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EFFICIENCY CRITERIA IN GAS CHROMATOGRAPHY

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PART I

The study of the operating characteristics of chromatographic apparatus and of the efficiency of the resulting separations is of great relevance to the development of this important technique for physicochemical analysis. Contemporary gas chromatography includes a variety of different methods, each of which involves numerous parameters. Industrial concerns in many countries are marketing very diverse chromatographic assemblies, the types of which already exceed several dozen.

One is often faced with the problem of comparing different methods and their analytical results and thus defining the optimum experimental parameters. Unfortunately, the literature is strangely silent on the selection of the correct procedures for evaluating the effectiveness of the operation of chromatographic equipment, in spite of the large number of *ad hoc* criteria suggested by different authors. The necessary distinction between apparatus parameters and characteristics of the separation process is not always made. Many important questions (for instance, the effect of the ratio of the concentration of components) are not analysed in sufficient detail.

The present article attempts a critical survey of the efficiency characteristics for the chromatographic process which have been proposed, and suggests ways of improving on them. The reader is assumed to be familiar with the basic concepts of the theory of chromatography, given in Keulemans' monograph[1] and in an article by one of the present authors, previously published in this journal[2].

Before the criteria given in the literature can be correctly classified, it is necessary to specify them. Considerable divergence of opinion is evident from the many papers on this subject. The number of necessary criteria must be determined by the number of essential characteristics of the apparatus and of the process. One should first of all evaluate the extent of separation from the final chromatogram. However, as will be shown below, one cannot rely on a single criterion for characterising the degree of separation. According to the nature of the chromatographic curve, three criteria may present themselves: these make up one group, since they all characterise the degree of separation. However, the overall separation effect does not provide a sufficiently detailed description of the various aspects of the operation of a particular apparatus.

The selectivity of the adsorbent (or solvent) is an essential characteristic and the main design parameter of the apparatus. Selectivity considerations make up the second group of chromatographic criteria. For a given selectivity, the separation is limited by the spreading of the bands. Experimental parameters (gas flow rate, particle size, pressure, column geometry, etc.) as well as characteristics of the sample injector and of the detector have a considerable effect on the spreading of the bands.

The third group of criteria describes those properties of the column which are largely independent of the sorbent, being determined by the kinetics and the dynamics of the process and by the properties of the detector and the injector. These criteria describe the extent to which band spreading can be suppressed in a given apparatus.

All these groups of criteria are needed to characterise the degree of separation. Some characteristics of the apparatus, however, do not affect the degree of separation. The most important of these are the resistance to gas flow and the time required for the analysis. Automation, and industrial process control, require short analysis times. The fourth group of criteria will characterise all the properties of the chromatographic equipment, including the degree of separation, the resistance to gas flow, and the analysis time.

We shall discuss these four groups of criteria in the order given above.

PART II

The degree of separation is a measure of the purity of a fraction, expressed by the dimensionless quantity θ which gives the proportion of the main component in a particular fraction. This quantity is derived from the most characteristic features of the chromatogram.

The chromatogram for a component with a linear adsorption isotherm is defined by three quantities: the position of the maximum (*e.g.* the retention volume, v_g, per unit column area), the concentration at the maximum, c_m, and the parameter β, which describes the shape of the chromatogram by means of the equation

$$c = c_m e^{-\beta x^2} \tag{1}$$

where x is measured from the ordinate of the maximum.

The so-called band width μ (distance between points at which $c = c_m/e$) is related to the quantity β:

$$\mu = 2\sqrt{\frac{1}{\beta}}. \tag{2}$$

For a chromatogram characterised by a single parameter all the other characteristics are expressed in terms of these three (v_g, c_m, and β).

θ must obviously depend on differences in v_g, not on the absolute values of v_g, since the degree of separation is not affected by displacing the chromatogram along the volume axis.

The values of β for neighbouring components may be assumed identical, since β is generally independent of the nature of the component in turbulent diffusion, and all other processes which can lead to band spreading have very similar β values for components in close proximity.

The degree of separation may depend on the ratio between c_{m_1} and c_{m_2} ($\Phi = c_{m_1}/c_{m_2}$) but not on the absolute values of c_m, since θ does not vary with concentration in the case of a linear isotherm. Being a dimensionless quantity, θ may depend on dimensionless expressions.

From the three chromatogram parameters discussed above we can construct two dimensionless expressions: Φ and $K = \Delta v_g \sqrt{\beta}$.

Thus,

$$\theta = f(\Phi, K). \tag{3}$$

It must be stressed that Φ and c_m refer to the peaks of pure components. Φ therefore gives the ratio of the starting materials in the original mixture.

Methods for evaluating K and Φ from the chromatogram and for deducing the degree of separation will now be discussed.

The procedure used for analysing the chromatogram will depend on the completeness of the separation achieved. If the separation is good, Δv_g and μ may be determined directly from the chromatogram. In this case it is advantageous to replace K by a new criterion[3,4] differing from K by some factor:

$$K_1 = \frac{\Delta v_g}{\mu_1 + \mu_2} = \frac{\Delta v_g}{2\mu}. \tag{4}$$

When separation is incomplete neither Δv_g nor μ can be measured, since the appearance of the maxima is altered when two peaks are in close proximity. If the chromatogram has a minimum we can choose the quantities c_{min} (concentration at the minimum) and c_m as the basic parameters.

Two criteria based on this approach[5,9] are discussed in the literature:

$$K_2 = \frac{c_{m_1} + c_{m_2}}{c_{min}}, \tag{5}$$

$$K_B = \frac{c_B - c_{min}}{c_B}, \tag{6}$$

where c_B is the concentration corresponding to the intersection of the straight line joining the two maxima with the ordinate passing through the minimum (see Fig. 1).

