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Basic Equations Relating Separation Time to Relevant Operational Parameters in Chromatography

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Summary

Basic equations are derived to relate the chromatographic separation time to operational parameters, which are chosen to ensure that they can be experimentally measured. The most important of these parameters are the available pressure-drop across the column, the extracolumn contributions to band broadening, the plate height of the column itself, the parameters that determine the plate height, the column length, and the separation factor. The derivation is presented in such a way as to stress the assumptions often implicitly introduced in the theory.

The time required for the analysis of mixtures by means of chromatography is an important practical aspect of the technique, and methods for its reduction are currently being studied (*1–10*).

Although impressive progress has already been reported (*9, 11–14*), there appears to be some debate about which properties of a chromatograph can most profitably be adjusted in order to diminish separation times. Thus, some authors contend that the available pressure-drop across the column should be increased, since this permits the favorable arrangement of the separating column's characteristics such as small packing particles or long column lengths, while others (*15*) suggest

that it will never be really necessary to utilize high pressures in order to effect fast analyses. Confusion arising from the arbitrary choice of limiting parameters is also apparent from the diametrically opposed answers that often emerge from theoretical studies. Thus we have shown (*3*) that when the pressure drop across the column is limited, the optimum flow velocity for minimum analysis time corresponds with the flow velocity that also minimizes the plate height. This contrasts sharply with the widely quoted (*16*) generalization that the flow velocitv most favorable for fast analysis is significantly above that for which the plate height is a minimum. Of course, each of the above conclusions is correct within some well-specified framework of assumptions. Since these assumptions have, very often, not been stated explicitly, it is not always simple to determine them in practice.

The choice of the parameters which would be most significant in the present problem is further complicated by the fact that a unique set of such parameters cannot be selected on the basis of some scientific principle. The relative importance of the parameters relevant to the speed of analysis is determined largely by the personal preferences of the chromatographer and his specific circumstances. It must, therefore, be conceded that there exist many "best" ways of reducing analysis time in chromatography.

It would appear, however, that a very general approach which incorporates a large number of specific situations as special cases would contribute to the general understanding of various methods for the reduction of analysis time and their relationship to each other. Such an approach should be general in the sense that it must take into consideration many features of the chromatograph relevant to speed of analysis over as wide a range of parametric values consistent not only with present practice, but also with possible improvements of the technique. An important example is that the role of the flow velocity of the mobile carrier should be considered in both the laminar and turbulent flow regions. Furthermore, in most existing studies the extracolumn effects have not explicitly been taken into account. The advantage of an attack of the problem in completely general terms is that attention may be drawn by such an analysis to solutions that may not be obvious on the basis of simple physical arguments and/or the consideration of a limited number of parameters. In addition, such a study would clearly indicate under which circumstances a more simplified approach may validly be relied upon.

Although a general approach, such as that advocated here, involves

fewer assumptions, chromatographic processes are so complex that assumptions of some sort have to be made. Obviously, these must be particularly clearly defined.

GENERAL CONSIDERATIONS

In practice, chromatography is most often concerned with complex mixtures. A fundamental treatment of separation time in this context is prohibitively difficult and, not surprisingly, most studies of this problem have been limited to separations of binary mixtures (*1, 17–20*). The scope and depth of this study imposes a similar restriction. Although it has been contended (*1, 16*) that the conclusions which result from a study of binary mixtures can validly be applied to multicomponent mixtures, this statement is questionable. To demonstrate this, consider a complex mixture in which the last two eluted components are the most difficult to separate. Since it would appear (*16, 18*) that for a two-component mixture the optimum mass distribution coefficient is approximately unity, this implies that the mass distribution coefficients for the other solutes must be much smaller. For the mass distribution coefficient in the range smaller than 1, chromatographic columns operate very inefficiently (*21, 16*). It is thus, in general, unlikely that all the earlier components of such a mixture will be separated. Since this study is necessarily confined to the separation of binary mixtures, the fact that the results and conclusions that will be obtained cannot be directly applied to multicomponent mixtures is recognized and accepted. Nevertheless, these conclusions would, to a greater or lesser extent, have some bearing on the conditions under which complex mixtures can be resolved in short times.

