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MASS TRANSFER IN IDEAL AND GEOMETRICALLY DEFORMED OPEN TUBES

II*. POTENTIAL APPLICATION OF IDEAL AND COILED OPEN TUBES IN LIQUID CHROMATOGRAPHY

ISTVÁN HALÁSZ

Angewandte Physikalische Chemie, Universität des Saarlandes, 6600 Saarbrücken (G.F.R.)

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SUMMARY

It has been shown experimentally in Part I that the peak broadening in an open tube with a liquid mobile phase can be described solely by the $C_m u$ term of the Golay equation, if the inner diameter is small ($< 100\ \mu$m) and the linear velocity is not extremely high (< 1 m/sec). With this assumption, optimal values achievable in capillary columns are calculated for the number of theoretical and effective plates, the speed of analysis, the number of plates per unit pressure drop and the peak volume. These parameters yield results which are hardly, if at all, better than those generated in packed columns in routine liquid chromatography. Even if the instrumental problems, including the coating of the open tube, are neglected, capillary columns will be of interest in liquid chromatography only if secondary flow can be generated within the open tubes.

INTRODUCTION

In earlier publications[1,2] it was shown experimentally that in ideal tubes the band broadening for an inert peak can be described with the help of the equations of Taylor[3], Aris[4] or Golay[5–7] if (a) the linear velocity of the eluent is less than 20 cm/sec, (b) the inner diameter of the tube is less than 500 μm and (c) the unevenness of the wall is negligible. This limiting velocity increases with decreasing inner diameter of the open tube, and with decreasing kinematic viscosity of the eluent. The linear velocity limit given above is valid for the "worst" eluent used in liquid chromatography (LC), *i.e.*, for *ca.* 45% (v/v) methanol in water.

Coiling the column to a diameter of about 12 cm stabilizes the laminar flow. In the laminar region secondary flow[8,9] diminishes the dispersion. It was shown experimentally that although there is no firm theoretical basis for it, the desired influence of the secondary flow declines with decreasing inner diameter of the tube. With the boundary conditions mentioned above the effect of the secondary flow can be neglected.

* Part I: ref. 2.

The application of open tubes in LC in the turbulent region will not be discussed in this paper for the following reasons:

(a) In this region the specific permeability of an open tube is at least a factor of 3 less than that for laminar flow[1,2].

(b) The h values in the turbulent region are about ten times higher[1,2] than those calculated on the basis of the friction theory of Taylor[10], because laminar conditions prevail in an appreciable portion of the cross-section of the tube.

(c) The pressure drop over the column is high, because of the high linear velocities required and because of the great pneumatic resistance of a long column with a small inner diameter.

(d) The injection of small samples is difficult if the inlet pressure is high.

On the basis of the experimental results for the laminar region discussed above, it will be assumed that the dispersion of a sample in ideal or coiled tubes (with circular cross-sections) can be described by the Taylor[3], Aris[4] and Golay[5–7] equations, if the inner diameter of the tube is less than 500 μm and the linear velocity of the eluent is less than 20 cm/sec. The limiting velocity can be increased to 100 cm/sec if the inner diameter of the open tube is less than 100 μm. A coil diameter of about 10 cm or more is assumed.

In this paper the B/u and $C_s u$ terms of the Golay equations[5–7] will be neglected, and consequently for retarded peaks in ideal open tubes the maximum efficiency is calculated. In a following paper these maximum values will be compared with the experimental data. The relative advantages and disadvantages of capillary and packed columns will be discussed.

MAXIMUM NUMBER OF PLATES GENERATED IN AN OPEN TUBE

In an ideal open tube, the height equivalent to a theoretical plate, h, can be calculated on the basis of the Golay equation[5–7]:

$$h = \underbrace{\frac{2\gamma D}{u}} + \underbrace{\frac{1 + 6k' + 11(k')^2}{(1 + k')^2}} \cdot \frac{d^2}{96D} \cdot u + \frac{2k'}{3(1 + k')^2} \cdot u \qquad (1)$$

$$= \frac{B}{u} + \underbrace{f \cdot C_m^* u} + C_s u =$$

$$= \frac{B}{u} + C_m u + C_s u$$

where

$$f = \frac{1 + 6k' + 11(k')^2}{(1 + k')^2} \qquad (2)$$

The factor f is given in Table I as a function of k', including also the extreme values for the capacity ratios.

It is sometimes overlooked that the Golay equation is valid only for straight tubes, as is implicit in the statement of Golay[7]: "...the average speed of flow has a parabolic profile along any cross-section parallel to the direction of flow,...". This statement, however, is valid only for straight tubes, and elsewhere it is impossible to describe explicitly the flow profile. Further, the Golay equation is an "extension of

TABLE I

FACTORS f, f^*, F' AND F^* AS A FUNCTION OF THE CAPACITY RATIO, k'

k'	f	f^*	F'	F^*
0	1.000	∞	∞	∞
0.05	1.204	441.0	531.0	557.6
0.075	1.308	205.4	268.8	289.0
0.1	1.413	121	171.0	188.1
0.15	1.624	58.78	95.44	109.8
0.25	2.040	25.00	51.00	63.75
0.30	2.243	18.78	42.11	54.74
0.40	2.633	12.25	32.25	45.15
0.50	3.000	9.000	27.00	40.50
0.75	3.816	5.444	20.78	36.37
0.914	4.278	4.385	18.76	35.91
1.0	4.500	4.000	18.00	36.
1.25	5.074	3.240	16.44	36.99
1.50	5.560	2.778	15.44	38.60
1.75	5.975	2.469	14.76	40.59
2.0	6.333	2.250	14.25	42.75
2.5	6.918	1.960	13.56	47.46
3.0	7.375	1.778	13.11	52.44
5.0	8.500	1.440	12.24	73.44
10.0	9.595	1.210	11.61	127.7
20.0	10.252	1.103	11.30	272.3
∞	11.000	1.000	11.00	∞

Taylor's method"[7] and eqn. 1 is reduced to the Taylor or Aris equations for an inert peak ($k' = 0$). These equations again are valid only for straight tubes, as pointed out by Aris[4]: "In three recent papers, Sir Geoffrey Taylor has discussed the dispersion of soluble matter in a fluid flowing in a straight tube[3,10,11]".

On the other hand, in gas chromatography the Golay equation is always an excellent approximation for coiled tubes, because of the high interdiffusion coefficients of gases ($D_g \approx 10^{-1}$ cm²/sec).