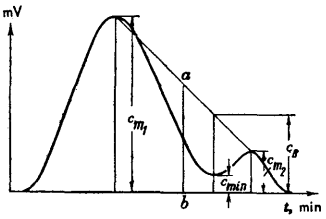


Fig. 1. Definition of the criteria K_2 and K_B.

It can readily be shown that if $\Phi \simeq 1$

$$K_B = \frac{K_2 - 2}{K_2}.$$

Finally, if the separation is very poor, and no minimum appears on the chromatogram, the values of Δv_g and μ may be calculated from the shape of the chromatogram.

For small values of Δv_g the expression

$$c = c_{m_1}[\Phi e^{-\beta x^2} + e^{-\beta (x-\Delta v_g)^2}]$$

is reduced to the form

$$\ln \frac{c_{m_2}}{c} = \beta x^2 - \ln \Phi - \ln\left(1 + \frac{1}{\Phi}\right) - \frac{2x\beta\Delta v_g}{1+1/\Phi}. \quad (7)$$

If Φ is known, or if $\Phi \simeq 1$, β and Δv_g may be determined and the criterion K_1 calculated by fitting Eqn. (7) to the experimental chromatogram. All the criteria discussed here may be expressed in terms of any one of them. Thus, it can be shown that for $\Phi \simeq 1$, $K_2 = 2e^{4K_1^2}$ and therefore $K_B = 1 - e^{-4K_1^2}$.

Thus, if Φ is known, the criterion K_1 is in principle calculable for any chromatogram. Since $\theta = f(K, \Phi)$, Φ must be kept constant when comparing different methods or discussing the effect of various parameters. All the expressions are considerably simplified if $\Phi = 1$. In particular, if Δv_g is large, a quantitative relationship between θ and K_1 can easily be derived:

$$\theta = \frac{1}{4\sqrt{\pi} K_1} e^{-4K_1^2}.$$

If Φ varies between experiments, comparison of the criteria will lead to an incorrect evaluation of the difference in the degree of separation. The criterion which is least sensitive to the value of Φ will therefore be the most satisfactory from this point of view. K_B has this property. The criterion K_B has a twofold advantage over K_2: not only does K_B vary between more physically meaningful limits than K_2 (K_2 varies between +1 and ∞, K_B between 0 and 1), but K_B also varies little with Φ. The use of K_2 can therefore only be recommended in cases when $\Phi \simeq 1$. The difference between K_2 and K_B can be appreciated from Fig. 1. In place of $c_B - c_{min}$, K_2 contains double the value of the ordinate ab, which equals the arithmetic mean of the maxima. Obviously, if $\Phi \neq 1$, c_m should be compared with c_B or $c_B - c_{min}$ rather than with ab. On these grounds we can think of the criterion K_B as a modified form of K_2 which is less sensitive to Φ.

The criterion K_1 may also be modified so as to decrease its sensitivity to Φ. Let $c_{m_1} > c_{m_2}$. In this case we measure μ not between the points at which the concentration is c_{m_1}/e, as is done when calculating K_1, but between points on the first peak of concentration c_{m_2}/e. The resulting criterion $\left(K_1 = \frac{\Delta x}{\mu_1 + \mu_2}\right)$ is considerably less sensitive to Φ.

If we wish the criteria to have certain specified values (for example, we may wish to control K_1, the purity of the fraction), the values of the parameters of the chromatographic experiment must be under our control.

We shall derive the relationship between K_1 and these values for the simplest case ($\Phi = 1$). It is known that

$$\Delta x = \Gamma_2 L (m - 1), \quad (8)$$

where $m = \Gamma_1/\Gamma_2$ and Γ is Henry's constant used in the calculation of the amount of adsorption per unit volume of the tube:

$$\mu_1 = 4\Gamma_1 \sqrt{\frac{DL}{\alpha}}, \qquad \mu_2 = 4\Gamma_2 \sqrt{\frac{DL}{\alpha}}. \quad (9)$$

Here α is the linear velocity of the carrier gas, D is the effective coefficient of longitudinal diffusion, which we assume to be the same for both components, and L is the length of the column.

It follows that

$$K_1 = \frac{1}{4}\frac{m-1}{m+1}\sqrt{\frac{L\alpha}{D}}.$$

If the values of A in the equation $\Gamma = Ae^{Q/RT}$ are the same for both components, $\Delta Q \ll RT$, and $\Gamma_1 = \Gamma_2$, we have[7]

$$K_1 = \frac{\Delta Q}{8RT}\sqrt{\frac{L\alpha}{D}},$$

where D/α characterises the spreading of the bands in the particular apparatus. Applying the well-known formula $2D/\alpha = H$, where H is the height of a theoretical plate, we have

$$K_1 = \frac{1}{4}\frac{m-1}{m+1}\sqrt{\frac{2L}{H}}. \quad (10)$$

Therefore, in order to achieve a given value of K_1 (or a given fraction purity) we require a certain minimum length L:

$$L = 8K_1^2\left(\frac{m+1}{m-1}\right)^2 H, \quad (11)$$

$$N = 8K_1^2\left(\frac{m+1}{m-1}\right)^2, \quad (12)$$

where $N = L/H$ is the number of plates.

