Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Support-Coated Open Tubular Columns, V. Columns with Various Liquid-Phase Loadings

L. S. Ettre[a]; J. E. Purcell[a]; K. Billeb[a]
[a] The Perkin-Elmer Corporation, Norwalk, Connecticut

To cite this Article Ettre, L. S. , Purcell, J. E. and Billeb, K.(1966) 'Support-Coated Open Tubular Columns, V. Columns with Various Liquid-Phase Loadings', Separation Science and Technology, 1: 6, 777 — 802
To link to this Article: DOI: 10.1080/01496396608049480
URL: http://dx.doi.org/10.1080/01496396608049480

SEPARATION SCIENCE, 1(6), 777–802 (1966)

Support-Coated Open Tubular Columns, V. Columns with Various Liquid-Phase Loadings*

L. S. ETTRE, J. E. PURCELL, and K. BILLEB
THE PERKIN-ELMER CORPORATION,
NORWALK, CONNECTICUT

Summary

Support-coated open tubular columns of a wide range of phase ratio (β) are considered. Efficiency, comparison with maximum theoretical efficiency, and length and temperature of analysis are discussed for various liquid loadings.

Comparison with classical open tubular columns and packed columns is made.

Support-coated open tubular columns were first introduced in 1963, by Halász and Horváth (*1*). Their development represents the realization of Golay's original suggestion for increasing the inside surface of column tubing without increasing its diameter (*2*). In this way, additional liquid phase may be applied in a relatively thin film, while the phase-ratio value—the value of β—is reduced. The advantages of such columns are obvious:

1. The sample capacity of the column is increased as compared to the classical open tubular columns, where the liquid phase is coated on the inside tube wall. Sample charges, similar to those used with small-diameter packed columns, are possible.

2. The partition ratio (k) of a given component is increased. As a conclusion, fewer theoretical plates—i.e., shorter columns—are

* This article will be published later in a volume entitled *Separation Techniques: Proceedings of the Nineteenth Annual Summer Symposium on Analytical Chemistry.*

required for a given resolution or with a given column length, and better separation can be achieved.

3. The relatively thin film and the generally shorter column length will result in a reduction of the analysis time for a given component as compared with a packed column (if such column exists at all). Even compared with wall-coated open tubular columns, the analysis time is frequently shorter.

Our previous papers (*3–6*) have dealt with the various aspects of the support-coated columns. In the work reported there, columns with relatively high liquid-phase loading were used: The phase-ratio value of those columns was in the range of 20 to 30, i.e., close to the value of standard packed columns. With these columns, it was necessary to use temperatures about 50°C higher than those normally used with the classical wall-coated open tubular columns. Owing to the relatively high liquid-phase volume, sample amounts as high as 0.2 μl could be injected, and thus the minimum detectability could be improved as compared with the classical wall-coated open tubular columns.

The aim of the investigations reported in the present paper was to evaluate the influence of lowering the liquid-phase loading (i.e., increasing the value of the phase ratio) on column performance. In connection with this work, certain measurements and calculations on the support material were also carried out.

EXPERIMENTAL

Columns

The columns used in our work were prepared according to the method described by Halász and Horváth (*1*): dissolving the liquid phase in a high-density solvent such as Freon, suspending the support in this solution, filling the empty column tubing with the suspension, and evaporating the solvent by drawing the filled tube through an oven heated above the boiling point of the solvent. Except for those mentioned specifically, all columns were made of thin-walled stainless-steel tubing of 0.020-in. I.D., in 50-ft segments. If longer columns were needed, the 50-ft segments were joined using Swagelok unions.

The phase-ratio (β) values of the squalane columns were calcu-

lated from the well-known equation (1), where K is the partition

$$K = \frac{V_G}{V_L} k = \beta k \quad (1)$$

coefficient and k the partition ratio for a certain solute, and V_G and V_L are the respective volumes of the gas and liquid phases, in the column. Normal paraffins were analyzed on the columns and the value of the partition ratio established; the partition-coefficient values for the normal paraffins were taken from the publication of Desty and Goldup (7).

For columns prepared with liquid phases other than squalane, the phase-ratio values were approximated by comparing the relative amount of liquid phase present with the various squalane columns, assuming the same density for the liquid phase.

Support Material

The support material used in our work is a very fine diatomaceous earth type of support obtained from the Johns-Manville Corp. (R-6470-1). This support is characterized by the physical constants listed in Table 1 and from the pore-size distribution curve shown in Fig. 1. The surface area, total pore volume, and pore-size distribution were determined using the continuous-flow method. The total pore volume was also measured using water or alcohol titration method of Innes and was found to be 25 to 28 μl/g. Both this method and the mercury-penetration method established that there are no pores greater than 1000 A in diameter. Particle size was measured using the Hitachi PSA-2 particle-size analyzer.

TABLE 1

Physical Constants of the Support Material Used in the Preparation of Support-Coated Open Tubular Columns

True density, g/ml	2.10
Loose density, g/ml	0.13
Particle size, μ	<2
Specific surface area (BET), m^2/g	5.34
Accumulative pore volume (up to 1000-A pore diameter), μl/g	28

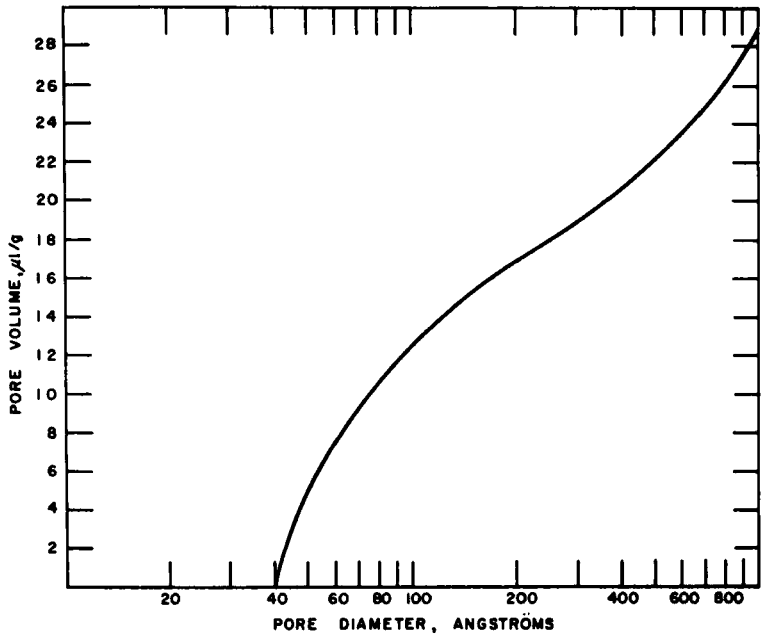

FIG. 1. Pore-size distribution of the support used in column preparation.

Instrumentation

The analyses reported here were carried out with either the Model 880 or the Model 226 gas chromatographs of the Perkin-Elmer Corp. Both instruments were equipped with flame-ionization detectors and connected to Leeds & Northrup Speedomax "G" 1- or 5-mV recorders. With a 5-mV recorder, these systems correspond to a full-scale pen deflection of 1.1×10^{-11} amp at attenuation × 1.

Helium was used as the carrier gas. The flow rates reported were measured at column outlet and ambient temperature. The average linear gas velocities ($\bar{u}$) were calculated from the column length (L) and the retention time of methane (t_M) [Eq. (2)].

$$\bar{u} = L/t_M \tag{2}$$

Samples were introduced with help of Hamilton 1- or 10-μl syringes. Usually, 1 to 2 μl total sample volumes were injected and the homogeneous mixture of carrier gas plus sample vapor split

in a 1:10 to 1:40 ratio. The sample volumes listed refer to the actual volumes entering the column.

RESULTS AND DISCUSSIONS

Column Characteristics

The columns prepared for the investigation belong to four categories as given in Table 2. As shown the amount of support was kept constant, while the amount of liquid phase in the column was varied.

