

## PREDICTION OF SEPARATION AND SPECIFICATIONS OF CHROMATOGRAPHIC COLUMNS

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### INTRODUCTION

Employing the techniques of ROHRSCHEIDER<sup>1</sup>, columns of commercial manufacture were classified according to relative polarity. ROHRSCHEIDER also showed that the combination of two stationary phases will result in a column of polarity intermediate between the two pure materials. Various methods of combining two different stationary phases were investigated. The effects of column pressure and length on absolute retention times were obtained.

### CLASSIFICATION OF CHROMATOGRAPHIC COLUMNS BY RELATIVE POLARITY

Utilizing the construction techniques of ROHRSCHEIDER<sup>1</sup>, a graph of relative polarity for many of the commercially available chromatographic columns was constructed (Fig. 1). Table I identifies the liquid phases represented in Fig. 1. Also shown is the position of a column "K-1" which is a homogeneous mixture of bis-(2-methoxyethyl) adipate on GC-22 solid support and di-2-ethylhexyl sebacate on GC-22 solid support in the ratio 2.1 to 1 respectively. The construction was made for saturated hydrocarbons through carbon number 5, unsaturated hydrocarbons through carbon number 4, acetylene, propane, and butadiene-1,3.

Previous data<sup>1</sup> showed that squalane and  $\beta,\beta$ -oxydipropionitrile were the least polar and most polar stationary phases respectively; they were arbitrarily assigned polarity numbers of 0 and 100, respectively. The relative retention times of individual components were plotted vertically on a common logarithmic scale at opposite ends of a linear "polarity" scale. Normal pentane has a relative retention time of 1. Compounds of like structure and carbon number were interconnected by straight lines. All other polarity lines were located by fitting the relative retention times of the individual stationary phases to the skew lines. In each case, a suitable fit of all data for a single stationary phase was accomplished by a straight line having only a single value of polarity.

In general, the C<sub>2</sub> and C<sub>3</sub> hydrocarbons showed the largest deviations from the skew lines. The deviations for all components could have been reduced if an intermediate component such as iso-butane had been chosen as the reference. However, since most of the available data is based on normal pentane as the reference, it was

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also used in this study. Acetylenes (also observed by ROHRSCHEIDER) showed the greatest deviations, although some form of linear trend did exist. Hydrocarbons of carbon number greater than 5 and oxygenated and halogenated hydrocarbons have not been plotted, but it is believed that similar charts could be constructed for them. It has also been found that data will fit the polarity lines better if separate charts are constructed for components of similar structure (e.g., separate charts for saturated and unsaturated hydrocarbons); however, the value of having all data on a single chart has outweighed this refinement.

