GRAPHICAL AND NUMERICAL METHODS FOR SELECTING EXPONENTIAL FLOW PROGRAMMES IN CAPILLARY COLUMN GAS CHROMATOGRAPHY

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SUMMARY

Equations have been derived for predicting the results of exponentially flow programmed flow separations in gas chromatography. Relationships between retention volume, retention time, and a three-parameter flow programme are discussed, and the effects of different forms of the flow programme, as determined by those parameters, are illustrated in several diagrams and simulated chromatograms. Experimental results indicate that the predictive value of the relationships presented is very good.

INTRODUCTION

The flow programming technique for controlling gas chromatographic (GC) separations[1–9] has so far found only limited application, maybe because of the former predominance of packed columns. In packed columns the flow resistance is relatively high and therefore the range over which the flow-rates can be varied is more limited than in capillary columns. The high gas permeability in capillary columns makes it easy to produce fast changes in the flow-rate. An exponential increase of the flow-rate corresponds to a linear temperature programme. Hence exponential flow programming in capillary columns has been developed as an alternative to temperature programming. In flow-programmed GC the linear velocity of the eluting medium varies both with position along the column and with time. It is then not possible to obtain a solution in closed form of the equation that describes the rate of migration of an analyte peak. In order to get an analytical solution, Kelley and Walker[10] assumed that the actual velocity of the carrier gas could be replaced by its average velocity at the current pressure drop in the column. Calculations were carried out for a flow programme in which the inlet pressure increased linearly with time. It was found that the retention time computed from the approximate equation agreed, to within a few percent, with the value obtained from a numerical solution of the exact equation. This result was also verified experimentally.

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The approximation introduced[10] is equivalent to assuming that the corrected retention volume, *i.e.* the retention volume multiplied by the pressure-gradient correction factor, is independent of the flow programme. This concept has been termed the first general rule of flow-programmed GC[1]. Hence from a knowledge or estimate of such volumes it should be possible to predict the positions of the peaks in chromatograms obtained with various flow-rate programmes. Experimental results will be presented here to indicate that retention volumes obtained with exponential flow programming are close to the values obtained under isorheic (constant flow-rate) conditions. The concept of constant retention volume is then used to discuss the influence of the parameters in the exponential flow function on retention time and peak dispersion.

THEORY

The migration rate of a solute peak is governed by

$$\mathrm{d}x/\mathrm{d}t = Ru(x, t) \tag{1}$$

where $u(x, t)$ is the linear velocity of the carrier gas at the position of the peak, x is the distance travelled by the peak at time instant t, and R the retention factor of the solute. If $u(x, t)$ is replaced by the average linear velocity, $\bar{u}(t)$, as suggested in ref. 10, then eqn. 1 can be integrated (L = column length, t_R = retention time):

$$\int_0^L \mathrm{d}x = R \int_0^{t_R} \bar{u}(t)\mathrm{d}t = L$$

or

$$R \int_0^{t_R} \bar{Q}(t)\mathrm{d}t = V_m = RV_R^0 \tag{2}$$

where $\bar{Q}(t)$ is the time-dependent average volumetric flow-rate of the carrier gas, V_m is the interstitial volume of the column, and V_R^0 is the corrected retention volume under isorheic conditions.

Eqn. 2 shows that V_R^0 is independent of the flow programme used provided that the approximation $u(x, t) \approx \bar{u}(t)$ is valid. Thus a knowledge of the V_R^0 values of the components in a sample can be used to find a suitable $\bar{Q}(t)$ that will elute the components within a reasonable time.

The flow-rate is regulated by changes in the inlet pressure. The relationship between the average flow-rate and the inlet pressure, p_i, and the outlet pressure, p_0, of the column is

$$\bar{Q} = K(p_i - p_0)\left(1 + \frac{1}{1 + p + p^{-1}}\right) \tag{3}$$

$$p = p_i/p_0$$

where K is a constant that depends on the dimensions of the column and the viscosity of the carrier gas. When the change in $\bar{Q}$ is moderate, $\bar{Q}$ is approximately proportional to $p_i - p_0$. The flow can then be programmed by a proportional change in the pressure after an experimental determination has been made of the constant of proportionality. Taking $\bar{Q}$ proportional to $p_i - p_0$ is only a fair approximation since the last factor in eqn. 3 varies between 1.33 and 1.0 as p changes from unity to infinity. The approximate relationship may be useful with simple pressure-control systems[2], but full use of eqn. 3 should be made when possible[9].