Microscopic investigations were also carried out to check the actual physical appearance of the support-substrate layer. On the inside wall of the stainless-steel tubing, the solid coating represents a fairly symmetric ring with a thickness of about 20 to 30 μ. However, when using copper tubing, the solid layer became fairly irregular. This may be explained by the unevenness of the inside surface of copper tubing as compared with the stainless-steel tubing.

Influence of Changes in Liquid-Phase Loading

Efficiency. Reduction in the relative amount of the liquid phase improves column efficiency. Figure 2 plots the values of HETP for three squalane columns against the average carrier-gas velocity ($\bar{u}$). All three plots were obtained at 75°C, and no attempt was made to optimize the temperature for the particular sample analyzed. With a fixed average carrier-gas velocity, there is always an optimum temperature where the value of HETP is the smallest; Table 3 lists some data.

TABLE 2

Characteristic Values of the Support-Coated Open Tubular Columns Used for the Investigations

Tube I.D. (nominal), mm	0.50	0.50	0.50	0.50
Geometric surface area of the tube, cm^2/m	15.7	15.7	15.7	15.7
Amount of solid support in the column, mg/m	8.75	8.75	8.75	8.75
Amount of liquid phase in the column, mg/m	8.2	4.1	2.6	0.51
Value of the phase ratio (β)	22	50	67	360

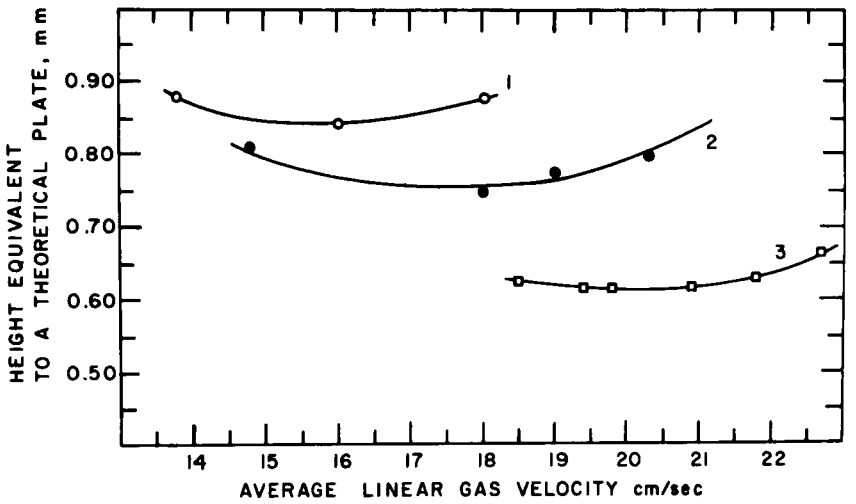

FIG. 2. HETP curves for three support-coated columns prepared with squalane liquid phase having different phase-ratio values. Column length, 100 ft; phase ratios, (1) 22, (2) 50, (3) 67. Sample and the value of the partition ratio (k): (1) methylcyclohexane (k = 11.1); (2) methylcyclohexane (k = 5.0); (3) n-heptane (k = 2.8). Carrier gas, helium.

TABLE 3

HETP Values for Certain Hydrocarbons at Different Temperatures[a]

Substance	Boiling point, °C	Column temperature, °C			
		60	77	82	90
		Value of HETP, mm			
2-Methylbutane	27.85	0.56	0.44	0.43	0.58
2,2-Dimethylbutane	49.74	0.59	0.53	0.48	0.50
n-Hexane	68.74	0.58	0.44	0.51	0.52
Benzene	80.10	0.60	0.59	0.60	0.61
Cyclohexane	80.74	0.64	0.57	0.57	0.57
3-Methylhexane	91.85	0.59	0.56	0.53	0.49
n-Heptane	98.43	0.61	0.57	0.54	0.54
2,2,4-Trimethylpentane	99.24	0.65	0.59	0.58	0.56

[a] Column: 100-ft × 0.020-in. I.D. support-coated open tubular, prepared with squalane liquid phase. Phase ratio (β), 67. Average linear carrier-gas velocity, 19.4 ± 0.5 cm/sec.

Figure 2 illustrates the general trend resulting from lowering the liquid-phase loading: The over-all column efficiency improves and, at the same time, the HETP versus $\bar{u}$ plot flattens. This means that, when working at flow rates above optimum, the increase in the HETP is relatively small. As a conclusion, analysis time can be reduced without severe loss in efficiency; this is illustrated later with the help of Fig. 6.

The increase in the gas velocity will increase N/t_R, i.e., the value of the number of effective plates produced per unit time up to a certain point. This is the region where—if necessary—increase of the column length can compensate for the loss in efficiency while still permitting an analysis time shorter than obtained with the original column length and optimum gas velocity. This concept was discussed in detail by Desty et al. (8) and, recently, by Halász and Gerlach (9). Figure 3 plots the HETP and the N/t_R values for a squalane column having a phase ratio of 67, using *n*-heptane as

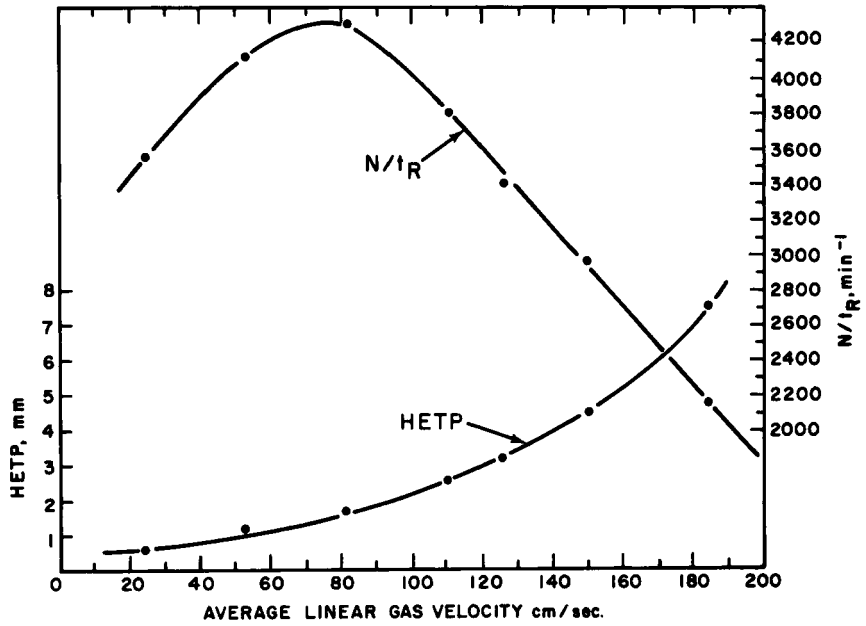

FIG. 3. Plot of HETP and N/t_R against the average linear gas velocity for a 100-ft-long support-coated column prepared with squalane liquid phase (β = 67). Sample, *n*-heptane; column temperature, 90°C; partition ratio (k), 1.74; carrier gas, helium.

sample, at 90°C. As can be seen, the maximum of the N/t_R plot is at about 70 cm/sec average gas velocity, whereas the optimum flow (the minimum of the HETP plot) is below 20 cm/sec.

Figure 3 illustrates one more effect. Recently, Littlewood (*10*) discussed in detail the so-called anastomosis in gas-chromatographic columns which—in packed columns—may result in a concave curvature of the HETP versus $\bar{u}$ plot at high $\bar{u}$ values. In the case of open tubular columns where there are no multiple paths, there ought to be no anastomosis. Figure 3 is an additional proof of the validity of this statement.

Sample Capacity. The lowering of the liquid-phase loading naturally reduces the sample capacity of the columns. This, however, does not necessarily result in a worsening of the actual minimum detectable limit. The reason for this is that one is able to use shorter columns (because, generally, the support-coated columns with lower loading have an increased efficiency); thus the retention times were reduced and the peaks became sharper. As a conclusion, although the *absolute* amount that can be introduced into the column will be less than with heavier-loaded columns, the *practical* minimum detectability—expressed as concentration in the sample—will remain almost the same, or may even be improved.