Röck[8] derived a similar formula for the criterion K_B:

$$N = \left(\ln\frac{4}{1-K_B}\right)\left(\frac{m+1}{m-1}\right)^2. \quad (13)$$

It can be seen that if the values of K_B (or K_1) and H are given, the required length is described by a factor which we shall call, after Purnell[9], the selectivity coefficient K_c:

$$K_c = \frac{m-1}{m+1}.$$

K_c refers to a single separation. This coefficient vanishes when there is no separation of the components, and tends to one if separation is complete.

It must be remembered, when comparing the efficiency of different methods, that the Henry coefficients (Γ) refer to sorption by unit volume of the tube. A decrease in the absolute value of the coefficient Γ (*e.g.* by decreasing the amount of stationary phase) will therefore lead to a decrease in K_c.

If κ_1 is the fraction of the cross-sectional area occupied by the stationary phase and κ is the fraction of free space we have, as will be shown in Part III,

$$\Gamma = \kappa + \Gamma_i \kappa_1,$$

where Γ_i describes the sorption by unit volume of the stationary phase. Hence

$$m = \frac{\kappa + \Gamma_{i_1}\kappa_1}{\kappa + \Gamma_{i_2}\kappa_1}. \qquad (14)$$

We can see that if the Henry coefficient is small a decrease in κ_1 for a given stationary phase will sharply lower the value of m and therefore also of K_c, and consequently increase the length required. For large values of Γ_i we can neglect κ and write

$$m = \frac{\Gamma_{i_1}}{\Gamma_{i_2}}.$$

Consequently, the separation coefficient K_c is independent of the amount of stationary phase. However, if κ and Γ_i are both small, a decrease in κ_1 will considerably impair the separation, since if $\kappa_1 = 0$, $m = 1$, and $K_c = 0$, and the required length $L \to \infty$. This conclusion, first put forward by Purnell, stresses the inadequacies of capillary chromatography in comparison with the conventional gas–liquid variant.

We shall illustrate this point by considering two typical examples taken from gas–liquid and capillary chromatography respectively.

If the stationary phase is the same in the two cases and the true Henry coefficients are 30 and 20 respectively, we shall have $\kappa = 0.5$ and $\kappa_1 = 0.1$ for the gas–liquid chromatography. Then

$$m = \frac{30\times0.1 + 0.5}{20\times0.1 + 0.5} = 1.4.$$

For the capillary chromatography $\kappa = 1$, $\kappa_1 = 10^{-2}$, whence

$$m = \frac{30\times10^{-2} + 1}{20\times10^{-2} + 1} = 1,1,$$

and the K_c values will be 0.17 and 0.045 respectively. A greater column length is needed in the second case in spite of the fact that the H values are the same.

Formulae (11) and (12) express the length, or the plateage L/H, required if the criterion K_1 is to have the stated value. At $\Phi = 1$, K_1 uniquely determines the degree of separation, θ.

In general, as has already been pointed out, $\theta = f(\Phi, K)$. The most obvious choice of a separation condition in this case is:

$$\Delta x > \frac{\mu_1 + \mu_2}{2}. \qquad (15)$$

However, when $\Phi \neq 1$, the width of the band corresponding to the first component, which is also the major component, must be measured at the concentration c_{m_2}/e:

$$\mu_2 = 4\Gamma_2\sqrt{\frac{DL}{\alpha}}$$

and

$$\mu_1 = 4\Gamma_1\sqrt{\frac{DL}{\alpha}\ln\frac{c_{m_1}e}{c_{m_2}}} = 4\Gamma_1\sqrt{\frac{DL}{\alpha}(1 + \ln\Phi)}.$$

Making use of (15):

$$\Gamma_2 L\left(\frac{\Gamma_1}{\Gamma_2} - 1\right) > 2\Gamma_2\sqrt{\frac{DL}{\alpha}} + 2\Gamma_1\sqrt{\frac{DL}{\alpha}(1 + \ln\Phi)}.$$

After some manipulation, and substituting H for $2D/L$, we obtain:

$$L > H\frac{2[1 + m\sqrt{1 + \ln\Phi}]^2}{(m-1)^2}. \qquad (16)$$

Condition (15) corresponds to the requirement that $K > 1/2$. For $\Phi = 1$ Eqn. (16) corresponds to Eqn. (11).

Formula (16) differs from that derived by van Deemter[10] in that the value of Φ is considered.

The variation of N_Φ/N_1 with Φ is shown in Fig. 2 for m close to 1. N_Φ/N_1 is the increase in plateage required if the ratio between the two components is changed from 1 to Φ. The variation of N_1 with Φ may be determined by comparing (15) and (11) for a given value of θ, whence:

$$\frac{N_\Phi}{N_1} = \frac{[1 + m\sqrt{1 + \ln\Phi}]^2}{(1+m)^2}. \qquad (17)$$

N_Φ/N_1 gives the increase in N_1 needed to change from $\Phi = 1$ to $\Phi = \Phi$, keeping the degree of separation constant. The formula is only true when the separation is good. It shows that an increase in Φ makes the requirements in N much more stringent. Thus, if $m = 0.5$ and $\Phi = 100$, $N_\Phi/N_1 = 2.2$.

Formula (17) predicts that the increase in N with Φ depends on the value of m, and decreases when the difference in adsorbability increases.