The separation time of a two-component mixture is operationally defined as the time that elapses from the moment of sample introduction until the center of mass of the second eluted solute coincides with the detector attached to the column exit, provided that a prescribed degree of separation between the components has been attained. The separation time clearly depends on the conditions under which this prescribed degree of resolution is obtained, i.e., the necessary column length, L_r, and the migration rate of the center of mass of the second eluted solute band, $u_s(x)$. Since the latter quantities change, in general, with the distance from the sample introduction point, the analysis time is given

by

$$t_2 = \int_{0-\Delta'}^{L_r+\Delta} [(1 + k_2)/u(x)]\, dx \tag{1}$$

where $u(x)$ is the radial average of the mobile phase velocity and is related to $u_s(x)$ by

$$u_s(x) = u(x)/(1 + k) \tag{2}$$

Equation (1) is considerably simplified provided that two assumptions apply. The first is that k does not change with time (e.g., in programmed temperature chromatography) or with $\bar{x}$ (e.g., when the amount per unit column length or the type of stationary phase changes along the column length). The second is that Δ', $\Delta \ll L_r$, i.e., the residence time of the solute band in the region between the sample inlet point, the column inlet, and between the column exit and the actual detection sensor must be much shorter than the residence time in the column itself. These provisions then clearly allow us to write

$$t_2 = (1 + k_2) \int_0^{L_r} dx/u(x) \tag{3}$$

The separation time, as given by Eq. (3), is determined by L_r, $u(x)$, and k_2. These quantities are related to each other and to the many other relevant parameters that determine the column performance. For the purpose of establishing such relations in a very general way, a logical starting point is a criterion for the degree of separation between two solute bands. The internationally accepted (*21*, *16*) norm for this purpose is the peak resolution

$$R = (t_2 - t_1)/2(\sigma_{tT02} + \sigma_{tT01}) \tag{4}$$

where t_1 and t_2 are the retention times of the first and second eluted components, respectively. σ_{tT02} and σ_{tT01} are the standard deviations of the concentration distributions of the first and last eluted solutes measured at the column outlet in units of time, respectively.

The general form of Eq. (4) leads to relatively clumsy expressions even where extracolumn effects are ignored (*21*). To avoid this difficulty, simplifying assumptions are usually introduced (*22*). The best known of these is that first proposed by Purnell (*16*, *23*), viz.

$$\sigma_{tT02} = \sigma_{tT01} = \sigma_{tT0} \tag{5}$$

In practice this condition is approached only in the limit where $t_2 \simeq t_1$,

i.e., for relatively difficult separations, ($t_2 > t_1$); this assumption is no longer valid, and it may lead to erroneous conclusions (*21*, *22*). It has been shown (*21–24*) that ($\sigma_{tT02} + \sigma_{tT01}$) is a function of the detailed characteristics of the chromatographic column as well as of the mobile-phase–stationary-phase system and that, in general, the value of R predicted by Eq. (5) is too small by as much as 50% in extreme situations. For most practical circumstances, however, the error introduced by the Purnell assumption does not amount to more than about 10%, which is not excessive for the present purpose, and because of its simplicity it will be used here. Quantities t and σ_{tT0} are logically expressed in time units since they normally result from a time measuring device at the column outlet. For the convenience of the later discussion, it is useful also to express these quantities in units of length. For this purpose, the following transformations are used

$$u_s(x) = \sigma_T(x)/\sigma_{tT}(x) \tag{6}$$

$$u_s(x) = d\bar{x}/dt \tag{7}$$

$\sigma_T(x)$ is the standard deviation of the concentration distribution measured at $\bar{x}$ in units of length. $\bar{x}$ is the position of the center of mass of the solute band as measured from the sample introduction point. Strictly speaking, the standard deviation of the solute concentration distribution changes during the time of measurement. Consequently, σ_{T0} can only be regarded as the standard deviation of the solute concentration distribution within the column as long as $L_r \gg \sigma_{T0}$.

