77. *The Speed of Analysis by Gas Chromatography.*

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Expressions are derived for the minimum possible analysis times on capillary and packed columns in terms of the separation S and the column-pressure drop Δp. It is shown that there is little to choose between the speed of packed and of capillary columns.

THERE is still some difference of opinion as to whether analysis by gas chromatography is faster on a packed or on a capillary column. Soon after capillary columns were first described [1] it was clear that their use enabled columns of very high theoretical plate efficiency to be operated successfully, and analyses of a given plate efficiency to be carried out much faster than had been possible with packed columns. It was therefore natural that capillary columns were considered to be faster than packed columns, but Purnell [2,3] has claimed that in certain circumstances the packed column may be faster than the capillary. His analysis is based upon the differences in the operating conditions of the two types of column and rests particularly on the difference between the experimentally important separation factor S and the theoretically important plate number N (see equations 1, 2, and 4 below). As we now show, there is little to choose between the two types of column if one evaluates the minimum analysis time consistent with certain experimental limitations.

An isothermally operated gas-chromatographic column, packed or capillary, can be regarded as a system of five degrees of freedom. The most convenient independent variables are: (1) the column length, l; (2) the column radius for a capillary or the particle radius for a packed column, r; (3) the thickness of the liquid film, d, or alternatively the ratio of film thickness to radius, $\rho = d/r$; (4) the linear gas velocity, u; (5) the solubility, α, of the substance being chromatographed or the closely related column capacity coefficient k (see equation 3).

Two other factors can be varied, but for practical reasons they cannot be regarded as truly independent variables, *viz.*, the properties of the carrier gas and of the liquid phase. They enter into the theoretical equations for the speed of analysis in the form of the diffusion coefficients D_g and D_l of substances in the gas and the liquid phase, and the viscosity η of the gas. Change of carrier gas or liquid phase alters these properties discontinuously, but changes of the column temperature and pressure alter them continuously. In practice, however, both the nature of the phases and their temperature and pressure are fixed by considerations other than the attainment of high analysis speeds. We therefore regard them as variables fixed beforehand and we take D_g, D_l, and η as constants.

The number of theoretical plates, which is the basic measure of the efficiency of any column, is denoted by N and is related to the shape of individual chromatographic peaks by any of several well-known formulæ, one of which is

$$N = 8(V_R/w_e)^2 = 8[(V'_R + v_g)/w_e]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V_R = total retention volume from the beginning of the chromatogram; V'_R = retention volume from the " air peak," the net retention volume; v_g = gas phase volume of the column = retention volume of the " air peak "; w_e = peak breadth (in same units as V_R) at 1/2·718 of the maximum peak height.*

* All the mathematical symbols used are summarised in an appendix (p. 441).

[1] Golay, in " Gas Chromatography (Report of Symposium), 1958," ed. Desty, Butterworths, London, p. 36.

[2] Purnell, *J.*, 1960, 1268.

[3] Purnell, *Nature*, 1959, **184**, 2009.

For the purpose of evaluating the efficiency with which a column can separate substances, a more useful quantity is the separation factor S, defined as

$$S = 8(V'_R/w_e)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The net retention volume, rather than the total retention volume, is related directly to the solubility,

$$\begin{aligned} V'_R/v_g = k &= \alpha v_l/v_g \\ &= \alpha\beta d/r = \alpha\beta\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

where v_l and v_g are the volumes of the liquid and the gas phase in the column and β is a constant for any type of column. For a capillary $\beta = 2$; for a packed column $\beta = 3(1 - e)/e$ where $e =$ the porosity of the packed column (fraction of total volume occupied by gas). Generally e is about 0·4 and $\beta \approx 4$. S and N are thus related by the equation

$$N = S[(1 + k)/k]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For a column of length l the height of a theoretical plate (HETP) is

$$H = l/N = (l/S)[k/(1 + k)]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Theoretical equations for H in terms of column parameters already defined have been given by van Deempter (see Desty *et al.*[4]) for packed columns

$$H = 4\lambda r + \frac{2\gamma D_g}{u} + \left\{\frac{1}{25}\cdot\left(\frac{k}{(1+k)}\right)^2\frac{r^2}{D_g} + \frac{2}{3}\cdot\frac{k}{(1+k)^2}\cdot\frac{d^2}{D_l}\right\}u \quad . \quad . \quad (5a)$$

