256. *The Correlation of Separating Power and Efficiency of Gas-chromatographic Columns.*

By J. H. PURNELL.

A new measure of gas-chromatographic column efficiency, the separation factor S, is proposed and defined. Methods of calculating its value, both empirically from elution curves and from relative volatility data, are described. A general equation relating theoretical-plate requirements with relative volatility, retention volume, and free space in the column is derived. This equation is used to explain inconsistencies in the apparent separating power of different columns, in particular, for capillary and packed columns. Application of the equation to prediction of experimental efficiency requirements, with consequent elimination of much experimental work, is discussed.

THE theoretical-plate concept, introduced into chromatography by Martin and Synge [1] and later refined by Glueckauf,[2] has proved the most profitable approach to quantitative description of the efficiency of chromatographic columns. The theory is based on a model in which a single substance is eluted through a column by a carrier fluid; although Glueckauf discussed impurity ratios, the theory has never been explicitly applied to the problem of the separation of mixed solutes, except in a rudimentary fashion by van Deemter, Zuiderweg, and Klinkenberg.[3] The number (N) of theoretical plates in a column can be evaulated from experimental elution curves by use of the equation of van Deemter, Zuiderweg, and Klinkenberg:

$$N = 16(V_R'/w)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where V_R' is the retention volume (or time) measured from the moment of injection of the eluted substance into the column to the moment when its concentration maximum emerges at the column outlet, and w is the distance between the intercepts on the base line of the tangents to the inflexion points of the gaussian elution curve.

Since this method of determining N is universally adopted it will be used here, although there is good reason to believe that the alternative method suggested by Glueckauf's equations, identical in theory, yields more reproducible results.

Apart from those interested in the theoretical aspects of chromatography few workers use theoretical plate numbers: analysts, for instance, are concerned more with the degree of separation attainable with a column than with its apparent efficiency. Besides, more satisfactory results have often been claimed for columns of low "efficiency" than for others of higher plate numbers. Experiment has shown too that N depends upon almost all the variables and is, therefore, so inconstant as to mean little except when it is stated

[1] Martin and Synge, *Biochem. J.*, 1941, **35**, 1358.
[2] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.
[3] van Deemter, Zuiderweg, and Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271.

that it is the best, or the worst, value attainable with a given column. Finally, the possible relation between the value of N necessary for the separation of two substances of relative volatility α does not seem to have been explored and so, since α is the function of practical importance, N seems to be of no use since its value cannot be determined before an experiment.

On the other hand, measurements of N have provided the basis for the studies of column performance [4] which have recently much improved packed-column efficiency. The dependence of N upon many variables is now at least semiquantitatively known and the work has improved our understanding of the nature and kinetics of column processes. Further, it is now a relatively simple matter to construct and operate packed columns of as many as 50,000 theoretical plates. Simultaneously with the development of highly efficient packed columns, Golay [5] studied the theoretical and practical aspects of open capillary columns. His theoretical predictions of high efficiency, in terms of N, appear to be borne out by the finding of plate efficiencies as high as 750,000 in some cases.[6] However, where it has proved possible, comparison of chromatograms obtained with reasonably efficient packed columns and with capillaries reveals the disturbing fact that from the point of view of the actual separations achieved there is little to choose between them even when, as in some cases, plate efficiencies differ by as much as a factor of 100.

It thus remains uncertain whether the apparently high efficiencies make for improved analysis, and there is a need for a measure of column performance accurately related to the degree of separation attainable, as well as for a direct link to the quantity familiar to most analysts, the relative volatility and, possibly, to the theoretical-plate number. The work presented here attempts to achieve these aims.

