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EFFICIENCY, RESOLUTION AND SPEED OF OPEN TUBULAR COLUMNS AS COMPARED TO PACKED COLUMNS

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SUMMARY

Three ways are proposed for the comparison of true column performance: calculating the retention time needed for a given resolution, or the resolution obtained in a given time, or plotting resolution vs. retention time for various column types. The utilization of these methods is shown for three columns of different types (packed, wall-coated open tubular and support-coated open tubular) containing diethylene glycol succinate as the stationary phase and a fatty acid methyl ester mixture as the test substance, and the influence of various parameters on resolution and the time of analysis is discussed. Finally, the way this concept can be utilized to express true column performance is illustrated with a hypothetical case.

INTRODUCTION

When we consider the facts which helped in the immediate acceptance of gas chromatography at its introduction, two special advantages must be mentioned together. The first was the ability of the new technique to separate the components of complicated mixtures consisting of substances having similar chemical and/or physical characteristics. However, this fact alone would not have been enough to explain the unparalleled development of chromatography and to account for becoming in a short time the most widely used analytical technique. After all, some of the other analytical methods in use at the introduction of gas chromatography also permitted the separation and analysis of complex mixtures. However, gas chromatography had the advantage in that it permitted the separation in shorter analysis time. Thus, when speaking about chromatography, separation and speed must always be considered together.

The usual ways to express the efficiency of chromatographic columns is to give the number of theoretical plates or the HETP. However, neither of these gives an indication of the analysis time, although, naturally, in their calculation the retention time was utilized. A further complication is that the resolution which can be achieved for a given peak pair specified by their relative retention also depends on the partition ratio of the peaks*:

* For explanation of symbols, see the listing at the end of the paper.

$$R = \frac{\sqrt{n}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k}{k + 1} \right) \quad (1)$$

where k refers to the second peak. Investigation of the values of $k/(k + 1)$ vs. k (see Table I) shows that at lower k values the reduction in the resolution can be considerable as compared to the resolution which can be obtained with the same plate number but at higher partition ratios. Let us take, for example, the case of $\alpha = 1.1$ and $n = 20,000$. If $k = 0.5$, only a resolution of $R = 1.07$ can be achieved while if $k = 2.5$, the resolution will be $R = 2.30$.

TABLE I
VALUES OF DIFFERENT k FUNCTIONS

k	$k/(k + 1)$	$(k + 1)/k$	$[(k + 1)/k]^2$	$(k + 1)^3/k^2$
0.1	0.0909	11.000	121.000	133.100
0.2	0.1667	6.000	36.000	43.200
0.5	0.3333	3.000	9.000	13.500
1.0	0.5000	2.000	4.000	8.000
1.5	0.6000	1.667	2.778	6.944
2.0	0.6667	1.500	2.250	6.750
2.5	0.7143	1.400	1.960	6.860
3.0	0.7500	1.333	1.778	7.111
3.5	0.7778	1.286	1.653	7.439
4.0	0.8000	1.250	1.563	7.812
4.5	0.8182	1.222	1.494	8.216
5.0	0.8333	1.200	1.444	8.640
6.0	0.8571	1.167	1.361	9.528
7.0	0.8750	1.143	1.306	10.449
8.0	0.8889	1.125	1.266	11.391
9.0	0.9000	1.111	1.235	12.346
10.0	0.9091	1.100	1.210	13.310
20.0	0.9524	1.050	1.103	23.152
30.0	0.9677	1.033	1.068	33.101
40.0	0.9756	1.025	1.051	43.076
50.0	0.9804	1.020	1.040	53.060
100.0	0.9901	1.010	1.020	103.030

This fact is very important in the comparison of columns. If we assume the same liquid phase and analysis at the same temperature, the same solute will have a larger partition ratio on a packed column than *e.g.* on an open tubular column and thus, one would need more plates for the latter to achieve the same resolution. This is clear if we express n from eqn. 1:

$$n = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k + 1}{k} \right)^2 \quad (2)$$

The need for more plates, of course, means a longer column since

$$n = \frac{L}{h} \quad (3)$$

and the HETP values of different column types do not significantly differ from each other. However, the length of columns is not directly involved in the "relative good-

ness" of various column types if we compare them from the point of efficiency and speed.

Recognizing these problems, various ways have been proposed to express column efficiency in a comparable way. Golay, in 1957, proposed the performance index¹ to express the relationship between the resolving power of a column, the time of analysis, and the pressure drop. Purnell², in 1960, introduced the separation factor, which is identical to the number of effective plates of Desty *et al.*³ described one year later. These two terms eliminate the difference in the partition ratio and thus, the number of effective plates needed to achieve a given resolution

$$N = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \quad (4)$$

will be the same for a given relative retention regardless of the difference in the partition ratio. Desty *et al.* also proposed to define column performance as the rate of production of the effective plates, *i.e.* N/t_R , the effective plates per retention time; the higher this value the better the column. However, as will be explained later, this value is no longer independent of the partition ratio and —unless one is working at a high velocity— also depends on the average linear gas velocity.

The problem with all of these values is that while they give an indication of the relative performance of various column types, this is not done in a way which can be translated to a practical evaluation; also, one cannot demonstrate easily that resolving power and the speed of analysis are two characteristics which can be traded against each other nor can they be used *e.g.* to compare columns on an equal resolution or equal time basis. It is also interesting to note that, although the theory and practice of the various column types is well established, very little data are available in the literature comparing the performance of the various column types on this basis.

In this paper we want to report on a systematic investigation comparing the performance of the three column types: packed, wall-coated open tubular (WCOT) and support-coated open tubular (SCOT). For the comparison, one model was selected and the discussion is based on the data obtained under these conditions. However, it is easy to realize that the conclusions drawn here can be generalized for other phases and samples, and this will also be demonstrated at the end of the paper. In essence, the present discussion can be considered as a continuation of an earlier, more general, treatment of the same subject⁴. Our goal is to demonstrate the usefulness of comparing true column performance on three bases:

- (a) retention time needed to achieve equal resolution;
- (b) resolution obtained in equal time;
- (c) resolution *vs.* retention time plots.