Although many methods are available which offer more precise tabulations of

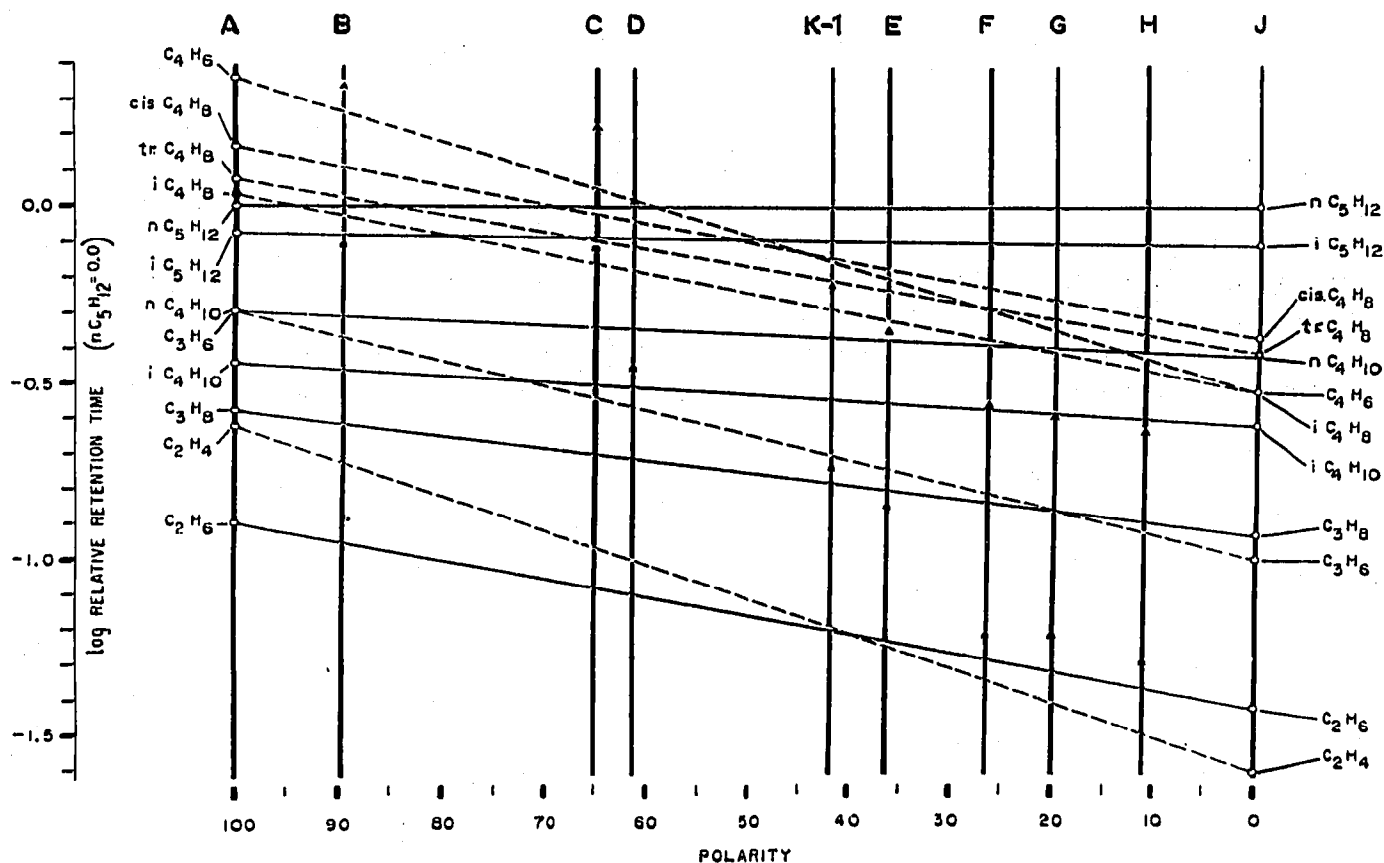


Fig. 1. Relative polarity chart for various commercially available chromatographic columns. — paraffins; - - - olefins; ● acetylene; ▲ propyne.

chromatographic data, none, other than the polarity classification, presents the data for all columns on a single graph in an orderly manner. It is important to note that the polarity classification of data gives no actual data of column parameters such as length, flow rate, etc., or the resolution obtainable between adjacent components.

Although the polarity classification is useful for the selection of a column to achieve a desired separation, it is most useful for the evaluation of new stationary phases or special chromatographic columns. When the polarity classification is employed for the latter purpose, the retention times of only two components are required for the estimation of the retention times of all other components. One of the required components must be normal pentane.

TABLE I  
IDENTIFICATION OF COLUMNS OF FIG. 1

A = $\beta,\beta$ -Oxydipropionitrile	H = Silicone oil D. C. No. 200
B = Polydiethylene glycol succinate	J = Squalane
C = Carbowax 400	K-1 = Homogeneous mixture of bis-(2-methoxyethyl) adipate and di-2-ethylhexyl sebacate in the ratio 2:1 to 1, respectively.
D = Bis-(2-methoxyethyl) adipate	
E = Ucon polyglycol LB-550-X	
F = Diisodecyl phthalate	
G = Di-2-ethylhexyl sebacate	

The above designation of columns is alphabetical for identification purposes only.

### CHROMATOGRAPHIC COLUMNS WITH MIXED STATIONARY PHASES

It is not unusual to find that a desired chromatographic separation cannot be accomplished in one step with any of the known chromatographic columns. The usual solution is to perform the analysis in two steps using two chromatographic columns, or if the desired analysis must be made frequently (as in a control laboratory or process chromatograph), effort may be expended to find a stationary phase which will most nearly accomplish the desired separation.

ROHRSCHEIDER<sup>1</sup> described a technique whereby it is possible to combine two column materials of different polarity in order to achieve a particular separation.