Equation (4) may now be extended, by substituting Eqs. (3), (2), and (6) and by introducing the simplification implied by Eq. (5), and after rearrangement, to

$$R = \tfrac{1}{4}[(\alpha - 1)/\alpha][k/(1 + k)]\sqrt{\frac{L_r}{\frac{L_r}{u_0^3}\left[\sigma_{T0}/\int_0^{L_r} dx/u(x)\right]^2}} \tag{8}$$

where

$$\alpha = k_2/k_1 > 1 \tag{9}$$

and, furthermore,

$$H_V = (L_r/u_0^2)\left[\sigma_{T0}/\int_0^{L_r} dx/u(x)\right]^2 \tag{10}$$

and

$$N_V = L_r/H_V \tag{11}$$

σ_{T0} incorporates all causes of band spreading. Broadly speaking, these may be divided into those originating outside the chromatographic system and those residing within it. It is assumed that these causes contribute independently to the total band width

$$\sigma_{T0} = [(\sigma_{e0}')^2 + \sigma_0^2]^{1/2} \tag{12}$$

σ_0^2 and $(\sigma_{e0}')^2$ are the contributions to σ_{T0}^2, measured at the column exit, of the processes in the column itself and those external to it. The extracolumn contributions may be further attributed to inlet and detector effects. Provided that the peak measured at the column outlet is Gaussian, a formal variance may be ascribed to each of the extracolumn band spreading effects and it may be assumed that they are additive, i.e.

$$(\sigma_{e0}')^2 = \sigma_{i0}^2 + \sigma_{00}^2 \tag{13}$$

Although the inlet band will seldom be Gaussian, it will be assumed that a variance σ_{ii}^2 can formally be defined which would be the equivalent of σ_{i0}^2 corrected, if necessary, for compressibility. The interpretation of σ_{i0}^2 and σ_{00}^2 is sufficiently subtle to warrant a few remarks at this point. Since σ_{ii}^2 is the variance of the inlet concentration distribution as measured at the column inlet *inside the packing*, its value is influenced by k. However, it would be more desirable to so define σ_{ii}^2 that it is k-independent and only reflects parameters such as sample volume and band broadening effects in the inlet and the connecting pipes. Let, therefore, σ_{iP}^2 be the variance of the solute band measured immediately prior to its entering the packing. σ_{iP}^2 is related to σ_{ii}^2 via Eqs. (6) and (7) by

$$\sigma_{ii}^2 = \sigma_{iP}^2/(1 + k)^2 \tag{14}$$

Secondly, the σ_{00}^2 is measured at the column outlet but it includes the effect that arises between the outlet and the actual detector. Here, again, take σ_{0A}^2 to be the variance contributed by the detection process. This represents band dispersion originating in the connecting tubes, dead volumes, as well as those resulting from the slow response speeds of the primary detection process and associated electronics. This quantity can also be measured without a column attached to the detector. Here then

$$\sigma_{00}^2 = \sigma_{0A}^2/(1 + k)^2 \tag{15}$$

TABLE 1

Expressions for B_0 (*25*)

Column type	Re range	B_0
Open tube	Re < 2000	$B_0 = 1/8$
	Re > 2000	$B_0 = 25.1/\mathrm{Re}^{0.75}$
Packed	Re < 15	$B_0 = \{150[(1 - \epsilon/\epsilon)]^2\}^{-1}$
	Re > 15	$B_0 = \{150[(1 - \epsilon)/\epsilon]^2\} + \{1.75[(1 - \epsilon)/\epsilon]\mathrm{Re}\}^{-1}$

A further problem arises from the introduction of σ_{0A}^2. The second assumption on which Eq. (3) is based and which is necessary to secure the relatively simple form of Eq. (8) makes σ_{0A}^2 physically an invalid concept. Thus, as will emerge below, physically unacceptable pressure corrections of σ_{0A}^2 arise in the case of compressible mobile phases. This error will, in the present framework, be corrected somewhat artificially.

The pressure drop across the column may, generally, be obtained from (*25*)

$$dP = -[\eta u(x)/B_0 s^2]\,dx \tag{16}$$

where B_0 is a constant, does not vary along the column length (*25*), and is usually a function of the Reynolds number. A summary of the expressions for B_0 used in this study is given in Table 1 (*25*). The functional form of Eq. (16) is valid for both open tubes and packed beds in the sense that $s = d_t$ in the case of open tubular columns and that $s = d_p$ for packed columns.