$$= 4\lambda r + \frac{2\gamma D_g}{u} + \left\{\frac{1}{25}\left(\frac{k}{1+k}\right)^2\frac{1}{D_g} + \frac{2}{3}\cdot\frac{k}{(1+k)^2}\cdot\frac{\rho^2}{D_l}\right\}ur^2 \quad . \quad . \quad . \quad (5b)$$

$$= A + B/u + (C_1 + C_2)u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5c)$$

and by Golay [1] for capillary columns

$$H = \frac{2D_g}{u} + \left\{\frac{1 + 6k + 11k^2}{24(1+k)^2}\cdot\frac{r^2}{D_g} + \frac{2}{3}\frac{k}{(1+k)^2}\cdot\frac{d^2}{D_l}\right\}u \quad . \quad . \quad (6a)$$

$$= \frac{2D_g}{u} + \left\{\frac{1 + 6k + 11k^2}{26(1+k)^2}\cdot\frac{1}{D_g} + \frac{2}{3}\frac{k}{(1+k)^2}\cdot\frac{\rho^2}{D_l}\right\}ur^2 \quad . \quad . \quad (6b)$$

$$= B/u + (C_1 + C_2)u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6c)$$

There are four terms in the equation for a packed column, and three in that for a capillary column. They are respectively the contributions of: (A) eddy diffusion due to different paths round particles in a packed column, where λ is a constant of the order of unity; this effect is absent in a capillary column; (B) longitudinal diffusion, where γ is a constant of the order of unity; (C_1) and (C_2) the slowness of transverse diffusion in the gas and the liquid phase respectively. It may be noted that the liquid transverse diffusion term is the same for both packed and capillary columns, while the gas-phase transverse diffusion term is generally greater for capillary columns.

Experimentally (A) is apparently relatively unimportant for packed columns with small particles,[5,6] and for convenience we set $A = 0$, noting that we thereby make the packed column rather more efficient than it would actually be in practice. Since we are

[4] Desty, Goldup, and Whyman, *J. Inst. Petroleum*, 1959, **45**, 287.
[5] Littlewood, in ref. 1, p. 23.
[6] Bohemen and Purnell, in ref. 1, p. 6.

interested in the separation factor rather than theoretical plate number, we replace H by the value given in equation (4*a*):

$$\text{Packed: } S^{-1} = \left(\frac{1+k}{k}\right)^2 \cdot \frac{2\gamma D_g}{ul} + \left\{\frac{1}{25D_g} + \frac{2}{3}\cdot\frac{1}{k}\cdot\frac{\rho^2}{D_l}\right\} ur^2/l \quad . \quad . \quad . \quad (7)$$

$$\text{Capillary: } S^{-1} = \left(\frac{1+k}{k}\right)^2 \cdot \frac{2D_g}{ul} + \left\{\frac{1+6k+11k^2}{24k^2D_g} + \frac{2}{3}\cdot\frac{1}{k}\cdot\frac{\rho^2}{D_l}\right\} ur^2/l \quad . \quad (8)$$

The two equations may be summarised in the form

$$S^{-1} = P/ul + Qur^2/l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The retention time of any substance whose column partition coefficient is k is

$$t = (1+k)l/u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The linear gas velocity is related to column length, the column or particle radius, and the pressure drop Δp across the column by the Poiseuille equation for a capillary tube and by the Kozeny–Carman equation [7] for a packed column. These equations are:

Poiseuille equation: $$u = \Delta p r^2/8\eta l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Kozeny–Carman equation: $$u = (\Delta p r^2/9\eta l)e^2/\mu(1-e)^2$$

$$= f/ae = f/a_g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

where μ is a constant between 4·5 and 5·0 for spheres; f = volume flow rate through column; a = total cross-sectional area of column. Direct experiment [8] shows that for randomly packed spheres the porosity lies between 0·36 and 0·42. This is confirmed by experiments described later for columns packed by the conventional gas-chromatographic procedure. With $e = 0{\cdot}38$ and $\mu = 4{\cdot}8$, equation (12*a*) becomes

$$u = \Delta p r^2/115\eta l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12b)$$

Both equations may be summarised in the form

$$u = r^2/Dl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The variables u and l can thus be replaced by t and D in equation (9), giving

$$S^{-1} = PD/r^2 + Q(1+k)r^2/t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This equation involves the variables S, k, r, Δp, ρ, and t.