EXPERIMENTAL

Table II lists the three columns used for the investigations. These were prepared by standard production methods. A mixture of C_6 – C_{18} saturated fatty acid methyl esters also containing methyl oleate was selected as the test sample; unless otherwise specified, all data reported refer to the methyl oleate peak and the resolution of the methyl stearate–oleate peaks. The analyses were carried out at 180 ° using

TABLE II
COLUMNS USED FOR THE MEASUREMENTS

	Column		
	Packed	WCOT	SCOT
Length, ft.	8	150	50
cm	243.84	4572	1524
Internal diameter, in.	0.085	0.010	0.020
mm	2.16	0.25	0.50
Liquid phase	Diethylene glycol succinate (DEGS)		
Support	Chromosorb W*, 80-100 mesh	—	Aerosil** + Minusil***
Liquid phase loading, wt. %	10	—	—
Phase ratio	10.3	120	54

* Johns-Manville, New York, N.Y., U.S.A.

** Degussa, New York, N.Y., U.S.A.

*** Pennsylvania Glass Sand, Pittsburgh, Pa., U.S.A.

helium as the carrier gas. At this temperature, the relative retention (α) of methyl stearate/oleate is 1.12; this is the average value of the measurements carried out on the different columns.

We analyzed the fatty acid methyl ester sample on the three columns at twelve different carrier gas velocities each time also measuring the gas holdup time using methane as the non-retarded solute. From these chromatograms we calculated for each case the HETP, average linear gas velocity and partition ratio values as well as the resolution for the methyl stearate-oleate pair. These values are used for the calculations and plots reported below. The chromatograms shown in Figs. 2, 4 and 7 were obtained by calculating from the respective theoretical plate and retention time values the standard deviation of the Gaussian peak and with its help reconstructing the particular part of the chromatogram; Figs. 6, 10, and 11 represent direct copies of actual chromatograms.

All the measurements were carried out with a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector; the sample introduction system and the connecting lines were always optimized for the particular column used.

Table III lists, among others, the mean values of the partition ratio. From these and the phase ratio values (see Table II) the partition coefficient of methyl oleate (on DEGS at 180°) was calculated. The mean of the three values listed in Table III is 604.7 and the deviation of the individually calculated values is -1.2% (packed), +1.01% (WCOT) and +0.02% (SCOT). We could not find any data in the literature for the partition coefficient of methyl oleate to which we could compare the values determined here.

RESULTS AND DISCUSSION

Van Deemter plots

Fig. 1 shows the Van Deemter plots for the methyl oleate peak. Let us first investigate the values corresponding to the minimum of the plots. These are listed in Table III and the reconstructed chromatograms are shown in Fig. 2. As seen, the

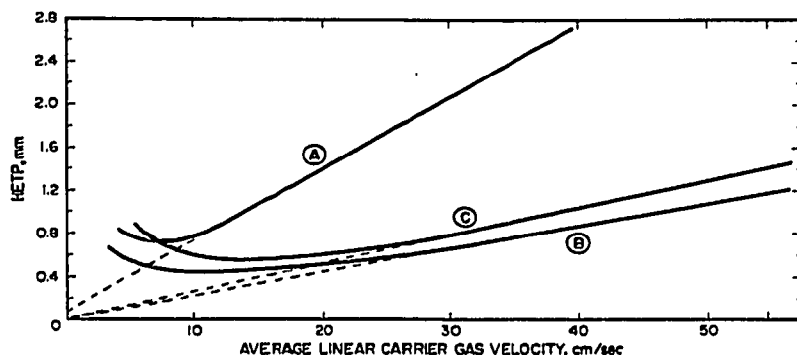


Fig. 1. Van Deemter plots of methyl oleate on the three columns, at 180° using helium as the carrier gas. A = Packed column; B = WCOT column; C = SCOT column.

TABLE III

CHARACTERISTIC DATA FOR METHYL OLEATE ON THE THREE DEGS COLUMNS

	Column		
	Packed	WCOT	SCOT
Partition ratio*	58.6	5.1	11.2
Partition coefficient	597.4	612.0	604.8
Optimum average carrier gas velocity, cm/sec	6.8	9.0	13.5
HETP _{min.} , mm	0.71	0.46	0.55
Retention time at \bar{u}_{opt} , min	35.62	51.65	22.95
Resolution of the methyl stearate/methyl oleate peaks	1.54	7.06	4.09

* Average of 12 determinations.

value of the optimum linear average gas velocity is the lowest for the packed column followed by the WCOT column while it is the highest for the SCOT column. Under these conditions, we obtained base line resolution on the packed column for the stearate/oleate pair (in case of base line resolution, $R = 1.5$) while the resolution obtained on the open tubular columns at \bar{u}_{opt} was much better. Table III also lists the corresponding retention times. These data will be used below for the comparison of column efficiency.

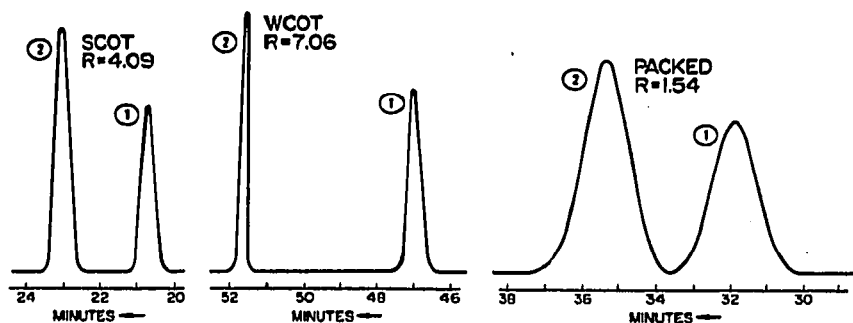


Fig. 2. Reconstructed chromatograms showing the methyl stearate-methyl oleate peak pair on the three columns, at optimum average linear gas velocity. 1 = Methyl stearate; 2 = methyl oleate.

