, and stored in a dry bottle for characterization. The amount of bonded ligands on the silica surface was determined by elemental carbon analysis of the dried samples.

Column packing

The bonded phases were packed into pretreated stainless steel tubes (2.0 m × 1.07-mm i.d.; No. 304) fitted with Swagelok low dead volume connectors. The columns were dry packed in vertical position. One end was loosely plugged with silanized glass wool. The column was attached to a vacuum pump, and the packing material was added to a small stainless steel reservoir connected to the open end of the column. The

### Table I. Percent Carbon Load of Bidentate Bonded Phases*

Column	Silanizing agent	Percent carbon
1	1,3-Dichlorotetramethyldisiloxane	1.81
2	1,3-Dichlorotetraisopropyldisiloxane	1.74
3	1,6-Bis(chlorodimethylsilyl)hexane	2.63
4	1,8-Bis(chlorodimethylsilyl)octane	3.31
5	1,8-Bis(trichlorosilyl)octane	4.05
6	1,1,4,4-Tetramethyl-1,4-dichlorodisilylethylene	1.64

*Porasil C silica (80/100 mesh) was used.

Table II. Gas Flow Characteristics of the Columns*

Column	Packing density (g/cm³)	Interstitial porosity (ε)	Specific permeability (B_s) (x 10^{-7} cm²)	Flow resistance parameter (Φ)
1	0.492	0.40	2.54	1046.0
2	0.488	0.42	2.42	1097.9
3	0.490	0.40	2.41	1102.4
4	0.498	0.39	2.62	1014.1
5	0.499	0.41	2.59	1025.8
6	0.490	0.43	2.45	1084.4

* The columns all had dimensions of 2.0 m × 1.07-mm i.d. Helium was used as the carrier gas at 25°C. The average particle diameter was 163 µm.
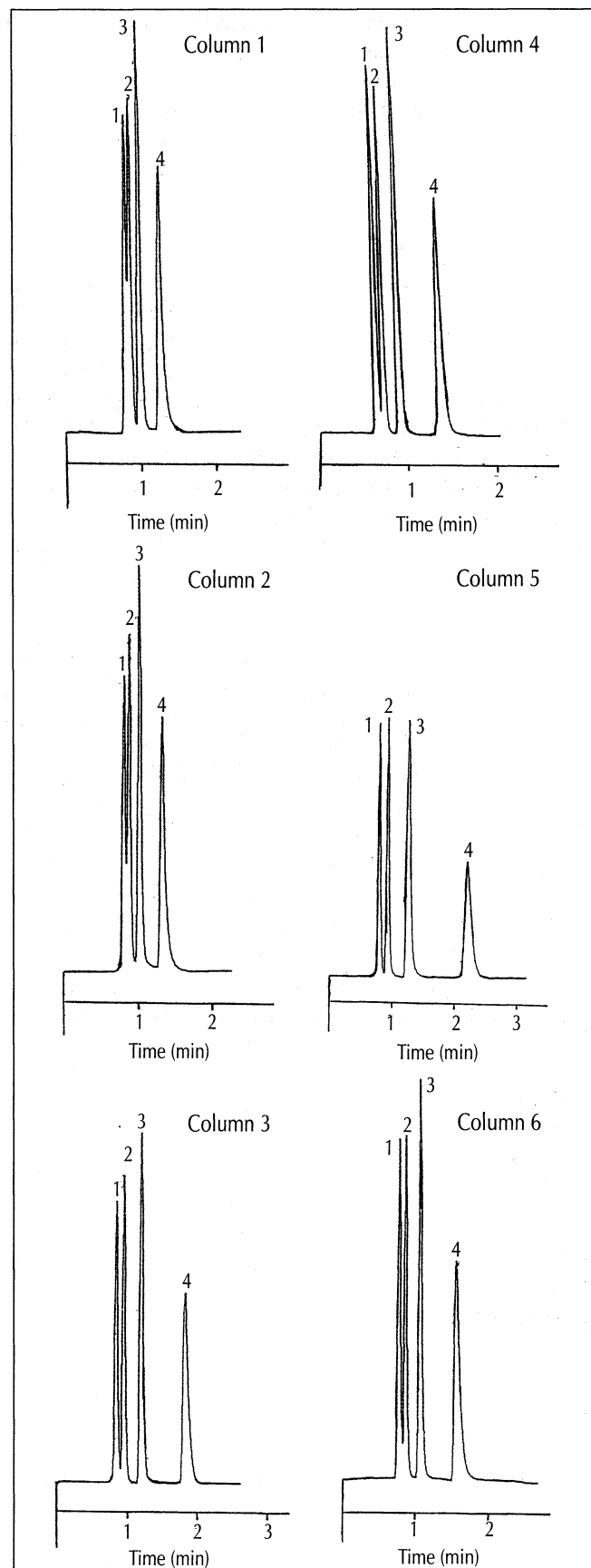
Figure 1. Chromatograms of the test solutes on micropacked bidentate alkyl-bonded silica columns. Conditions: temperature, 25°C; carrier gas, helium (5.0 mL/min); injection loop, 100 µL; column length, 2 m. Peak identification: 1, methane; 2, ethane; 3, propane; 4, butane.