Compressible Mobile Phase

The expressions (Eqs. 2–16) derived above are general in that they do not depend on the functional form of $u(x)$. In general, however, provided that $\rho'(x)$ and $u(x)$ do not vary with time, conservation of mass requires that (*25*)

$$\rho'(x)u(x) = \text{constant} \tag{17}$$

It is convenient for the subsequent discussion to know $u(P)$. This can be attained from Eq. (17) provided that the PV-relationship for the mobile fluid is known. It would appear that, for most practical operating conditions, the ideal gas law holds sufficiently well. If it is now assumed

that the mobile fluid is a gas that behaves ideally, Eq. (17) leads to

$$P(x)u(x) = P_0u_0 \tag{18}$$

$u(x)$ can now immediately be obtained from Eqs. (16) and (18)

$$u^2(x) = u_0^2/[p^2 - (x/L)(p^2 - 1)] \tag{19}$$

where

$$p = P_i/P_0 \tag{20}$$

The variance of the concentration distribution of the solute band measured at the column outlet, σ_{T0}^2, may be taken as the sum of the contributions to the variance resulting from the movement of the band through dx at x, each such elementary contribution being corrected for the differences in pressure at x and at the column outlet (*24*, *26*, *27*). This may be written in differential form as (*24*, *26*)

$$d\sigma_{T0}^2 = [p^2(x)/p_0^2]\, d\sigma_x^2 \tag{21}$$

The total variance of the solute band can now be obtained by integrating the right-hand side of Eq. (21) between 0 and $L + \Delta$. If it is assumed that the pressure drop across Δ is negligible, and upon substitution from Eq. (18), it follows that

$$\int_0^{L_r+\Delta} d\sigma_{T0}^2 = \int_0^{L_r+\Delta} [p^2(x)/p_0^2]\, d\sigma_x^2$$

$$= u_0^2 \int_0^{L_r} [H(x)/u^2(x)]\, d\bar{x} + \int_{L^r}^{L_r+\Delta} d\sigma_x^2$$

or

$$\sigma_{T0}^2 = u_0^2 \int_0^{L_r} [H(x)/u^2(x)]\, d\bar{x} + \sigma_{i0}^2 + \sigma_{00}^2 \tag{22}$$

where the local plate height

$$H(x) = d\sigma^2(x)/d\bar{x} \tag{23}$$

is a particularly significant parameter and is closely related to the more fundamental band broadening processes in the column itself. Theoretical studies, most often, attend to the relation between the local plate height and column parameters such as particle diameters and linear mobile phase flow rates.

H_V can now be expressed in terms of $H(x)$ and any other parameters introduced thus far through Eqs. (10), (22), (19), and (20) together with

$$\sigma_{i0}^2 = p^2\sigma_{ii}^2 \tag{24}$$

as

$$H_V = H + [(\sigma_{e0}')/L_r]^2 \tag{25}$$

where

$$H = \frac{u_0^2 f_1 \int_0^{L_r} [H(x)/u^2(x)]\,dx}{L_r} \tag{26}$$

f_1 is a correction for compressibility, i.e.,

$$f_1 = 9/4[(p^2 - 1)^2/(p^3 - 1)^2] \tag{27}$$

Furthermore

$$(\sigma_{e0}')^2 = f_2\sigma_{ii}^2 + f_1\sigma_{00}^2 \tag{28}$$

where

$$f_2 = 9/4[p^2(p^2 - 1)^2/(p^3 - 1)^2] \tag{29}$$

It is instructive to summarize the foregoing bv writing the plate height measured by a chromatograph, H_V, explicitly in terms of all the operational parameters representing (relevant) phenomena present between the inlet and the detector. Thus from Eqs. (14), (15), (25), (26), and (28) it follows

$$H_V = \frac{u_0^2 f_1 \int^{L_r} [H(x)/u^2(x)]\,dx}{L_r} + \frac{1}{L_r(1 + k)^2}\{f_2\sigma_{ip}^2 + \sigma_{0A}^2\} \tag{30}$$