The peak broadening with a liquid mobile phase can only be calculated using the Golay equation if the inner diameter of the tube is less than 100 μm (coil diameter about 10 cm) and the linear velocity of the eluent is less than 100 cm/sec, as is usual in LC. A further assumption is that no secondary flow is caused by the unevenness of the wall.

From experience, it is a tolerable approximation that in eqn. 1 $\gamma = 1$. By differentiation of eqn. 1 the velocity at the minimum of the h *versus* u curve, u_{Min}, is

$$u_{\mathrm{Min}} = \frac{D}{d}\sqrt{\frac{192}{f}} = \frac{13.86D}{d\sqrt{f}} \tag{3}$$

In routine LC, $u \gg u_{\mathrm{Min}}$. Consequently, the B/u term in eqn. 1 will be neglected. The upper limit for this approach, however, must be stated: in a 15-μm I.D. tube with n-heptane as eluent, u_{Min} for an inert peak is 0.28 cm/sec.

Also for an inert peak the $C_s u$ term is zero. Consequently, the minimum h value, h_0, is generated for an inert peak.

The maximum number of theoretical plates, n_{max}, for a retarded peak is generated if we assume an extremely rapid mass transfer in the stationary phase, *i.e.*, we neglect also the $C_s u$ term in eqn. 1:

$$n_{max} = \frac{L}{h_{min}} = \frac{96DL}{fd^2u} = \frac{96Dt_0}{fd^2} = \frac{n_0}{f} \tag{4}$$

where n_0 is the number of theoretical plates generated for an inert peak ($k' = 0$). In eqn. 4 the B/u and the $C_s u$ terms of in eqn. 1 are neglected. It can be seen in eqn. 4 that for a retarded peak n_{max} is always less than n_0, because $f > 1$.

Using the same assumption, the minimum h value for a retarded peak (h_{min}) is

$$h_{min} = \frac{fd^2u}{96D} = fh_0u \tag{5}$$

Apart from the factor f in eqn. 4, the validity of the Taylor equation is assumed for calculating h in both inert and retarded peaks.

As is shown in eqn. 4 n_{max} is a linear function of the hold-up time, t_0, of the column only if the eluent and sample (*i.e.*, D for a given temperature) and the inner diameter of the column, d, are given. If the column is elongated by a given factor β, the linear velocity has to be increased by the same factor β to achieve the same hold-up time. Consequently, h also increases by a factor of β while n_{max} remains unchanged. Therefore, n_{max} is a function of the ratio of the column length over the linear velocity of the eluent ($t_0 = L/u$), as was shown in eqn. 4.

For difficult separations in chromatography, the relative retention α is small and it is a reasonable approximation[12,13] that

$$R \equiv \frac{\Delta t_R}{w} = \frac{\alpha - 1}{4\alpha} \cdot \frac{k'}{1 + k'} \cdot \sqrt{n_2} = \frac{\alpha - 1}{4\alpha} \cdot \sqrt{N_2} \tag{6}$$

with

$$n = \left(\frac{1 + k'}{k'}\right)^2 N = f^* N \tag{7}$$

In eqn. 6 the theoretical plate number, n_2, and the effective plate number, N_2, both refer to the later emerging peak. Thus, for difficult separations ($\alpha < 1.2$) the resolution is an extremely sensitive function of α and of $R \approx \sqrt{N}$. From the point of view of the separation, N (not n alone) is of interest, as is shown in eqn. 6.

The maximum number of effective plates, N_{max}, (the B/u and $C_s u$ terms of the Golay equation are again neglected) can be calculated if eqns. 4 and 7 are combined:

$$N_{max} = \frac{96Dt_0}{d^2 f f^*} = \frac{n_0}{f f^*} = \frac{n_0}{F'} \tag{8}$$

where

$$F' = \frac{1 + 6k' + 11(k')^2}{(k')^2} \tag{9}$$

The dimensionless factors f^* and F' as functions of k' are given in Table I together with their extreme values. As shown in Fig. 1, f increases slowly, but f^* and F' decrease extremely sharply with increasing capacity when $0 \leqslant k' \leqslant 2$. It is this region which is the most important in practice.

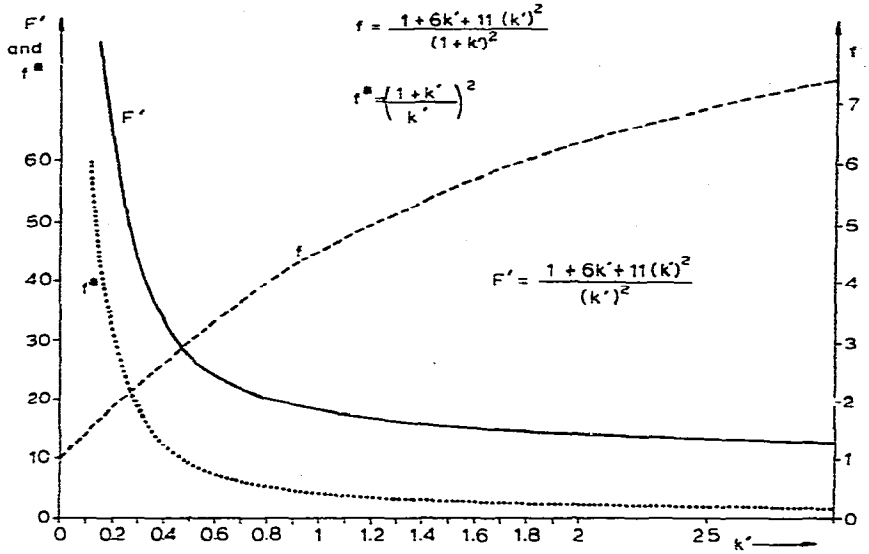


Fig. 1. The factors f, f^* and F' as functions of the capacity ratios.

IMPORTANCE OF THE REGION OF SMALL CAPACITY RATIOS ($k' < 2$)

The hold-up time, t_0, of a capillary column is usually long compared with that of a packed column of similar efficiency. Therefore, with increasing k' the analysis time increases rapidly.

