Characterization of micropacked alkyl-bonded silica columns for gas chromatographic analyses of light hydrocarbons in planetary atmospheres

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Abstract

Micropacked columns of different types of chemically bonded n-octyl- and n-octadecyl stationary phases were prepared and evaluated for the separation of light hydrocarbons under isothermal conditions. Column selectivities and efficiencies varied with surface coverage and the functionality of the silanizing agents. As might be expected, solute retentions are higher on the C_{18} phases than on the C_8 phases due to the increased effective interactive surface between the solute and the stationary phase. Among the phases examined, the polymeric n-octadecyl packings gave the highest plate number and better retention characteristics for the test solutes. The H versus $\bar{u}$ plots obtained revealed the applicability of the columns for fast analysis at low linear carrier-gas velocities and correspondingly low volumetric flow-rates without any substantial loss in efficiency. Within the temperature range investigated, thermal-stability experiments indicate that the polymeric n-octadecyl phase can be used at temperatures up to 250°C with little or no column bleed.

1. Introduction

The understanding of chemical evolution and the origin of life in the solar system form part of NASA's exobiology program. Clearly such investigations require the development of analytical techniques that are both highly sensitive and precise for the identification of compounds that might be present in planetary atmospheres. Even though conventional chromatography was successfully used for in situ analyses of the atmospheric constituents of Mars [1,2] and Venus [3], the relatively long time required to complete each analysis prevented the collection and analyses of more samples while the probe descends [4]. Similar problems are anticipated in future planetary missions such as the Galileo, Cassini, Mars Pathfinder, Mars Surveyor, and Rosetta missions. For instance, the proposed NASA–ESA Cassini mission, planned to be launched in 1997 [5] to explore the atmosphere of Titan, will involve the collection and analyses of complex mixtures of low-molecular-mass hydrocarbons, nitriles, dinitriles, CO, H_2, and CO_2 in the presence of large amounts of methane, N_2, and Ar during the probe descent.

To solve some of these problems, Do and Raulin [6,7] studied the chromatographic behavior of PoraPLOT and Al_2O_3–KCl porous-layer open tubular (PLOT) capillary columns for the analysis of light gases. While the columns produced good resolution of the test solutes in a

relatively short time, they were, however, found unsuitable for gas chromatographic experiments aboard spacecraft due to their poor mechanical strength. Also, bleeding of the stationary phase encountered during temperature programming make CP-Sil-5 CB WCOT capillary columns unviable for space applications [8]. Although a Molsieve PLOT capillary column allows the separation of permanent gases in the presence of hydrocarbons and nitriles, its mechanical strength appears too weak to withstand the rigors of launch and space flight [9,10].

In the light of the aforementioned, micropacked columns might be a suitable alternative for capillary columns because of their high sample-loading capacity, low flow-rate, low bleeding of the liquid phase, and small value of the mass-transfer coefficient, C, of the van Deemter equation [11-14]. Such columns with narrow inner column diameter ($d_c \leqslant 1$ mm) have been shown to give high efficiency and outlet flow-rates that satisfy the optimum flow conditions into the mass spectrometer, making them suitable for gas chromatography-mass spectrometry (GC-MS) coupling [15-17]. In view of the anticipated limitations in terms of size, weight, power, and consumables in future planetary missions, the above properties of micropacked columns could be of special benefit for GC-MS experiments aboard a spacecraft [4,18].

More recently, de Vanssay et al. [10] showed that molecular sieve 5A micropacked could be used for fast analysis of permanent gases under isothermal conditions with high efficiency and low column-head pressure. However, the C_2 hydrocarbons were poorly resolved on this column due to their long retention times and poor peak shape. Therefore, micropacked GC columns containing chemically bonded stationary phases with the $\equiv$ Si-O-Si bond type may be a better choice for the determination of low-molecular-mass hydrocarbons. Since this type of packing material can provide high separation efficiency, sample capacity, and high stability capable of withstanding the rigors of launch and space flight, its potential importance in future space missions is currently under investigation.

The present paper describes the synthesis of a series of alkyl-bonded silica packings using mono-, di-, and trifunctional chlorosilanes. Data on gas flow and chromatographic characteristics of the columns, including van Deemter curves for selected light hydrocarbons, are reported.

2. Experimental

2.1. Materials and chemicals

Porasil C (particle size 149-177 μm, surface area 100 m^2/g, pore diameter 300 Å) silica was purchased from Waters Associates (Millipore, Milford, MA, USA). Octyldimethylchlorosilane, octylmethyldichlorosilane, and octyltrichlorosilane were prepared by hydrosilation reaction [19] of distilled octene (Aldrich, Milwaukee, WI, USA) with the appropriate hydrosilane (United Chemical Technologies, Bristol, PA, USA). Each reaction was catalyzed by chloroplatinic acid (Aldrich). Octadecyldimethylchlorosilane and octadecyltrichlorosilane were obtained from United Chemical Technologies and used as received. Toluene, tetrahydrofuran, methylene chloride, and methanol were obtained from general sources and used as received.