columns were agitated, and the vacuum continued until the quantity of the packing material in the reservoir remained unchanged. The open end of the columns were then sealed with silanized glass wool, and the columns were installed in the gas chromatograph. Each column was conditioned overnight at 110°C under helium–gas purge at 5 mL/min before use.

Gas chromatography

The columns were evaluated on a gas chromatograph equipped with a micro thermal conductivity detector (TCD) and control (Carle Instruments; Fullerton, CA) and a Hewlett-Packard HP 3396 Series II integrator (Hewlett-Packard; Avondale, PA). The analyses were carried out at 25°C using helium (99.999% UHP He) as the carrier gas. A Matheson Hydrox Purifier (Model 8301, Matheson Gas Products; Secaucus, NJ) was connected to the carrier gas line to remove traces of water and oxygen from the carrier gas. A gas mixture of 1000 ppm each of methane (C_1), ethane (C_2), propane (C_3), and butane (C_4) in helium (Matheson Gas Products) was used as the test sample.

Chromatographic parameters

The capacity factor, k', was calculated from the expression $k'= (t_R - t_0)/t_0$, where t_R is the solute retention time, and t_0 is the gas hold-up time determined with dry nitrogen gas. The average linear gas velocities, $\bar{u}$, calculated from the expression $\bar{u} = L/t_0$ (where L is the column length), were obtained by varying the carrier gas inlet pressures from 1.41 to 4.22 kg/cm^2 at 25°C. The carrier gas flow rates were measured at the column outlet using a soap-bubble flow meter. The separation factor, α, was determined from the equation $\alpha = k'_2 / k'_1$, where 1 and 2 refer to peaks 1 and 2 and $k'_2 > k'_1$. The peak resolution, R_S, was calculated from the following expression:

$$R_s = \frac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{1 + k'}\right)\left(\sqrt{N}\right) \qquad \text{Eq 1}$$

where N is the theoretical plate number defined as

$$N = \frac{L}{H} \qquad \text{Eq 2a}$$

The theoretical plate height, H, for the test solutes were calculated from the following equation:

$$H = \frac{L}{5.54}\left(\frac{w_h}{t_R}\right)^2 \qquad \text{Eq 2b}$$

where w_h is the peak width at half height. The peak is assumed to be symmetrical and Gaussian.

Results and Discussion

Surface coverage

The surface coverage of the packings, expressed as a percentage of bound carbon, are presented in Table I. The data show the effect of different hydrocarbon spacer lengths and bulky groups attached to the silicon atoms on the coverage of the phases. Thus, the slight increase in the carbon load of column 1 compared with column 2 can be attributed to the steric effect of the attached groups. Also, the observed increase in the carbon load of column 4 compared with column 3 is presumably due to the increase in the hydrocarbon spacer lengths (12,13). The possibility of forming more multiple bonds on the silica surface with 1,8-bis(trichlorosilyl)octane may account for the high carbon load of column 5 (13).