Of particular importance concerning any investigation of resolution vs. time (see below) is the slope of the ascending part of the Van Deemter curves because a smaller slope means that we can use a higher velocity without too much loss in column efficiency. It can be seen that the slope of the packed column curve is significantly larger than for the two open tubular columns. This can be explained from the well known Van Deemter-Golay equations written for packed (eqn. 5a) and open tubular (eqn. 6a) columns:

$$\text{HETP} = A + B/\bar{u} + C\bar{u} \quad (5a)$$

$$\text{HETP} = B/\bar{u} + C\bar{u} \quad (6a)$$

It is easy to realize that the linear ascending part of the curves can be described by the respective eqns. 5b and 6b:

$$\text{HETP} \simeq A + C\bar{u} \quad (5b)$$

$$\text{HETP} \simeq C\bar{u} \quad (6b)$$

in which C represents the slope of this part of the curve. Its value can be expressed as:

$$C \simeq \frac{\text{HETP} - A}{\bar{u}} \quad (5c)$$

$$C \simeq \frac{\text{HETP}}{\bar{u}} \quad (6c)$$

The C term in the Van Deemter-Golay equations represents the resistance to mass transfer related to the diffusion in the gaseous and liquid phases. Its value for an open tubular column will be smaller than for a packed column because in the latter, the slowness of diffusion of the solute molecules in the gas phase, within the pores of the packing material, is the limiting factor. Comparing the two open tubular column types, the C term —or in other words, the slope of this part of the curve— will generally be slightly larger for a SCOT column than for a WCOT column because in the former some pores are present while they are absent in the latter where the liquid phase is coated on the smooth metal wall. This can be seen in Fig. 3, plotting the HETP/\bar{u} values against the velocity for the three columns; the HETP/\bar{u} value corresponding to the asymptotic part of the curves represents the C term*.

The importance of the smallness of the HETP/\bar{u} value will be detailed below, when investigating the factors influencing the retention time related to a certain resolution.

Comparison of true column performance

We are suggesting three ways to compare the true performance of various column types: compare the retention time corresponding to the same resolution, or

* Since $A \ll \text{HETP}$, the HETP/\bar{u} plot can also be taken as an approximate value for the C term on the packed column. In our case A is about 0.006 cm (see Fig. 1) and thus, the C term would be about 0.0067 sec against 0.00685 sec, the value of HETP/\bar{u} calculated for the high velocities.

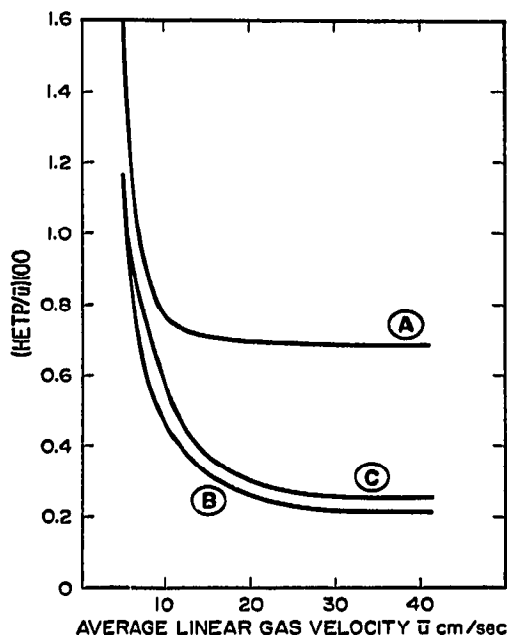


Fig. 3. Plot of $HETP/\bar{u}$ vs. \bar{u} for the three columns calculated from the Van Deemter plots shown in Fig. 1. A = Packed column; B = WCOT column; C = SCOT column.

the resolution corresponding to the same retention time, or by preparing resolution vs. retention time plots.

For the first comparison, we start with the data obtained at the minimum of the Van Deemter plot (see Table III). These data are repeated in columns *a*, *b* and *d* of Table IV. We recalculated the data to the same resolution, in other words established the length of column with the same efficiency (HETP) and operated at opti-

TABLE IV

COMPARATIVE DATA

I. DATA CORRESPONDING TO THE OPTIMUM AVERAGE LINEAR GAS VELOCITY*

	Column				
	Packed	WCOT		SCOT	
		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
\bar{u}_{opt} , cm/sec	6.8	9.0	9.0	13.5	13.5
$HETP_{min.}$, mm	0.71	0.46	0.46	0.55	0.55
Column length, ft.	8	150	7.14	50	7.08
cm	243.84	4572	217.63	1524	215.80
Resolution of the methyl stearate/ methyl oleate peaks	1.54	7.06	1.54	4.09	1.54
Retention time of methyl oleate, min	35.62	51.65	2.46	22.95	3.25

* Columns *a*, *b* and *d*: measured at \bar{u}_{opt} and $HETP_{min.}$; columns *c* and *e*: column length calculated to give equal resolution to the 8-ft. packed column.

imum velocity which would give the same (base line) resolution as the packed column and then, calculated the respective retention times. This calculation is carried out using the following two equations*:

$$L = 16 R^2 h \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k + 1}{k} \right)^2 \quad (7)$$

$$t_R = \frac{L}{\bar{u}} (k + 1) \quad (8)$$

The new data for the packed and SCOT columns are given in columns *c* and *e* of Table IV, respectively. As seen, one would have to use only a 7.14-ft.-long WCOT column and the retention time would be only 7% of that needed on the packed column. In the case of the SCOT column, a 7.08-ft.-long column would give the same resolution and the retention time would be 9% of that obtained on the packed column.

In other words, while it takes over 30 min to get a base line resolution on the 8-ft.-long packed column, the same can be achieved in a few minutes on the open tubular columns.