The weight (or volume) of the stationary phase per unit column volume is much smaller in coated open tubes than in packed columns. Therefore, the maximum sample size per unit column volume is smaller if open tubes are used. Consequently, the concentration of the sample in the eluent at the peak maximum is usually smaller by a factor of 10 (or even more) in conventional open tubes. As the retention time of the compounds increases the peak height decreases, if the sample size remains constant. Because of the higher density of the eluent the concentrations of the sample in LC are smaller than in gas chromatography. Hence in LC, with increasing k', the possibility that the signal from the detector will become smaller than the noise level of the detector becomes much greater. *With increasing capacity ratios not only does the time of analyses increase, but the peaks can become undetectable.*

In efficient open tubes the first retarded peak with $k' = 0.05$ used to be separated from the inert peak. Let us assume that the relative retention of the first and second retarded peak is $\alpha = 1.2$. Rearranging eqn. 6 the effective number of plates necessary for a given separation, N_{ne}, is

$$N_{ne} = \left(\frac{4R\alpha}{\alpha - 1}\right)^2 \qquad (10)$$

For example, if $\alpha = 1.2$ and baseline resolution ($R = 1.5$) is wanted, then 1296 effective plates are required for this separation. All of the other pairs of peaks with $\alpha = 1.2$ (or higher) will have a resolution of $R > 1.5$ because N increases with increasing capacity ratios (because of the increase in factor f) if the mass transfer in the stationary phase (*i.e.*, the $C_s u$ term in eqn. 1) is neglected. Approximately constant α values are typical if homologous series are to be separated. With these assumptions, thirteen peaks (excluding the inert peak) can be resolved if $0.05 \leqslant k' < 0.5$. Between $k' = 0.5$ and 1 only four peaks can be separated, and also between $k' = 1$ and 2.

Qualitatively, the picture remains unchanged (as shown in Table II) if the opposite assumption is made: $n_0 = 30{,}000$ and $R = 1.5$ are required for all the neighbouring peaks. Further, in a hypothetical sample the retentions of the compounds should be free to change, as demonstrated in Table II. In the third column of Table II the relative retentions, α, of the pair of compounds with $k' = 0.05$ and 0.09473 are in the lane of $k' = 0.09473$ tabulated. The same is true for the effective number of plates necessary for the seperation of these two compounds, N, in the last column. As shown in the third column, the relative retentions, α, decrease considerably with increasing k' in the range $0 < k' < 0.5$ (*i.e.*, from $\alpha = 1.90$ to 1.22). The number of effective plates for the first retarded compound is only $N = 56$, although here $n \approx 25{,}000$. The N values increase and the n values decrease with increasing k'. For infinite

TABLE II

SEPARATION OF A HYPOTHETICAL MIXTURE IN AN OPEN TUBE WITH BASELINE RESOLUTION ($R = 1.5$) IF $n_0 = 30{,}000$

$B/u = C_s u = 0$.

Number of samples	k'	α	n	N
0	0	—	30 000	0
1	0.05000	—	24 915	56
2	0.09473	1.89453	21 566	161
3	0.14493	1.53003	18 721	300
4	0.20137	1.38940	16 313	458
5	0.26488	1.31538	14 281	626
6	0.33641	1.27003	12 568	796
7	0.41702	1.23962	11 124	963
8	0.50791	1.21797	9 907	1124
9	0.61045	1.20188	8 880	1276
10	0.72616	1.18955	8 012	1418
11	0.85677	1.17986	7 276	1549
12	1.00422	1.17210	6 651	1670
13	1.17072	1.16580	6 119	1780
14	1.35874	1.16060	5 666	1880
15	1.57109	1.15629	5 277	1971
16	1.81094	1.15266	4 945	2052
17	2.08187	1.14960	4 658	2126
18	2.38791	1.14700	4 412	2192
19	2.73363	1.14478	4 199	2251
20	3.12418	1.14287	4 014	2304
21	3.56539	1.14123	3 854	2351
22	4.06385	1.13980	3 715	2393
23	4.62698	1.13857	3 595	2430
24	5.26317	1.13750	3 489	2464

k' the maximum number of theoretical plates is $n_{max} = 2727$, and of course $N_{max} = 2727$ also. If $R = 1.5$ is required the optimal resolution is $\alpha = 1.13$. This relative retention, however, is achieved in practice in the capacity ratio region around $k' = 5$, as shown in Table II.

In calculating the values in Table II, it was again assumed that $B/u = C_s u = 0$. In practice, the higher the capacity ratios the less this approach is valid. With increasing k' the $C_s u$ term usually increases, and consequently the plate numbers will become smaller than is indicated in Table II and the α values will remain more or less constant if R is constant as is claimed.

The maximum speed of separation, *i.e.*, N_{max}/t_R, occurs at $k' = 0.914$, as will be shown later. If only a few compounds have to be separated, the stationary phase and eluent have to be selected so that the compounds will be eluted around $k' = 1$. If the capacity ratios are smaller, longer columns have to be used to generate enough plates for the required resolution and the velocity of the eluent has to be increased to achieve unchanged hold-up times. For both of these reasons the inlet pressure must be increased.

To summarize, the region of small capacity ratios ($k' < 2$) is of extreme importance in LC with open tubes because of (a) the time of analysis, (b) the detectability, (c) the peak capacity, (d) the speed of analysis in this region and (e) possible pressure limitations.

CALCULATED MAXIMUM PLATE NUMBERS FOR DIFFERENT ELUENTS

It will be demonstrated with some numerical values that in capillary-column LC only the effective plate numbers are of importance. Further, the required geometry of the open tubes will be outlined.

In the following it will be assumed that the molecular weight of the compounds to be separated is smaller than 400 and that room temperature applies. The product of the diffusion coefficient, D, and the viscosity of the eluent, η, is constant. The values for *n*-heptane are

$$\begin{aligned} D\eta &= (3 \cdot 10^{-5}\ \mathrm{cm^2/sec}) \cdot (4 \cdot 10^{-3}\ \mathrm{poise}) \\ &= 1.2 \cdot 10^{-7}\ \mathrm{dyne} \\ &= 1.2 \cdot 10^{-12}\ \mathrm{newton} \end{aligned} \qquad (11)$$

As shown in eqns. 4 and 8, the plate number is linear in t_0. To generate enough plates, $t_0 = 10$ min was assumed, *i.e.*, the time of analysis for $k' = 2$ is 30 min. For routine work a longer time of analysis is not usually acceptable.