Gas flow characteristics

The specific permeabilities, B_S, of the columns were determined from the slopes of the plots of F_0 versus $(p_i^2 - p_0^2)$ obtained from the following relation (14):

$$F_0 = \frac{3.0 \times 10^7 \, AB_S\left[p_i^2 - p_0^2\right]}{\eta L p_0} \qquad \text{Eq 3}$$

where F_0 is the carrier gas flow rate at the column outlet, A is the cross-sectional area of the column, η is the helium gas viscosity (2.018×10^{-4} at 25°C) (15) and p_i and p_0 are the column inlet and outlet pressures, respectively. The gas flow characteristics of the columns are summarized in Table II. The flow resistance parameter, Φ, was calculated from the expression $\Phi = d_p^2 / B_S$ where d_p is the average particle diameter. The value of Φ is constant for well-packed columns. This can be seen in Table II where Φ remains almost constant (mean = 1061.8 ± 38.2) for all

Table III. Chromatographic Properties of the Columns*

Property	Column 1	2	3	4	5	6
Capacity factor						
k'_{C1}	0.06	0.05	0.06	0.05	0.07	0.07
k'_{C2}	0.15	0.13	0.19	0.18	0.25	0.20
k'_{C3}	0.33	0.29	0.50	0.47	0.68	0.48
k'_{C4}	0.74	0.66	1.29	1.20	1.90	1.17
Separation factor						
α_1^2	2.51	2.64	3.46	3.67	3.72	2.79
α_2^3	2.20	2.25	2.59	2.62	2.74	2.42
α_3^4	2.22	2.23	2.57	2.58	2.80	2.47
Efficiency (plate/m)						
Propane	997	1027	1169	1216	1205	1263
Butane	782	817	1039	1076	1056	1102
Resolution						
Propane–ethane	1.35	1.28	2.34	2.28	2.95	2.22
Butane–propane	1.63	1.56	2.77	2.74	3.42	2.67