Lu P'ei-chang[11] adopted $\sqrt{\ln(c_{m_1}/c_{\min})}$, *i.e.* $\ln\sqrt{N_2/2}$, as the separation criterion for the case $\Phi = 1$ and $c_{m_1} = c_{m_2}$. He showed that his criterion was the product of two factors, S and F:

$$\sqrt{\ln\frac{c_{m_1}}{c_{\min}}} = SF. \qquad (18)$$

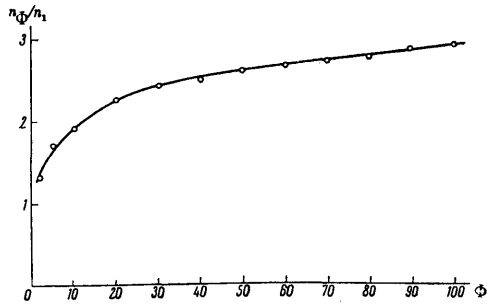


Fig. 2. Variation of n_Φ/n_1 with Φ.

TABLE 1.

Type of chromatography	S	F
Adsorption development	$\frac{V_{g_2}-V_{g_1}}{V_{g_2}+V_{g_1}}$	$\sim D^{0.5}\gamma^{0.5}L^{0.5}$
Gas-liquid	$\frac{V_{g_2}-V_{g_1}}{V_{g_1}^{0.5}+V_{g_2}^{0.5}}$	$2.75\frac{0.5}{g}\alpha^{0.42}$
Chromathermography	$\frac{Q_2-Q_1}{\sqrt{Q_1}+\sqrt{Q_2}}$	$\frac{1}{\sqrt{2R}}\sqrt{\frac{\alpha}{D_{\text{eff}}\gamma}}$

S is determined by the statistical characteristics of the column, F by the spreading of the bands, *i.e.* by the kinetics and the dynamics of the process.

Lu P'ei-chang's values for S and F are set out in Table 1 for different types of chromatography: R is the gas constant, γ is the temperature gradient, and q is the amount of stationary phase.

Lu P'ei-chang's factorisation has the desirable effect of distinguishing the influence of experimental parameters (F) from the properties of the adsorbent (S).

PART III

The second group of criteria characterises the column selectivity.

It was shown in the above discussion that the criteria K are expressed as the products of factors which are separately determined by statistical and by kinetic characteristics. Formulae (10), (13), and (18) show these properties. The selectivity of the column is given in every case by the criterion:

$$K_c = \frac{m-1}{m+1}. \tag{19}$$

K_c is obviously a characteristic of the column rather than of the adsorbent, since both m and K_c decrease, as was shown above, if the amount of adsorbent is decreased.

The value of m can be determined directly from the retention volumes by means of the formula:

$$m = \frac{v_{g_1}}{v_{g_2}}.$$

In addition to (19), a number of other selectivity criteria are to be found in the literature. Thus, Janak[12] suggests making use of the difference in retention volumes, $\Delta v_g = v_{g_1} - v_{g_2}$. This is of doubtful value, since it is the relative difference in retention volume which is important, not its absolute value. The requirement in Δv_g depends on v_g itself, since H is proportional to Γ and therefore also to v_g, and a small value of Δv_g is sufficient if the v_g values are small. Consequently, the requirements in Δv_g are less stringent if the materials are not readily adsorbed.

It may not be out of place to stress that in the case of non-linear isotherms not all the criteria discussed, such as v_g, are applicable.

In a number of publications[1,13] m is used directly as a selectivity criterion. K_c is to be preferred, however, not only because it varies over more physically meaningful limits (from 0 to 1 instead of from 0 to ∞), but also because the separation criteria follow directly from it through formulae (10), (11), and (12).

Selectivity criteria have on occasions been defined on the basis of the distribution coefficients Γ_i rather than in terms of the ratio of the coefficients Γ. This procedure is less attractive, since it is the selectivity of the column as a whole which is important, not that of the sorbent. In practice, this concerns the method used for determining the Henry coefficient from the chromatogram, and, in particular, the need for introducing the dead space correction into the calculation of the retention volume. The literature has little to offer on these questions. We shall therefore confine our attention to the Henry coefficients, which may be derived directly from chromatographic experiments. Considering only the v_g measurement, we can only derive the Henry coefficient which appears in the formulae presented above, *i.e.*

$$\Gamma = \frac{v_g}{w},$$

where w is the volume of the column or, if v_g is expressed per unit cross-sectional area, the column length. Γ defines the capacity of unit volume of the column: it is related to Γ_i, which expresses the capacity of unit volume of the stationary phase.

Let, as before, κ be the fraction of free volume, κ_1 the fraction of the volume occupied by the solvent. In the case of adsorption chromatography we have

$$\kappa_1 = 1 - \kappa.$$

The capacity of unit volume is then given by

$$\kappa \times c + \kappa_1 \times \Gamma_i \times c, \tag{20}$$

and therefore $\Gamma = \kappa + \kappa_1\Gamma_i$. The smallest value of Γ is obviously given by κ. If κ_1 tends to zero, Γ assumes the universal value κ for all substances.

The values of κ and Γ_i cannot be determined from measurements of v_g alone. A knowledge of v_{g_0}, the retention volume of a virtually non-adsorbed component, such as hydrogen or helium, is also required. In this case

$$\kappa = \frac{v_{g_0}}{w}.$$

From Eqn. (20),

$$\Gamma_i = \frac{\Gamma - \kappa}{\kappa_1} = \frac{v_{g_1}/w - v_{g_0}/w}{\frac{v_{liq}}{w}}$$

where v_{liq} is the volume of the stationary phase.

Thus

$$\Gamma_i = \frac{v_g - v_{g_0}}{v_{liq}}. \tag{21}$$

The Henry coefficient calculated per unit volume of adsorbent, Γ_a, is occasionally of interest:

$$\Gamma_a = \frac{v_g - v_{g_0}}{v_a} \tag{22}$$

where v_a is the volume of the adsorbent.