Temperature of Analysis. It has already been mentioned that the columns used in our early work (which were characterized by phase ratios in the range of 20 to 30) had to be used at temperatures about 50°C higher than the temperature normally used with classical wall-coated open tubular columns.

Lowering of the liquid loading (i.e., increase in the phase-ratio value) reduces the necessary analytical temperature. However, the temperatures will still be higher than those usually required for wall-coated columns. In a wide range of applications—particularly in the hydrocarbon field—the analysis temperatures required, being higher than those used with wall-coated columns, will fall within the accurately controlled range of commercial gas chromatographs. Frequently, the need for subambient temperatures is also eliminated.

Examples. The following examples illustrate the effects discussed above.

Figures 4 and 5 show chromatograms of a high-purity (99.5+ %) *n*-heptane sample with some added components. For the analysis

of such a sample the ASTM method No. D-2268-64T specifies a wall-coated open tubular column of 0.010-in. I.D. with squalane liquid phase, in a length of at least 200 ft, and at room temperature. The chromatograms shown here were obtained with support-coated columns prepared with squalane liquid phase. Figure 4 was obtained on a heavier-loaded column ($\beta = 22$), at 85°C, whereas Fig. 5 is the result of the analysis on a lower-loaded column ($\beta = 67$), at 65°C. Table 4 compares the operating parameters and the analytical results. From these data, the following evaluation is possible:

1. The HETP value of the second column ($\beta = 67$) is much better than that of the first; thus the total number of theoretical plates is practically the same, although the second column was 33% shorter.

2. Owing to the lower temperature (to the increase of the relative retention), peaks 1 and 2 corresponding to the added cyclo-

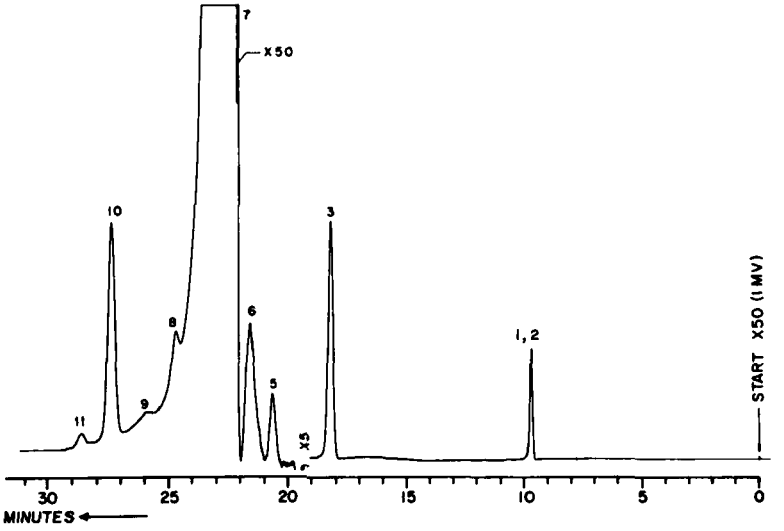

FIG. 4. Analysis of a high-purity *n*-heptane, I. Column, 150-ft × 0.020-in. I.D. support-coated open tubular, prepared with squalane liquid phase. Phase ratio (β), 22; column temperature, 85°C; sample (column), 0.21 μl; carrier gas, He; flow rate at outlet, 3 ml/min; 1-mV recorder. Peaks: (1) cyclopentane (100 ppm, added); (2) 2-methylpentane (100 ppm, added); (3) cyclohexane (600 ppm, added); (7) *n*-heptane.

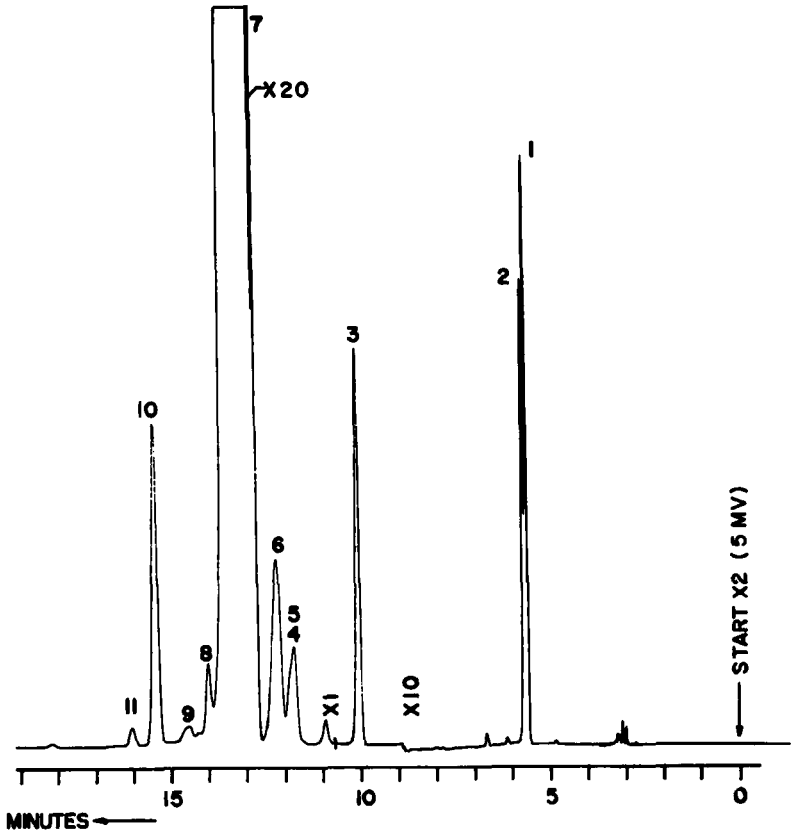

FIG. 5. Analysis of a high-purity *n*-heptane, II. Column, 100-ft × 0.020-in. I.D. support-coated open tubular, prepared with squalane liquid phase. Phase ratio (β), 67; column temperature, 65°C; sample (column), 0.08 μl; carrier gas, He; flow rate at outlet, 3.3 ml/min; 5-mV recorder. Peaks as listed in Fig. 4.

pentane and 2-methylpentane could be partly separated in Fig. 5, whereas they overlapped in Fig. 4. The excellent efficiency of the second column is well illustrated by the fact that the relative retention of these two peaks is only 1.024.

3. The minimum detectable limit is arbitrarily calculated as the concentration of cyclohexane in the actual sample introduced into the column, which would result in a peak having 4 mm height*

* The reason for the selection of this value is that, with attenuation × 1 on a 1-mV recorder, this is about the smallest peak which can be evaluated.

TABLE 4

Comparative Data on the Three Chromatograms Shown in Figs. 4 to 6

		Fig. 4	Fig. 5	Fig. 6
L	Column length, m	45.720	30.480	30.480
β	Phase ratio	22	67	67
	Column temperature, °C	85	65	65
k	Partition ratio of cyclohexane	4.66	2.72	2.72
k	Partition ratio of peak no. 11	7.94	4.93	4.93
F_o	Carrier-gas flow rate at outlet, ml/min	3.0	3.3	8.7
u_o	Carrier-gas outlet velocity, cm/sec	28.93	22.15	40.48
p_i/p_o	Ratio of inlet and outlet pressures	1.41	1.34	1.61
j	Compressibility correction factor	0.822	0.849	0.753
B_0	Specific permeability, 10^{-7} cm^2	586	354	320
$\bar{u}$	Carrier-gas average velocity, cm/sec	23.78	18.81	30.48
t_R	Retention time of cyclohexane, min	18.14	10.04	4.79
t_R	Retention time of peak no. 11, min	28.7	16.02	7.48
HETP	HETP for the cyclohexane peak, mm	1.05	0.66	0.95
n	Number of theoretical plates for the cyclohexane peak	43,540	45,950	32,050
N	Number of effective plates for the cyclohexane peak	29,490	24,560	17,130
N/t_R	Effective plate number/retention time for the cyclohexane peak, min^{-1}	1,630	2,450	3,575
	Sample volume (column), μl	0.21	0.08	0.01
	Minimum detectable limit (cyclohexane) in the given sample, ppm	0.40	0.36	

on the original recorder chart, with a 1-mV recorder and attenuation × 1. As seen in Table 4, the minimum detectable limit was practically the same in both cases, although the absolute sample amount in the second case was only 40% of the first sample.