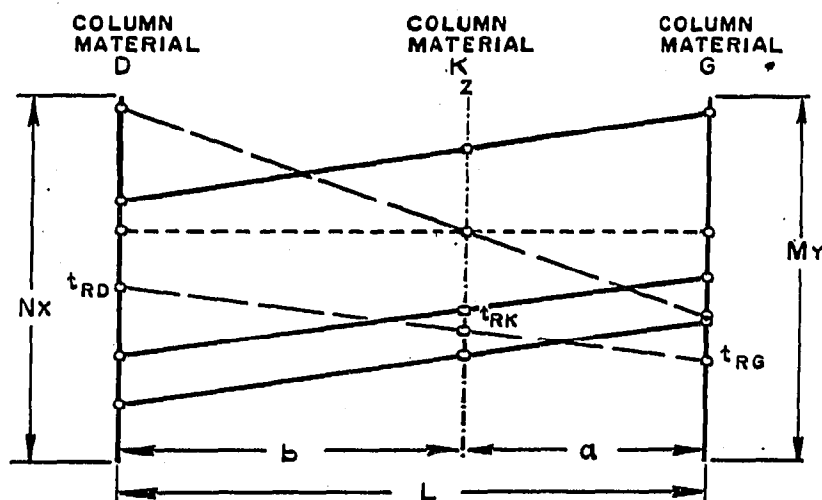


Fig. 2. Nomenclature and illustration of the column prediction chart.

The purpose of this phase of the investigation was to determine under what conditions this technique is applicable and how the column materials must be combined in order to give the greatest accuracy. Fig. 2 illustrates the technique, as modified by the authors, for predicting a column to give a desired separation. The technique will be illustrated using columns D and G as examples. See Table I.

To construct this graph, retention times for the desired components for the two columns, D and G, of lengths  $x$  and  $y$ , respectively, must be determined at the same outlet flow rates, percent liquid phase, and temperatures. However, if those retention

times, so determined, were plotted on the heavy lines as shown, it would be found that the points on one side or the other would be too close for accurate estimation. Therefore, the retention times of columns D and G are multiplied by  $N$  and  $M$  respectively. The length of the columns are likewise multiplied by  $N$  and  $M$ , respectively. The new values of retention time are plotted linearly on the chart as shown, where:

- $x$  = length of column having liquid phase of material D
- $y$  = length of column having liquid phase of material G
- $t_{RD}$  = retention time of component R measured on column D of length  $x$
- $t_{RG}$  = retention time of component R measured on column G of length  $y$
- $N$  = multiplication factor for column D
- $M$  = multiplication factor for column G
- $K$  = identification of predicted column
- $Z$  = length of predicted column
- $L$  = distance between lines D and G
- $a$  = distance between lines K and G
- $b$  = distance between lines K and D
- $t_{RK}$  = predicted retention time of component R for column K.

Like components are interconnected by straight lines. A vertical line,  $Z$ , is drawn where the components have the desired separation. If the desired separation is nowhere attainable, a different pair of columns must be tried. In general, the polarity chart will enable one to pick the proper pair rapidly.

Having determined that line  $Z$  would give the desired separation, the question arises as to how materials D and G should be combined and in what proportions. The following cases exist:

*Case 1.* Column materials D and G in series, respectively, in predetermined lengths.

*Case 2.* Column materials G and D in series, respectively, in predetermined lengths.

*Case 3.* Coated solid supports D and G intimately mixed in predetermined proportions by weight percent, and a column of a predetermined length.

*Case 4.* Stationary phases D and G intimately mixed in predetermined proportions by weight percent and coated on solid support in a column of predetermined length.

Based on ROHRSCHEIDER's work, the lengths for cases 1 and 2 above are:

$$\text{Length of column D} = \frac{aNx}{L} \quad (1)$$

$$\text{Length of column G} = \frac{bMy}{L} \quad (2)$$

The ratio of D and G materials for cases 3 and 4 above are:

$$\frac{D}{G} = \frac{aNx}{bMy} \quad (3)$$

The length of columns for cases 3 and 4 above are:

$$\text{Length of column} = \frac{aNx + bMy}{L} \quad (4)$$

To determine which of the four cases above would give the most accurate results, new columns were predicted using bis-(2-methoxyethyl) adipate as the D material and di-2-ethylhexyl sebacate as the G material. Each column was 2 m in length, 1/8 in. o.d., 15 % liquid phase, 100-120 mesh solid support, carrier gas: helium. The fractograms are shown in Figs. 3 and 4 respectively. The column prediction chart is shown in Fig. 5. For clarity, it does not show all the components. Identification of all components is given in Table II. K-1 and K-2 are the predicted columns.