Theoretical

The retention volume V_R' of equation 1 is really the sum of two retention volumes: the first is the volume (V_d) of carrier fluid required to sweep a solute through the free space of the column and, in practice though not in theory, its ancillary apparatus; the second is the true retention volume (V_R) due only to the solvent or adsorbent present in the column. Thus, rewriting equation 1, we have

$$N = 16[(V_d + V_R)/w]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here lies the clue to the apparent discrepancy between the plate efficiency N and the ability of a column to separate mixtures. For a given column, V_d is constant; hence, when V_R is reduced relatively to V_d (*e.g.*, by reducing the weight of solvent in the column), then for a given value of N the ratio (V_R/w) decreases. For the separation of mixtures it is the latter ratio which is important. This is illustrated in Figs. 1 and 2. Fig. 1 shows the imagined chromatograms (with peaks drawn as triangles for simplicity) for two substances of relative volatility 1·22 with each of four columns identical in all respects save that the weight of solvent is halved on passing from one to another. Since the columns are geometrically identical the dead space is the same in each case and since temperature and flow rate are assumed the same for all four columns, V_d is the same for all. The peaks are drawn so that the plate efficiency of each column is 680 (the base of the triangle is assumed to be w). With reduction of solvent weight, as the solute and air peaks move together, less separation would be observed. Evidently, as V_R approaches zero, more theoretical plates are required to bring about a given separation. This is further illustrated in Fig. 2 in which the chromatograms of Fig. 1 are redrawn to show complete

[4] Purnell, *Ann. New York Acad. Sci.*, 1959, **72**, 592; Bohemen and Purnell (p. 6) and Scott (p. 36), in "Gas Chromatography," Butterworths, London, 1958, ed. D. H. Desty; Scott and Cheshire, *Nature*, 1957, **180**, 702.

[5] Golay, *Analyt. Chem.*, 1957, **29**, 928.

[6] Golay in "Gas Chromatography," Butterworths, London, 1958, ed. D. H. Desty, p. 13; Desty, Goldup, and Swanton, *Nature*, 1959, **183**, 107; Lipsky, Landowne, and Lovelock, *Analyt. Chem.*, 1959, **31**, 852; Scott, 3rd Informal Symp. Gas Chromatography Discussion Group, London, April, 1959.

separation of the two solutes with each column, the number of plates necessary in each case being shown. In going from column *a* to column *d* the theoretical plate requirement for separation rises from 680 to 2850.

Separation Factor.—Fig. 2 shows that although N increases from column to column the ratio (V_R/w) remains the same. Thus, some unit proportional to this ratio would be a satisfactory unit of column efficiency. For reasons which emerge later, a separation factor, S, is proposed, to be defined by:

$$S = 16(V_R/w)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Each of the chromatograms in Fig. 2 yields $S = 480$, this value defining the separation of two substances of relative volatility 1·22; and any column for which $S = 480$ would bring about the separation shown in Fig. 2. Again, Fig. 1 shows that, although N is constant from column to column, S falls from 480 for column *a* to 117 for column *d*.

FIG. 1. *Illustrative chromatograms of separation of two component mixture of* $\alpha = 1{\cdot}22$. *Solvent weights are*: for *a*, x; for *b*, $x/2$; for *c*, $x/4$; for *d*, $x/8$. *All columns have same* V_d *and* N.

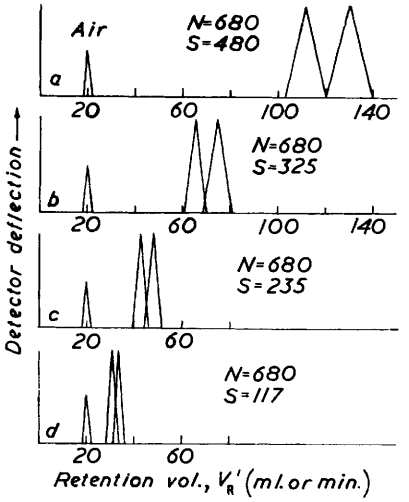
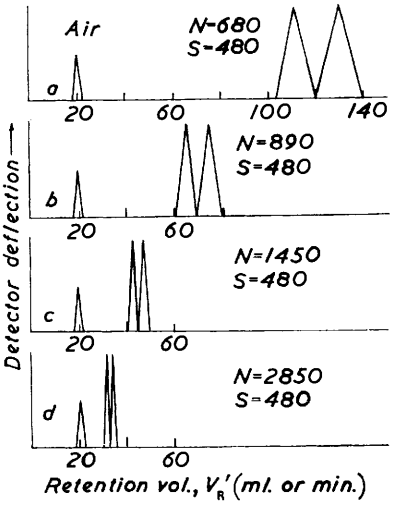


FIG. 2. *Illustrative chromatograms, as in Fig.* 1, *drawn to show exact separation of two components of mixture by all columns. All columns have same* V_d *and* S.