For the second comparison we arbitrarily selected a retention time of 15 min for methyl oleate and established the resolution which could be obtained on the three columns. The calculation is straightforward; we calculate \bar{u} from eqn. 8, determine from Fig. 1 the corresponding HETP value, calculate from eqn. 3 the corresponding number of theoretical plates and then, from eqn. 1 the resolution. The data obtained are listed in Table V; the reconstructed chromatograms are shown in Fig. 4. In the

TABLE V
COMPARATIVE DATA
II. RESOLUTION CORRESPONDING TO THE SAME RETENTION TIME

	Column		
	Packed	WCOT	SCOT
Column length, ft.	8	150	50
cm	243.84	4572	1524
Average linear gas velocity, cm/sec	16.15	30.99	20.66
Relative velocity*	2.37	3.44	1.53
HETP, mm	1.14	0.67	0.62
Relative HETP**	1.61	1.46	1.13
Resolution of the methyl stearate/ methyl oleate peaks	1.22	5.85	3.85
Retention time of methyl oleate, min	15.00	15.00	15.00

* $\bar{u}/\bar{u}_{opt.}$

** HETP/HETP_{min.}

table we also list the values of the relative velocity and HETP, *i.e.* the ratio of the actual value and the one corresponding to the minimum of the Van Deemter plot. These are informative values as *e.g.* they show that while in case of the packed column a 2.37-fold increase of the optimum velocity gave a 61% raise in the HETP_{min.} value,

* Here *h* and *k* refer to the second peak.

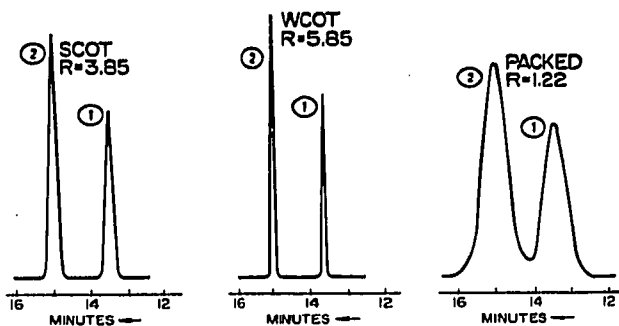


Fig. 4. Reconstructed chromatograms showing the methyl stearate/methyl oleate peak pair on the three columns, having a retention time of 15 min for the methyl oleate peak. 1 = Methyl stearate, 2 = methyl oleate.

in case of the WCOT column a 3.44-fold increase in velocity gave only a 46% raise in the corresponding $HETP_{min.}$

This type of relative evaluation clearly shows that in the same analysis time, the open tubular columns gave a much better resolution than the packed column.

Finally, the third and the best way which, in our opinion, permits the comparison of the true performance of columns is to plot resolution vs. retention time for a given peak pair. Fig. 5 shows these plots for the three columns investigated by us, for the methyl stearate/methyl oleate peak pair. It can be seen that the best we could obtain from this packed column is about base line resolution and it takes about 27–30 min to achieve it. On the other hand, in a shorter time, we can get a much better resolution on the open tubular columns.

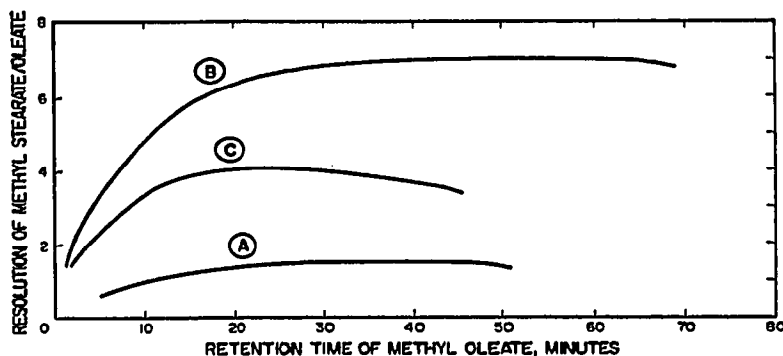


Fig. 5. Plots of resolution of the methyl stearate/methyl oleate peak pair against the retention time of methyl oleate, on the three columns. A = Packed column; B = WCOT column; C = SCOT column.

Separation of closely spaced peaks

In the model investigated until now, the peak pair of methyl stearate and methyl oleate, the true merit of open tubular columns is not so evident because base line resolution—which can be obtained without too much trouble on the packed column—

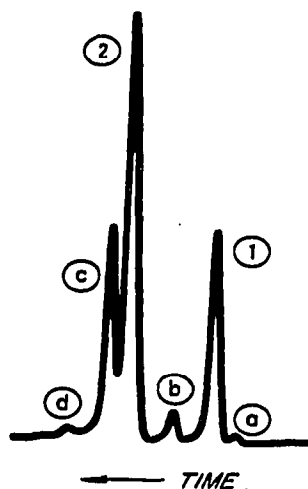


Fig. 6. Segment of a chromatogram obtained when analyzing at 180° the fatty acids (in methyl ester form) from a menhaden oil on a 150 ft. \times 0.010 in. I.D. WCOT column coated with DEGS stationary phase. 1 = Methyl stearate; 2 = methyl oleate.

is satisfactory in most of the cases and the possibility of decreasing the analysis time is not always of special importance.

However, the possibility of high resolution in fatty acid analysis — taking this as the example — is important because in many natural samples components other than these present in our test sample are also present. Fig. 6, for example, shows part of a chromatogram obtained when analyzing the fatty acids (in methyl ester form) in the oil of menhaden. Here, four more peaks are present in the C_{18} region: as listed in Table VI, their relative retention is very small. If we would analyze this sample on a standard packed column, all these small peaks would be overlapped by the two main peaks, those of methyl stearate and methyl oleate. This is demonstrated in Fig. 7, which, similar to Fig. 4, shows the reconstructed chromatograms for the case when the retention time of methyl oleate is 15 min.