4. The analysis of such a sample on a wall-coated column at room temperature—as illustrated in the referenced ASTM method —takes about 36 min. The use of the heavier-loaded (β = 22) column reduced the analysis time by about 20%. However, when utilizing the lower-loaded (β = 67) column, the analysis time was

reduced by an additional 40%. The number of effective plates produced in unit time (N/t_R) increased by more than 50%, as compared with the result obtained on the heavier-loaded column.

The chromatogram shown in Fig. 5 was obtained at a flow rate close to optimum. An increase in the flow rate can even further reduce the analysis time. Figure 6 was obtained with a flow rate of 8.7 ml/min, and the total analysis time was reduced to 8 min,

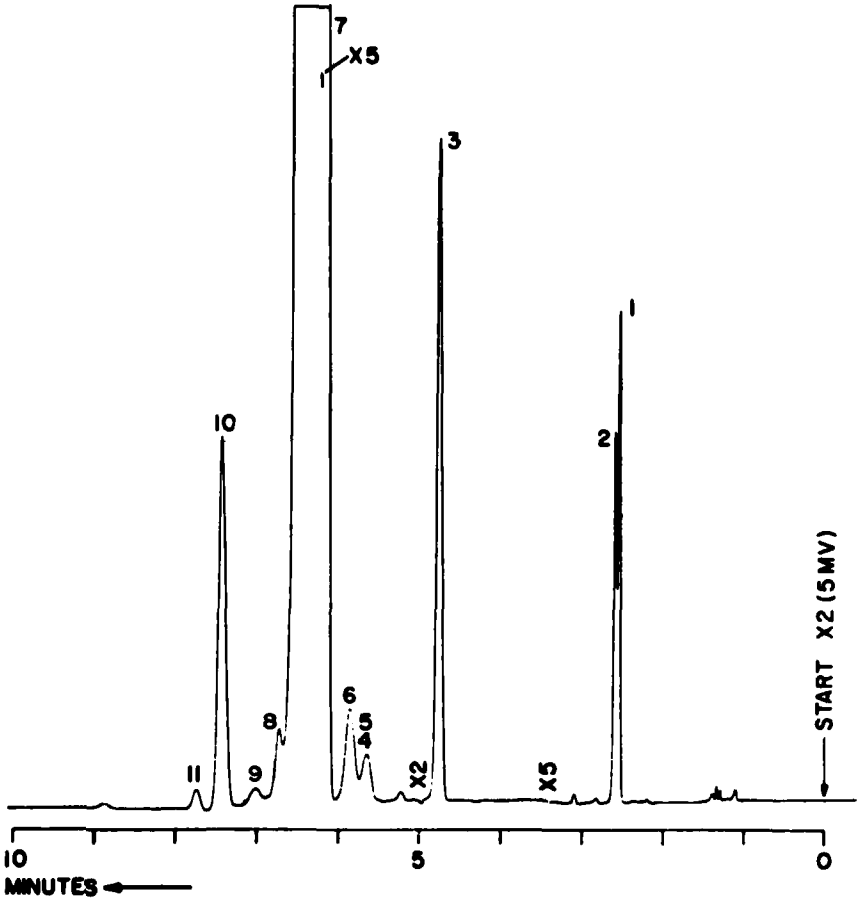

FIG. 6. Analysis of a high-purity *n*-heptane, III. Column, as in Fig. 5. Column temperature, 65°C; sample (column), 0.01 μl; carrier gas, He; flow rate at outlet, 8.7 ml/min; 5-mV recorder. Peaks as listed in Fig. 4.

while the column still had sufficient efficiency for the necessary separations.

A further illustration on the relative efficiency of columns with different loading is shown in Fig. 7; see also Table 5. This chromatogram represents the analysis of a complex natural sample consisting mainly of the isomeric heptanes. The analysis was carried out on a 100-ft support-coated open tubular column prepared with

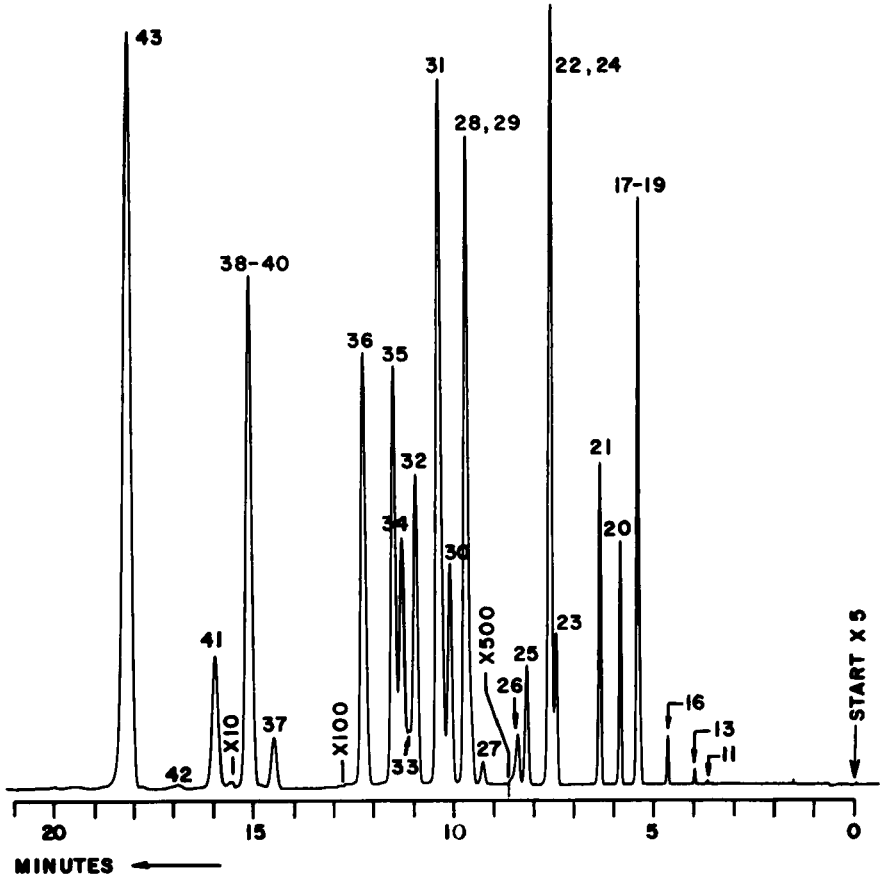

FIG. 7. Analysis of a complex hydrocarbon sample. Column, 100-ft × 0.020-in. I.D. support-coated open tubular, prepared with squalane liquid phase. Phase ratio (β), 67; column temperature, 65°C; sample (column), 0.025 μl; carrier gas, He; flow rate at outlet, 2.9 ml/min; 5-mV recorder. Peaks as listed in Table 5.