Finally the capacity of the support is sometimes referred to unit free volume:

$$\Gamma' = \frac{v_g - v_{g_0}}{w\kappa} = \Gamma_i \frac{\kappa_1}{\kappa}. \tag{23}$$

The most direct and useful characteristic is undoubtedly Γ. This quantity can be calculated without measuring v_{g_0} and subtracting it from v_g. The use of Γ in calculations is to be recommended.

When the properties of the solvent or the adsorbent are being studied, the need sometimes arises to use formulae (21)–(23). Thus, low values are obtained if the heat of adsorption is derived from the temperature variation of Γ.

PART IV

Two criteria have so far been suggested for describing band spreading in a column. The criterion most commonly used in the literature is H, the height of a theoretical plate, or N, the number of theoretical plates[14]. The other criterion is the effective longitudinal diffusion coefficient, D. The two criteria are related by the following well-known expression

$$H = \frac{2D}{\alpha},$$

and are therefore equivalent.

The values of H and D are calculated from measurements of v_g and μ. Replacing Γ by v_g/L we obtain the familiar relation

$$\frac{D}{\alpha} = \frac{1}{16} L \left(\frac{\mu}{v_g}\right)^2,$$

whence

$$H = \frac{1}{8} L \left(\frac{\mu}{v_g}\right)^2,$$

or the number of theoretical plates

$$N = \frac{L}{H} = 8 \left(\frac{v_g}{\mu}\right)^2.$$

Many other similar methods of calculating H and N are available. They have been reviewed by Glueckauf[3] and by Struppe[15].

In the calculation of v_g, and even of μ, an unnecessary correction is often made for the retention volume of the dead space. This correction is justified only if the dead volume is located outside the packing.

Conceptually, the theoretical plate approach has the advantage of generality, as it is unrelated to any specific mechanism of band spreading. However, this formal generality can lead to an erroneous interpretation. Since the selectivity coefficient does not appear in the expression for the plate height, it is not possible to characterise the separation efficiency of the apparatus by means of the latter quantity. In this respect the quantity D has certain advantages over H, since its physical significance is clear, and it is not likely to be incorrectly interpreted.

It is not always true to say that decreasing H (or increasing N) must necessarily improve the separation. For instance, H always decreases when the quantity of solvent is decreased in cases where inner diffusion is the controlling process. The selectivity criterion is also decreased and the number of plates required for the separation will now increase, as indicated by Eqn. (10).

We shall now consider how the separation criterion K_1 (and therefore also the purity of the fraction, θ) varies when the amount of solvent is decreased in gas–liquid and in capillary chromatography. This requires an analysis of the dependence of the selectivity criterion K_c and the plate height H on the amount of solvent. We shall discuss the case, typical in gas–liquid chromatography, of combined turbulent and inner diffusion[2].

In this case

$$H = A + C\alpha,$$

where A represents the turbulent diffusion, and is independent of the amount of material, and

$$C = \frac{8}{\pi^2} \frac{\Gamma' \delta^2}{(1+\Gamma')^2 D_{\text{liq}}}.$$

In this formula δ is the thickness of the film, D_{liq} is the inner diffusion coefficient, and Γ' is given by Eqn. (23) in terms of κ and κ'.

To calculate the variation of κ with δ we require the volume of solvent per unit volume of the packing, given by

$$\frac{1-\kappa}{4/3\pi r^3} \times 4\pi r^2 \delta.$$

The first factor defines the number of spherical particles per unit volume, the second factor gives the volume of the layer of solvent on each particle.

The quantity $\frac{3(1-\kappa)\delta}{r}$ gives the required value of κ_1, since it is calculated per unit area and per unit volume of packing.

Thus

$$C\alpha = \frac{Z\delta^3}{(1+M\delta)^2},$$

and

$$H = A + \frac{Z\delta^3}{(1+M\delta)^2}, \qquad (24)$$

where Z and M are constants.

To calculate K_1 we require to know the function $m = f(\delta)$. It follows from what has been said above that

$$m = \frac{\kappa + 3\left(\frac{1-\kappa}{r}\right)\delta\Gamma_1}{\kappa + 3\left(\frac{1-\kappa}{r}\right)\delta\Gamma_2}.$$

If $\Gamma_1 = \Gamma_2 + \Delta\Gamma$ and $\Delta\Gamma$ is small, we have

$$m = 1 + \frac{3(1-\kappa)\delta}{r}\Delta\Gamma \text{ and } K_c = \frac{3(1-\kappa)\delta}{r}\frac{\Delta\Gamma}{\Gamma}.$$

Therefore

$$K_1 = \frac{\delta(1+M\delta)}{\sqrt{A(1+M\delta)^2 + Z\delta^3}}.$$

It can be seen that K_1 goes through a maximum. This is particularly evident when Γ is small and $\mu \to 0$. In this case

$$K_1 = \frac{\delta}{\sqrt{A + Z\delta^3}}.$$

Thus, an increase in the amount of material is beneficial at low values of δ, in spite of the fact that it invariably decreases the number of plates, because the resulting gain in selectivity will offset the loss introduced by the increased spreading.

PART V

It is arguable whether an overall criterion of the performance of a chromatographic apparatus, which included the efficiency of separation, the resistance to flow, and the analysis time, would be desirable.

Some attempts have been made in the past to derive general criteria for complicated assemblies. On the whole, they have not been very successful. It is better to find separate answers to the various questions (for example, to that of speed) than to search for a general criterion. This does not mean that one should consider only the separation efficiency when comparing different chromatographic procedures.