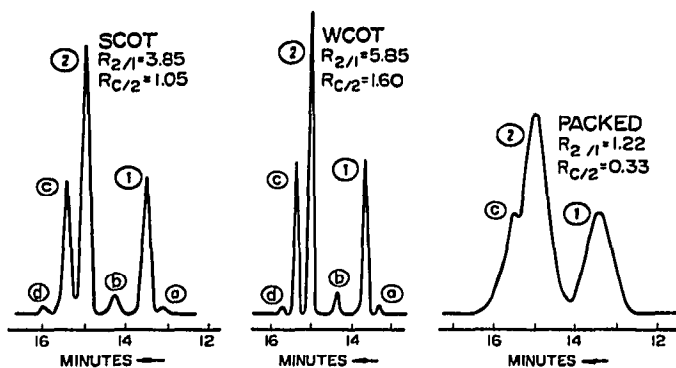


Fig. 7. Reconstructed chromatogram of the C_{18} region of a menhaden oil sample on the three columns having a retention time of 15 min for the methyl oleate peak. 1 = Methyl stearate; 2 = methyl oleate.

From the relative retention values listed in Table VI the one for the peak pair *c* and methyl oleate is the smallest ($\alpha = 1.030$). In order to be able to investigate the performance of our columns for this separation we present the R vs. t_R plots in Fig. 8*. Besides the three columns used for our investigations, we also give plots for a 24-ft.-long packed and a 150-ft.-long SCOT column assuming the same efficiency (the same

TABLE VI

RELATIVE RETENTION OF TWO CONSECUTIVE PEAKS PRESENT IN THE CHROMATOGRAM SHOWN IN FIG. 6

Peak pair	Relative retention
1/a	1.033
b/1	1.056
2/b	1.061
c/2	1.030
d/c	1.036

Van Deemter plot). As seen, the best resolution we could get on the 24-ft.-long packed column would be about 0.7 and we would need about 1.5 h for this; in this time, a resolution of $R = 1.9$ could be obtained on both 150-ft.-long open tubular columns, and for base line resolution, we need only about 13 min on the WCOT and about twice of that on the 150-ft.-long SCOT column.

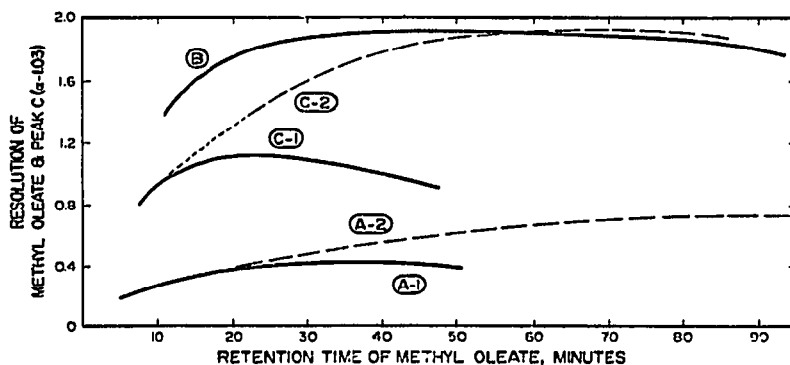


Fig. 8. Plot of resolution of the methyl oleate/peak *c* pair against the retention time of methyl oleate, on the three columns. A-1 = 8-ft.-long packed column, A-2 = 24-ft.-long packed column, B = 150-ft.-long WCOT column; C-1 = 50-ft.-long SCOT column; C-2 = 150-ft.-long SCOT column.

The plots shown in Fig. 8 permit one more conclusion. As seen, at high velocities there is no gain anymore in increasing the column length. For example, at a retention time of 17 min the resolution of the 8- and 24-ft.-long packed columns would be identical ($R = 0.35$) and the same is true at $t_R = 11$ min for the 50- and 150-ft.-

* In order to permit comparison between the plots in Figs. 5 and 8, we plot in both cases resolution against the retention time of methyl oleate which is the second peak in case of the stearate/oleate separation but the first peak in case of the separation from peak *c*.

long SCOT columns ($R = 0.95$). This observation is due to the fact that behind the so-called optimum practical gas velocity (OPGV) the value of $HETP/\bar{u}$ is constant and we do not gain anything in increasing column length⁵.

Factors influencing retention time

Combining eqns. 3 and 8 we get

$$t_R = \frac{nh}{\bar{u}}(k + 1) \quad (9)$$

If we now substitute the r.h.s. of eqn. 2 for n , we get that

$$t_R = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left[\frac{(k + 1)^3}{k^2} \frac{h}{\bar{u}} \right] \quad (10)$$

This equation relates resolution, relative retention, partition ratio, column efficiency (HETP), and average linear gas velocity to retention time (h , k , and t_R refer to the second peak).

If we carry out the comparison at the same temperature and investigate the retention time obtained when the resolution is equal, then the first part of eqn. 10 will have the same value for the different columns and the difference will be only in the last two terms given in brackets.

Fig. 9 plots the first term in the brackets against k . As seen, its value has a minimum at $k = 2$. In other words, looking at this term only, the shortest retention time can be obtained if the partition ratio is close to this value. On packed columns, we usually have large partition ratio values and thus, the value of this term is high.

The behavior of the last term in the brackets, $HETP/\bar{u}$, was already investigated and its value for the case investigated was plotted in Fig. 3; as discussed, if we work at the linear portion of the Van Deemter curve (*i.e.* at or above the OPGV), its

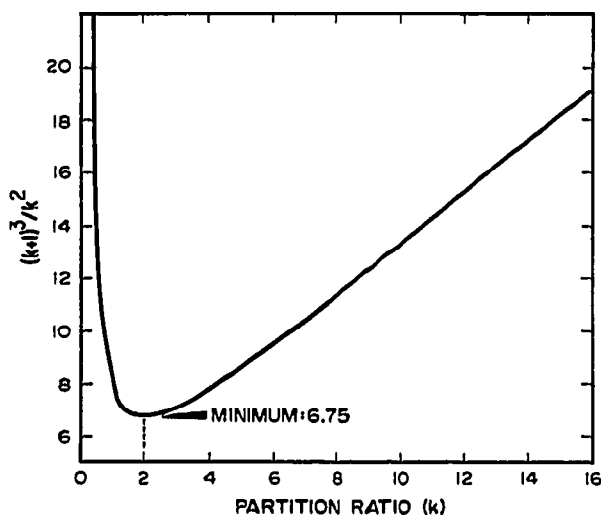


Fig. 9. Plot of $(k + 1)^3/k^2$ vs. k .

value approaches the C term of the Van Deemter–Golay equations. Since this term is generally higher for packed columns than for open tubular columns, the retention time for the former will be longer.