TABLE 5

Peak Identification for Chromatograms of Figs. 7 to 9

Peak no.	Substance	Peak no.	Substance
1	Methane	24	2,4-Dimethylpentane
2	Ethane	25	2,2,3-Trimethylbutane
3	Propene	26	Benzene
4	Propane	27	3,3-Dimethylpentane
5	2-Methylpropane	28	Cyclohexane
6	2-Methylpropene	29	2-Methylhexane
7	Butene-1	30	2,3-Dimethylpentane
8	*n*-Butane	31	3-Methylhexane
9	*trans*-Butene-2	32	Dimethylcyclopentane isomer (?)
10	*cis*-Butene-2	33	3-Ethylpentane
11	2-Methylbutane	34	Dimethylcyclopentane isomer (?)
12	Pentene-1	35	2,2,4-Trimethylpentane
13	*n*-Pentane	36	*n*-Heptane
14	*trans*-Pentene-2	37	2,2-Dimethylhexane
15	*cis*-Pentene-2	38	2,5-Dimethylhexane
16	2,2-Dimethylbutane	39	Methylcyclohexane
17	Cyclopentane	40	2,2,3,3-Tetramethylbutane
18	2,3-Dimethylbutane	41	2,4-Dimethylhexane
19	2-Methylpentane	42	2,2,3-Trimethylpentane
20	3-Methylpentane	43	3,3-Dimethylhexane
21	*n*-Hexane	44	Toluene
22	Methylcyclopentane	45	2,3,4-Trimethylpentane
23	2,2-Dimethylpentane	46	2,3-Dimethylhexane

squalane liquid phase having a phase ratio of 67, at 65°C. As seen, the retention time of the last peak is 18 min; the HETP values for peaks 20 and 36 are 0.48 and 0.65 mm, respectively. Analyzing the same sample on a column with a phase ratio of 22, a 150-ft long column was needed and had to be operated at 90°C. The retention time of the last peak was over 30 min, and the HETP values of the given peaks were in the range of 1.1 to 1.3 mm.

Finally, Fig. 8 illustrates the possibility of eliminating sub-ambient programming. The sample analyzed here was a wide-range hydrocarbon mixture starting with methane. As seen, the C_1 to C_5 hydrocarbons were eluted at room temperature, whereas the rest was analyzed by programming the column temperature up to 75°C with a linear of 2°C/min.

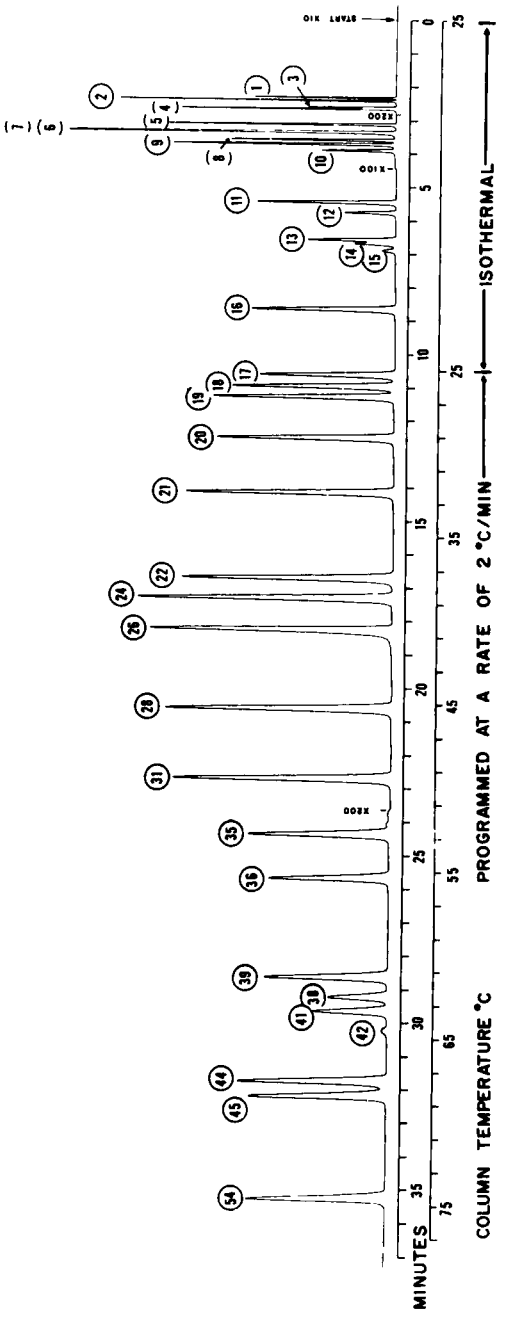

FIG. 8. Analysis of a C_1–C_9 hydrocarbon mixture. Column, 100-ft × 0.020-in. I.D. support-coated open tubular prepared with squalane liquid phase. Phase ratio (β), 67; column temperature, programmed as given; sample (column), 0.02 μl; carrier gas, He; flow rate at outlet, 3.24 ml/min; 5-mV recorder. Peaks as listed in Table 5.

COMPARISON WITH THEORETICAL EFFICIENCY VALUES

From the original Golay equation for HETP (*11*), the theoretical minimum value (at optimum gas velocity) for a wall-coated open tubular column—considering that the resistance to mass transfer in the liquid phase (the C_L term) is negligibly small—can be expressed by Eq. (3), where r is the inside radius of the column

$$\mathrm{HETP}_{\min} = r\left[\frac{1 + 6k + 11k^2}{3(1 + k)^2}\right]^{1/2} \tag{3}$$

tubing and k is the partition ratio of the particular solute.

In a more recent publication (*12*), Golay modified his original equation for open tubular columns lined with a porous layer. Similarly to the previous deduction, the theoretical minimum HETP value can be derived from Eq. (4), where r_g is the inner

$$\mathrm{HETP}_{\min} = r_g\left[\frac{1 + 6k + 11k^2}{3(1 + k)^2} + \frac{8a}{3} + \frac{16ka}{3(1 + k)^2}\right]^{1/2} \tag{4}$$

radius of the porous layer, i.e., the radius of the unobstructed gas path, and a is the ratio of porous layer thickness (d_p) to inner radius (r_g):

$$d_p = ar_g \tag{5}$$

It is discussed in the literature (*13–15*) that with wall-coated open tubular columns, only 20 to 60% of the theoretical best efficiency can be utilized in practice, higher utilization being achieved for earlier peaks and for columns with smaller diameter. The reason for this is that in the above calculation, ideal columns and gas-chromatographic systems are assumed and the C_L term is neglected.

In our first paper (*3*), we have shown for a heavier-loaded column, at $k = 7.25$, a 57% utilization of the theoretical best efficiency, whereas with a wall-coated column at the same k values, only about 40% can be achieved. It can be expected that for a lower-loaded column, where the average film thickness is even less, the actual values should be closer to those calculated from Eq. (4). Therefore, we have calculated these values for the chromatogram shown in Fig. 7. Taking $d_p = 25\,\mu$, the value of a will be 25/225 =

0.111. Table 6 lists the values calculated for peaks 20 and 36 and compares them with the values actually obtained.

The best value that we have obtained is 81%. This was calculated for the *n*-heptane peak in Fig. 9. The corresponding values for this peak are $k = 3.07$, $HETP_{min} = 0.38$ mm, and HETP = 0.47 mm.

It should be emphasized that the difference between the respective values calculated by using Eqs. (3) and (4) is small and that even gross error in the estimation of the average thickness of the porous layer (d_p) has only little influence on the final value of