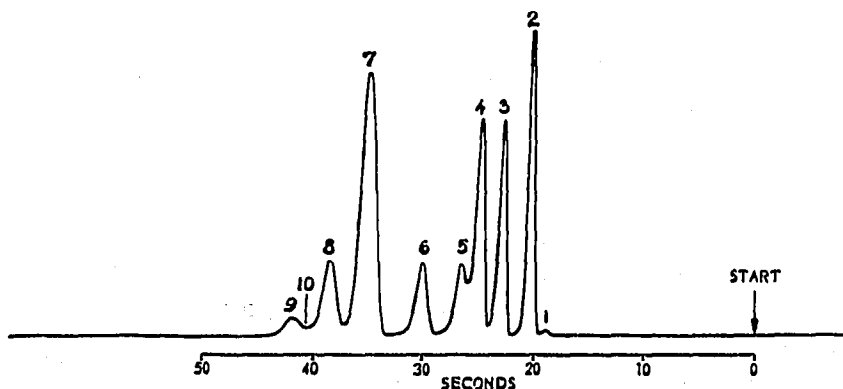


Fig. 3. Chromatograph of various hydrocarbons on a high speed bis-(2-methoxyethyl) adipate column. Length: 2 m; carrier: 39 p.s.i.g.; flow rate: 50 c.c./min.

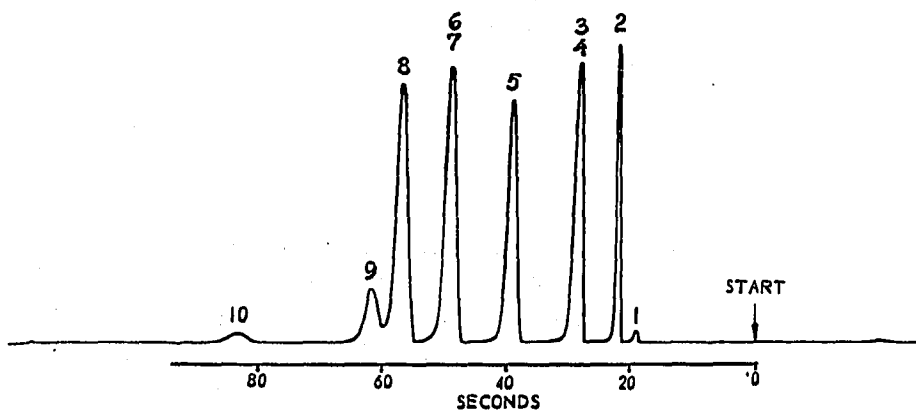


Fig. 4. Chromatograph of various hydrocarbons on a high speed di-2-ethylhexyl sebacate column. Length: 2 m; carrier: 39 p.s.i.g.; flow rate: 50 c.c./min.

Table II columns 1 and 6, lists the relative retention times for columns K-1 and K-2 as determined from the column prediction chart, Fig. 5. Relative retention times from fractograms based on cases 1 through 4 above and column K-1 are listed in columns 2 through 5, respectively. Relative retention times from a fractogram based on case 3 for column K-2 are listed in column 7. The actual total column length used in each test was only 2 m, but the proportions of materials or column lengths were precisely adhered to. It is readily seen that for both columns K-1 and K-2, the most accurate results were obtained when case (3), the intimate mixing of coated supports in the proportions determined by eqn. 3, is used. Although case 4 gave good results, it was removed from consideration since it was felt that the resolving power of a mixed liquid phase would not be a linear function of the pure liquid phases.

As a part of the investigation, it was also of interest to determine if the predicted retention times had any relation to the column length prediction by eqn. (4). It was found that the predicted retention times could not be achieved unless the carrier flow was altered (*i.e.*, other than 50 c.c./min as used with the pure columns).