2.2. Synthesis of stationary phases

Prior to the preparation of the stationary phases, about 20 g of silica were refluxed with 3 M HCl at 100°C for 2 h, rinsed thoroughly with deionized water, and dried overnight at ca. 150°C in an oven. The monomeric phases were prepared under anhydrous conditions, as follows. About 3 g of silica was added to a warm solution of 30 ml dry toluene and 10 ml of the appropriate monofunctional silane in a 100-ml two-neck round-bottom flask. The slurry was refluxed for 4 h at 110°C under gentle helium (99.999% UHP He) flow. After cooling, the silylated silica was transferred into a sintered glass crucible and washed with dry toluene, methylene chloride, methanol, methanol-water (50:50, v/v), and finally with 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 (hexamethyldisilaxane–trimethylchlorosilane, 1:1 molar ratio) at 100°C. The final product was again washed as described above, dried under vacuum in a desiccator, and stored in a dry bottle for characterization. In a similar manner, monomeric phases using di- or trifunctional silanes were prepared. However, prior to endcapping, the bonded phases were refluxed with 50% THF–H$_2$O for 1 h at 80°C to remove any unreacted chlorine atoms.

The following procedure was employed for the preparation of the polymeric phases using di- or trifunctional silanes. About 3 g of silica were dispersed in a warm solution of 30 ml dry toluene and 10 ml of the appropriate silane in a two-neck round-bottom flask. One milliliter of water was immediately added to the mixture to initiate self-polymerization of the silane and the slurry was refluxed for 5 h under a slow helium flow. The derivatized silica was filtered using a sintered glass crucible and washed as described above. Samples were dried under vacuum in a desiccator and kept in dry bottles for evaluation.

The amounts of stationary phase on the bonded supports were determined by elemental carbon analysis of the dried samples.

2.3. Column packing

The bonded phases were packed into stainless-steel tubes (2.0 m × 1.07 mm I.D.: No. 304) which had been pretreated by washing successively with HCl (20%), distilled water, methanol, and acetone and then purged with helium gas. The tubes were fitted with Swagelok low dead volume connectors. The columns were dry packed in vertical position with one end, loosely plugged with silanized glass wool, connected to a vacuum pump and a small stainless-steel reservoir was attached to the open end. The packing material was slowly added to the reservoir on starting the vacuum pump and the particles were continuously transported into the column while moving a hand vibrator along the column. The column was considered filled when there was no

reduction in the volume of the packing material after a few minutes of vibration. The column inlet was then sealed with silanized glass wool and installed in the gas chromatograph. All columns were conditioned overnight at 110°C under helium-gas purge at 5 ml/min before use.

2.4. Gas chromatograph

The columns were evaluated on a gas chromatograph equipped with a micro thermal conductivity detector (TCD) and control (Carle Instruments, Fullerton, CA, USA) and a Hewlett-Packard HP 3396 Series II integrator (Hewlett-Packard, Avondale, PA, USA). UHP helium (99.999% He) was used as carrier gas for all measurements. To remove traces of water and oxygen from the helium, the carrier gas line was connected to a Matheson Hydrox purifier, Model 8301 (Matheson Gas Products, Secaucus, NJ, USA). 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 to evaluate the chromatographic performance of the columns. The sample mixture was injected into the column with an eight-port Valco (Alltech, Deerfield, IL, USA) valve fitted with two 100-μl sample loops. All experiments were performed under isothermal conditions.

2.5. Chromatographic parameters

The capacity factor, k', was determined from the expression $k' = (t_R - t_o)/t_o$, where t_R is the retention time of the solute and t_o is the hold-up time determined by injecting nitrogen as a marker. The average linear gas velocity values ($\bar{u}$), calculated from the expression $\bar{u} = L/t_o$ (where L is the column length in cm), were obtained by varying the inlet pressures of the carrier gas from 1.38 to 4.14·10^5 Pa at the operating temperature. The carrier gas flow-rate was measured at the column outlet using a soap-bubble flow meter. Assuming the peaks to be symmetrical and Gaussian, the theoretical plate height, H, for the test solutes were calculated from

$$H = \frac{L}{5.54}\left[\frac{w_{0.5}}{t_R}\right]^2, \tag{1}$$

where $w_{0.5}$ is the peak width at half height in time units. The separation factor, α, and column plate number, N, were calculated in the usual manner.
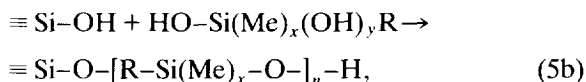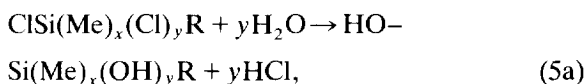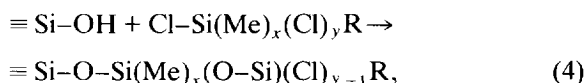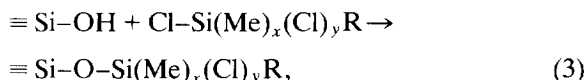
3. Results and discussion