Table VII lists numerical values for the bracketed terms for the cases investigated, at high velocities (over the OPGV). It is clear that the value is the largest for the packed column explaining the long analysis time.

TABLE VII

VALUES OF THE LAST TWO TERMS IN THE RETENTION TIME EQUATION FOR METHYL OLEATE, AT HIGH VELOCITIES

Column	k	$\frac{(k+1)^3}{k^2}$	$\frac{h}{\bar{u}}$ (sec)	$\left[\frac{(k+1)^3}{k^2} \frac{h}{\bar{u}} \right]$ (sec)
Packed	58.6	61.65	0.00685	0.422
WCOT	5.1	8.73	0.00215	0.019
SCOT	11.2	14.48	0.00255	0.037

Finally, let us investigate the meaning of the bracketed term of eqn. 10. We have seen that

$$N = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \quad (4)$$

Thus substituting N for the first part of the r.h.s. of eqn. 10 we obtain that

$$t_R = N \left[\frac{h}{\bar{u}} \frac{(k+1)^3}{k^2} \right] \quad (11)$$

$$\frac{N}{t_R} = \frac{\bar{u}}{h} \frac{k^2}{(k+1)^3} \quad (12)$$

In other words the reciprocal of the bracketed term is equal to the number of effective plates generated in unit time, the expression used by Desty *et al.* to describe column performance.

However, this derivation also shows that, in spite of the general beliefs, the value of N/t_R is not independent of the partition ratio and — unless we work at high velocities — it will also be influenced by the average linear gas velocity because, at lower velocities, \bar{u}/h is not a constant. Thus, by cleverly selecting the conditions, the values of N/t_R can be adjusted at will. This can be illustrated well by calculating the N/t_R values for the cases already discussed. Table VIII lists values for the “bracketed term”, *i.e.*

$$\left[\frac{h}{\bar{u}} \frac{(k+1)^3}{k^2} \right]$$

and its reciprocal value, corresponding to N/t_R for three cases: methyl oleate at optimum and high velocities and methyl laurate at high velocities. It is clear that *e.g.* by proper selection of the conditions, the N/t_R value for the same solute can be more

TABLE VIII

COMPARATIVE DATA FOR THE NUMBER OF EFFECTIVE PLATES PRODUCED IN UNIT TIME, IN THREE CASES, ON THE THREE COLUMNS

	Column		
	Packed	WCOT	SCOT
<i>Data for methyl oleate</i>			
<i>At optimum velocity</i>			
Bracketed term, sec	0.6412	0.0445	0.0594
N/t_R , sec ⁻¹	1.560	22.472	16.835
<i>At high velocities</i>			
Bracketed term, sec	0.4223	0.0188	0.0369
N/t_R , sec ⁻¹	2.370	52.632	27.027
<i>Data for methyl laurate</i>			
<i>At high velocities</i>			
Bracketed term, sec	0.0710	0.0256	0.0183
N/t_R , sec ⁻¹	14.085	39.063	54.645

than doubled, while by proper selection of the solute, its value can also be increased significantly.

These values show that the N/t_R value is not an absolute value either and depends on the solute and the analytical conditions. Therefore, if it is to be used to express column performance, the conditions under which it is determined should be agreed upon. For example, one could agree to give its values always at $k = 2$ where the $k^2/(k + 1)^3$ term will have a maximum corresponding to $1/6.75 = 0.1482$, and at high velocities where h/\bar{u} is a constant approximating the C term. However, the problem with this is that while it would permit the absolute comparison of columns, it will not be satisfactory to compare their performance for the same sample because if the partition ratio is $k = 2$ for a given solute on one column, it will certainly be different on the other column or columns and thus data given at $k = 2$ for each column will need further calculation before they could be used for real column comparison. Besides this, since one cannot find a solute having a partition ratio of exactly $k = 2$, one would have to get data for a number of solutes and then interpolate for $k = 2$. In our opinion, the ways proposed here to express true column performance where the comparison is based on a common denominator—either resolution or speed—are better for the practice.

Comparison of the two open tubular column types

In the particular case investigated, the SCOT column was "slower" than the WCOT column. The reason for this can be explained from the first term in the brackets in eqn. 10, which is larger for the SCOT column. However, if we would have a critical separation at an earlier part of the chromatogram, the situation would be different. For example, if we would have a separation problem adjacent to the methyl laurate (C_{12} fatty acid) peak, the SCOT column would be in a more favorable position. This can be seen from Table IX, which lists the values of the bracketed terms for the methyl laurate peak at high velocities (assuming the same C term for both methyl oleate and methyl laurate). As seen, here, the value for the SCOT column is about 30% less than

TABLE IX

VALUES OF THE LAST TWO TERMS IN THE RETENTION TIME EQUATION FOR METHYL LAURATE, AT HIGH VELOCITIES

Column	k	$\frac{(k+1)^3}{k^2}$	$\frac{h}{\bar{u}}$ (sec)	$\left[\frac{(k+1)^3}{k^2} \frac{h}{\bar{u}} \right]$ (sec)
Packed	6.92	10.37	0.00685	0.071
WCOT	0.57	11.91	0.00215	0.026
SCOT	1.32	7.17	0.00255	0.018

for the WCOT column and 75% less than for the packed column. The same relative values would also be obtained for the retention times.