Separation Factor and Relative Volatility.—Since the true retention volume V_R is inversely proportional to the activity of a substance eluted from a chromatographic column, the relative volatility can be defined by:

$$\alpha = V_{R,2}/V_{R,1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the subscripts 1 and 2 refer to two solutes in their order of elution. If the effective base width of a gaussian curve is taken as $1{\cdot}5w$ for exact separation of two substances giving such curves, their retention volumes should differ according to:

$$V_{R,2} - V_{R,1} = 1{\cdot}5[(w_1 + w_2)/2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Asymmetry usually takes the form of sharpened fronts and extended tails. These roughly cancel and so the assumption of gaussian form for the curves will not affect the conclusions greatly.

Making the reasonable approximation that $w_1 = w_2$ and substituting for w_2 in equation 3 gives

$$S = 36[V_{R,2}/(V_{R,2} - V_{R,1})]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which, with the aid of equation 4, leads to:

$$S = 36[\alpha/(\alpha - 1)]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This connects the separation factor directly with the relative volatility and so, if α is known, the necessary value of S for any separation can readily be calculated.

Separation Factor, Relative Volatility, and Theoretical Plates.—If equation 2 is divided by equation 3 we get:

$$N = S[1 + 2(V_d/V_R) + (V_d/V_R)^2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or, when the value of S given by equation 7 is inserted:

$$N = 36\left(\frac{\alpha}{\alpha - 1}\right)^2\left[1 + 2\left(\frac{V_d}{V_R}\right) + \left(\frac{V_d}{V_R}\right)^2\right] \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Equation 9, which is a general one, permits calculation of N for any values of α, V_R, and V_d. These are quantities which, if not already known, can be established easily and quickly by a few experiments with single substances eluted from very short columns. It should be borne in mind that the values of S or N deduced from the above equations are those necessary to separate exactly two components of given α, and that V_R is the true retention volume of the second component of the pair.

The limiting values of N are clearly given by:

$$V_d/V_R \longrightarrow 0\text{: } N = S = 36[\alpha/(\alpha - 1)]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and,

$$V_d \gg V_R\text{: } N = S(V_d/V_R)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

As V_R tends to zero, N tends to infinity, as expected.

The values of N and S become identical if $V_R \gg V_d$, and it is for this reason and because " conventional " columns fall into this category that S was defined as in equation 3. In these conditions too, we may compare directly the number of plates required to carry out separations in gas chromatography and in distillation. The annexed Table shows calculations from equation 10 and distillation data calculated from the approximate empirical fractionation rule $\alpha^N = 850$. Columns N_{GC} and N_{dist}^2 establish again that the

Comparison of theoretical-plate requirements for gas chromatography and distillation.

α	N_{dist}	N_{GC}	N_{dist}^2	α	N_{dist}	N_{GC}	N_{dist}^2
1·015	460	162,000	200,000	1·375	21	485	440
1·075	93	7,100	8,700	2·000	10	144	100
1·157	46	1,940	2,100	2·830	7	87	49
1·245	31	940	960	3·950	5	64	25

number of theoretical plates required in gas chromatography is roughly the square of the number required in distillation. At high values of α, however, even more than this are needed and it can readily be shown graphically that N_{GC} tends to the value $5N_{dist}^2$, the value, incidentally, which can be deduced by consideration of the events in a continuous circular chromatographic column.

From equation 11 we see that even very simple separations require enormous column efficiencies when V_R is small; and, further, that

$$\log N = -2 \log V_R + 2 \log V_d + \log S$$

i.e.,

$$\log N = -2 \log V_R + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The " Constant " will not, in fact, be constant in practice, because of the changing value of S, but even so there should be general behaviour in accord with the form of equation 12. Phillips [7] quotes unpublished results which fit such an equation, and Scott [6] shows curves of N against V_R' which might also agree with equation 12.

[7] Phillips, " Gas Chromatography," Butterworths, London, 1956, p. 78.