The objective of this study was to investigate the viability of micropacked columns containing alkyl-bonded silicas for GC analysis of light hydrocarbons in planetary atmospheres. These columns are considered suitable for this application due to their high efficiency, speed, selectivity, and thermal stability when compared with conventionally coated columns. The physical characteristics of the packing materials are shown in Table 1. The surface coverage of each bonded phase was calculated from its percentage carbon load (%C) according to the equation [20]

$$\text{surface coverage } (\mu\text{mol}/\text{m}^2) = \frac{\%C \times 10^6}{1200N_c \times S_{BET}}. \tag{2}$$

where N_c is the number of carbon atoms in the bonded ligand and S_{BET} is the surface area of the silica as given by the manufacturers. As can be seen, the carbon contents of the polymeric phases are relatively higher than the corresponding monomeric phases and this, in a few cases, results in exceptionally high surface coverage of the packing. Thus, beside the di- and trifunctional silanes undergoing a 1:1 or 1:2 stoichiometric reaction with the silanols [21] as expressed by Eqs. 3 and 4, respectively, addition of water to the reaction mixture probably increased the carbon content of the phases by increasing the amount of bonded chains through self-polymerization of the hydrolyzed product of the silanes according to Eqs. 5a and 5b [22]:

$$\equiv\text{Si–OH} + \text{Cl–Si(Me)}_x(\text{Cl})_y\text{R} \rightarrow$$
$$\equiv\text{Si–O–Si(Me)}_x(\text{Cl})_y\text{R}, \tag{3}$$

$$\equiv\text{Si–OH} + \text{Cl–Si(Me)}_x(\text{Cl})_y\text{R} \rightarrow$$
$$\equiv\text{Si–O–Si(Me)}_x(\text{O–Si})(\text{Cl})_{y-1}\text{R}, \tag{4}$$

$$\text{ClSi(Me)}_x(\text{Cl})_y\text{R} + y\text{H}_2\text{O} \rightarrow \text{HO–}$$
$$\text{Si(Me)}_x(\text{OH})_y\text{R} + y\text{HCl}, \tag{5a}$$

$$\equiv\text{Si–OH} + \text{HO–Si(Me)}_x(\text{OH})_y\text{R} \rightarrow$$
$$\equiv\text{Si–O–[R–Si(Me)}_x\text{–O–]}_n\text{–H}, \tag{5b}$$

where $x = 1$ or 0 and $y = 1$ or 2 for di- or trifunctional silane, respectively; R is $\text{CH}_3(\text{CH}_2)_{17}$ – or $\text{CH}_3(\text{CH}_2)_7$ – and n is an integer equal to or greater than 1.

The gas flow properties of the columns are presented in Table 2. Using a value of $2.018 \cdot 10^{-4}$ g cm^{-1} s^{-1} for the viscosity, η, of helium at 25°C [23], the specific permeabilities, κ_o, were

Table 1
Characteristics of the bonded phases[a]

Column no.	Phase type	%C	Surface coverage (μmol/m^2)
1	monomeric monofunctional C_8	2.46	2.05
2	monomeric difunctional C_8	3.58	3.31
3	polymeric difunctional C_8	4.22	3.91
4	monomeric trifunctional C_8	4.67	4.86
5	polymeric trifunctional C_8	4.78	4.98
6	monomeric monofunctional C_{18}	8.60	3.98
7	monomeric trifunctional C_{18}	8.81	4.08
8	polymeric trifunctional C_{18}	10.72	4.96

[a] Silica: Porasil C, 80/100 mesh.

Table 2
Columns gas flow characteristics[a]

Column no.	Packing density (g/cm³)	Porosity, ϵ	Permeability, κ_0 ($\times 10^{-7}$ cm²)
1	0.508	0.404	2.74
2	0.497	0.402	2.69
3	0.502	0.398	2.57
4	0.499	0.405	2.78
5	0.510	0.398	2.57
6	0.498	0.401	2.66
7	0.500	0.400	2.64
8	0.503	0.407	2.83
Mean ± S.D.	0.502 ± 0.005	0.402 + 0.003	2.69 ± 0.09
C.V. (%)	1.0	0.7	0.3

[a] Columns: 2.0 m × 1.07 mm I.D.; helium, 25°C.
S.D. = standard deviation; C.V. = coefficient of variation.