With these assumptions (*i.e.*, $B/u = C_s u = 0$, $t_0 = 10$ min and $D\eta = 1.2 \cdot 10^{-7}$ dyne) and with the help of eqns. 4 and 8 the maximum plate numbers for different eluents were calculated as functions of the inner diameter of the column and of the capacity ratios of the samples at room temperature. In Table III the eluent is *n*-heptane. The results are impressive: for an open tube of 30-μm I.D. 192,000 theoretical plates are calculated for the inert peak. As a consequence of the *f versus* k' function (Table I), n decreases with increasing capacity ratio. However, for $k' = 2$ more than 30,000 theoretical plates are calculated. On the other hand, n_0 is inversely

TABLE III

MAXIMUM NUMBER OF THEORETICAL PLATES, n, GENERATED IN OPEN TUBES OF DIFFERENT INNER DIAMETERS AND FOR VARIOUS k' VALUES

t_0 = 10 min. Eluent, n-heptane. $D = 3 \cdot 10^{-5}$ cm²/sec. $\eta = 4 \cdot 10^{-3}$ poise. Room temperature.

I.D. (*μm*)	*k'*								
	0	*0.1*	*0.25*	*0.5*	*0.75*	*1.0*	*1.5*	*2.0*	*2.5*
30	192,000	135,860	94,118	64,000	50,344	42,667	34,532	30,316	27,752
50	69,120	48,909	33,882	23,040	18,112	15,360	12,432	10,914	9991
65	40,889	28,941	20,049	13,633	10,717	9089	7356	6458	5912
85	23,917	16,924	11,724	7972	6267	5315	4302	3776	3457
100	17,280	12,227	8471	5760	4528	3840	3108	2728	2498

proportional to d^2. If only $n_0 = 30{,}000$ is required, the inner diameter of the tube has only to be smaller than 77 μm.

The picture becomes worse, but more realistic, if the effective plate numbers, N, are calculated for n-heptane as eluent (Table IV). The baseline separation ($R = 1.5$) of a pair of compounds with $\alpha = 1.3$ is a simple problem in chromatography. They can be resolved with $N = 675$, as can be calculated with eqn. 10. This condition, however, is fulfilled only above the dashed line in Table IV. If a pair of compounds emerge around $k' = 0.1$, and $\alpha = 1.3$ is required, only columns with an inner diameter smaller than 30 μm can be used if $t_0 = 10$ min.

TABLE IV

NUMBER OF EFFECTIVE PLATES, N, GENERATED IN OPEN TUBES OF DIFFERENT INNER DIAMETERS AND FOR VARIOUS k' VALUES

t_0 = 10 min. Eluent, n-heptane. $D = 3 \cdot 10^{-5}$ cm²/sec. $\eta = 4 \cdot 10^{-3}$ poise. Room temperature.

I.D. (*μm*)	*k'*							
	0.1	*0.25*	*0.5*	*0.75*	*1.0*	*1.5*	*2.0*	*2.5*
30	1123	3765	7111	9241	10,667	12,432	13,474	14,159
50	404	1355	2560	3327	3840	4475	4851	5097
65	239	802	1515	1968	2272	2648	2870	3016
85	140	469	886	1151	1329	1549	1678	1764
100	101	339	640	832	960	1119	1213	1274

Diffusion coefficients in water are about 2.5 times less than in n-heptane. Consequently, the corresponding plate numbers are smaller by the same factor, as shown in Tables V and VI. As demonstrated in Table V with water as eluent, the inner diameter of the open tube has to be less than 50 μm if $n_0 = 30{,}000$ is required. With a 30-μm I.D. column, baseline separation for $\alpha = 1.3$ is with $k' < 0.12$ not achieved. Here, as in Table IV, baseline separations for $\alpha = 1.3$ are only achieved

TABLE V

NUMBER OF THEORETICAL PLATES, n, GENERATED IN OPEN TUBES OF DIFFERENT INNER DIAMETERS AND FOR VARIOUS k' VALUES

$t_0 = 10$ min. Eluent, water. $D = 1.2 \cdot 10^{-5}$ cm²/sec. $\eta = 1.0 \cdot 10^{-2}$ poise. Room temperature.

I.D. (μm)	k'								
	0	*0.1*	*0.25*	*0.5*	*0.75*	*1.0*	*1.5*	*2.0*	*2.5*
30	76,800	54,344	37,647	25,600	20,124	17,067	13,813	12,126	11,101
50	27,648	19,564	13,553	9216	7245	6144	4973	4365	3996
65	16,360	11,576	8019	5453	4287	3636	2942	2583	2365
85	9567	6769	4690	3189	2507	2126	1721	1511	1453
100	6912	4891	3388	2304	1811	1536	1243	1091	999

TABLE VI

NUMBER OF EFFECTIVE PLATES, N, GENERATED IN OPEN TUBES OF DIFFERENT INNER DIAMETERS AND FOR VARIOUS k' VALUES

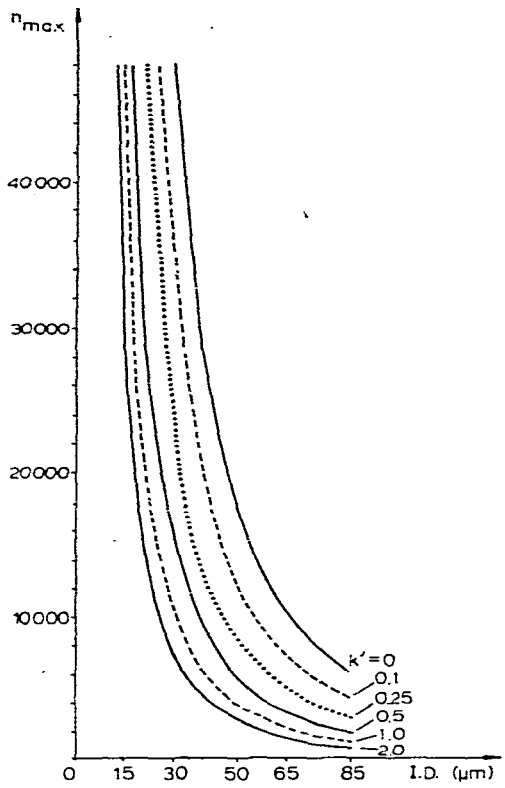
$t_0 = 10$ min. Eluent, water. $D = 1.2 \cdot 10^{-5}$ cm²/sec. $\eta = 1.0 \cdot 10^{-2}$ poise. Room temperature.

I.D. (μm)	k'							
	0.1	*0.25*	*0.5*	*0.75*	*1.0*	*1.5*	*2.0*	*2.5*
30	449	1506	2844	3696	4267	4973	5389	5664
50	162	542	1024	1331	1536	1790	1940	2039
65	96	321	606	787	909	1059	1148	1206
85	56	188	354	460	531	619	671	687
100	40	136	256	333	384	448	485	510

with the conditions above the dashed line in Table VI. With water as eluent only columns with I.D. < 50 μm are of interest.