At an earlier peak, the difference would be even more significant and here, the WCOT column could simply not have enough efficiency to achieve separation. This can be seen by evaluating Figs. 10 and 11, which show the analysis of our test mixture on the two open tubular columns at relatively high velocities. In the SCOT column chromatogram (Fig. 11) there is a peak before the first numbered peak which is overlapped by peak No. 1 on the WCOT column chromatogram (Fig. 10). It can also be seen that the retention time of methyl laurate (peak No. 4) is about 3 min on the

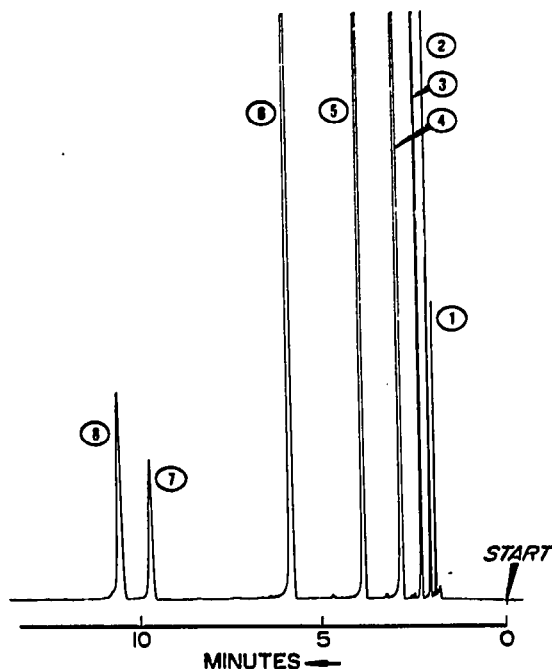


Fig. 10. Chromatogram of a fatty acid methyl ester mixture obtained on a 150 ft. \times 0.010 in. I.D. WCOT column coated with DEGS stationary phase. Temperature, 180°; average linear carrier gas (helium) velocity, 42.3 cm/sec; resolution of the methyl stearate/oleate peaks, 4.75; 1 = Methyl caproate (C_6), 2 = methyl caprylate (C_8), 3 = methyl caprate (C_{10}), 4 = methyl laurate (C_{12}), 5 = methyl myristate (C_{14}), 6 = methyl palmitate (C_{16}), 7 = methyl stearate (C_{18}), 8 = methyl oleate (C_{18}).

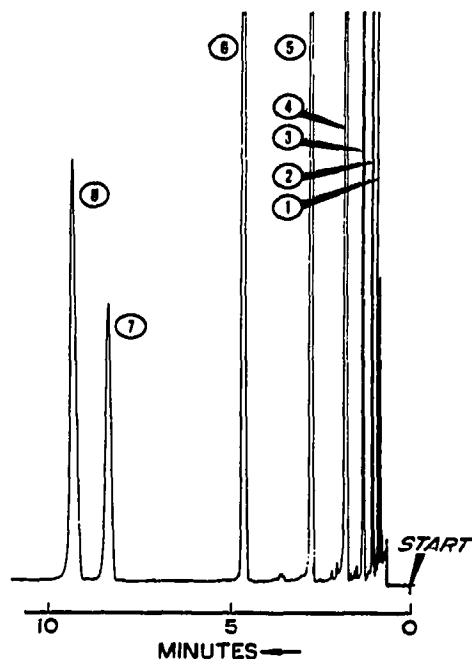


Fig. 11. Chromatogram of a fatty acid methyl ester mixture obtained on a 50 ft. \times 0.020 in. I.D. SCOT column prepared with DEGS stationary phase. Temperature, 180°; average linear carrier gas (helium) velocity, 34.0 cm/sec; resolution of the methyl stearate/oleate peaks, 3.2. For peak identification, see the legend to Fig. 10.

WCOT column and 2 min on the SCOT column although the velocity used in the former case was higher.

Utilization of the proposed ways to express true column performance

Finally, we would like to illustrate the utilization of the proposed ways to express true column performance by taking an extreme case.

In 1959, Zlatkis and Kaufman⁶ described the use of a 1-mile-long open tubular column resulting in over one million theoretical plates. Table X lists the pertinent data;

TABLE X

DATA OBTAINED ON THE ONE-MILE-LONG COLUMN OF ZLATKIS AND KAUFMAN

Length, m	1,609.3
Internal diameter, mm	1.676
Liquid phase	<i>n</i> -Hexadecane
Temperature, °C	25
Carrier gas	Nitrogen
Flow-rate at outlet, ml/min	250
Number of theoretical plates	1,000,000
HETP, mm	1.61
Phase ratio	840
Carrier gas outlet velocity, cm/sec	188.89
Pressure drop, atm gauge	2.647
Compressibility correction factor	0.3884
Average linear carrier gas velocity, cm/sec	73.36

from these, the phase ratio and the pressure drop are calculated; the former by assuming a liquid film thickness of $0.5 \mu\text{m}$ and the latter by calculating the outlet velocity (u_o) from the given flow-rate and then, the inlet pressure from the outlet velocity:

$$u_o = \frac{F_c}{r^2 \pi} = \frac{r^2}{16 \eta L} \frac{p_i^2 - p_o^2}{p_o} \quad (13)$$

In this equation, u_o is in cm/sec, F_c in ml/sec; r (the inside radius of the column) and L (the column length) in cm, and p_i and p_o (the absolute inlet and outlet pressures) in dyn/cm². From the pressure drop, the compressibility correction factor and from it and u_o , the average linear gas velocity can be established.

Let us now assume a peak pair with a partition ratio of $k = 5$ for the second peak*; using eqn. 8 we can calculate its retention time as 219.38 min (3.66 h).

We are now asking two questions: (a) if $R = 1.5$, what can be the relative retention of the two peaks, and (b) if $\alpha = 1.05$, what resolution can be achieved? The answers can be calculated using eqn. 2:

$$(a) \text{ if } R = 1.5, \alpha = 1.0072$$

$$(b) \text{ if } \alpha = 1.05, R = 9.92$$

The next question is: what kind of packed column would give the same results and in what time? In order to get answer to these questions, a number of assumptions have to be made. Assuming a $\beta = 10$ for this column, the partition ratio of the second peak would be $k_2 = 420$. This is much too high and one would certainly use this packed column at a higher temperature. We assumed 75° and calculated the partition ratio by assuming that the solutes to be separated are hydrocarbons and that a plot of the log of the partition coefficient against the carbon number on hexadecane is identical to that obtained on squalane, for which such data are available⁷. As a result, we obtain $k = 49$ at 75° .