determined from the slopes of the plots of F_0 versus $p_i^2 - p_0^2$ derived from [24]

$$F_0 = \frac{3.0 \cdot 10^7 \, A\kappa_0 [p_i^2 - p_0^2]}{\eta L p_0}.$$ (6)

where F_0 is the carrier gas flow-rate at the column outlet, A is the cross-sectional area of the column, and p_i and p_0 are the column inlet and outlet pressure, respectively. The column porosity, ϵ, was calculated from the expression $\epsilon = 1 - m\rho_b / V_c$, where ρ_b and m are the bulk density and mass of packing, respectively, and V_c is the column volume. As can be seen, column porosities were almost identical and very close to the theoretical value of 0.42 reported for random close packing of spheres with small diameter range [25]. The insignificant differences in column permeability (coefficient of variation, C.V. = 0.3%) and packing densities (C.V. = 1.0%) showed that the packing procedure is reasonably uniform and reproducible.

Fig. 1 shows the chromatograms illustrating the separation performance of the selected columns. Better separation of the analytes was possible using the polymeric surface modification process, as indicated by the resolution of the test solutes which improved from monomeric to polymeric phases. While baseline separation was achieved only on the polymeric C_{18} column

(column 8), the overall time required for the elution of butane (last peak) ranged from about 1.0 min in column 1 to 2.2 min in column 8 at the operating conditions.

The chromatographic properties of the columns in terms of their capacity factor, selectivity, and efficiency of the solutes are listed in Table 3. In general, higher k' and plate numbers were obtained on the polymeric phases than on the monomeric phases and these were greater on octadecyl columns, as expected. Also, the solutes were retained longer on the octadecyl phases than on the corresponding octyl phases. This is probably the result of their high carbon content rather than the nature of the stationary phase. Therefore, the analytes interact with the bonded ligands almost exclusively by dispersive forces which increase with the molecular contact area between the solutes and the hydrocarbonaceous layer of the stationary phases. As might be expected, the k' for methane remains substantially constant ($k' = 0.06 \pm 0.01$) on all the columns, since it's dispersive interaction with the stationary phase is very small compared to, for example, that of butane, where the overlap between the chains leads to a significant dispersive interaction.

According to Ettre and March [26], plots of resolution versus retention time for a given pair of peaks provides a good comparison of the
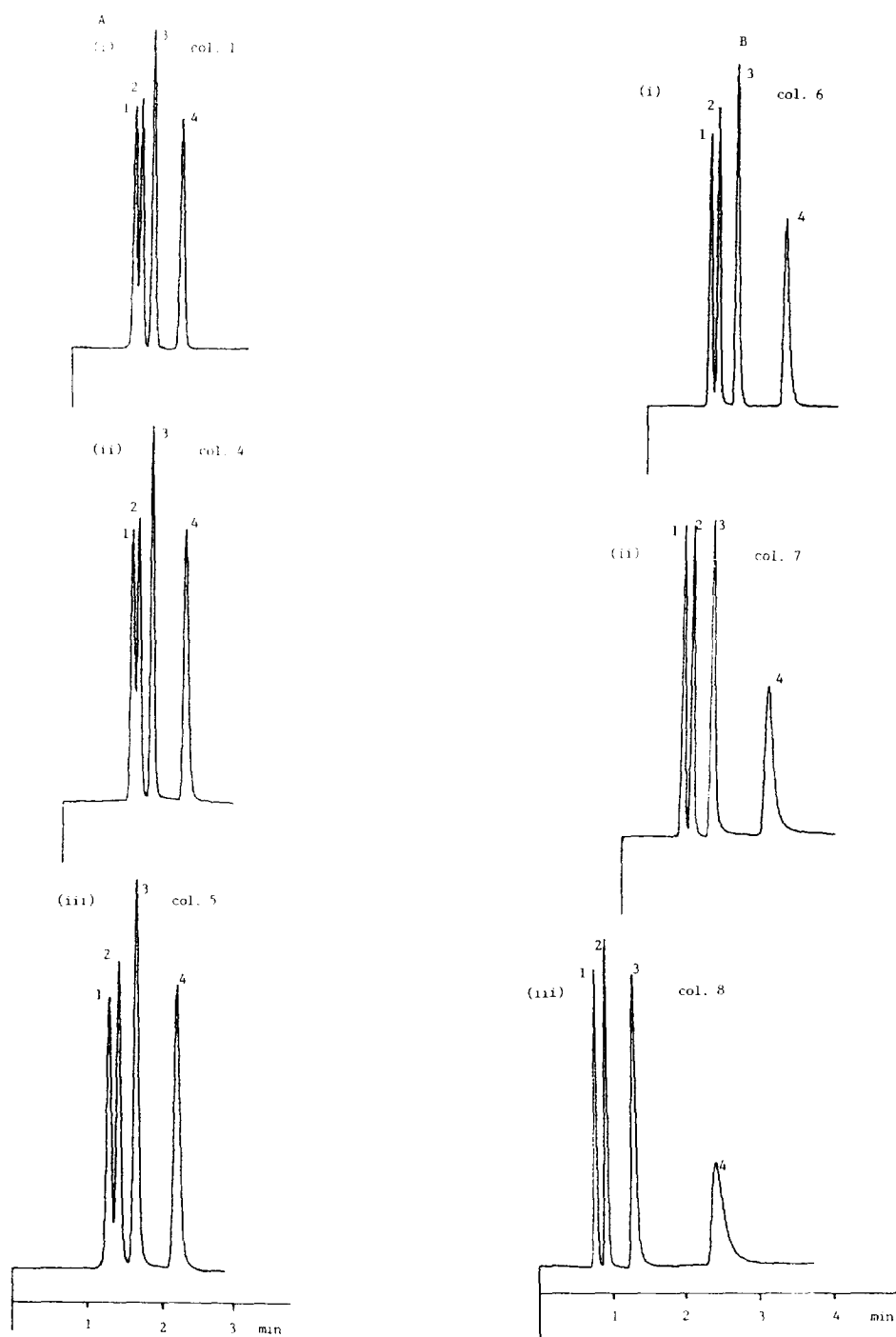
Fig. 1. Gas chromatogram of light hydrocarbons on 2.0 m × 1.07 mm I.D. columns of various: (A) octyl- and (B) octadecyl phases. (i) Monomeric monofunctional. (ii) monomeric trifunctional, (iii) polymeric trifunctional syntheses. Conditions: temperature, 25°C; TC detector; carrier gas: He, 5.5 ml/min; 100-μl injection loop. Peaks: (1) methane, (2) ethane, (3) propane, (4) butane.