Finally, the condition for the attainment of any prescribed value of the peak resolution, R_s, follows from Eqs. 8 and 11 as

$$N_V \geq \beta \tag{31}$$

where

$$\beta = 16R^2[\alpha/(\alpha - 1)]^2[(1 + k)/k]^2 \tag{32}$$

The minimum column length, L_r, which is required to attain the pre-

scribed resolution can be solved for from Eqs. (25), (11), (28), (31), (14), and (15), i.e.,

$$L_r = \beta H(\tfrac{1}{2} + \{\tfrac{1}{4} + [\sigma_E^2/\beta(1 + k)^2H^2]\}^{-1/2}) \tag{33}$$

where

$$\sigma_E^2 = f_2^2\sigma_{iP}^2 + \sigma_{0A}^2 \tag{34}$$

The pressure drop across the column follows from Eqs. (16) and (18) as

$$\Delta P = 2\eta u_0 L_r/s^2 B_0(1 + p) \tag{35}$$

Finally, the analysis time follows from Eqs. (3) and (19) as

$$t = (1 + k)L_r/u_0(f_1)^{1/2} \tag{36}$$

Incompressible Mobile Fluid

When the compressibility of the mobile fluid can be ignored, as is the case with most liquids, the equations derived above can be considerably simplified since obviously

$$\begin{aligned} u(x) &= u_0 = u \\ \sigma_{ii}^2 &= \sigma_{i0}^2 \\ (\sigma_{e0}')^2 &= \sigma_{e0}^2 \\ f_1 &= 1 \\ f_2 &= 1 \end{aligned} \tag{37}$$

and, formally, for Eq. (36)

$$p = 1$$

DISCUSSION

Equation (36), via Eqs. (26), (30–35), and (37), gives a general expression for the analysis time, based on assumptions stated during the derivation outlined above and in terms of operationally defined parameters. These equations are completely general and can be employed in most practical situations to compute the optimum analysis time.

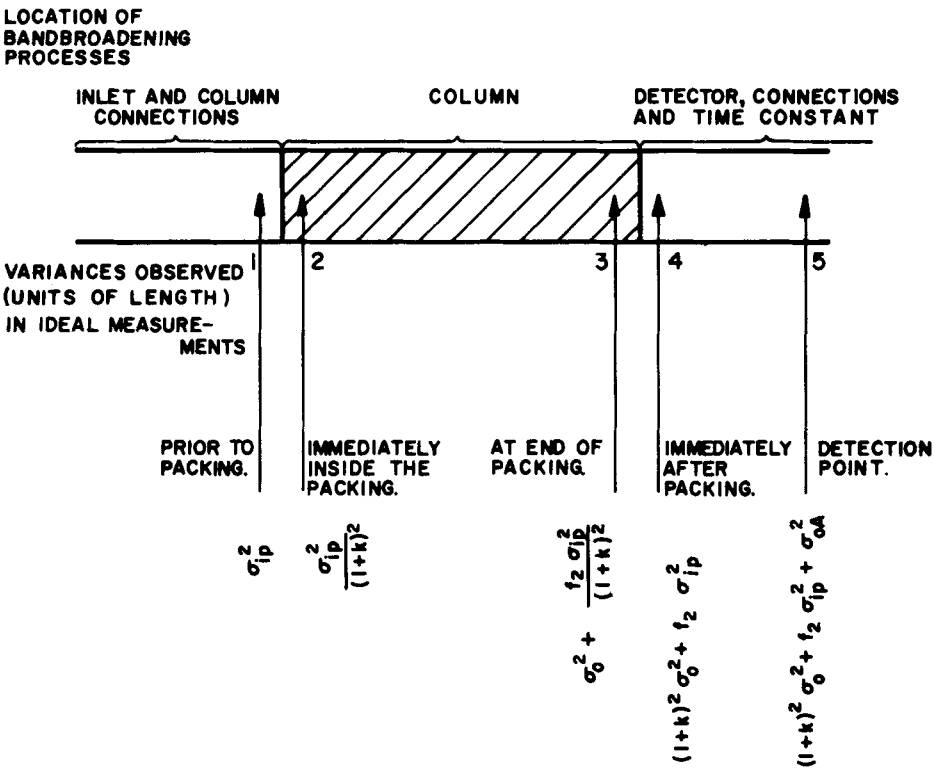

FIG. 1. Standard deviation measured at various positions in the chromatograph.