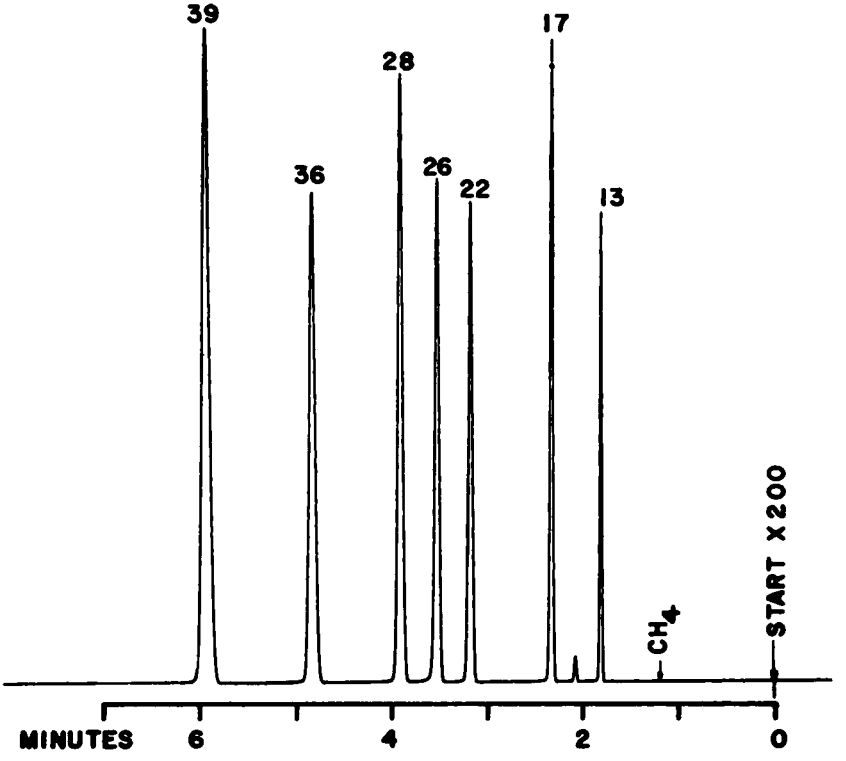

FIG. 9. Analysis of a hydrocarbon mixture. Column, 50-ft × 0.020-in. I.D. support-coated open tubular prepared with squalane liquid phase. Phase ratio (β), 67; column temperature, 75°C; sample (column), 0.01 μl; carrier gas, He; average velocity, 21.5 cm/sec; 5-mV recorder. Peaks as listed in Table 5.

TABLE 6

Comparison of Theoretical and Actual Efficiencies for Peaks 20 and 36 in Fig. 7

		Peak	
		20	36
k	Partition ratio	1.31	3.83
$HETP_{min}$	Theoretical minimum HETP calculated from Eq. (4), mm	0.33	0.38
HETP	Obtained HETP, mm	0.48	0.66
	Utilization of the theoretical best efficiency, %	69	59

$HETP_{min}$. For example, let us take a case where $r = 0.25$ mm and $d_p = 25\ \mu$ (identical to our columns used for the calculation above); for a peak at $k = 3.0$, the respective values for $HETP_{min}$ calculated using Eqs. (3) and (4) are 0.392 and 0.381 mm, the difference being only 2.8%. If we make a ±20% error in the estimation of the value of d_p, the $HETP_{min}$ value will vary only between 0.378 and 0.383 mm, which—compared to the mean value obtained for $d_p = 25\ \mu$—means only a ±0.66% change in the value of $HETP_{min}$. Thus, if Golay's equation is assumed to be valid, the values calculated for the support-coated columns represent true efficiencies and illustrate that these columns are closer to an ideal column than the standard wall-coated open tubular columns.

COMPARISON WITH RESULTS OBTAINED ON PACKED COLUMNS

It is very instructive to compare the performance of support-coated open tubular columns with results that can be expected from packed columns. For this comparison, we select two examples.

High-Purity *n*-Heptane

The analysis of this sample was shown in Figs. 4 to 6, and Table 4 summarized the analytical parameters and the results calculated from these chromatograms. As the number of effective plates is a value that permits a direct comparison of column performance regardless of the column type, we shall investigate the analytical parameters of a packed column operated at the same temperature that would result in the same effective plate number. For this comparison, we assume for the packed column an I.D. of 2.2 mm

($\frac{1}{8}$-in. O.D. column), an HETP of 0.6 mm, a specific permeability of 1.96×10^{-7} cm^2, a phase ratio of 19, an interparticle porosity of 0.40, and a carrier-gas outlet flow rate of 40 ml/min. From these data, column length, partition ratios, carrier-gas inlet pressure, average gas velocity, retention times, and effective plates produced in unit time can be calculated. The calculation is straightforward and was explained in our previous paper (6). Table 7 lists the values obtained for column operations at 65 and 85°C. As seen, the total analysis time in both cases would be over 1 hr and 18- and 25-m-long columns would be necessary.

Fatty Acid Analysis

One of the most widely used applications of gas chromatography is the analysis of fatty acids in the form of their methyl esters on columns prepared with polyester liquid phases. The efficiency of such columns is usually characterized by the resolution (R) of the

TABLE 7

Calculated Comparative Data for a Packed Column, in the Analysis of the High-Purity *n*-Heptane Sample

	Column temperature	85	65
β	Phase ratio	19	19
k	Partition ratio of cyclohexane	5.37	9.59
k	Partition ratio of peak no. 11	9.15	17.39
	HETP for the cyclohexane peak, mm	0.60	0.60
N	Number of effective plates for cyclohexane peak	29,490	24,560
n	Number of theoretical plates for cyclohexane peak	41,490	29,950
L	Column length, m	24.894	17.971
F_o	Carrier-gas flow rate at outlet, ml/min	40	40
u_o	Carrier-gas outlet velocity, cm/sec	43.85	43.85
B_0	Specific permeability, 10^{-7} cm^2	1.96	1.96
p_i/p_o	Ratio of inlet and outlet pressures	9.95	8.28
Δp	Pressure drop along the column, psig	131.5	107.0
j	Compressibility correction factor	0.149	0.179
$\bar{u}$	Carrier-gas average velocity, cm/sec	6.53	7.85
t_R	Retention time for cyclohexane, min	40.47	40.41
t_R	Retention time for peak no. 11, min	64.5	70.17
N/t_R	Effective plate number/retention time for the cyclohexane peak, min^{-1}	730	608

methyl stearate and oleate peaks, calculated according to Eq. (6),

$$R = \frac{2(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} \tag{6}$$

where t_R is the retention time and w_b the peak width at base (base intercept) subindices 1 and 2, referring to the stearate and oleate peaks, respectively.

With a 6-ft-long packed column of HETP = 0.6 mm, resolution values of 1.2 to 1.5 can generally be achieved, whereas with 150-ft-long, 0.010-in. I.D. standard wall-coated open tubular columns, resolution values of 3.5 to 4.2 are reported (*16*).

Figure 10 shows the chromatogram of a fatty acid methyl ester

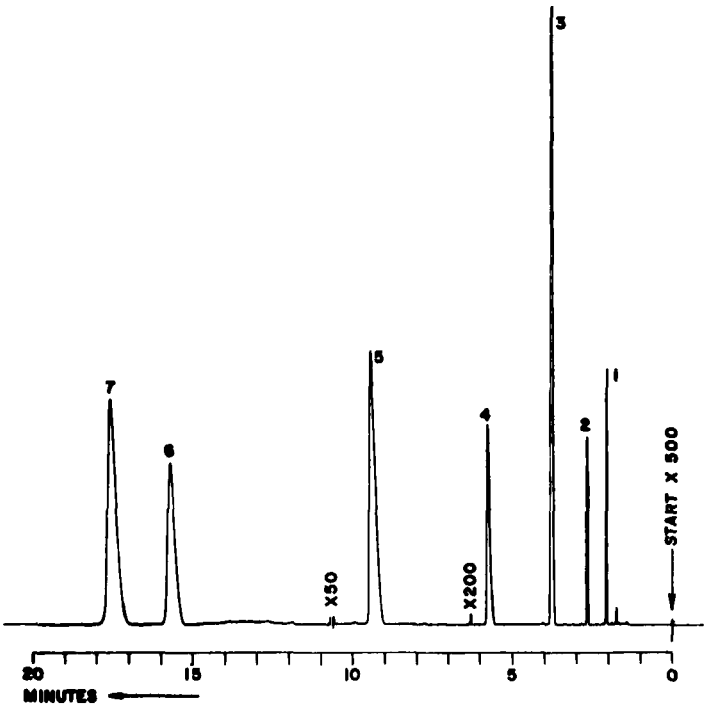

FIG. 10. Analysis of a fatty acid methyl ester mixture. Column, 50-ft × 0.020-in. I.D. support-coated open tubular prepared with diethylene glycol succinate liquid phase. Phase ratio (β), 50; column temperature, 200°C; sample (column), 0.1 μl; carrier gas, He; flow rate at outlet, 4 ml/min; 5-mV recorder. Peaks: methyl (1) caprylate, (2) caprate, (3) laurate, (4) myristate, (5) palmitate, (6) stearate, (7) oleate.