Table 3
Chromatographic properties of columns[a]

Column no.	Capacity factor				Separation factor			Efficiency[b] (plates/m)
	k'_{C_1}	k'_{C_2}	k'_{C_3}	k'_{C_4}	α^2_1	α^3_2	α^4_3	
1	0.05	0.12	0.30	0.65	2.40	2.50	2.17	1112
2	0.06	0.18	0.38	0.85	3.00	2.11	2.24	1217
3	0.07	0.19	0.39	0.87	2.05	2.47	2.23	1264
4	0.06	0.15	0.34	0.76	2.50	2.27	2.24	1246
5	0.06	0.16	0.35	0.78	2.67	2.19	2.23	1263
6	0.06	0.19	0.50	1.30	3.17	2.63	2.60	1332
7	0.06	0.22	0.58	2.22	3.67	2.64	3.83	1477
8	0.07	0.28	0.85	2.67	4.00	3.04	3.14	1513

[a] Temperature: 25°C; column length: 2.0 m; carrier gas: He, 5.5 ml/min.
[b] Column efficiency based on butane peak.

"true" performance of different columns in gas chromatography. Fig. 2 shows these plots for the propane/butane peak pair for all the columns. The resolution, R_s, for the two peaks was calculated from the expression

$$R_s = \frac{1}{4} \frac{\alpha - 1}{\alpha} \frac{k'}{1 + k'} \sqrt{N}. \qquad (7)$$

The differences in selectivity of the columns is reflected in the shape of the curves. Thus, the high retention capacity of the solutes on columns 7 and 8 results in high resolution. As shown in Fig. 2, column 8 gave a much better resolution
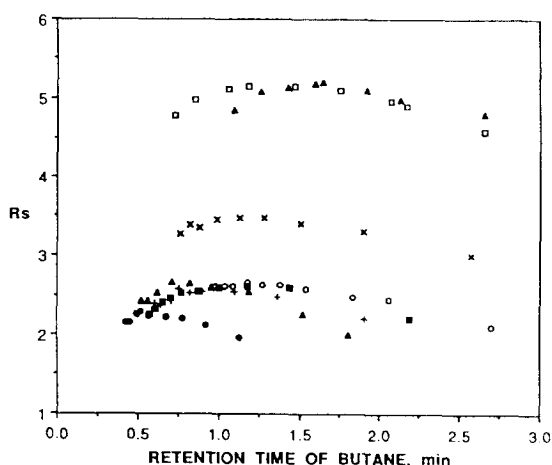