The time for analysis can be varied by changing any of the first five variables and can theoretically be reduced to zero. However, this possibility is not of practical importance since it involves making S zero or Δp infinite. In order to obtain a practicable value for the minimum time these two variables must be restricted. One inevitably works with an apparatus which can develop a maximum pressure drop across any column. Since any increase in Δp (*i.e.*, decrease in D) can be made to increase the speed of analysis we can, for the purpose of evaluating the maximum speed, regard Δp as being a constant.

Further, one is always interested in obtaining a given degree of separation between substances. This implies a minimum S. The separation factor required for any two substances has been evaluated by Glueckauf [9] in terms of the desired purity of the two substances and their relative solubilities in the liquid phase. The closer the solubilities and the higher the purity required the greater is the separation factor required. Purnell

[7] Carman, " Flow of Gases Through Porous Media," Butterworths Scient. Publ., 1956.
[8] Carman, *Trans. Inst. Chem. Engineers*, 1937, **15**, 150.
[9] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.

has deduced that the separation factor required, when the peaks are separated by six standard deviations, is approximately

$$S = 36[(\alpha_{12}/(1 - \alpha_{12})]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where α_{12} is the ratio of the solubilities of the two substances.

The problem is therefore to derive the minimum time for the elution of a substance from a column with a given separation factor S and working with a pressure drop Δp. We assume, first, that k and ρ are constant and determine the optimum column radius. This is equivalent to considering the elution of a given substance from a series of columns all containing the same percentage of liquid phase. We then examine how the analysis time at the optimum column radius can be further reduced by altering k and ρ.

Differentiating equation (14) and setting $dt/dr = 0$, we have

$$-2PD/r^3 + 2Qr(1 + k)/t = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

$$t = Q(1 + k)r^4/PD \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16b)$$

Substituting into equation (14), we obtain

$$t = 4PDQ(1 + k)S^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$r^2 = 2PDS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The other parameters can then be evaluated from equations (4*a*), (10), and (13). They are given in Table 1.

The values of H and u evaluated in this way are readily shown to be those for the minimum in the well-known HETP–u curve. Equations (5) and (6) may be written in the form

$$H = 2\gamma D_g/u + [k/(1 + k)]^2 Qr^2u \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$
$$= B/u + Cu$$

The plot of H against u is a curve with a minimum H value given by $H^2 = 4BC$ at a linear velocity given by $u^2 = B/C$; *i.e.*,

$$H^2 = 8\gamma D_g[k/(1 + k)]^2 Qr^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$u^2 = 2D_g[(1 + k)/k]^2/Qr^2 = (2DSQ)^{-1} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

These values are identical with those of Table 1.

TABLE 1. *Columns parameters for minimum analysis times.*

Time: $t = 8\gamma DD_g[(1 + k)^3/k^2]S^2Q$
Radius: $r^2 = 4\gamma DD_g[(1 + k)/k]^2S$
Length: $l^2 = 2r^4SQ/D$
Gas velocity: $u^2 = (2DSQ)^{-1}$
HETP: $H^2 = 8\gamma D_g[k/(1 + k)]^2Qr^2$

$D_{\text{capillary}} = 8\eta/\Delta p$	$D_{\text{packed}} = (43\eta/\Delta p)(1 - e)^2/e^2$	$e = 0{\cdot}38$
$\gamma_{\text{capillary}} = 1{\cdot}00$	$\gamma_{\text{packed}} =$ constant of order of unity	
$Q_{\text{capillary}} = \left\{\frac{1 + 6k + 11k^2}{24k^2D_g} + \frac{2}{3k} \cdot \frac{\rho^2}{D_l}\right\}$	$Q_{\text{packed}} = \left\{\frac{1}{25D_g} + \frac{2}{3k} \cdot \frac{\rho^2}{D_l}\right\}$	

If therefore one has a given Δp and requires a definite S value, and if one can choose the column radius freely, there is no possibility of obtaining a faster analysis by using a longer, wider column with intrinsically a higher S value, even if a high gas velocity is used. Only if one is limited to the available column radii or particle diameters can one hope to increase speed by using too high a gas velocity. In such a situation the column length is

decreased and the velocity increased until the separation has declined to the minimum acceptable value. In view of this, the device described by Desty [10] for winding glass capillaries of any desired radius will be a valuable aid in the experimental approach to high-speed gas chromatography.