Extracolumn Effects

Figure 1 serves to demonstrate the variance of the solute band that will be observed with an ideal measurement probe in various locations in the chromatographic apparatus. It is particularly interesting to note how the relationship between the extracolumn and column contributions to the variance, measured in units of length, changes from point to point. This impression can be amplified by relating σ_{T0}^2 to the variances originating external to the column and to those resulting from the usual column band broadening effects via Eqs. (12), (14), (15), and (28) as

$$\sigma_{T0}^2 = \sigma_0^2 + [1/(1 + k)^2] \{f_2 \sigma_{iP}^2 + \sigma_{0A}^2\} \quad (38)$$

The $1/(1 + k)^2$-dependent form of Eq. (38) is not without practical significance. It shows, for instance, that in a liquid chromatograph for

which $\sigma_{iP}^2 + \sigma_{0A}^2 \simeq \sigma_0^2$ when $k = 0$, i.e., the inlet and detectors are dynamically very badly designed, $[1/(1 + k)^2](\sigma_{iP}^2 + \sigma_{0A}^2) \ll \sigma_0^2$ when k becomes large, say $k \simeq 10$. This explains why chromatographs with badly designed extracolumn features may have a reasonable performance in practice.

That the inclusion of extracolumn effects into the general expressions for the analysis time are necessary can be seen from Eqs. (33) and

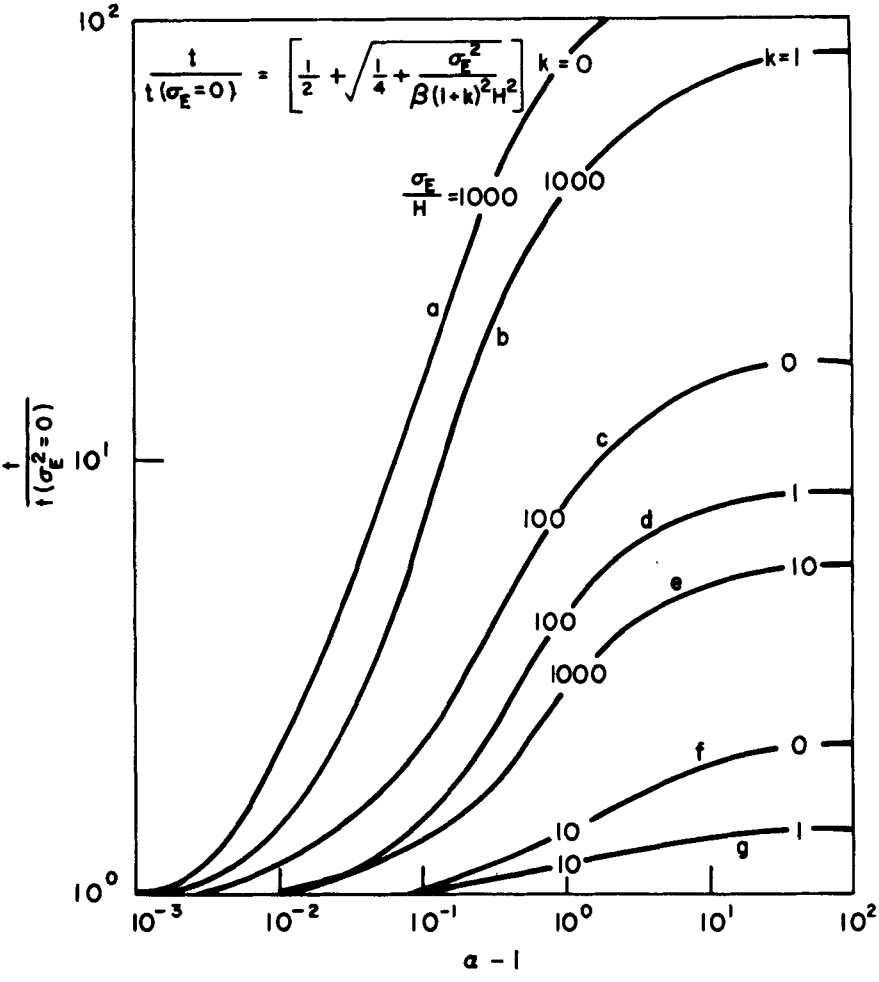

FIG. 2. Dependence of the separation time on extra-column effects.