Fig. 2. Plots of resolution of the propane/butane peak pair against the retention time of butane. Column identifications: (●) 1, (■) 2, (+) 3, (△) 4, (○) 5, (×) 6, (▲) 7, (□) 8.
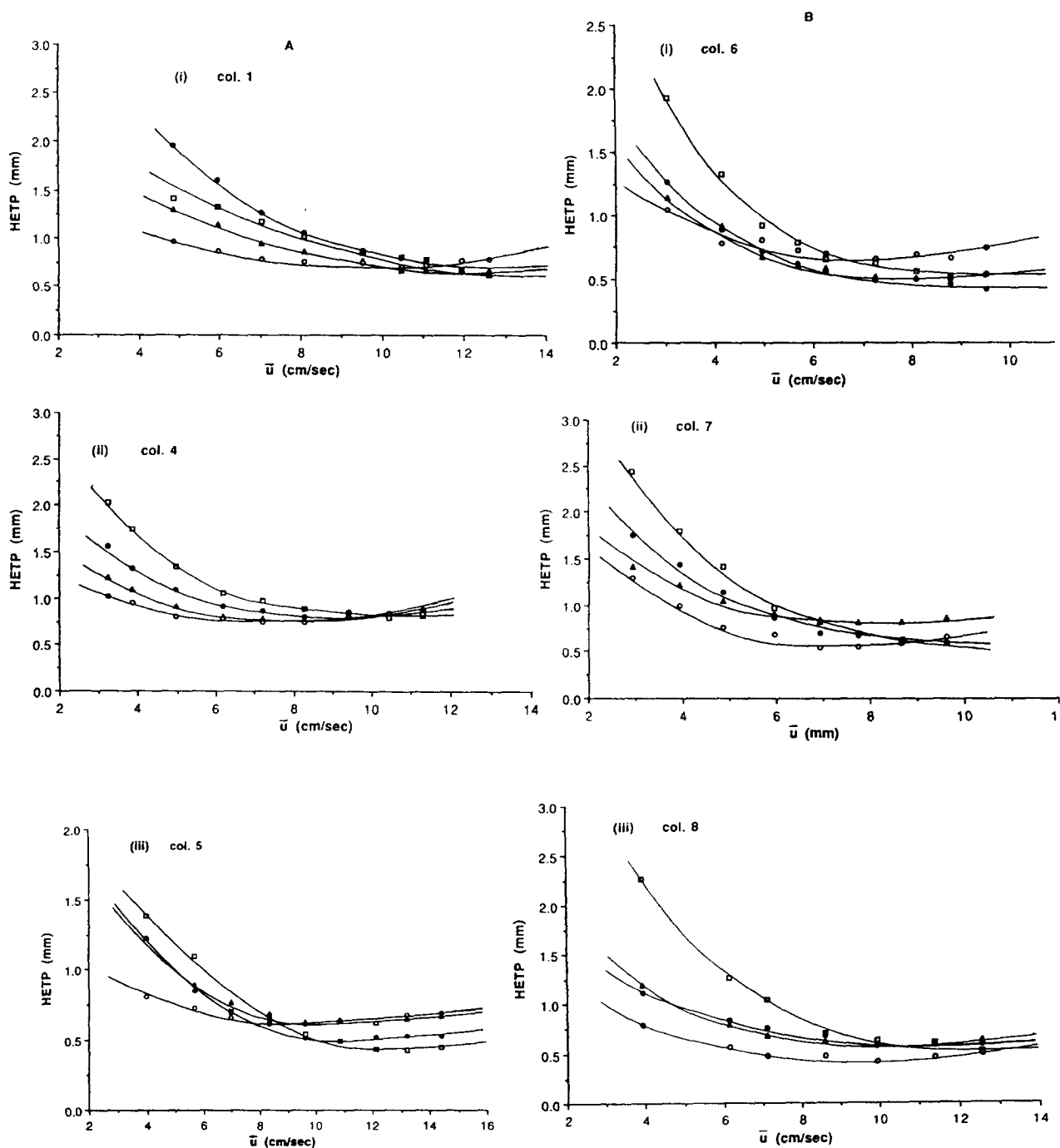
than column 7 in a short analysis time. The best resolution that could be achieved on column 1 is about 2.3, after which the resolution decreases markedly with increasing analysis time. At high velocities, the maximum R-values for columns 2, 3, 4, and 5 are almost identical. In general, the resolutions of the octadecyl phases are significantly higher than those of the octyl phases, presumably due to their high hydrocarbon character and hence high retention capacity of the solutes.

Fig. 3 shows the column efficiencies expressed in terms of HETP (height equivalent of a theoretical plate) as a function of average linear gas velocity, $\bar{u}$. The fit of the experimental data to the van Deemter equation ($H = A + B/\bar{u} + C\bar{u}$) [27] by the least-squares method gave negative values for the constant A. Therefore, in agreement with previous data for packed columns [28,29], a constant value of zero was assumed and the contributions of B (axial diffusion in the column) and C (mass transfer in the column packing material) terms of the equation to the total plate height for butane are listed in Table 4 together with the minimum column plate heights (H_{min}) at optimum carrier gas velocities ($\bar{u}_{opt}$). The plots show the expected improvement in column efficiency as the B term contribution diminishes, with each plot exhibiting a shallow and broad minimum at the optimum region. While the linear part of the curves for methane

Fig. 3. Dependence of H on average linear gas velocity ($\bar{u}$) of test solutes on 2.0 m × 1.07 mm I.D. columns of various (A) octyl-
and (B) octadecyl phases. (i) Monomeric monofunctional, (ii) monomeric trifunctional, (iii) polymeric trifunctional syntheses.
Carrier gas: helium, $T = 25°C$. Symbols represent: (□) methane, (●) ethane, (△) propane, (○) butane.