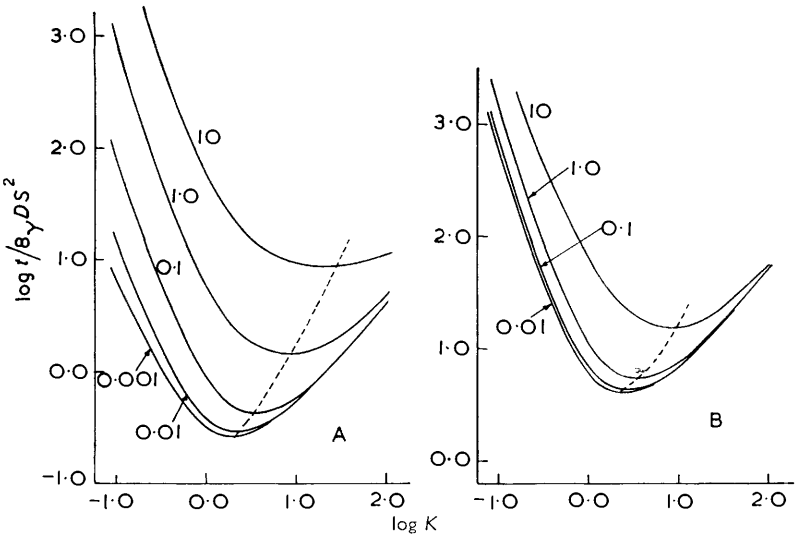
The explicit equations for the minimum time are

Packed: $$t = 8\gamma DS^2 \cdot \frac{(1+k)^3}{k^2} \cdot \left\{0{\cdot}040 + \frac{2}{3}\frac{\rho^2}{k}\frac{D_g}{D_l}\right\} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Capillary: $$t = 8DS^2 \cdot \frac{(1+k)^3}{k^2} \cdot \left\{\frac{1+6k+11k^2}{24k^2} + \frac{2}{3}\frac{\rho^2}{k}\frac{D_g}{D_l}\right\} \quad . \quad . \quad . \quad (23)$$

t can always be reduced by reducing ρ, and a minimum for t is obtained at $\rho = 0$. Variation of k for $\rho = 0$ shows that the ultimate minimum occurs for a value of k close to 2 for both types of column. However, this minimum is unattainable in practice since a value of

Plots of log $(t/8\gamma DS^2)$ *against* log K *for* (A) *packed columns and* (B) *capillary columns.*



$\rho = 0$, with $k = 2$, means that the solubility α must be infinite. In order to obtain minimum times for the two types of column which have any physical significance it is necessary to consider a series of values of ρ, which are within a physically acceptable range from the point of view of the solubilities demanded. For organic vapours in hydrogen and nitrogen at atmospheric pressure, D_g takes the values of approximately 0·6 and 0·1 cm.^{2} sec.$^{-1}$. D_l for organic substances in the type of liquid used for gas chromatography is probably between 5×10^{-6} and 5×10^{-7} cm.^{2} sec.$^{-1}$. The ratio D_g/D_l is thus likely to be in the range of 10^4—10^6. In the Figures the values of $t/8\gamma DS^2$ have been plotted against k for the values of $\rho^2 D_g/D_l$ given against the individual curves. The curves have minima depending upon the value of $\rho^2 D_g/D_l$ from $k = 2$ to $k = 30$. The values of k and α for the minimum times are given in Table 2 for both types of column. One notes that the minimum values of $t/8\gamma DS^2$ for the packed column are lower than for the capillary by factors ranging from 2 for rather thick liquid films to 15 for the thinnest films. However, D is about 15 times larger for the packed column than for the

[10] Desty, *Analyt. Chem.*, 1960, **32**, 302.

capillary. The minimum analysis times are thus comparable on the two columns for very thin films but greater on the packed column for the thicker films. It should, however, be pointed out that this dependence upon relative film thickness results from the different dependence of Q upon k for the two types of column. A unified theoretical treatment of the capillary and packed columns might well eliminate this difference.