*Conditions: temperature, 25°C; column length, 2.0 m; carrier gas, He (5.3 mL/min).
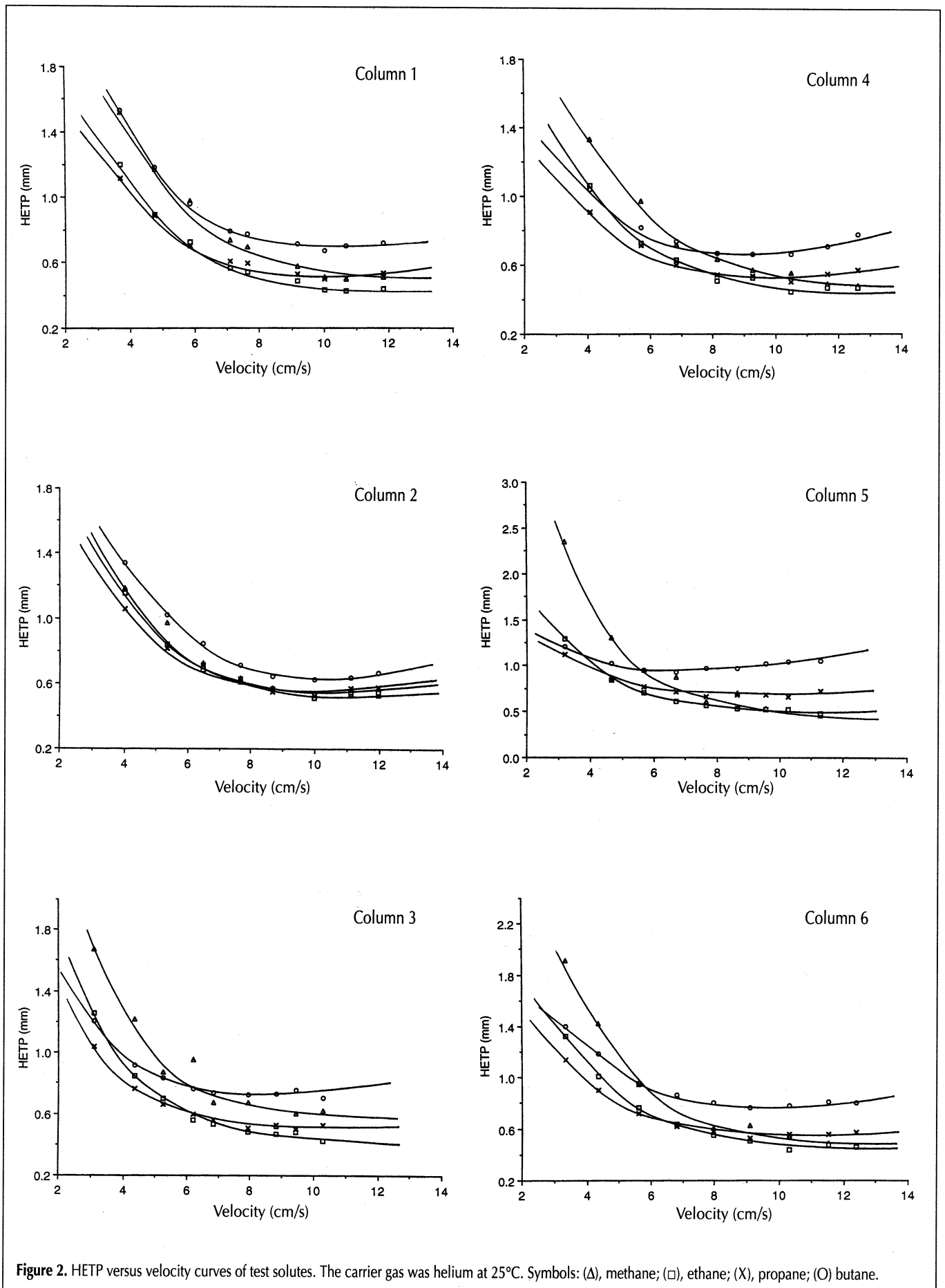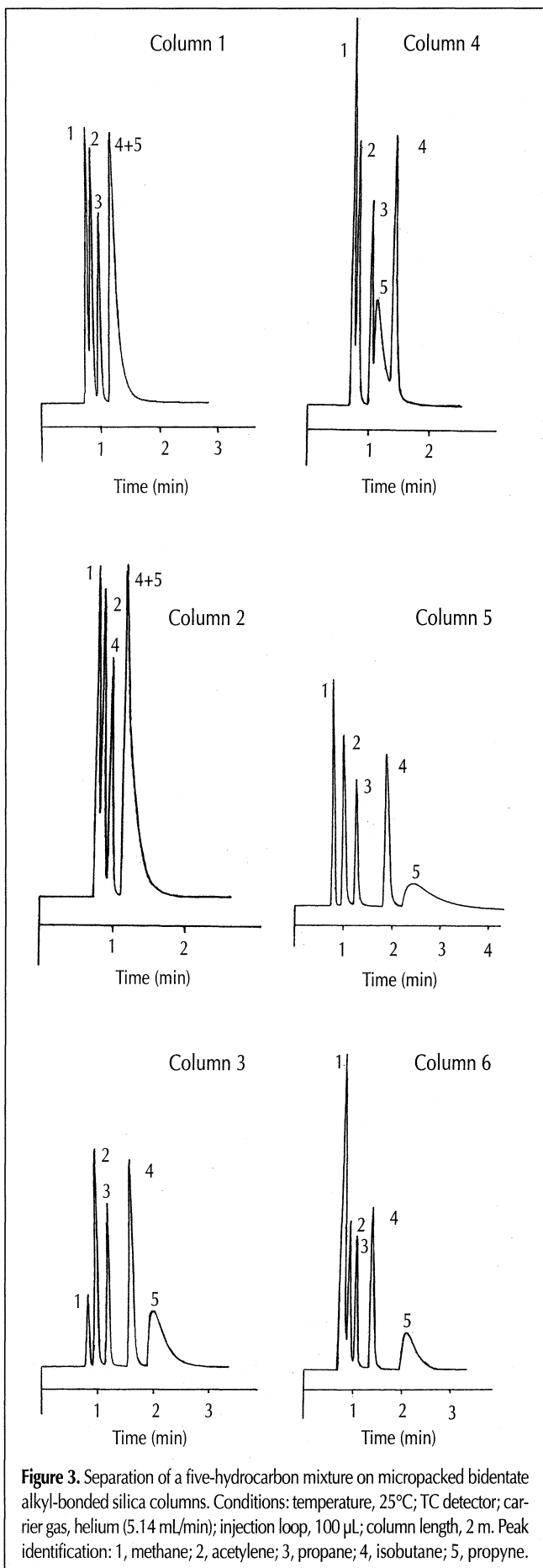
Figure 2. HETP versus velocity curves of test solutes. The carrier gas was helium at 25°C. Symbols: (Δ), methane; (□), ethane; (X), propane; (O) butane.