Discussion

Equation 9 can be used to construct families of curves from which the plate efficiences needed for the exact separation of components of given α for any value of (V_d/V_R) can be quickly determined, as in Fig. 3. In consequence of the enormous change in N, a logarithmic scale must be employed. As an example of the use of the curves we may consider the separation of a pair of substances of $\alpha = 1{\cdot}15$. Fig. 3 shows that, when V_d is negligible, only 1500 plates are needed whereas, when $(V_d/V_R) = 10$, as is not uncommon in capillary analysis, 160,000 plates are required. Again, for a pair of solutes of $\alpha = 1{\cdot}5$, in principle a very simple separation requiring only 300 plates when $V_d = 0$, when $(V_d/V_R) = 10$, no less than 40,000 plates are essential for separation. Evidently, curves such as those in Fig. 3 can be very useful for rapid calculations.

Some practical applications of equation 9 are now possible. Bohemen and the author [4] attempted to separate *m*- and *p*-xylene in a 30-ft. column of polyethylene glycol (2% by

Fig. 3. *Plots of* log N *required for exact separation of pairs of mixed materials against* V_d/V_R at *various values of* α. *Data calculated from equation* (10).

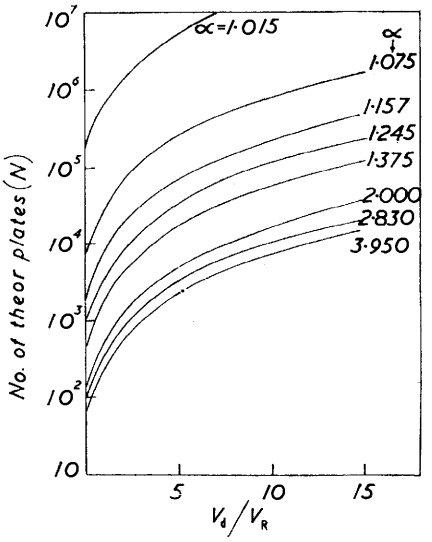
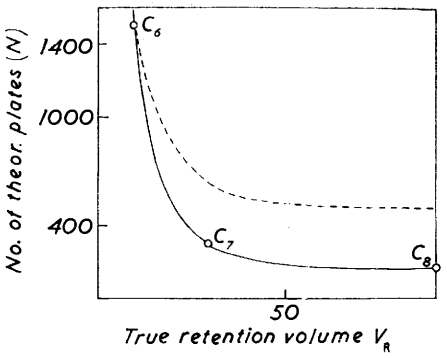


Fig. 4. *Plot of* N *against* V_R *for series of n-alkanes* (C_6, C_7, C_8) *for* $V_d/V_R = 30$, V_R (*butane*) $= 1$. *Ordinate plotted in multiples of* S. S *for* $\alpha = 3$ *is* 81.



weight on firebrick) at 50° where $\alpha = 1{\cdot}03$. For this column $(V_d/V_R) = 0{\cdot}1$. Putting these values into equation 11 gives $N = 28{,}000$. They did not quite achieve complete separation at 24,000 plates. As a second example, Desty, Goldup, and Swanton [6] state that at 78·5° the relative volatility of the xylenes over 7,8-benzoquinoline is 1·083; they achieved complete separation with what appears to be a very heavily loaded capillary column for which $(V_d/V_R) = 0{\cdot}215$. Equation 9 yields the value $N = 16{,}000$ for these conditions, which may be compared with the experimentally determined value of about 15,000. It is to be expected that the calculated value of N will always be slightly high in view of the approximation made in going from equation 5 to equation 6.