(36). This point is probably best demonstrated by comparing separation times with and without extracolumn effects, i.e., $t/t(\sigma_E^2 = 0)$, as has been done in Fig. 2. It is interesting to note that Eqs. (33) and (36) indicate that extracolumn effects may be ignored as soon as $\sigma_E^2/\beta(1 + k)^2H^2 \ll \frac{1}{4}$.

I.e.,

$$\sigma_E \leq [1/(20)^{1/2}](1 + k)(H + L)^{1/2}$$

which conforms to previously reported results (*28*, *29*).

The k-dependence of the relation between column and extracolumn effects is effectively brought to light by curves *a*, *b*, and *e* of Fig. 2.

It may occur that operation at large k-values will solve all the problems of badly designed extracolumn components. That this is not the case in practice, however, will become clear if the dilution effect of elution at large k-values is kept in mind. The concentration of an eluted band changes roughly proportionally to $1/(1 + k)$. Operation in large k-areas will very often, therefore, push the solute concentration outside the detection limits of most detectors. Furthermore, in Fig. 2 the analysis time has been referred to $t(\sigma_E = 0)$, which in turn may be and is (*30*) a strongly ascending function of k.

List of Symbols

B_0	constant defined by Eq. (16)
d_p	particle diameter (L)
d_t	column diameter (L)
H_V	convenient parameter, defined by Eq. (10) (L)
$H(x)$	local plate height defined by Eq. (23) (L)
k	mass distribution coefficient; ratio of the solute mass in the stationary phase to the solute mass in the mobile phase at equilibrium
L	column length (L)
L_r	value of L necessary to effect a separation to a prescribed degree of resolution (L)
N_V	efficiency parameter of a chromatographic column, taking extra column contributions to band width into account, defined by Eq. (11)
P	pressure ($ML^{-1}T^{-2}$)
P_i	value of P measured at the column inlet ($ML^{-1}T^{-2}$)
P_0	value of P measured at the column outlet ($ML^{-1}T^{-2}$)

p	ratio of inlet to outlet pressure (P_i/P_0)
R	resolution of a solute pair, defined by Eq. (4)
Re	Reynolds number; Re $= 2r_t u(x)/\nu(x)$, for open tubular columns; Re $= d_p u(x)/\nu(x)$, for packed columns
s	convenient parameter; $s = dt/2$ for open tubular columns and $s = d_p$ for packed columns (L)
t	elution time of a solute; equal to separation time if this solute is the last eluted solute (T)
u	radial average of the linear flow velocity of mobile phase in the axial direction (LT^{-1})
u_0	value of u measured at the column outlet (LT^{-1})
u_s	linear velocity of the center of mass of the solute (LT^{-1})
x	axial column coordinate with the sample inlet point chosen as the origin (L)
$\bar{x}$	position of the center of mass of the solute band as measured from the sample inlet (L)
α	separation factor $= k_2/k_1 > 1$
ϵ	porosity of column packing
η	viscosity in the mobile phase ($ML^{-1}T^{-1}$)
ρ'	density of the mobile phase (ML^{-3})
σ_{0A}	contribution to σ_T by the detection process as measured by the detector (L)
σ_{iP}	standard deviation of solute concentration distribution measured prior to its entering the packing (L)
σ_{00}^2	contribution of band broadening effects, originating beyond the column exit, to σ_t (L)
σ_{i0}	contribution of inlet effects to σ_T as measured at the column outlet (L)
σ_{ii}	value of σ_{i0} measured at the column inlet, inside the packing (L)
σ_0	value of σ measured at the column outlet (L)
σ	contribution of band broadening effects, originating inside the column, to σ_T (L)
σ_{e0}'	contribution of extracolumn effects to σ_T, measured at the column outlet (L)
σ_{tT0}	value of σ_{tT} measured at the column outlet (T)
σ_{tT}	total standard deviation of solute concentration distribution in units of time (T)
σ_T	total standard deviation of solute concentration distribution in units of length (L)

σ_{T0} value of σ_T measured at the column outlet (L)

Δ distance between column exist and actual point of detection (L)

Δ' distance between injection point and beginning of the column packing (L)

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