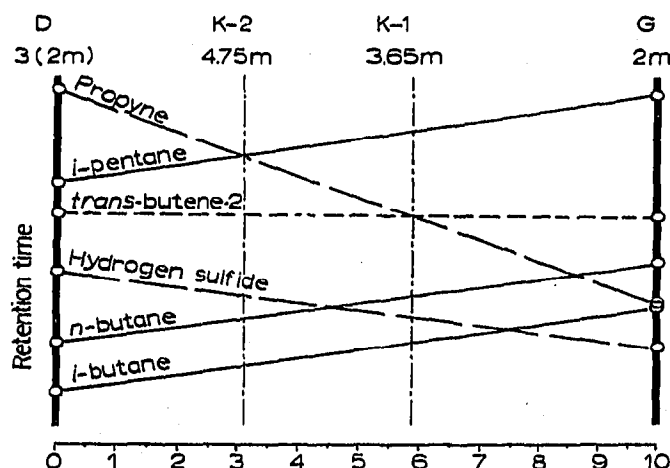


Fig. 5. Column prediction chart for bis-(2-methoxyethyl) adipate and di-2-ethylhexyl sebacate column materials.

However, it was found that if the retention times were reduced by linear proportions to a column length of 2 m, which is the length of either of the pure columns, the predicted retention times are equal to the actual retention times of a 2 m column at a carrier gas flow rate of 50 c.c./min. Fig. 6 is a fractogram of a 2 m K-1 column with a carrier flow rate of 50 c.c./min. Fig. 7 is a fractogram of a 2 m K-2 column with a carrier flow rate of 50 c.c./min. Table III compares the predicted retention times with

TABLE II  
RELATIVE RETENTION TIMES ( $nC_5 = 1.0$ )

Component	1	2	3	4	5	6	7
	Predicted K-1	Actual K-1 case 1	Actual K-1 case 2	Actual K-1 case 3	Actual K-1 case 4	Predicted K-2	Actual K-2 case 3
2 Ethane	0.043	0.047	0.023	0.0475	0.049	0.045	0.04
3 Propane	0.123	0.132	0.124	0.125	0.128	0.127	0.137
4 Propylene	0.175	0.177	0.173	0.183	0.186	0.205	0.21
5 Isobutane	0.260	0.265	0.284	0.27	0.266	0.267	0.269
6 <i>n</i> -Butane	0.373	0.386	0.379	0.386	0.384	0.383	0.386
7 Isobutylene	0.466	0.495	0.448	0.483	0.48	0.541	0.53
8 <i>trans</i> -Butene-2	0.579	0.61	0.55	0.594	0.591	0.650	0.65
9 <i>cis</i> -Butene-2	0.655	0.675	0.63	0.654	0.674	0.740	0.75
10 Isopentane	0.792	0.788	0.765	0.792	0.792	0.790	0.79
Maximum error	$\times$	+0.031	-0.029	+0.017	+0.019	$\times$	-0.011
Average error	$\times$	+0.0121	-0.010	+0.0075	+0.093	$\times$	+0.0065

the actual retention times for 2 m columns. Columns 1 and 4 are the predicted retention times for K-1 and K-2 respectively. Columns 2 and 5 are the retention times obtained from actual 2 m K-1 and K-2 fractograms, Figs. 6 and 7, respectively.

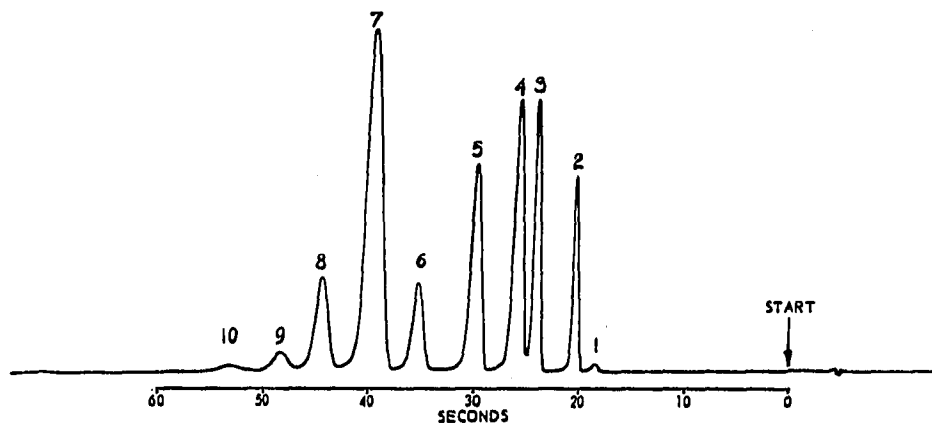


Fig. 6. Chromatograph of various hydrocarbons on column K-1 as specified by the column prediction chart in Fig. 5. Length: 2 m; carrier: 45 p.s.i.g.; flow rate: 50 c.c./min.