Golay[16] introduced the so-called performance index of the column (*PI*) to describe the advantages of capillary chromatography over the gas–liquid variant. His approach can be summarised as follows. One must obviously express the optimum conditions (minimum plate height $H_{\min}$) in a form which involves the basic experimental parameters, such as the pressure drop Δp, the width of the band, etc., since Golay's index must necessarily involve the pressure drop. We know that the pressure drop can be expressed as

$$p_1^2 = p_0^2 + \frac{16\eta}{r^2} p_0 L\alpha$$

where p_0 and p_1 are the outlet and the inlet pressures, η is the viscosity, r is the radius of the capillary column, v_0 is the outlet velocity, and L is the length of the column.

In addition, we shall consider the half-width of the band (Δt^x, expressed in seconds) under conditions of carrier gas velocity corresponding to minimum plate height.

Golay, taking only longitudinal and radial diffusion into consideration, expresses the plate height by the formula:

$$H = 2\frac{D}{\alpha} + \frac{1 + 6\Gamma' + 11\Gamma'^2}{24(1+\Gamma')^2} \times \frac{\alpha r^2}{D} .$$

From the condition $\partial H/\partial\alpha = 0$ we have:

$$H_{\min} = \left(\frac{1 + 6\Gamma' + 11\Gamma'^2}{3(1+\Gamma')^2}\right)^{1/2} r . \qquad (25)$$

It should be noted that the minimum plate height in capillary chromatography is a function of the radius of the capillary. From Eqn. (25) Golay obtains an expression for Δt_x:

$$\frac{\Delta t_x^2}{t_x^2} = \frac{144 \ln 2 (p_1^2 - p_0^2)(p_1^2 + p_0^2)\eta\alpha p_0 h}{(p_1^3 - p_0^3) r^2} .$$

Introducing the retention time for the non-adsorbed component:

$$t_a = \frac{(p_1^3 - p_0^3) r^2}{24\eta\alpha^2 p_0^2} ,$$

Golay obtains an expression for the viscosity in terms of the quantities under discussion:

$$\eta = \frac{1}{64(\ln 2)^2}\left(\frac{\Delta t_x}{t_x}\right)^4 \frac{t_a}{C_K} \frac{16}{27} \frac{(p_1^3 - p_0^3)^2}{(p_1^4 - p_0^4)^2} ,$$

where

$$C_K = \frac{8}{3} \frac{1 + 6\Gamma' + 11\Gamma'^2}{(1+\Gamma')^2} ,$$

or, approximately,

$$C_K = \frac{4}{3}\left(1 + 15\frac{\Gamma}{1+\Gamma}\right) .$$

We make the further approximation

$$\frac{(p_1^3 - p_0^3)^3}{(p_1^4 - p_0^4)^2} = \Delta p = p_1 - p_0 .$$

The maximum error in this treatment arises when Δp is large, and amounts to 40%:

$$\eta \times {}^1/_3 \times 2^{10} (\ln 2)^2 \simeq \frac{\Delta t_x^4 \times t_a \Delta p}{t_x^3\left(t_x - \frac{15 t_a}{16}\right)} .$$

Golay calls this quantity, which is proportional to the viscosity, the performance index of the column:

$$PI = \frac{\Delta t_x^4 \times t_a \times \Delta p}{t_x^3 (t_x - t_a^{15}/_{16})} . \qquad (26)$$

Since *PI* increases with the width of the band, it must increase when the optimum velocity is replaced by realisable velocities and when subsidiary factors conducive to spreading, which had not been considered, become appreciable (*e.g.* inner diffusion).

The expression for *PI* may be re-written as follows:

$$PI = \left(\frac{\Delta t_x}{t_x - t_a}\right)^4 \frac{(t_x - t_a)^4 t_a}{t_x^4 (t_x - \frac{15 t_a}{16})} t_x \Delta p .$$

The first term describes the spreading in the column and therefore varies inversely as the column efficiency; the third term expresses the price which has to be paid for this efficiency, since it involves the work expended and the time required for the analysis.

PI is dimensionally a viscosity, and its numerical value equals the viscosity under optimum conditions (for helium, *PI* = 0.08 poise). The larger the performance index, the worse the performance of the column [$\Delta t_x/(t_x - t_a)$, or the analysis time, will be large, or much work will be expended]. *PI* is not a function of the dimensions of the column: it depends only on the nature of the solvent. Representative *PI* values for gas–liquid chromatography are 4 orders of magnitude higher than the minimum calculated value, whereas in capillary chromatography the discrepancy is only 2 powers of ten.

Golay's method of comparing different techniques is not particularly successful. One should certainly not compare different methods under conditions of minimum plate height: conditions of optimum separation should be chosen instead (optimum K_1, for instance).

The choice of conditions corresponding to a minimum H implies a constant length of packed column. However, it follows directly from Eqn. (10) that if L is constant K_1 is a maximum when H is a minimum. It should be noted that constant length is frequently assumed in publications dealing with the choice of parameters[17,18].

If the work expended is chosen as the main characteristic an expression is obtained in which the other parameters (analysis time, resistance to flow) play a more or less fortuitous part.

The inadequacy of Golay's criterion is best illustrated by pointing to an example in which the separation is impaired by decreasing *PI*. It is well known, for instance, that the separation is worse at higher temperatures in spite of the fact that *PI* decreases.

Different methods are best compared under their respective most favourable conditions, keeping constant whatever parameter is dictated by practical considerations.

The main practical requirement is undoubtedly a reasonably short analysis time (t); the second involves the resistance to flow (Δp).