The methanol–water mixture has its maximum viscosity (0.016 poise) if the volume ratio is around 45–55. Unfortunately, similar eluent compositions are often required if the separation is made with reversed phases. In Fig. 2 the curves of n_{max} *versus* inner diameter of the column are shown for different capacity ratios. The corresponding plate numbers here are four times less than with *n*-heptane as eluent. Therefore, 15 μm I.D. is also included in Fig. 2. The higher the viscosity of the eluent (*i.e.*, the lower the diffusion coefficients), the smaller are the inner diameters required to solve routine problems in LC. On increasing the viscosity of the eluent by a factor of four, the columns have to be elongated by the same factor in order to generate identical plate numbers. The curves in Fig. 2 demonstrate again one of the problems of comparing the efficiency of open tubes and packed columns in LC: in contrast to the well packed columns in open tubes, n is a sensitive function of the capacity ratios.

It was shown in eqn. 10 that for a baseline resolution ($R = 1.5$) the relative retention, α, is only a function of the effective plate number, N. In Fig. 3 both N and α are shown as a function of the inner diameter of the open tube. The eluent here is the same as in Fig. 2. For example, in Fig. 3 it can be seen directly that if two com-



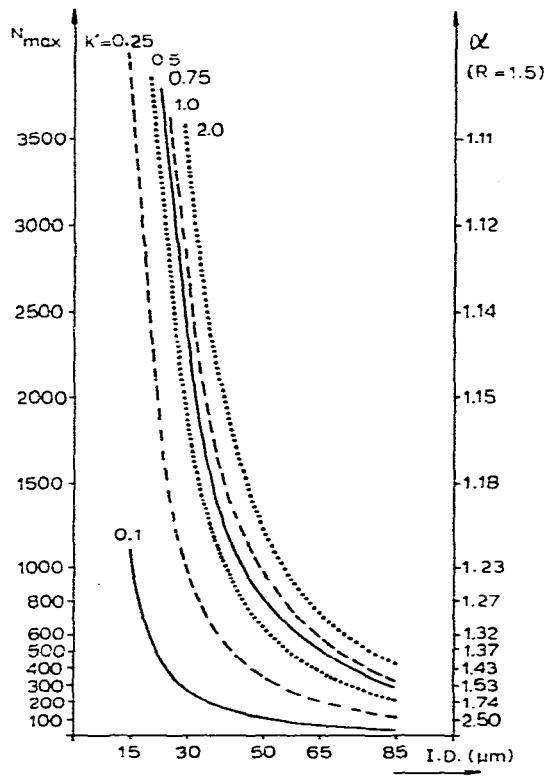


Fig. 2. Maximum number of theoretical plates as a function of the inner diameter of the capillary column for different capacity ratios. Eluent, methanol–water (45:55, v/v). Hold-up time, 10 min.

Fig. 3. Curves of N_{max} and α *versus* inner diameter for different k' values. Eluent, methanol–water (45:55). t_0, 10 min.

pounds emerge around $k' = 0.25$ and baseline resolution is required in a 30-μm I.D. column, then the relative retention of these substances has to be greater than $\alpha = 1.23$. With a 50-μm I.D. capillary column only compounds with $\alpha > 2.5$ can be resolved in the neighbourhood of $k' = 0.1$. Bearing in mind that in all of the calculations $B/u = C_s u = 0$ was assumed, it seems to be evident that for routine separations in LC, open tubes of I.D. 30 μm or less are required if the viscosity of the eluent is about $1 \cdot 10^{-2}$ poise.

Rearranging the Hagen–Poiseuille equation[14,15] for ideal tubes we obtain

$$L = \frac{d^2 \Delta P}{32 u \eta} \tag{12}$$

On combining eqns. 4 and 12:

$$n_{max} = \frac{3 D \Delta P}{f u^2 \eta} \tag{13}$$

or, at room temperature with the approximation described in eqn. 11

$$n_{max} = \frac{3.6 \cdot 10^{-7} \Delta P}{f u^2 \eta^2} \tag{14}$$

In eqn. 14 all of the parameters are given in c.g.s. units (1 bar $\approx 10^6$ dyne). The maximum outlet pressure of the micropumps is limited. If ΔP is constant, n_{max} is inversely proportional to the square of the linear velocity and to the square of the viscosity of the eluent. It can be seen in eqn. 13 that, with ΔP constant, n_{max} will be achieved at u_{Min} (*i.e.*, the minimum of the *h versus u* curve), as described in eqn. 3. Of course, in this u region the B/u term is not negligible. Comparing eqn. 13 or 14 with eqn. 12 it can be seen that if u, η and ΔP are given, the ratio d^2/L has to be constant. Otherwise, for a given d the value of L can be calculated.

If u is small (and consequently h is also small) the column length, L, has to be short in order to achieve reasonable analysis times. A short column and a small h value result in a very small peak volume, and consequently the volume of the detector has to be extremely small. Because of the volume of the detector cell, long columns (and high linear velocities) are required in LC with open tubes. Between the two contradictory statements in this paragraph, a compromise has to be found. The best choice is dependent on the maximum outlet pressure of the pump and the cell volume of the detector. It should be mentioned that the velocity at the minimum of the *h versus u* curve is inversely proportional to the inner diameter of the open tube, as shown in eqn. 3.

SPEED OF ANALYSIS IN OPEN TUBES

Rearranging eqn. 8 and bearing in mind that $t_R = t_0(1+k')$, the maximum number of plates generated per unit time is

$$\frac{n_{max}}{t_R} = \frac{96D}{fd^2(1+k')} \tag{15}$$

or

$$\frac{N_{max}}{t_R} = \frac{96D}{d^2F'(1+k')} = \frac{96D}{d^2F^*} = \frac{n_0}{t_0F^*} \tag{16}$$

where

$$F^* = F'(1+k') = \frac{1+6k'+11(k')^2}{(k')^2} \cdot (1+k') \tag{17}$$

The factor F^* as a function of k' is given in Table I and has its minimum at $k' = 0.914$. The optimal speed of analysis, defined in terms of the number of effective plates generated per unit time, is achieved in this capacity ratio region. It should be remembered that with packed columns the maximum of N/t_R is generated with $k' = 2$ if n is not a function of k', because the $(k')^2/(1+k')^3$ *versus* k' curve has its maximum at this point.

The assumption in this paper is that $u \gg u_{Min}$. Consequently, the speed of analysis is independent of the velocity of the eluent, because h is a linear function of u.