TABLE 8
Comparative Data for the Analysis of Fatty Acid Methyl Esters

		Fig. 10	Packed column
L	Column length, m	15.240	8.790
β	Phase ratio	50	19
HETP	HETP for methyl oleate, mm	0.94	0.6
n	Number of theoretical plates for methyl oleate	16,170	14,650
R	Resolution, oleate/stearate	3.37	3.37
k	Partition ratio of methyl oleate	11.36	29.9
α	Relative retention, oleate/stearate	1.13	1.13
t_R	Retention time of methyl oleate, min	17.52	>45

mixture obtained on a 50-ft-long support-coated open tubular column prepared with diethylene glycol succinate liquid phase ($\beta \simeq 50$). Table 8 lists the characteristic data. As seen, we obtained a resolution of 3.37 in 17.5 min. If we assume a packed column with an HETP of 0.6 mm and a phase-ratio value of 19, we can calculate the corresponding partition ratio of methyl oleate. From this value and the relative retention (α), we can calculate the number of theoretical plates necessary (n_{ne}) in order to obtain a resolution of 3.37 [Eq. (7)]. As we assumed an HETP of 0.6 mm, we can

$$n_{ne} = 16R^2 \left(\frac{\alpha}{\alpha - 1}\right)^2 \left(\frac{k+1}{k}\right)^2 \tag{7}$$

calculate the length of the packed column that would give the necessary theoretical plates. As given in Table 8, it is 8.79 m (28.8 ft). The corresponding retention time would be at least 45 min.

Assuming the given values for k and α, we would need a 5.7-ft-long packed column to obtain a resolution of 1.5 for the stearate and oleate peaks. It is easy to calculate from the data given in Table 8 that, if we do not want a better resolution than $R = 1.5$, a 2.73-m (8.95-ft) long support-coated column would be sufficient, and the retention time of methyl oleate would only be 3.13 min.

COLUMNS WITH VERY LOW LIQUID-PHASE LOADING

The chromatograms shown until now were obtained on columns characterized by phase ratios of 22 to 67. For special high-boiling

samples, columns with even higher phase-ratio values should be utilized. Such columns can be fabricated by using the standard process without any difficulty. We have utilized in our work columns having a phase ratio (β) of 360; Table 2 listed the characteristic values of such columns. The performance of such columns is illustrated in Figs. 11 and 12.

Figure 11 was obtained on a 50-ft-long SE-30 column, at 220°C. The test mixture again consisted of the fatty acid methyl esters. The value of HETP calculated for the stearate peak is 0.70 mm, and the resolution for the oleate/stearate peaks is $R = 2.1$.

Figure 12 was obtained by using two 50-ft-long columns in series. The first column was prepared with diethylene glycol succinate and the second with SE-30 liquid phase. The sample consisted of the *n*-butyl N-trifluoroacetyl esters of five amino acids prepared according to the procedure of Gehrke et al. (*17,18*); the

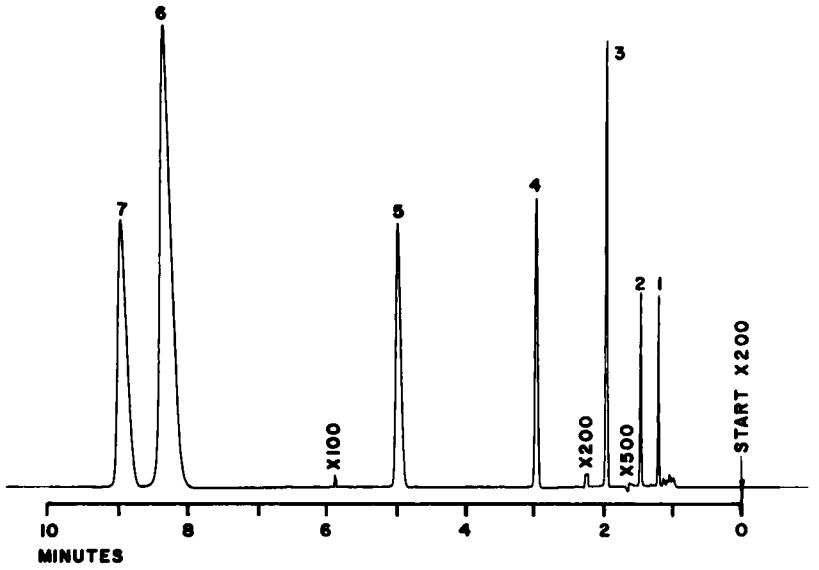

FIG. 11. Analysis of a fatty acid methyl ester mixture. Column, 50-ft × 0.020-in. I.D. support-coated open tubular prepared with SE-30 silicone gum rubber liquid phase; phase ratio (β), 360; column temperature, 220°C; sample (column), 0.03 μl; carrier gas, He; flow rate at outlet, 4 ml/min; 5-mV recorder. Peaks: methyl (1) caprylate, (2) caprate, (3) laurate, (4) myristate, (5) palmitate, (6) oleate, (7) stearate.

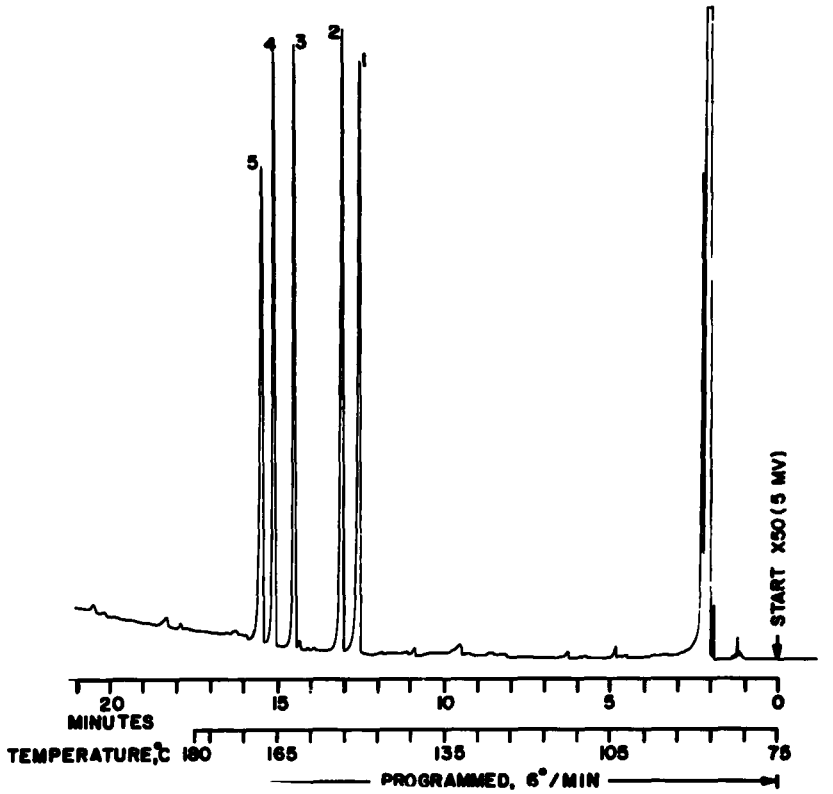

FIG. 12. Analysis of the mixture of the *n*-butyl N-trifluoroacetyl esters of five amino acids. Column, two 50-ft × 0.020-in. I.D. support-coated open tubular columns in series, the first prepared with diethylene glycol succinate and the second with SE-30 liquid phase. Phase ratio (β) for both columns, 360; column temperature, programmed as given; sample (column), 0.13 μl; carrier gas, He; flow rate at outlet, 3.5 ml/min; 5-mV recorder. Peaks: *n*-butyl N-trifluoroacetyl esters of (1) alanine, (2) valine, (3) isoleucine, (4) glycine, (5) leucine.

advantages of using series columns containing liquid phases of different polarity for the analysis of the volatile amino acid derivatives was demonstrated recently by Gehrke and Shahrokhi (*19*).*

* Separate investigations on the possibility of the utilization of support-coated open tubular columns for the analysis of complex natural amino acid mixtures are under way in cooperation with Dr. Gehrke's group at the University of Missouri, Columbia, Mo.