Figure 3. Separation of a five-hydrocarbon mixture on micropacked bidentate alkyl-bonded silica columns. Conditions: temperature, 25°C; TC detector; carrier gas, helium (5.14 mL/min); injection loop, 100 μL; column length, 2 m. Peak identification: 1, methane; 2, acetylene; 3, propane; 4, isobutane; 5, propyne.

the columns. The interstitial porosities of the columns (mean = 0.41 ± 0.01) are close to the theoretical value of 0.42 reported for random close packings of spheres with a small diameter range (16).

Retention data

The basic separation performances of the columns were evaluated with a mixture of saturated C_1–C_4 hydrocarbons. The chromatograms and the retention data obtained are shown in Figure 1 and Table III, respectively. With the exception of columns 1 and 2, where methane and ethane are partially resolved, the rest of the columns gave better separation of the test solutes with good resolution (R_S >1.5) and symmetrical peaks. The retention times of the late peak, butane, on the columns are lower than those obtained on Spherosil XOB (17) and Porapak N and Q (18–20) columns and almost identical to those obtained on isocyanate columns (10) at a much lower flow rate.

An examination of the chromatograms in Figure 1 showed that the solutes are retained longer on column 5. However, in terms of efficiency, the number of theoretical plates computed for the propane and butane peaks are slightly better on column 6 than other columns irrespective of its low carbon load. The higher value of N obtained with column 6 is attributed to effective nonspecific dispersive interactions between the solutes and the bonded ligand (21–24). On the other hand, the possibility of forming a more cross-linked polymer structure on the silica surface with trifunctional silane may result in slow diffusion of the solute molecules in the gas phase within the pores of the packing materials (9). Such a phenomenon could account for the long retention times and hence high k' values of the solutes on column 5. The high resolution obtained on column 5 demonstrates the large influence of retention capacity on resolution.

As shown in Table III, increasing the hydrocarbon spacer lengths (columns 3 and 4) and the molecular size of the bulky groups (columns 1 and 2) results in a slight increase in the separation factor and efficiency of the columns. However, a comparison of columns 1 and 6 showed that the introduction of an ethylene group in the bonded molecule results in a significant increase in column performance. These results reflect a reduction in steric hindrance of the attached groups, which in turn increased the dispersive interactions of the test solutes with the bonded ligand. The very small and almost identical k' values of methane (0.06 ± 0.01) in all the columns is consistent with the expected small dispersive interactions between the solute and the bonded ligand.