In a 30-μm I.D. tube with *n*-heptane as eluent, analyses are very rapid, as shown in Fig. 4. N_{max}/t_R is extremely low at small k' values, passes through a maximum at $k' = 0.914$ and decreases sharply with increasing capacity ratios. There is only a narrow range of capacity ratios where the optimal speed of analysis is achieved. If only a few compounds have to be separated, a system (*i.e.*, stationary phase, eluent composition and sample) has to be chosen where the compounds emerge in the neighbourhood of $k' = 1$. As was pointed out earlier and as shown in Fig. 4, capacity ratios greater than $k' = 2$ are of limited interest in routine LC if open tubes are to be used.

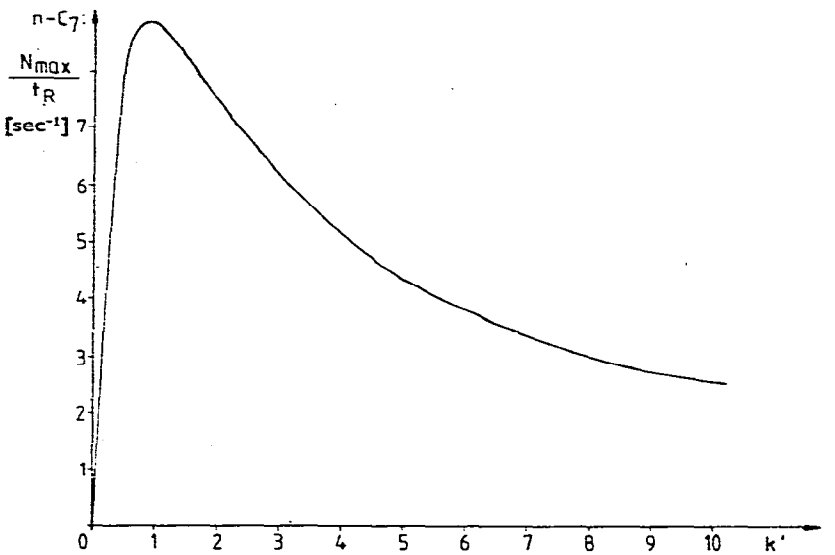


Fig. 4. Maximum speed of analysis, N_{max}/t_R, *versus* k' in a 30-μm I.D. capillary column. Eluent, *n*-heptane.

In Fig. 5 the speed of analysis is shown for water and methanol–water eluents in capillary columns with different inner diameter as a function of k'. Although optimal boundary conditions ($B/u = C_s u = 0$) are assumed, the speed of analysis in the 50-μm I.D. column is again surprisingly low compared with the N/t_R values generated in columns packed with 10- or 5-μm particles.

PEAK VOLUME AND SAMPLING SYSTEM

The minimum peak volume (*i.e.*, $B/u = C_s u = 0$), defined as 4ω, can be calculated with eqn. 5 and with $\sigma = \sqrt{hL}$:

$$\begin{aligned} 4\omega_{min} &= 4\sigma r^2 \pi = \pi d^2 \sqrt{hL} \\ &= 0.32 d^3 \sqrt{\frac{fuL}{D}} \\ &= 0.32 u d^3 \sqrt{\frac{ft_0}{D}} \end{aligned} \tag{18}$$

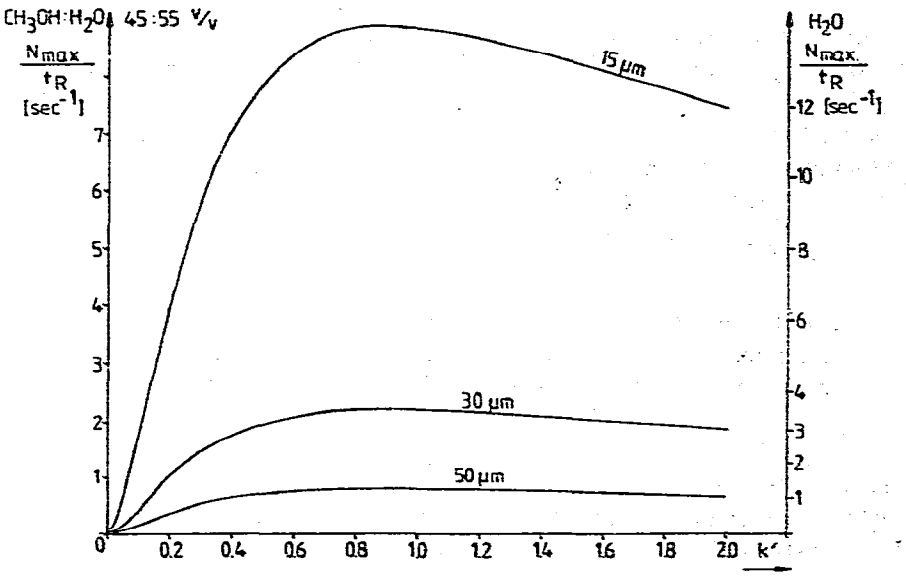


Fig. 5. N_{max}/t_R *versus* k' curves for open tubes with different inner diameters. Eluent, water (right-hand axis) and methanol–water (45:55) (left-hand axis).

N.B., the peak volume is proportional to d^3. Because of the factor f, which is a function of k', the minimum $4\,\omega_{min}$ will be calculated or measured for the inert peak.

It must be pointed out again that ω is a linear function of u, as shown in eqn. 18. If the peak volume has to be increased by a given factor β (because of the problem of the cell volume of the detector), the linear velocity (*i.e.*, the pressure drop over the column) has to be increased by the same factor β. To keep the number of plates and the time of analysis constant, the length of the column therefore has to be increased. Consequently, the pressure drop over the column must increase by a factor of β^2.

Because of the sampling system, peak broadening outside the column and the restricted speed of mass transfer in the stationary phase (*i.e.*, $C_s u > 0$), the measured peak volumes will be greater than that calculated above, and will increase with increasing k'.

NUMBER OF PLATES GENERATED PER UNIT PRESSURE

As pointed out by Golay, the primary advantage of open tubes (also called Golay or capillary columns) in gas chromatography is the substantially greater number of plates generated per unit pressure drop compared with packed columns. High efficiency can then be achieved using long columns. However, the linear velocity must be sufficiently high to obtain acceptable analysis times.