The column prediction chart indicates that a simple linear relationship between the predicted and pure columns exists. Furthermore, since the retention times of the predicted 2 m columns are identical to the actual retention times, a simple mathematical relationship must exist<sup>2</sup>.

$$Q_{RD} = \frac{t_{mDx}}{t_{RDx}} \quad (5)$$

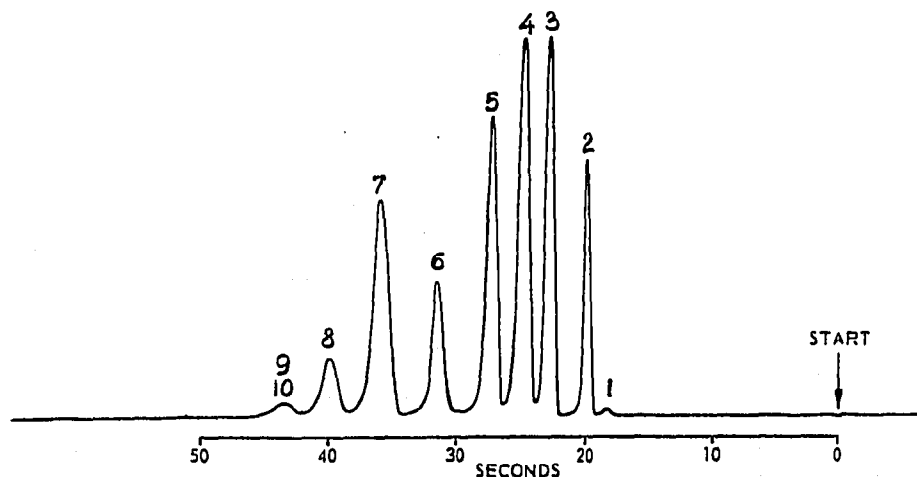


Fig. 7. Chromatograph of various hydrocarbons on column K-2 as specified by the column prediction chart in Fig. 5. Length: 2 m; carrier: 43 p.s.i.g.; flow rate: 50 c.c./min.

where:

$t_{mDx}$  = retention time of air for column D of length  $x$

$t_{RDx}$  = retention time for component R for column D of length  $x$

$Q_{RD}$  = retardation factor of component R for column D, dimensionless.

TABLE III  
RETENTION TIMES (IN SEC)

Component	1	2	3	4	5
	Predicted K-1	Actual K-1	Calculated K-1	Predicted K-2	Actual K-2
1 Air	19.0	18.25	19.13	19.0	18.5
2 Ethane	20.86	20.35	20.9	20.52	20.1
3 Propane	24.36	23.75	24.5	23.25	23.05
4 Propylene	26.65	26.25	26.3	25.85	25.5
5 Isobutane	30.4	30.1	30.4	27.94	27.45
6 <i>n</i> -Butane	35.3	35.3	35.5	31.82	31.35
7 Isobutylene	40.0	39.6	39.4	37.1	36.4
8 <i>trans</i> -Butene-2	44.6	44.5	44.3	40.75	40.3
9 <i>cis</i> -Butene-2	47.6	47.15	47.8	45.85	43.6
10 Isopentane	53.6	53.25	53.9	45.7	44.95
Maximum error	$\pi$	-0.75	-0.60	$\pi$	-2.25
Average error	$\pi$	-0.387	-0.24	$\pi$	-0.659