Table 4
Kinetic properties of the columns for butane at 25°C

Column no.	ΔP ($\times 10^5$ Pa)	ϕ_{min} (ml/min)	$\bar{u}_{opt}$ (cm/s)	$HETP_{min}$ (mm)	B (cm^2/s)	C ($\times 10^{-3}$ s)
1	2.39	11.1	6.69	0.66	0.28	5.2
2	2.38	10.9	7.35	0.59	0.20	5.0
3	2.21	11.2	7.08	0.62	0.22	5.5
4	2.12	12.0	7.09	0.68	0.28	5.2
5	2.20	11.0	8.43	0.64	0.23	6.3
6	2.40	11.8	7.69	0.69	0.21	6.4
7	2.17	12.0	7.94	0.58	0.25	6.6
8	2.28	12.3	7.72	0.46	0.23	7.0

(least retained solute) remains almost constant at high velocities, those of other solutes, especially butane, increased slowly with increasing gas velocity. This may be due to the low diffusion coefficient of butane in the gas phase, which probably leads to low plate heights at low velocities where the B term is large ($B/\bar{u}$&z.Gt;$C\bar{u}$) and large plate heights at higher gas velocities where the C term predominates ($C\bar{u}$&z.Gt;$B/\bar{u}$).

As shown in Table 4, the C terms for the polymeric packings are slightly higher than those of the corresponding monomeric phases. This is probably caused by the low diffusion coefficient of the solute within the cross-linked polymer structure of the bonded ligands. The above phenomenon might account for the relatively high C-value of column 5 compared to that of column 3. Thus, column 3 may be thought of possessing a less cross-linked polymer structure than column 5 and therefore offering a small resistance to mass transfer. Since B is directly proportional to the diffusion coefficient of the solute in the carrier gas, which is the same for molecules of the same size and shape, the value of B is almost constant for all the columns. Similar trends were observed for other solutes. The minimum flow-rate, ϕ_{min} (mean = 11.54 ml/min; C.V. = 4.72%), and $\bar{u}_{opt}$ (mean = 7.50 cm/s; C.V. = 7.42%) are not significantly different in all the columns and are within the range of values obtained in gas–liquid chromatography [30]. From the data presented in Table 4, column 8, which yields a minimum plate height of 0.46 mm (2174 theoretical plates/m) with butane, ap-

peared to be the best column. This minimum value of H was achieved at an average linear gas velocity of 7.72 cm/s, corresponding to a flow-rate of 12.3 ml/min and a pressure drop of $2.28 \cdot 10^5$ Pa.

The thermal stability of the phases was examined by determining the capacity factors of the test solutes at 25°C after purging the columns at high temperatures ranging from 100 to 250°C for 2 h under dry helium flow. A change of about 10% or higher in k'-values indicates that the packing material was affected at the purging temperature. Fig. 4 shows the effect of the purging temperature on the capacity factor of butane. It can be seen that the k' of butane did not vary greatly within the temperature range investigated. In fact, increasing the purging tem-
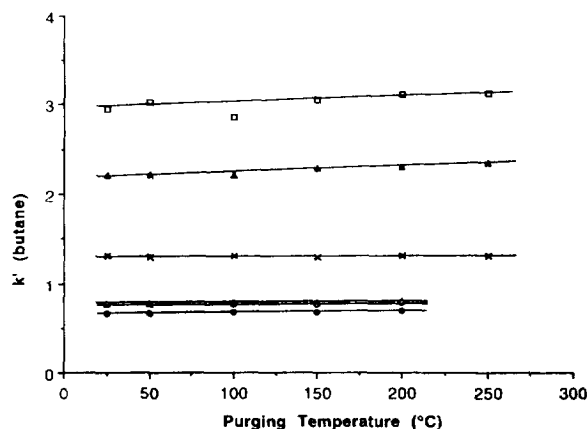

Fig. 4. Effect of purging temperature on capacity factor, k' of butane. Column identifications: (●) 1, (△) 4, (○) 5, (×) 6, (▲) 7. (□) 8.

perature of columns 6, 7, and 8 to 250°C results in 5.4, 6.0, and 6.5% loss, respectively, in k'-values of butane, which could well be due to removal of residual solvents from the pores of the packings at elevated temperatures. Therefore columns 6, 7, and 8 can be operated at temperatures up to 250°C without any appreciable column bleed. This temperature is notably higher than that obtained on isocyanate packings [31]. Consequently, the packing materials investigated in this study, particularly the polymeric C_{18} phase (column 8), can be employed with ionization detectors where high stability and minimum column bleed are required.