TABLE 2. *Values of k for minimum analysis times at different ρ values.*

$\text{Log}_{10}\rho$ for D_g/D_l			$\frac{t}{8\gamma\overline{DS^2}}$	k	Solubility for D_g/D_l		
10^4	10^5	10^6			10^4	10^5	10^6
Capillary columns							
−1·5	−2·0	−2·5	15·3	10	160	500	1600
−2·0	−2·5 *	−3·0	5·5 *	3·3 *	165	520 *	1650
−2·5	−3·0	−3·5	4·2	2·5	400	1250	4000
−3·0	−3·5	−4·0	4·0	2·0	1000	3200	10,000
	zero		4·0	2·0		infinite	
Packed columns							
−1·5	−2·0	−2·5	8·6	30	240	740	2400
−2·0	−2·5	−3·0	1·42	9	220	710	2200
−2·5	−3·0 *	−3·5	0·46 *	4 *	320	1000 *	3200
−3·0	−3·5	−4·0	0·29	2·5	630	2000	6300
−3·5	−4·0	−4·5	0·27	2·0	1700	5300	17,000
	zero		0·27	2·0		infinite	

* Conditions chosen for evaluation of minimum practicable analysis times given in Tables 3 and 4.

The solubility of the chromatographed vapour in the liquid phase at the minimum analysis time for any relative film thickness varies only slightly when the film is thick, but begins to increase rapidly as it decreases below a value for which $\rho^2 D_g/D_l \simeq 10^{-1}$. At this point the time for analysis is only about twice the ultimate minimum. This value thus makes a reasonable compromise between the desirability of a close approach to the ultimate minimum time and the difficulty of meeting the increasingly severe solubility requirements. It may be noted that a slightly higher solubility is required with a packed column for any given approach to the ultimate minimum analysis time than with a capillary column. The difference is however slight and may well result from differences in the methods of derivation of the van Deempter and the Golay equation. The rather high solubilities required for any reasonable approach to the minimum analysis time result from the great difference between the liquid- and the gas-phase diffusion coefficients. If this difference is decreased the solubility required is less. There will therefore be some practical advantage in using nitrogen or argon as carrier gases instead of hydrogen or helium, and in using high pressures (when D_g is lower). Nitrogen, however, has a disadvantage in having a higher viscosity than hydrogen (by a factor of about 2), and since D is proportional to the viscosity one loses some analytical speed if nitrogen is used, but since viscosity does not change with pressure this disadvantage is not encountered when higher operating pressure are used. However, the slight disadvantage of using nitrogen as carrier may be far outweighed by the difficulty of obtaining a high enough solubility to make full use of the advantages of hydrogen or helium. Nevertheless, solubilities of the order of 10^2—10^3 are normal in gas chromatography [11] and there should not be any serious difficulty on this score in approaching the conditions for high speed analysis except when one is dealing with highly volatile substances. For fast analysis of these it will be necessary to work with refrigerated columns. Several liquid phases have already been successfully used by the author for columns operating at −80°.

A rough idea of the minimum practicable analysis times along with the other column dimensions may be obtained by taking values of the parameters η, D_g, D_l, ρ, and Δp. The

[11] Kwantes and Rijnders, in ref. 1, p. 125.

relevant data are given in Tables 3 and 4 for capillary and packed columns. The value of $\rho = 10^{-2.5}$ taken for the capillary column is comparable with the current experimental values and represents a 0·65% by volume coating with liquid phase. The value of $\rho = 10^{-3}$ taken for the packed column represents a coating of approximately 0·2% of the total volume of the column. When using Celite, which has a packed density of about 0·25 g./ml., this is equivalent to a 0·6% loading by weight. This is rather less than is normal in high-efficiency columns but it is not unreasonably small.

From Tables 3 and 4 it is seen that the particle radius for the packed column is some three times the radius of the equivalent capillary, whereas ρ is about three times less. The

TABLE 3. *Capillary-column parameters for minimum analysis times: nitrogen as carrier gas.*

$D_g = 0{\cdot}10$. $\eta = 2{\cdot}0 \times 10^{-4}$. $k = 3{\cdot}3$. $\alpha = 520$. $D_l = 10^{-6}$. $D = 1{\cdot}6 \times 10^{-9}$. $Q = 7{\cdot}4$. $\Delta p = 10^6$ (1 atm.).

(All quantities expressed in c.g.s. units.)