CONCLUSIONS

Figure 13 compares the support-coated open tubular columns with two wall-coated open tubular columns having 0.010- and 0.020-in. (or in metric system, 0.25- and 0.50-mm) internal diameter. The figure plots the phase-ratio (β) value and the average liquid film thickness (d_f) against the volume of liquid phase per unit column length. The film thickness of the wall-coated columns was calculated from the well known equation (*20*) [Eq. (8)].

$$d_f = r/2\beta \tag{8}$$

Because on wall-coated open tubular columns, film thicknesses above 1.2 μ are generally considered not stable, the corresponding parts of the plots are indicated by broken lines. The average film

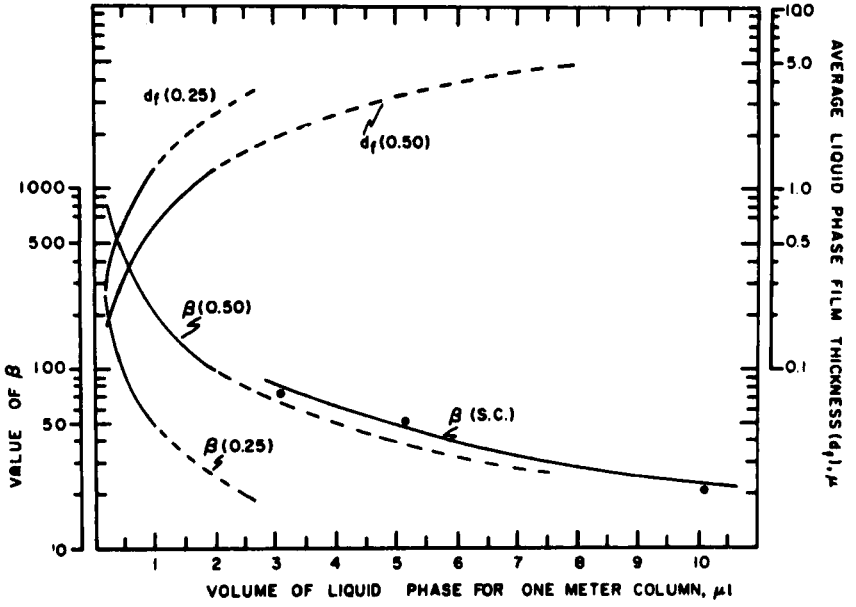

FIG. 13. Plots of the phase-ratio (β) values and average liquid film thicknesses (d_f) against the volume of liquid phase per unit column length for three columns. (S.C.) = support-coated open tubular column with 0.020-in. I.D.; (0.25) and (0.50), wall-coated open tubular columns with 0.25- and 0.50-mm (0.010- and 0.020-in.) I.D., respectively.

thickness in a support-coated column cannot be well-defined; thus such a plot is not given.

Figure 13 allows us to draw some general conclusions concerning the relative merits of support-coated open tubular columns prepared with various liquid loadings and makes it possible to give some directives for the selection of the best column type for a given application.

If we settle at a liquid-phase volume in the range of 3 to 5 μl/m, the phase ratio of the support-coated columns will be in the range between 55 and 85. These β values are still less than those of the wall-coated open tubular columns, whereas at the same time, the liquid-phase volume is almost one order of magnitude higher. These support-coated columns represent very good efficiency and a reasonable sample capacity, and, owing to the sharper peaks, the minimum detectable limit is very low. We would term these columns as the workhorse columns; most chromatograms shown here belong to this category.

If a high *absolute* sample capacity close to that of packed columns is desired, support-coated columns with 8 to 10 μl/m liquid phase have to be utilized; the corresponding β values are in the range between 20 and 30. Such heavier-loaded support-coated columns have to be used at temperatures 50 to 70°C higher than usual with wall-coated open tubular columns. These columns permit the direct injection of high absolute sample amounts; their efficiency will be poorer than that of the previous columns, and one can expect HETP values around 1 mm. As the pressure drop of these columns is practically nil, longer columns can be used without and difficulty, and thus the total number of plates is still much higher than that of packed columns, resulting in comparable analysis times.

For the analysis of high-boiling substances, support-coated columns with liquid loadings of 0.5 to 1 μl/m were utilized. Here, we are close to the phase-ratio range of 0.020-in. I.D. wall-coated columns; however, owing to the larger surface on which the liquid phase is distributed, more favorable column performance is obtained.

As a conclusion, one can state that, with the support-coated columns, one has the possibility of combining the high performance of open tubular columns with the sample capacity and minimum detectability of packed columns. By the selection of the proper liquid-phase loading, these columns can be tailored to best fit the analytical problems.

Acknowledgment

We acknowledge the cooperation of the Column Facility of our corporation, S. H. Wetriech, its supervisor, and L. Arthur, who prepared the columns used in our investigations, and of S. D. Norem, who was instrumental in the adaptation of the original column-fabrication methods for production and who helped us many times in theoretical considerations. We are grateful to Dr. Daeschner of Shell Development Co., Emeryville, Calif., who was kind enough to carry out for us the surface-area, pore-volume, and pore-size distribution measurements, and to D. L. Stalling of the University of Missouri, Columbia, Mo., for placing at our disposal the amino acid derivatives used in the analysis shown in Fig. 12.

REFERENCES

1. I. Halász and C. Horváth, *Anal. Chem.*, **35,** 499 (1963).
2. M. J. E. Golay, in *Gas Chromatography—1960* (R. P. W. Scott, ed.), Butterworth, London, 1960, pp. 139–143.
3. L. S. Ettre, J. E. Purcell, and S. D. Norem, *J. Gas Chromatog.*, **3,** 181 (1965).
4. J. E. Purcell and L. S. Ettre, *J. Gas Chromatog.*, **4,** 23 (1966).
5. L. S. Ettre and J. E. Purcell, *Journées Hellènes de Séparation Immédiate et de Chromatographie, Athens, Sept. 19–24, 1965*, Assoc. Greek Chemists, Athens, 1966, pp. 162–183.
6. L. S. Ettre, J. E. Purcell, and K. Billeb, *J. Chromatog.* (to be published).
7. D. H. Desty and A. Goldup, in *Gas Chromatography—1960* (R. P. W. Scott, ed.), Butterworth, London, 1960, pp. 162–183.
8. D. H. Desty, A. Goldup, and W. T. Swanton, in *Gas Chromatography* (N. Brenner, J. E. Callen, and M. D. Weiss, eds.), Academic, New York, 1962, pp. 105–135.
9. I. Halász and H. O. Gerlach, *Anal. Chem.*, **38,** 281 (1966).
10. A. B. Littlewood, *Anal. Chem.*, **38,** 2 (1966).
11. M. J. E. Golay, in *Gas Chromatography—1958* (D. H. Desty, ed.), Butterworth, London, 1958, pp. 139–143.
12. M. J. E. Golay, *Nature*, **199,** 370 (1963).
13. D. H. Desty, A. Goldup, and B. H. F. Whyman, *J. Inst. Petrol.*, **45,** 287 (1959).
14. L. S. Ettre, E. W. Cieplinski, and W. Averill, *J. Gas Chromatog.*, **1**(2), 7 (1963).
15. L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum, New York, 1965, pp. 15–20.
16. See Ref. *15*, p. 36.
17. W. M. Lamkin and C. W. Gehrke, *Anal. Chem.*, **37,** 383 (1965).
18. C. W. Gehrke, W. M. Lamkin, D. L. Stalling, and F. Shahrokhi, *Biochem. Biophys. Res. Commun.*, **19,** 328 (1965).
19. C. W. Gehrke and F. Shahrokhi, *Anal. Biochem.*, **15,** 97 (1966).
20. See Ref. *15*, p. 14.

Received by editor August 12, 1966
Submitted for publication September 8, 1966