Among the most characteristic requirements is the ability, essential in industrial chromatographic practice, to carry out the analysis in a stated time.

From Eqn. (10), introducing the relationship between the analysis time and the length of the column $t = L\Gamma/\alpha$, we obtain

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t\alpha}{\Gamma H}}.$$

Expressing H in terms of α,

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t}{\Gamma\left(\frac{A}{\alpha} + \frac{B}{\alpha^2} + C\right)}}.$$

We see from this equation that for a given analysis time K_1 increases with flow rate and therefore with length of the column, but that it cannot go on increasing indefinitely. There is a maximum limiting value of K_1 (K_{max}) which may be realised in the given time.

If $\alpha \to \infty$

$$K_{max} = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t}{\Gamma C}}. \qquad (27)$$

Different methods are best compared in terms of the value of K_{max}. The choice of a method is then dictated by the quantity

$$\nu_{I\text{-}II} = K^{I}_{max}/K^{II}_{max}$$

$$\nu_{I\text{-}II} = \frac{K_c^I}{K_c^{II}} \sqrt{\frac{\Gamma^{II}}{\Gamma^I}} \sqrt{\frac{C^{II}}{C^I}}. \qquad (28)$$

In the case of readily adsorbed materials, for which K_c decreases little if at all on going over to the capillary chromatographic technique, the last term in Eqn. (28) settles the verdict in favour of capillary chromatography as compared with the gas–liquid method.

The shortest time in which a given value of K_1 may be achieved can be derived from Eqn. (27):

$$t_{min} = \frac{8K_1^2 \Gamma C}{K_c^2}. \qquad (29)$$

Equations similar to (28) have been derived by Purnell[9] and by Loyd, Ayers, and Karasek[19].

If the resistance is given, the product $L\alpha = M_1$ must be treated as constant. In this case, it follows from (10) that

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_1}{\alpha H}},$$

or

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M}{A\alpha + B + C\alpha^2}}.$$

Thus, K_1 will decrease as α increases:

$$K_{max} = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_1}{B}}.$$

To compare different methods one determines the quantity

$$\nu_{I\text{-}II} = \frac{K_c^I}{K_c^{II}} \sqrt{\frac{B_{II}}{B_I}}.$$

In general, we shall need to fix the time (primarily) but also the resistance. In every concrete case we can define the product

$$t^n \Delta p^m = M_2,$$

which must be kept constant at a specified value, with the condition that $m + n = 1$. As before, using Eqn. (10), we obtain

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_2}{\Gamma^{\frac{n}{n+m}}} \times \frac{1}{A\alpha^{\frac{m-n}{m+n}} + B\alpha^{\frac{-2n}{m+n}} C\alpha^{\frac{2m}{m+n}}}}$$

In this case the optimum rate does not equal 0 or ∞ as in the earlier examples. A finite optimum value may be assigned to the rate (and therefore to the column length), so as to maximise K_1.

It should be stressed that the whole of this discussion of the relative advantages of different methods involves the assumption that the ratio of the concentrations of the components is close to unity ($\Phi = 1$). In the more general case the expressions should contain Φ.

A few practical cases will now be considered in order to illustrate the conclusions reached above on the usefulness of various criteria of the performance of chromatographic apparatus.

As we have pointed out, the very large plateage of capillary columns does not necessarily lead to improved separations, since the smaller volume of stationary phase in these columns entails a decrease in the selectivity coefficient. Tables 2 and 3 illustrate this state of affairs. The significance of the quoted values is defined in the tables.

In spite of the fact that the number of plates considered normal in capillary chromatography is higher than in the gas–liquid technique by about an order of magnitude, we see that the criterion K_1 is smaller. For example, in the system propane–butane on diatomite coated with liquid paraffin the number of theoretical plates for propane is 680. The same solvent, used in capillary chromatography, gives 50 times as many plates (33 600) but a smaller separation criterion: $K_1 = 6.1$ in gas–liquid chromatography, 2.0 in capillary chromatography. This is a consequence of the smaller selectivity coefficient K_c of the capillary technique.

Since the selectivity coefficient in capillary chromatography increases with thickness of the stationary phase, the value of K_1 will increase with amount of solvent. Thus, the separation criterion K_1 can be varied from 1.5 to 3.4 by changing the concentration of the solution of dibutyl phthalate in petroleum ether, used for coating the capillary, from 10% to 30%.

The selectivity coefficient can be increased by increasing the distribution coefficient whilst keeping constant the amount of solvent: replacing the dibutyl phthalate by petroleum jelly in gas–liquid chromatography results in an increase in K_1 too large to be accounted for by the increased plateage alone.

The relative effects of selectivity coefficient and of plate height depend on the nature of the mixture considered. Fig. 3 shows the variation of K_1^2 with N for the separation of a mixture of heptane and hexane by silicone oil supported on celite. The number of plates was calculated for heptane. The percentage of solvent is shown for each experimental point.

TABLE 2.

Substance	Gas-liquid chromatography																	
	diatomite + 20% dibutyl phthalate						diatomite + 25% dibutyl phthalate						diatomite + 25% paraffin oil					
	L, cm	v, $cm^3 \cdot min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \cdot min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \cdot min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1
Propane	200	17.5	61.5	3.7	1500	3.4	1000	25	156	12.5	860	5.0	1000	25	166	15.0	680	6.1
Butane			97.7	6.9	1070				330	22.8	1200				412.5	25	1500	

TABLE 3.