Separation factor	Time for elution (sec.)	Column diam. (mm.)	Column length (cm.)	Gas velocity (cm./sec.)
100	7×10^{-4}	0·0065	0·10	650
1000	7×10^{-2}	0·020	3·2	200
10,000	7	0·065	100	65
100,000	700	0·20	3,200	20
1,000,000	70,000	0·65	100,000	6·5
S	$7 \times 10^{-8}S^2$	$6{\cdot}5 \times 10^{-5}S^{\frac{1}{2}}$	$10^{-4}S^{\frac{3}{2}}$	$6{\cdot}5 \times 10^{3}S^{-\frac{1}{2}}$

TABLE 4. *Packed-column parameters for minimum analysis times: nitrogen as carrier gas.*

$D_g = 0{\cdot}10$. $\eta = 2{\cdot}0 \times 10^{-4}$. $k = 4{\cdot}0$. $\alpha = 1000$. $e = 0{\cdot}38$. $D_l = 10^{-6}$. $\Delta p = 10^6$. $Q = 0{\cdot}57$. $D = 2{\cdot}4 \times 10^{-8}$. $\gamma = 1{\cdot}5$.

(All quantities expressed in c.g.s. units.)

Separation factor	Time for elution (sec.)	Particle diam. (mm.)	B.S.S. mesh	Column length (cm.)	Gas velocity (cm./sec.)
100	0·0013	0·03	420	0·15	600
1000	0·13	0·09	130	5·0	190
10,000	13	0·3	42	155	60
100,000	1300	0·9	13	5,000	19
1,000,000	130,000	3·0	4·2	155,000	6
S	$1{\cdot}3 \times 10^{-7}S^2$	$3{\cdot}0 \times 10^{-4}S^{\frac{1}{2}}$	12·7/(diam.)	$1{\cdot}55 \times 10^{-4}S^{\frac{3}{2}}$	$6 \times 10^{3}S^{-\frac{1}{2}}$

liquid film thicknesses are thus similar. For columns giving an S value of 10^3 the film thickness will be only about 400 Å, although for an S value of 10^5 it is 4000 Å. Condon [12] has recently shown that in a working capillary column a film thickness of about 3000—4000 Å appeared quite stable and was evenly deposited. One might question whether thicknesses of less than 1000 Å could be deposited evenly, but this is till a matter for experiment. With such low liquid-phase loading it appears that normal gas-chromatographic supports such as Celite and firebrick should be replaced by more inert materials such as Nylon or glass beads. The rough porous materials which are generally used are only valuable if a high liquid-phase loading is required. They have the disadvantage that the liquid phase may well be trapped in pores which are relatively inaccessible, leading to larger values of C than would be predicted from the theoretical equation. Further, firebricks and Celite have undesirable adsorptive properties which will become increasingly noticeable as the amount of liquid phase is reduced.

It appears then that there is little to choose between the two types of column as far as practicable maximum analysis speeds are concerned. Both appear to be capable of considerably greater speeds than have so far been attained. Theory indicates that the

[12] Condon, *Analyt. Chem.*, 1959, **31**, 1717.

packed column is likely to be somewhat slower than the capillary especially if it is remembered that the eddy diffusion term has been taken as zero throughout the treatment given above.

We are therefore free to consider which type of column is the best for any type of analysis on grounds other than speed. It is clear that the operation of a capillary column with $S = 1000$ where diameter = 0·02 mm. and $l = 3{\cdot}2$ cm. is going to be exceedingly difficult in practice because of the exceedingly small column volume and the necessity of using an incredibly small sample size and very small injection systems and detectors. With a packed column, the gas-phase volume of the column can be some 100 times greater than that of the corresponding capillary. The sample size, injection system, and detector volume can be correspondingly increased in size. Thus the packed column is certainly the most convenient for analyses requiring values of S up to about 10,000. For higher values of S the size of the packed column makes it unwieldy, and the capillary column has obvious advantages.

Experimental

The Kozeny–Carman equation [7] is known to hold well for spherical particles with the constant $\mu = 5$. The particles used in gas chromatography are not normally spherical and may therefore offer rather different resistances to flow from that predicted by the equation.