Rearranging eqn. 13:

$$\frac{n_{max}}{\Delta P} = \frac{3D}{fu^2\eta} = \frac{3Dt_0}{fu\eta L} \qquad (19)$$

or with eqn. 9:

$$\frac{N_{max}}{\Delta P} = \frac{3D}{F'u^2\eta} \tag{20}$$

or at room temperature with the approximation described in eqn. 11:

$$\frac{N_{max}}{\Delta P} = \frac{3.6 \times 10^{-7}}{F'u^2\eta^2} \tag{21}$$

In eqn. 21 all of the parameters are again given in c.g.s. units. As shown in the equations above, the number of plates generated per unit time is independent of the inner diameter of the column, because both h and the permeability K are proportional to d^2.

As shown in eqn. 21, $N_{max}/\Delta P$ is inversely proportional to u^2 and η^2 and, because of the change in F', it increases with increasing capacity ratio. In Table VII some $N_{max}/\Delta P$ values are given for different eluents and different velocities when $k' = 1$. This capacity ratio (where $F = 18$) was chosen because the maximum speed of analysis is in this region. Of course, $N_{max}/\Delta P$ is smaller by a factor of about 30 for compounds with $k' = 0.05$ than for the values shown in Table VII. In the second column of Table VII, chromatographic column lengths, L, are given assuming a hold-up time of 10 min. The number of effective plates, of course, decreases with increasing velocity. In Table VII linear velocities of $u < 0.1$ cm/sec are of no interest, because $u \gg u_{Min}$. The problems of low velocities and short columns were discussed earlier.

TABLE VII

MAXIMUM NUMBER OF EFFECTIVE PLATES GENERATED PER UNIT PRESSURE (BAR) WITH DIFFERENT ELUENTS AND FOR $k' = 1$

u (cm/sec)	L^* (m)	Eluent		
		n-Heptane	*Water*	*Methanol–water (45:55, v/v)*
0.1	0.6	125,000	20,000	7810
0.5	3	5000	800	313
1	6	1250	200	78.1
10	60	12.5	2.00	0.781
50	300	0.5	0.08	0.031

* For the calculation of L it was assumed that $t_0 = 10$ min.

The number of theoretical plates generated per unit time, $n_{max}/\Delta P$, is a factor 4.5 smaller for an inert peak than for a retarded peak with $k' = 1$ because of the factor f in eqn. 19. This is also of importance if the efficiencies of capillary and packed columns are compared.

PROBLEMS WITH IDEAL OPEN TUBES IN LIQUID CHROMATOGRAPHY

In Table VIII some typical optimal parameters are given for open tubes without secondary flow for $t_0 = 10$ min. The inner diameters of the tubes ranged from 30 to

100 μm. The $u_{min,0}$ values in the second column were calculated with eqn. 3 for an inert peak, because this value is smaller than that for a retarded peak. Because the B/u term is always neglected, u was chosen so as to be always seven times greater than $u_{min,0}$. When $t_0 = 600$ sec and when u is defined, then the column length L is defined also. The other parameters in this table were calculated with the assumptions and equations described earlier. The effective plate numbers were calculated for $k' = 1$ (*i.e.*, N_1), because the speed of analysis is optimal in this range.

TABLE VIII

PEAK VOLUME, PRESSURE DROP AND SPEED OF ANALYSIS WITH IDEAL OPEN TUBES AND PACKED COLUMNS

Eluent, *n*-heptane. $t_0 = 600$ sec. $D = 3 \cdot 10^{-5}$ cm²/sec. $\eta = 4 \cdot 10^{-3}$ poise.

d (μm)	$u_{min,0}$* (cm/sec)	u (cm/sec)	L (m)	ΔP (bar)	n_0 ($k' = 0$)	N_1 ($k' = 1$)	$n_0/\Delta P$ (bar^{-1})	$N_1/\Delta P$ (bar^{-1})	n_0/t_0 (sec^{-1})	N_1/t_1 (sec^{-1})	$4\omega_0$ (μl)
30	0.14	1.0	6	8.53	192,000	10,667	22,500	1250	320	8.9	0.0386
30	0.14	10.0	60	853	192,000	10,667	225	12.5	320	8.9	0.386
50	0.083	0.6	3.6	1.11	69,120	3840	62,500	3460	115	3.2	0.107
50	0.083	2.0	12	12.3	69,120	3840	5625	312	115	3.2	0.357
100	0.042	0.3	20	0.77	17,280	960	22,442	1247	28.8	0.8	0.430
Packed column											
10**	0.1	0.1	0.6	24	14,630	3659	610	152	24.4	3.1	204

* u_{min} for $k' = 0$.

** Particle size of silica.

In the first row in Table VIII the plate numbers for the inert peak n_0 and the effective plate numbers for $k' = 1$ (N_1) are extremely high, as are the number of plates generated per unit pressure drop ($n_0/\Delta P$ and $N_1/\Delta P$) and the speed of analysis (n_0/t_0 and $N_1/t_1 = N_1/2t_0$). The peak volume, however, is extremely small: $4\omega \approx 0.04$ μl. The cell volume of the detector has to be about ten times greater than 4ω in order to avoid distortion of the peak.

To generate larger peak volumes, but to keep the efficiency and the speed of analysis constant, the column length must be increased by a factor of ten to 60 m and the linear velocity to $u = 10$ cm/sec. As shown in the second row in Table VIII, the peak volume is increased to $4\omega \approx 0.4$ μl (*i.e.*, a cell volume of 0.04 μl is acceptable), but at the same time the pressure drop increases to $\Delta P = 853$ bar. At the moment, it is hardly possible to generate inlet pressures of this order of magnitude with a micropump, and sample injection would also be difficult. In the second row the number of plates generated per unit pressure decreased dramatically. These values are comparable to or worse than those generated in routine LC with packed columns. Shorter columns of 30-μm I.D. and/or lower linear velocities would again result in intolerably small peak volumes.

The next two rows in Table VIII are the corresponding values calculated for open tubes of 50-μm I.D. The problem is again the peak volume. The N_1 and N_1/t_1 values in the fourth row are comparable (*i.e.*, the peak volume is acceptable) and the $N_1/\Delta P$ values are only twice as good as with packed columns.

In the fifth row in Table VIII the inner diameter of the ideal open tube is

100 μm. The number of plates generated per unit pressure drop is, of course, excellent. However, the efficiency and the speed of analysis are poor.

In the last row in Table VIII the corresponding parameters for packed columns are given. These values can easily be achieved experimentally using commercially available columns packed with irregular silica with a particle size of 10 μm. If the relevant parameters calculated for open tubes with acceptable peak volumes are compared with those generated experimentally using packed columns, the advantages of open tubes seem to disappear.