We further assume a column efficiency of HETP = 0.8 mm, a specific permeability of $2 \times 10^{-7} \text{ cm}^2$, an average linear gas velocity of 15 cm/sec and an inter-particle porosity of 0.40; these values correspond to a 1/8 in. O.D. (2.16 mm I.D.) packed column. From here on the calculation is straightforward and utilizes equations well established in gas chromatography:

$$n = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k + 1}{k} \right)^2 = (16)(9.92^2) \left(\frac{105}{5} \right)^2 \left(\frac{50}{49} \right)^2 = 722,960$$

$$L = n h = (722,960) (0.08) = 57,836.8 \text{ cm} = 578.4 \text{ m}$$

$$t_M = \frac{L}{\bar{u}} = \frac{57,836.8}{15} = 3855.79 \text{ sec} = 64.263 \text{ min}$$

$$t_R = t_M (k + 1) = (64.263) (50) = 3213.15 \text{ min} = 53.55 \text{ h}$$

* If we assume that the partition coefficients on hexadecane and squalane are identical, this peak would correspond to a hypothetical n -paraffin with 8.15 carbon atoms; this can be established from the log K vs. carbon number plots prepared using the data published by Desty and Goldup⁷.

$$\Delta p j' = \frac{\eta L \bar{u}}{B_0} = \frac{(2 \times 10^{-4})(5.784 \times 10^4)(15)}{2 \times 10^{-7}} =$$

$$867.6 \times 10^6 \text{ dyn/cm}^2 = 856.25 \text{ atm gauge}$$

$$j' = \frac{3}{4} \frac{P^2 + 2P + 1}{P^2 + P + 1}; \text{ if } P \text{ is large, } j' \simeq 0.75$$

$$\Delta p = \frac{856.25}{0.75} = 1141.7 \text{ atm gauge}$$

$$P = \frac{\Delta p + p_0}{p_0} = \frac{1141.7 + 1}{1} = 1142.7$$

$$= \frac{3}{2} \frac{P^2 - 1}{P^3 - 1} = \frac{3}{2} \frac{1142.7^2 - 1}{1142.7^3 - 1} = 1.313 \times 10^{-3}$$

$$u_0 = \frac{\bar{u}}{j} = \frac{15}{1.313 \times 10^{-3}} = 11,424.2 \text{ cm/sec}$$

$$F_c = u_0 \varepsilon (r^2 \pi) = (11,424.2) (0.40) (0.108^2) (\pi) = 167.45 \text{ cm}^3/\text{sec} = 10,047.0 \text{ cm}^3/\text{min}$$

$$F_a = F_c \left[\frac{T_a}{T_c} \frac{p_a}{p_a - p_w} \right] = (10,047.0) \frac{298}{348} \left[\frac{760}{760 - 23.8} \right] = 8,874.2 \text{ cm}^3/\text{min}$$

The most important values are summarized in Table XI. As seen, we would need an over half-km-long packed column and the inlet pressure would be over 1000 atm; the analysis would take over two days. At the same time, one would need only 3 h and 40 min on the 1-mile-long open tubular column to obtain the same performance.

TABLE XI

CHARACTERISTICS OF A PACKED COLUMN WHICH WOULD GIVE THE SAME RESOLUTION AS THE ONE-MILE-LONG OPEN TUBULAR COLUMN

Column temperature, °C	75
Column length, m	578.4
HETP, mm	0.8
Average linear carrier gas velocity, cm/sec	15.00
Flow-rate at outlet and room temperature*, ml/min	8,874.2
Pressure drop, atm gauge	1,141.7
Retention time of the second peak, h	53.55

* This is the flow-rate one would measure with a (wet) bubble flow meter; the value of F_c calculated to dry gas conditions and column temperature is 10,047 ml/min.

LISTS OF SYMBOLS

A	= multipath term in the Van Deemter equation
B	= longitudinal diffusion term in the Van Deemter–Golay equations
B_o	= specific permeability
C	= resistance to mass transfer term in the Van Deemter–Golay equations
F_a	= carrier gas flow-rate measured at column outlet and ambient temperature
F_c	= carrier gas flow-rate corrected to column temperature and dry gas conditions
h	= height equivalent to one theoretical plate, HETP [$h = L/n$]
HETP _{min.}	= HETP value corresponding to the minimum of the Van Deemter plot
j	= gas compressibility correction factor
j'	= Guiochon's term ⁸
k	= partition (capacity) ratio [$k = t_R'/t_M$]
K	= partition coefficient [$K = \beta k$]
L	= column length
n	= number of theoretical plates [$n = 16(t_R/w_b)^2$]
N	= number of effective plates [$N = 16(t_R'/w_b)^2$]
OPGV	= optimum practical gas velocity
p_a	= ambient pressure
p_i	= carrier gas inlet pressure
p_o	= carrier gas outlet pressure
Δp	= pressure drop along the column [$\Delta p = p_i - p_o$]
p_w	= partial pressure of water at ambient temperature
P	= carrier gas relative pressure [$P = p_i/p_o$]
r	= column inside radius
R	= peak resolution [$R = (t_{R2} - t_{R1})/w_{b2}$]
SCOT	= support-coated open tubular (column)
t_M	= gas hold-up time
t_R	= retention time (measured from start)
t_R'	= adjusted retention time (measured from the "air peak") [$t_R' = t_R - t_M$]
T_a	= ambient temperature (in °K)
T_c	= column temperature (in °K)
\bar{u}	= average linear carrier gas velocity [$\bar{u} = u_o j = L/t_M$]
u_o	= linear carrier gas velocity at column outlet, corrected to column temperature [$u_o = \bar{u}/j$]
\bar{u}_{opt}	= average linear carrier gas velocity corresponding to the minimum of the Van Deemter plot
V_G	= volume of gas phase in the column
V_L	= volume of stationary (liquid) phase in the column
w_b	= peak width at base
WCOT	= wall-coated open tubular (column)
α	= relative retention [$\alpha = t'_{R2}/t'_{R1}$]
β	= phase ratio [$\beta = V_G/V_L$]
ϵ	= interparticle porosity
η	= viscosity of the carrier gas at column temperature

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