In order to test this, columns were prepared by the usual gas-chromatographic procedure containing closely screened fractions of various supports, *viz.*, Celite, firebrick (Moler Products, Colchester), and glass beads. The true porosity of the glass beads was determined by measuring their packed volume and the volume of water displaced by them. Both 60—90 and 2·5—4 mesh beads had a porosity of 0·36—0·38, in agreement with the literature values.[7]

The volume-flow rates through the columns were measured with a soap-bubble flow meter and were linearly proportional to the pressure drop across the columns for all particles studied. The results are presented in Table 5, where the equation is tested by evaluating the viscosity of the gas (oxygen) on the assumption that $\mu = 4{\cdot}8$ and $e = 0{\cdot}38$. For glass beads and firebrick the agreement between the calculated and true values of the viscosity is good, but for Celite the calculated viscosities are low, indicating that the porosity is higher than 0·38. Calculations

Table 5. *The porosity of gas-chromatographic supports.*

Gas, oxygen. Viscosity of oxygen = $2{\cdot}0 \times 10^{-4}$ poise. Porosity assumed = 0·38. $\mu = 4{\cdot}8$.

Material	Mesh B.S.S.	Particle diam. (mm.)	$10^4 \times$ Viscosity by K.–C. eqn.	Calc. porosity
Firebrick	40—43	0·310	1·59	0·40
	60—65	0·203	1·95	0·38
	90—95	0·137	1·98	0·38
	140—150	0·085	1·40	0·41
Glass spheres	60—65	0·203	1·95	0·38
Celite	60—65	0·203	1·09	0·44
	90—95	0·137	0·75	0·47
	140—150	0·085	0·65	0·49

of the porosity assuming $\mu = 4{\cdot}8$, and taking the correct viscosity for oxygen give the values in the last column of the Table. For Celite the calculated porosity increases as the particle diameter decreases. This suggests that the particles are themselves somewhat porous and that the importance of flow through the particles increases as the space between them becomes more and more constricted. For high-speed chromatography diffusion in and out of the Celite granules may become a limiting process and could reduce efficiencies below the theoretically attainable limit.

Conclusions.—(1) There should in theory be no significant difference in the ultimate speeds attainable with capillary and packed columns if they are operated under the same external experimental conditions and if the same separation number is required. (2) For the highest speed, the column of the correct dimensions has to be operated at the gas

velocity which gives the minimum HETP. (3) Hydrogen and helium can give faster analysis than nitrogen and argon if the more severe solubility requirements can be met. (4) The solubility required for maximum speed on a packed column is slightly greater than that required for a capillary column. (5) Maximum speed is obtainable with a coating of roughly 0·5% (by vol.) in a capillary and of 0·2% (by vol.) for a packed column. These represent roughly the same film thickness for equivalent columns. (6) Since such low % coatings are required, it is likely that inert packings such as glass beads, nylon, or Teflon spheres may eventually prove the best supports. Firebrick should certainly not be used for high-performance columns except for the analysis of particular mixtures which are not adsorbed by it. (7) The speed of analysis can be increased by increasing the pressure drop across the column but the average column pressure has little effect upon the speed.

Appendix: Definitions of Symbols

a, a_g, a_l Cross-sectional areas of column, gas phase in column, and liquid phase in column.
α Solubility: concentration of chromatographed substance in liquid phase divided by concentration in gas phase.
A, B, C_1, C_2 Generalised coefficients in plate-height equations defined in equations (5*c*) and (6*c*).
β Constant characteristic of any type of column defined in equation (3).
γ Constant in the van Deempter equation.
d Average film thickness.
D Generalised coefficient in viscosity (equation 13).
D_g, D_l Diffusion coefficients of chromatographed substance in gas and liquid phases.
e Porosity of a packed column.
f Volume flow rate through column.
η Viscosity of carrier gas.
H Height equivalent to a theoretical plate, the HETP.
k Column capacity coefficient: amount of chromatographed substance per unit length of column in liquid phase divided by amount per unit length in gas phase.
l Length of column.
λ Constant in the van Deempter equation.
μ Constant in the Kozeny–Carman equation.
N Number of theoretical plates.
P, Q Generalised coefficients defined in equations 7, 8, and 9.
Δp Pressure drop across column.
r Radius of a capillary column, or radius of particles in a packed column.
ρ Ratio of film thickness to radius: $\rho = d/r$.
S Separation factor defined in equation (4).
t Elution time for any substance.
u Linear gas velocity in column.
v_g, v_l Volumes of gas and liquid phases in column.
V_R Total retention volume.
V_R' Net retention volume: $V_R' = V_R - v_g$.
w_e Peak breadth at a height 1/2·718 of the maximum.

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