When comparing capillary and packed columns with the help of Table VIII, it has to be re-emphasized that the parameters for open tubes obtained experimentally must be worse than those obtained by calculation, because of the neglected mass transfer term and because of the experimental problems (*i.e.*, peak broadening caused by sampling and extra-column effects). The peak volumes in open tubes as determined experimentally will be greater than the calculated values. This would be advantageous, but the overall picture will remain unchanged, because of the poorer efficiencies.

One possibility for increasing the peak volume would be to inject the eluent continuously between the column outlet and the detector inlet. The standard deviation of Gaussian peak in time units would thereby remain constant. Unfortunately, the inlet and outlet turbulence in this inverse splitting system would decrease the resolution achieved in the column. Further, the tolerable sample sizes for capillary columns of 50-μm I.D. or less is of the order of magnitude of nanograms. If the peak volume is about 1 μl the concentration of the sample at the end of the column would be, on average, less than 1 ppm. Because of the noise level of the UV detector only samples with unusually high molecular extinction coefficients could be so diluted.

PRESSURE LIMITATIONS

Finally, u_{Min} increases with decreasing diameter of the capillary column, as shown in eqn. 3. Because $u \gg u_{Min}$ and because the specific permeability, K, is proportional to d^2, the required pressure will increase sharply with decreasing inner diameter of the open tube. Although the figures in Table VIII are very impressive at low velocities, the pressure will become a limiting factor in LC in capillary columns, especially if micropumps have to be used.

CONCLUSIONS

The optimal parameters for separations by LC in capillary columns can be calculated if it is assumed that the dispersion of inert and retarded peaks can be described using only the $C_m u$ term of the Golay equation. This approximation is acceptable if (a) the inner diameter of the open tube is less than 100 μm, (b) the linear velocity is less than 1 m/sec, (c) the roughness of the wall is negligible, (d) the coil diameter is greater than 5 cm and (e) the flow is laminar. These conditions exclude secondary flow in the laminar region. Important parameters such as n, N, N/t_R, $N/\Delta P$ and peak volumes were calculated as a function of the inner diameter of the tubes, the capacity ratios of the compounds and the properties of the eluent. With the approximation given above, the speed of analysis, defined as the effective number of plates, N, generated per unit time, is independent of the velocity of the eluent. Further,

the number of plates generated per unit pressure drop is independent of the inner diameter of the capillary column. In LC, because of the high viscosity of the eluents and because of the small inner diameter of the open tubes, the $N/\Delta P$ values in capillary columns are comparable to the $N/\Delta P$ values generated in packed columns ($d_p = 10\ \mu m$).

It is shown that $0 < k' < 2$ is the most important range of capacity ratios if either simple or complicated mixtures are to be resolved. It contrast to packed columns in open tubes, h or n is an extremely sensitive function of k' in this range, and consequently only a narrow capacity ratio range gives optimal conditions for the separation.

The results achieved experimentally will always be worse than those calculated. It seems, therefore, that capillary columns with inner diameters greater than 30 μm will be of little practical interest in routine LC.

The extremely small peak volumes (*i.e.*, detection problems) and the required time of analysis will require long columns and high linear velocities. Consequently, the maximum available outlet pressure of the micropump will become a limiting factor. Micropumps are characterized by delivering the eluent at a small but constant flow-rate at high outlet pressures, as is required in LC with open tubes.

In LC with capillary columns, the peak dispersion can only be greater than calculated in this paper, because of the restricted rate of mass transfer in the stationary phase and because of instrumental difficulties. Consequently, it seems probable that open tubes cannot compete with packed columns in LC. This problem will be discussed in a following paper in which experimental results are compared for capillary and packed columns.

The above statement will not be true if columns are built in which the radial mass transfer in the laminar region is speeded up by secondary flow. This could be achieved in a geometrically deformed tube and/or by depositing the solid stationary thin layer in such a way that the wall of the open tube becomes rough. The smaller the inner diameter of the tube the less unevenness of the wall is required to generate secondary flow in a capillary column.

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SYMBOLS

B (cm²/sec)	constant in the Golay equation, longitudinal diffusion
C_m (sec)	constant in the Golay equation, mass transfer in the mobile phase
C_s (sec)	constant in the Golay equation, mass transfer in the stationary phase
d (cm)	inner diameter of the open tube
D (cm²/sec)	interdiffusion coefficient of the sample in the eluent
f	factor defined in eqn. 2

f^*	factor defined in eqn. 7
F'	factor defined in eqn. 9
F^*	factor defined in eqn. 17
h (cm)	height equivalent to a theoretical plate
h_0 (cm)	h at $k' = 0$
h_{min} (cm)	h for a retarded peak, if $B/u = C_s u = 0$
h_{Min} (cm)	h at the minimum of the h *versus* u curve
K (cm^2)	specific permeability
k'	$(t_R - t_0)/t_0$, capacity ratio
L (cm)	column length
n	$(4\,t_R/w)^2$, number of theoretical plates
n_0	n for the inert compound
n_{max}	n for a retarded sample, if $B/u = C_0 u = 0$
N	$(4\,t'_R/w)^2$, number of effective plates
N_{max}	N for a retarded sample, if $B/u = C_0 u = 0$
N_{ne}	$[4Ra/(a - 1)]^2$, necessary number of effective plates defined in eqn. 10
N_1	N at $k' = 1$
P (dyne/cm^2 $\approx 10^{-6}$ bar)	pressure
ΔP (dyne/cm^2 $\approx 10^{-6}$ bar)	pressure drop over the column
r (cm)	radius of the open tube
R	$2(t_{R2} - t_{R1})/(w_1 + w_2)$, resolution
t (sec)	time
t_0 (sec)	hold-up time, or retention time of an inert sample
t_R (sec)	retention time of a retarded peak
t'_R (sec)	$t_R - t_0$, net retention time
u (cm/sec)	cross-section averaged linear velocity of the mobile phase
u_{Min} (cm/sec)	u at the minimum of the h *versus* u curve
$u_{min,0}$ (cm/sec)	u_{min} for the inert compound
w (sec)	peak width at baseline
a	t'_{R2}/t'_{R1}, relative retention
η (g/cm sec or poise)	dynamic viscosity
σ (cm)	standard deviation of a Gaussian peak
ω (cm^3)	$\sigma r^2 \pi \cdot$ peak volume/4 = standard deviation of a Gaussian peak
ω_0 (cm^3)	ω for the inert compound
ω_{min} (cm^3)	ω for a retarded peak, if $B/u = C_s u = 0$

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