Highly Efficient Columns.—It seems to have been amply proved in the foregoing discussion that when columns are operated at high values of (V_d/V_R) very many plates will be required to effect very simple separations. Conversely, when simple separations are achieved at high values of (V_d/V_R) columns will appear to contain very many plates. This explains the apparent anomaly that extraordinarily high plate efficiencies in capillary chromatography often produce chromatograms no better than those from packed columns

of a mere few thousand plates. Indeed when extremely high efficiencies are quoted for capillary columns the underlying measurements are made on substances emerging very close to air. For instance, for fatty acid and ester separations on 200-ft. columns Lipsky, Landowne, and Lovelock [6] obtained $N = 180{,}000$ for substances emerging early. If, however, plate efficiencies are measured from peaks of high true retention volume, values of N near 30,000 are obtained. This, more realistic figure is, of course, very high but no better than can be achieved with good packed columns properly operated. The decrease in plate efficiency with increasing retention volume—the converse of what is generally observed with packed columns—has been described by Scott [6] and can also be predicted from equation 11 (see, for example, equation 12). Fig. 4 shows a plot of N against V_R which would be obtained from the chromatogram of some n-alkanes eluted from squalane at 25°. α is 3 for successive pairs of paraffins and the form of this curve is identical with those shown by Scott. In practice, if the first pair were just separated the second pair would be well separated, and N for the later peaks would be higher than those calculated from equation (10) and plotted in the Figure. However, this effect would hardly be great enough to change the shape of the curve significantly and something approximating to the broken line in Fig. 4 would be obtained.

In comparing the relative merits of capillary and packed columns, separation factors rather than plate efficiencies should be used. When this is done no anomalies exist. For example, the author has recently shown [8] that hydrocarbon analyses performed with very long capillary columns of up to a half-million plates can be closely reproduced by 7-ft. packed columns of 5000 plates in about one-hundredth of the time. The explanation is that the separation factor for the capillaries was only about 8000 while that for the packed column was the same as the plate efficiency. Since both S and N are defined in terms of the square of the peak width, the peak widths on the two types of chromatogram differed only by a factor of about 25%. The chromatograms obtained thus appeared little different.

One drawback at this time in the use of separation factors is that, in principle, nothing is known about the way in which, for a given column, they depend upon experimental variables. That is, it is not known precisely how change of column length or sample size, for example, affects the separating power of a column. However, it may be assumed from the similarity of equations (1) and (3) that the effects will parallel those already established for the dependence of N upon experimental parameters. Thus, we may expect to obtain higher values of S by increasing column length, reducing sample sizes, using highly uniform solid supports of the finest possible mesh size, employing elevated pressures, and choosing the solvent judiciously. The one way in which we may expect the two measures to differ is in the effect of reducing solvent weight in the column. It has several times been shown that more efficient columns are obtained if solvent weights are reduced. In the light of the present work it is not clear how far this is due purely to the effect of increasing the ratio (V_d/V_R) and how far it is a real increase in the separating power of a column. Superficially, equation (9) suggests that reduction of solvent weight must always reduce the separating power of a column. However, this is not true if the increase in N with reduction of solvent is greater than the increase in theoretical-plate requirements. Thus, there is likely to be an optimum solvent weight for maximum separation.

From the few experimental results at present available this seems to be the case, the optimum varying widely from solvent to solvent and being mainly determined by the mass-transfer term in the van Deemter rate equation. It is, thus, to some extent, determined also by the identity and properties of the substances analysed.

Experimental Application of Equation (9).—For practical use of equation (9) it is necessary to know V_d, V_R, and α. The dimensions of a column determine V_d: in a well-packed column, V_d is 45% ($\pm 5\%$) of the total column volume. Determination of V_R

[8] Purnell, Gas Chromatography Discussions, Ann. Mtg. Amer. Chem. Soc., Atlantic City, Sept., 1959.

and α is essentially the same problem. In many cases both will be available from tabulated specific retention volumes which can be quickly converted for use at any temperature for any weight of solvent; if not, they can very readily be determined since a short column of the chosen solvent can be used to provide V_R for each component. The number of plates needed to separate the pair of components of smallest α can then be calculated for various values of (V_d/V_R), or alternatively found from a graph such as Fig. 3. The column to be chosen is then that with which the required number of plates is most easily obtained. As a final check it should be ascertained that the first two components of the mixture [for which (V_d/V_R) is greatest] can be separated under the chosen conditions. It is possible that some compromise in the matter of column length or (V_d/V_R) ratio may then be necessary. If sufficiently detailed information about the dependence of N on various experimental parameters, and enough specific-retention data become available, it is conceivable that chromatograms can eventually be worked out completely by theory, thus eliminating the considerable time normally spent in the empirical approach to analytical problems.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

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