Similarly:

$$Q_{RG} = \frac{t_{mGy}}{t_{RGy}} \quad (6)$$

The  $Q_{RK}$  for the combination column is:

$$Q_{RK} = \frac{LQ_{RD}Q_{RG}t_{mKZ}}{aQ_{RG}t_{mDx} + bQ_{RD}t_{mGy}} \quad (7)$$

when

$$t_{mKZ} = t_{mDx} = t_{mGy} \quad (8)$$

$$Q_{RK} = \frac{LQ_{RD}Q_{RG}}{aQ_{RG} + bQ_{RD}}, \text{ and} \quad (9)$$

$$\frac{1}{Q_{RK}} = \frac{a}{LQ_{RD}} + \frac{b}{LQ_{RG}} \quad (10)$$

The retention time of air,  $t_{mKZ}$ , for the combined column is:

$$t_{mKZ} = \frac{a}{L}t_{mDx} + \frac{b}{L}t_{mGy} \quad (11)$$

The retention time for component "R" where the combined column is the same length as the pure column is:

$$\frac{t_{mKZ}}{Q_{RK}} \quad (12)$$

The calculated results based on the fractograms of the pure columns, Figs. 3 and 4, are shown in column 3 of Table III. It will be observed that the retention times deter-



mined by chart prediction, calculations from eqns. (5) through (12), and experimentally, are extremely close and verify the validity of both the graphical and analytical methods for predicting new combination results.

A comparison of the retention time of air as a function of column parameters for columns of mixed stationary phases and supports, and series-filled columns is shown below.

Retention time of air for columns of mixed stationary phases and supports:

$$t_{mRK} = U \frac{p_i^3 - p_o^3}{p_o^2} \quad (13)$$

Retention time of air for series-filled columns, D + G:

$$t'_{mRK} = U_1 \frac{(p_i^3 - p^3)}{p_o^2} + U_2 \frac{(p^3 - p_o^3)}{p_o^2} \quad (14)$$

Retention time of air for series-filled columns G + D:

$$t''_{mRK} = U_2 \frac{(p_i^3 - p^3)}{p_o^2} + U_1 \frac{(p^3 - p_o^3)}{p_o^2} \quad (15)$$

where:

$p_i$  = column inlet pressure

$p$  = column pressure at the interface of the two different column materials

$p_o$  = column outlet pressure

$U$  = is a proportionality factor and a function of gas viscosity, column permeability, column area, and volumetric flow rate.

It is seen from the above relationships that a simple linear relationship for retention times and relative retention times can exist only for eqn. (13), and then only if  $p_i$ ,  $p_o$  and  $U$  are approximately the same for both the pure and combined columns. Although relative retention times were found to be independent of the column length and pressure, and predictable if the column materials were intimately mixed, absolute retention times were not predictable until the column length and carrier flow rate of the combined column were identical to the pure columns.

In the general case, the chief limitation of the graphical technique is that in the preparation of the graph, the pure columns must be of equal length and operated under exactly identical conditions. However, if use of the polarity chart is made, very little data need be collected. Although column prediction can be accomplished analytically and without the previously mentioned restraints, the graphical technique is simple and much faster than the analytical approach.

It has also been found that where the ratio of inlet to outlet pressure is low, the column length predicted by eqn. (4) is very close to the actual length and the pure columns need not be of equal length. Although this effect has not been fully investigated, it is believed, none the less, to be true for the limiting case where the inlet pressure is equal to the outlet pressure, eqn. (13) reduces to a linear expression<sup>2</sup>.

#### RELATION OF RETENTION TIMES TO COLUMN PARAMETERS

It has previously been stated that the column lengths specified by eqn. (4) did not give the retention times determined by line K of the prediction chart unless the carrier

flow rate was suitably adjusted. It might be said that this is a very little consequence if it were not for the fact that in order to adjust the flow rate to achieve the predicted retention times, it might be necessary to raise the column inlet pressure above the capabilities or safe operating pressure of the instrument. The dashed line of Fig. 8 shows the relation of retention time of air to column length at the carrier flow rate of 50 c.c./min. It is seen that the relationship is non-linear.

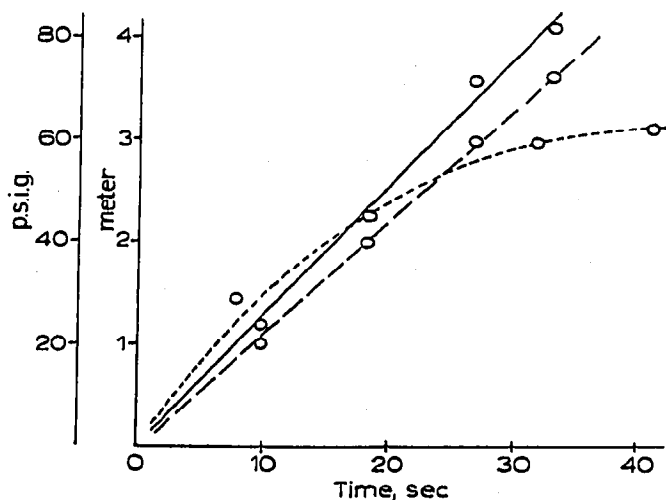


Fig. 8. The variation of the retention time of air with column pressure and length. ——— pressure; - - - - length; - · - · - pressure at 50 c.c./min.