Kinetic study

Figure 2 shows the plots of the experimental values of HETP against the average linear gas velocity. The shape of the curves is similar to those obtained by other authors (7,25–27), with each curve exhibiting a shallow and broad minimum at optimum gas velocity. The dependence of theoretical plate height on various process parameters in a chromatographic column can be described by the following equation (7):

$$H_i = a_d \frac{D_{im}}{\bar{u}} + \frac{a'_c \, d_p}{1 + a''_e (D_{im} \sqrt{u} d_p)^{\frac{1}{2}}} +$$

$$a_f \times \left(\frac{\bar{u}}{D_{im}} \right)^{\frac{1}{2}} d_p^{\frac{3}{2}} \left(\frac{k_i}{k_i + 1} \right)^2 +$$

$$a_b \times \frac{\bar{u}}{D_{ip}} \times d_p^2 \times \frac{k_i}{(k_i + 1)^2} \qquad \text{Eq 4}$$

where H_i is the HETP for component i, $\bar{u}$ is the linear gas velocity, D_{im} is the diffusion coefficient of component i in the mobile phase, d_p is the diameter of the column packing material, k_i is the capacity ratio of component i, D_{ip} is the total diffusion coefficient of component i in a particle; a_d, a'_c, a''_e, a_f, and a_b are factors representing the effects of the column geometry on diffusional mixing, convective mixing, dispersion arising from partial mass transfer in the moving part of the mobile phase, and dispersion due to mass transfer in a particle, that is, both in the stagnant part of the mobile phase and stationary phase. The diffusion coefficient in the mobile phase depends on pressure (P) according to the following relation:

$$D_{im} P = \text{constant} \qquad \text{Eq 5}$$

It follows from Equations 4 and 5 that H decreases with increasing pressure at low linear velocities and increases at high linear velocities. Furthermore, the minimum value of H decreases with increasing pressure and shifts to lower values of the flow velocity.

It can be said that the plots followed the predictions of Equations 4 and 5. At high flow velocities, the theoretical plate height, H, increases with increasing pressure, approaching a minimum with a decrease in k'. Thus, the crossing of the curves and the shift in H minimum to lower values of $\bar{u}$, particularly for the late peak (butane), result from the high resistance to mass transfer. This resistance predominates at high gas velocities, where the effect of pressure on D_{ip} is essentially controlled by the volume ratio of the stationary liquid and the stationary gas phase in the particle as well as their geometrical distribution. Consequently, D_{ip} decreased with increasing pressure, and the fourth term in Equation 3 increased because its value depends on the accessibility of the stationary mobile phase to the pores of the particles (7). This effect is more pronounced in column 5, where the value of H at optimum linear gas velocity is relatively large for the late peaks (e.g., butane, see Figure 2E) due to the polymeric nature of the bonded phase. Hence there is a decrease in the overall diffusion coefficient of the solute in the particles (D_{ip}) with an increase in pressure.