To further illustrate the performance of column 8, being the most efficient column, Fig. 5 shows the chromatogram of a ten-hydrocarbon mixture of C_1 to C_4 compounds. Although not capable of producing baseline separation of all the compounds (Fig. 5A), the analysis was much faster (<6 min) than that obtained on isocyanate columns (ca. 15 min) under similar conditions but at a lower carrier gas flow-rate [31]. At a column temperature of 50°C, the time required

for such analysis was reduced almost by half (Fig. 5B). Even though propadiene and propene and isobutane and butane co-eluted, respectively, ethane was separated from ethene under these conditions. Thus, column selectivity could presumably be improved by temperature programming and/or optimization of the column parameters such as column length and particle diameter. It is worth mentioning that the high power consumption of temperature programming may be detrimental to spacecraft applications since one of the major constraints in space missions is power budget.

4. Conclusion

This study has demonstrated the potential importance of micropacked alkyl-bonded silica columns, particularly polymeric octadecyl packings, for GC analysis of light hydrocarbons due to their good chromatographic performance compared to conventional packed columns. Even though a WCOT capillary column with chemical-
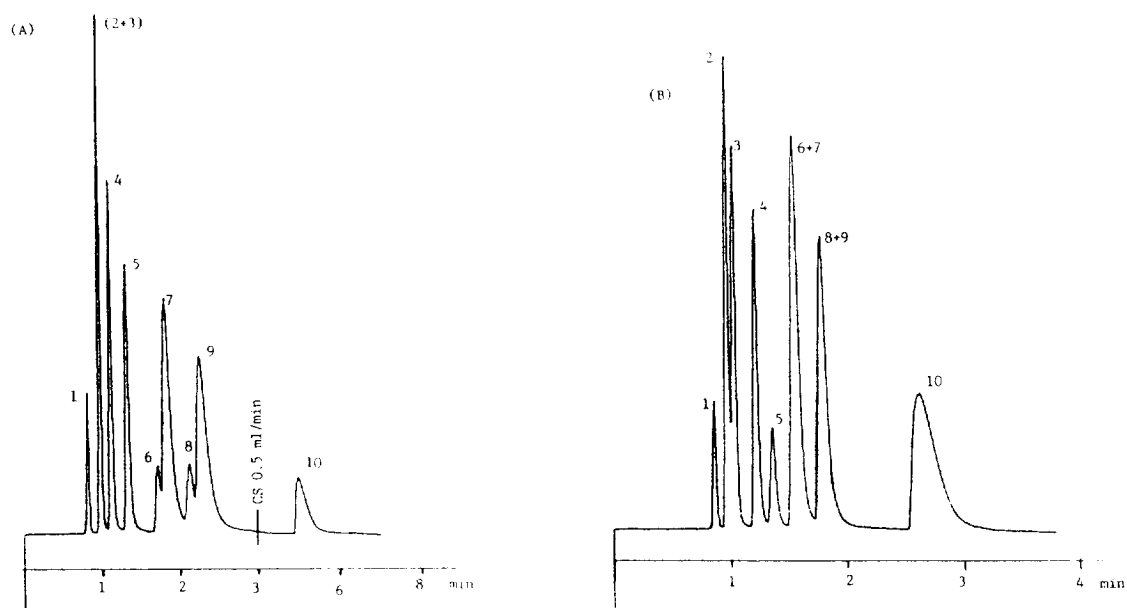

Fig. 5. Separation of hydrocarbon mixtures on polymeric octadecyl bonded phase (column 8). Conditions: temperature (A) 25°C, (B) 50°C; TC detector; carrier gas: He, 8.34 ml/min; 100-μl injection loop; chart speed (CS); 2.0 ml/min at start, changed to 0.5 ml/min at 3.0 min. Peaks: (1) methane, (2) ethane, (3) ethene, (4) propane, (5) acetylene, (6) propene, (7) propadiene, (8) isobutane, (9) butane, (10) propyne.

ly bonded stationary phase (dimethyl polysiloxane) provides fast and efficient analysis of low-molecular-mass hydrocarbons and nitrile [8], the high thermal stability of the present columns coupled to the capability of micropacked columns to handle much larger samples without overloading appear to make them suitable for GC instrumentation in future space missions. In view of the complex nature of gas mixtures in planetary atmospheres, the chromatographic behavior of the column with N-organics including nitriles is worth investigating.

Acknowledgements

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