Fig. 8 also shows the relation of column pressure and column length to actual retention times of air. It is seen that both relations are linear. The maximum and average pressure deviations are + 3.5 p.s.i.g. and -0.3 p.s.i.g. respectively. The maximum and average column length deviations are -0.05 m and -0.03 m respectively. Since the data pass through the origin, only one data point is required for each line. For the column length line, this can be the length of the pure column and the retention time of air for the predicted column when its length is equivalent to the length of the pure column. For the pressure line, the same retention time for air is used, and the inlet pressure of the pure columns is used if both have the same inlet pressures. If the inlet pressures of the pure columns are different, then the pressure may be estimated from the following relationships:

$$p_i^2 K = \frac{F_S}{F_K} (p_i s^2 - p_o^2) + p_o^2 \quad (16)$$

$$F_S = \frac{W}{p_i w^2 - p_o^2} \quad (17)$$

and:

$$F_K = \frac{a N x}{L} F_D + \frac{b M y}{L} F_G \quad (18)$$

where:

$F_S, W, p_S$  = either  $F_D, x, p_{iD}$  or  $F_G, y, p_{iG}$ , respectively  
 $p_i$  = column inlet pressure

$p_o$  = column outlet pressure which is assumed to be the same for both columns

$W, x, y$  = length of pure column which is the same for each column.

Eqn. (16) is valid only if the predicted column is of the same length as the pure columns.

To obtain the retention times for the desired components, the predicted retention times for air are divided by the appropriate  $Q_{RK}$  as defined by eqn. (7).

#### INSTRUMENTATION

A modified Perkin-Elmer Model 154-B Vapor Fractometer was used in this investigation. The instrument was modified as follows:

The original thermal conductivity detector was replaced by one with a smaller internal volume (10  $\mu$ l). The reference side of the detector had a separate carrier flow rate of 30 c.c./min. Because the columns would require high inlet pressures, the standard sample valve was replaced by a high-speed diaphragm valve (Perkin-Elmer Model 284). The sampling valve was located inside the air bath. The operating temperature of the instrument was 50° ( $\pm$  0.5°). The chromatographic columns were of 0.125 in. o.d., 0.085 in. i.d., and of No. 304 seamless stainless steel tubing. The chromatographic support material was 100–120 mesh GC-22 "super support" (Coast Engineering). The output of the measuring bridge is amplified by a DC amplifier (Magnetic Instruments Model 759-6). This signal was in turn amplified by a one-transistor amplifier in order to match the input signal to a 0–5 mA galvanometric recorder (Texas Instruments). Chart speeds used were 3 and 6 in./min in order to reduce the error of data interpretation.

#### SUMMARY

The purpose of this investigation was to arrive at a method whereby it is possible to:

1. Orderly classify all columns—the column polarity chart.
2. Minimize the effort required to develop new columns—the column prediction chart.
3. Predict the retention times of components as a simple function of the common column parameters—inlet pressure and length.

Although the methods do not lead to "exact" results, they are sufficiently accurate for most practical problems. These methods should help to minimize the analysis requirements of control laboratories; but perhaps even more important, they will help to reduce the complexity of process chromatographic solutions for they will minimize the number of separate columns required to accomplish wide range analysis.

In conclusion, the user of these methods must be reminded that they give no information with respect to separation between adjacent components. Unless this point is fully appreciated, considerable time can be expended in the development of new columns which may prove to be useless for their intended use.

#### REFERENCES

- <sup>1</sup> L. ROHRSCHEIDER, *Z. anal. Chem.*, 170 (1959) 256.
- <sup>2</sup> A. I. M. KEULEMANS, *Gas Chromatography*, 2nd Ed., Reinhold Publishing Corp., New York, 1959.