The fit of the experimental data to the simplified form of the van Deemter equation ($H = A + B/u + C\bar{u}$) by the least-squares method gave negative values for the constant A. Therefore, in agreement with the literature data for packed columns (28,29), a constant value of 0 was assumed, and the contribution of the B (axial diffusion in the column) and C (mass transfer in the column packing material) terms of the equation to the total plate height of each sample are given in Table IV together with the coefficients of determination and the standard errors of estimation(s). It can be seen that the highest value of C for each of the solutes was obtained on column 5. This high resistance to mass transfer could contribute to the long retention times that were observed for the test solutes. For a given solute, the value of B is almost constant in all the columns.
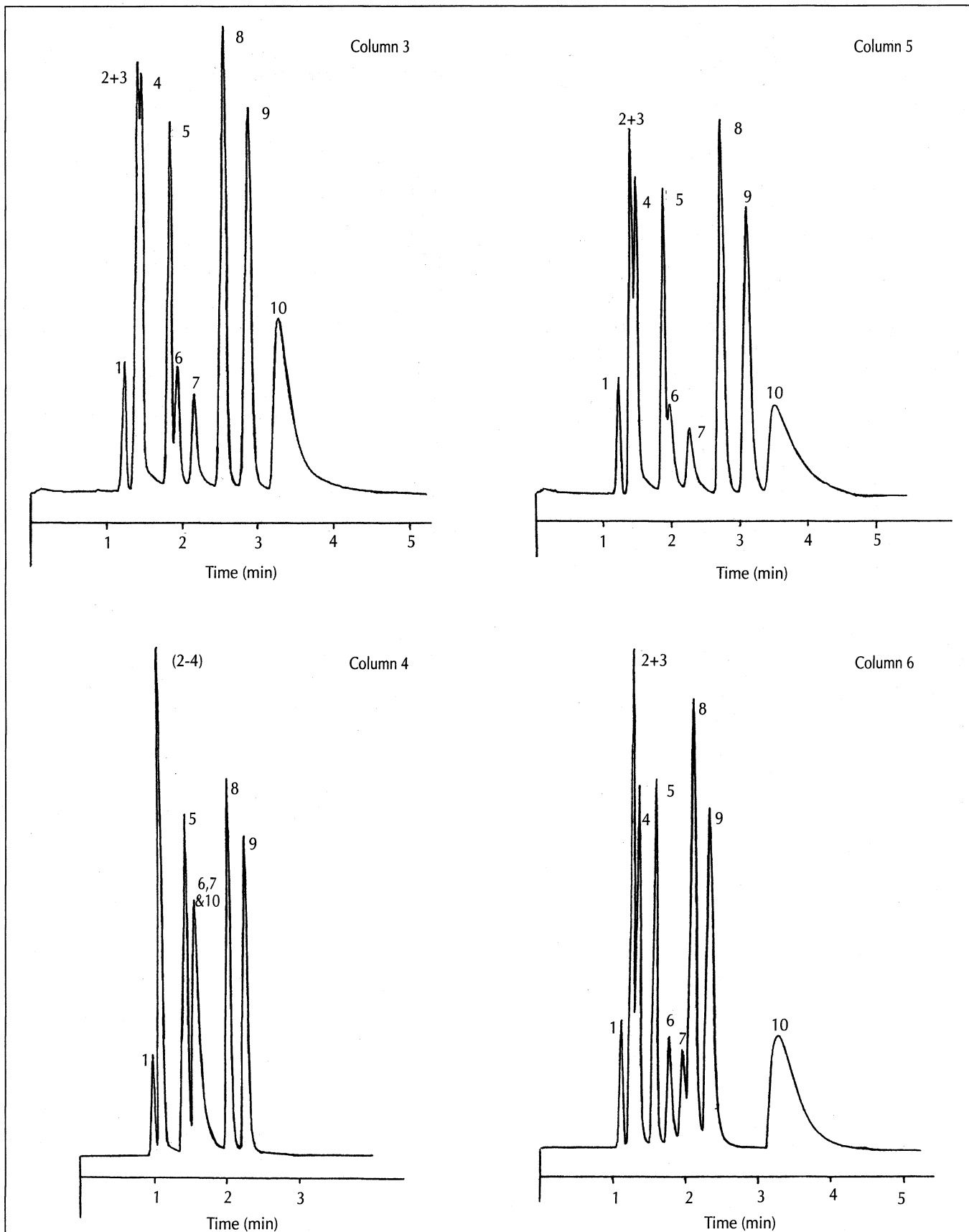
Separation of C_1–C_4 hydrocarbon mixtures

Figure 3 shows the separation of a five-component mixture of saturated and unsaturated hydrocarbons on the columns. With the exception of columns 1 and 2, better