Substance	Capillary chromatography in petroleum ether																							
	10% dibutyl phthalate						30% dibutyl phthalate						5% paraffin oil						8% paraffin oil						15% paraffin oil					
	L, cm	v, $cm^3 \times min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \times min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \times min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \times min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, $cm^3 \times min^{-1}$	v_g, cm^3	μ, cm^3	N	K_1
Propane	3200	0.8	6.0	0.2	5200		4500	0.5	8.7	0.3	4650		4700	0.1	5.3	0.1	15700		4700	0.1	7.8	0.1	33600		4700	0.6	9.0	0.1	11300	
						1.5						3.4						1.5						2.0						2.0
Butane			6.7	0.2	4600				11.2	0.4	4300				5.6	0.1	17400				8.2	0.1	37000				10.0	0.3	6200	

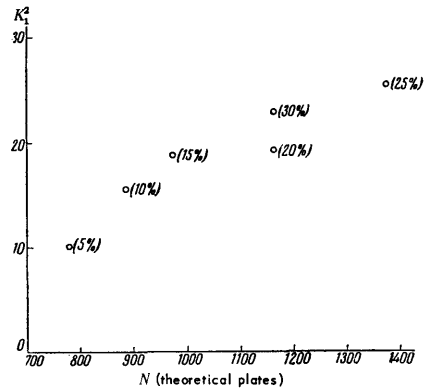


Fig. 3. Variation of K_1^2 with N for hexane–heptane mixtures.

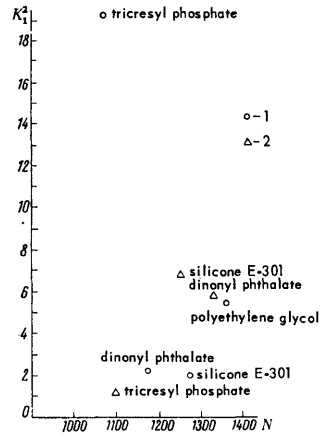


Fig. 4 Variation of K_1^2 with N for the following mixtures:
1) toluene–octane; 2) methylcyclohexane–octane.

From Eqn. (12), K_1^2 should be proportional to N if the selectivity coefficient is constant. For this particular mixture the relationship is more or less obeyed, but it fails completely with toluene–octane and methylcyclohexane–toluene mixtures, whose separation needs a higher selectivity (Fig. 4).

In these experiments the plateage was controlled by varying the solvent (as specified with each experimental point). A small change in the number of plates causes a sharp drop in K, since the separation in this case is largely determined by the selectivity rather than by the plateage.

The small thickness of the film in capillary chromatography introduces some substantial advantages in spite of the decreased selectivity. For readily adsorbed substances, the process of outer mass transfer is dominant in capillary chromatography. It follows that H and N are independent of the value of Γ_1 if the material is readily adsorbed. In the opposite case (sparingly adsorbed material) inner diffusion is the controlling process, and H increases with

Γ_i whilst N decreases. A decrease in N with Γ_i once again leads to a decrease in K_1, but with readily adsorbed substances the separation is improved more substantially than with weakly adsorbed materials if Γ_i is increased, *e.g.* the temperature is decreased, or the film thickness is increased.

The analysis and the results which have been presented demonstrate that a correct choice of method and of experimental parameters must involve both the static and the kinetic aspects of the separation criteria, which often present conflicting requirements.

To maximise the separation criterion certain conditions have to be fixed. A fixed analysis time is perhaps the commonest practical requirement, but we have considered the more general case in which limitations are imposed on the resistance to flow as well as on the time of the analysis.

For a fixed analysis time the separation criterion increases to a limiting value with flow rate. If the resistance to flow is fixed, the criterion decreases with flow rate to some other optimum value. High flow rates are desirable in the former case, low rates in the latter. The kinetic characteristics of the column are determined, in the two cases, by inner diffusion and by longitudinal diffusion, respectively.

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THE DIELECTRIC INVESTIGATION OF MOLECULAR RELAXATION IN POLYMERS

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I. INTRODUCTION

Owing to the structural peculiarities of polymers, molecular relaxation, a process representing the establishment of a statistical equilibrium, is one of the main factors determining their mechanical, electrical, and other properties [1].

The literature now contains a great deal of experimental data on the investigation of relaxation processes in polymers by both dielectric and mechanical methods, on the basis of which several conclusions can be reached about the nature and the mechanism of relaxation. This is done by comparing the structure of macromolecules with the temperature and the frequency dependence of the dielectric and the mechanical losses, characterised by the tangent of the loss angle, tan δ, and by the dielectric permittivity ϵ' (or by the elastic modulus in the case of the mechanical properties).

High polymers are characterised by the occurrence of several processes of molecular relaxation, which are due to the thermal motion of different types of kinetic units, which may be portions of the main chain of the polymer (segments), side-radicals, or simply certain groups of atoms, that behave as independent units in the thermal motion. All such kinetic units can be described by their most probable relaxation time τ; units of a single type, which have complicated molecular interactions with their environment, can yield a spectrum of relaxation times. At the present time, however, no rigorous theory of molecular relaxation in polymers yet exists. Therefore the only method for arriving at general conclusions is to compare the structure of the polymer with the above properties.

A peculiarity of relaxation observed by the dielectric method is that the energy of the electric field applied to a polymer specimen is dissipated mainly in relaxation regions containing polar groups. Dipoles taking part in thermal motion acquire a preferential orientation in the direction of the electric field. As a result, two maxima usually appear in the frequency (or temperature) variation of tan δ for polymers. The dielectric permittivity also undergoes marked changes, increasing with rise in temperature and falling with increase in frequency.