Column	Solute	B (cm²/s)	$C \times 10^{-3}$ (s)	Coefficient of determination	Standard estimation error
1	Methane	0.58	0.24	0.998	0.0018
	Ethane	0.42	0.35	0.992	0.0038
	Propane	0.33	1.34	0.993	0.0028
	Butane	0.42	1.78	0.992	0.0023
2	Methane	0.59	0.86	0.995	0.0028
	Ethane	0.42	1.23	0.990	0.0036
	Propane	0.34	1.52	0.995	0.0020
	Butane	0.40	1.76	0.998	0.0018
3	Methane	0.61	0.40	0.978	0.0089
	Ethane	0.39	0.43	0.986	0.0051
	Propane	0.35	2.03	0.991	0.0026
	Butane	0.43	3.43	0.992	0.0024
4	Methane	0.63	0.28	0.990	0.0039
	Ethane	0.40	0.89	0.987	0.0039
	Propane	0.33	2.15	0.995	0.0016
	Butane	0.41	3.39	0.998	0.0010
5	Methane	0.64	1.00	0.982	0.0094
	Ethane	0.40	1.53	0.983	0.0044
	Propane	0.35	4.13	0.981	0.0029
	Butane	0.39	4.36	0.994	0.0020
6	Methane	0.62	0.60	0.984	0.0086
	Ethane	0.42	0.73	0.992	0.0044
	Propane	0.35	2.06	0.988	0.0038
	Butane	0.43	3.58	0.998	0.0015

Table IV. Values of B and C Terms of the Van Deemter Equation ($A = 0$)*

*A 2.0-m × 1.07-mm i.d. column was used. Helium was used at 25°C

Figure. 4. Separation of a 10-hydrocarbon mixture on columns 3, 4, 5, and 6. Conditions: column length, 3 m; temperature, 25°C; TC detector; carrier gas, helium (5.14 mL/min); injection loop, 100 μL. Peak identification: 1, methane; 2, ethane; 3, ethene; 4, acetylene; 5, propane; 6, propene; 7, propadiene; 8, isobutane; 9, butane; 10, propyne.

separation of the sample components was achieved on other columns due to improved selectivity and higher column efficiency. It is interesting to note that propyne was eluted before isobutane on column 4. Besides the low diffusivity of the solutes within the bonded ligands, the observed tailing of the propyne peak on column 5 may be attributed to intermolecular interactions (pi-character) between the propyne molecule and the adsorptive sites (residual silanols) on the silica surface (22,23,30–32). The selectivities of columns 3, 4, 5, and 6 were further examined with a mixture of 10 hydrocarbons. The chromatograms of this mixture on each of the columns are shown in Figure 4. Although ethene and ethane coeluted on all the columns, these two compounds were poorly separated from acetylene on columns 3, 4, and 5 compared with column 6. Also, propyne coeluted with propene and propadiene on column 4. Nevertheless, all the columns allowed fast analysis of the sample components. It can be seen that the separation of the sample components was completed in less than 5 min, which is significantly less than the analysis time of the same mixture on alkyl-bonded silicas (9) and isocyanate (10) columns. Even though better resolution was achieved on Spherosil (17), Porapak N and Q (19,20), and Carbopack and Carbosieve (33), the present columns provide fast separation of similar hydrocarbons at conditions suitable for GC instrumentation in future planetary missions. For instance, isobutane was eluted within 3 min on each of the columns at 25°C (He flow rate, 5.14 mL/min) compared with approximately 44 min on Porapak Q at 76°C (He flow rate, 100 mL/min) (20).

Conclusion

This study has demonstrated the potential applicability of bidentate alkyl-bonded silica packings for the separation of light hydrocarbons. The chromatographic and kinetic properties of the columns varied with the nature of the bonded ligands. Column packings in which the methyl groups of the bonded ligand are separated by a short hydrocarbon chain, such as $-(CH_2)_2-$, exhibit better selectivity for the test mixtures. This is explained by the decrease in steric hindrance of the attached groups by the hydrocarbon spacer leading to effective dispersive interactions between the solutes and the stationary liquid phase. Finally, the packings described in this paper allowed further reduction in the analysis time of C_1–C_4 hydrocarbons at a lower carrier gas column head pressure under isothermal conditions.

Acknowledgments

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