The basic relationship between the instantaneous flow-rate, $Q(t)$, the retention time, t_R, and the retention volume, V_R, is

$$\int_0^{V_R} dV = \int_0^{t_R} Q(t)dt = V_R \tag{4}$$

Under isorheic conditions, with the average flow-rate $\bar{Q}_I$, the retention volume is given by

$$\int_0^{V_R^0} dV = \bar{Q}_I \int_0^{t_R} dt \qquad V_R^0 = \bar{Q}_I t_R \tag{5}$$

From here on $\bar{Q}$ and V_R^0 will be denoted by Q and V_R, respectively, in the text.

Eqn. 6 gives the exponential relationship between flow-rate and time; we shall call this relationship the "flow function":

$$Q = Q_0 e^{k_q t} \tag{6}$$

The usefulness of an exponentially programmed flow-rate can be further increased if a constant term is added to eqn. 6, which leads to the flow function

$$Q = Q_c + Q_0 e^{k_q t} \tag{7}$$

The symbols used in the flow function are: $Q_0 =$ pre-exponential factor; $Q_c =$ time-independent term of the flow function; $Q_s = Q_c + Q_0$ starting flow-rate; $Q_R =$ retention flow-rate, $i.e.$ the flow-rate when a component with retention time t_R is eluted; $k_q =$ programming rate or time constant. The starting flow-rate is an important parameter, since the efficiency of the column is strongly dependent on the velocity of the carrier gas. An initial flow-rate far from the optimal value results in a reduced separation efficiency.

Substitution of eqn. 7 into eqn. 4 yields

$$\int_0^{V_R} dV = \int_0^{t_R} (Q_c + Q_0 e^{k_q t}) \, dt$$

$$V_R = Q_c t_R + \frac{Q_0}{k_q} (e^{k_q t_R} - 1) \qquad (8)$$

The retention volume calculated from this equation should approximate the corrected retention volume determined under isorheic conditions if the simplification $u(x, t) \approx \bar{u}(t)$ is valid for exponential flow programming[11]. The flow-rates must, of course, be average flow-rates.

In practical work the time of analysis as well as the largest permissible values of the inlet pressure and flow-rate are important constraints. Therefore variations of eqn. 8 will often be needed when selecting the values of the parameters in the flow function. By combining eqns. 7 and 8 at $t = t_R$, the following relationship between V_R and Q_R is obtained

$$V_R = \frac{Q_R - Q_s}{k_q} + \frac{Q_c}{k_q} \ln \left(\frac{Q_R - Q_c}{Q_0} \right) \qquad (9)$$

and when $Q_c = 0$, eqn. 9 reduces to

$$Q_R = Q_0 + V_R k_q \qquad (10)$$

Eqns. 7 and 8 and variations thereof describe the behaviour of a single component. Since flow-programmed elution is used to overcome the general elution problem[12], some measure of the dispersion of the chromatographic peaks will be useful. The capacity factor, k', can be employed for this purpose. In an isorheic separation k' can be calculated from

$$k' = \frac{t_R}{t_m} - 1 = \frac{V_R}{V_m} - 1 \qquad (11)$$

where V_m and t_m refer to an unretained component.

In a flow-programmed separation a pseudo capacity factor can be defined by analogy with the isorheic case:

$$k'_{Fp} = \frac{t_{R,Fp}}{t_{m,Fp}} - 1 \neq \frac{V_R}{V_m} - 1 \qquad (12)$$

Since k'_{Fp} is flow-dependent, it has been called a pseudo capacity factor. Only when $Q_c = 0$ can an explicit relationship

$$k'_{Fp} = \frac{\ln[(k' + 1)V_m k_q Q_0^{-1} + 1]}{\ln(V_m k_q Q_0^{-1} + 1)} - 1 \qquad (13)$$

be found between k'_{Fp} and k'. For this case the flow function may be expressed as

$$Q_R = Q_0 \left(\frac{V_m k_q}{Q_0} + 1 \right)^{(k'_{Fp} + 1)} \qquad (14)$$

EXPERIMENTAL

The gas chromatographs were a Varian 1400 rebuilt for capillary columns[2] and equipped with a flame ionization detector and a Hewlett-Packard 5880A equipped with an electron-capture detector modified for flow programming. The columns were 25 m × 0.3 mm I.D., and the stationary phases were SE 30 and Apiezon L. Gas flow regulation was performed by means of flow programmers described previously[7,9].

RESULTS AND DISCUSSION

Comparison of corrected retention volumes obtained from isorheic and flow-programmed chromatograms

Table I contains the corrected retention volumes of nine chlorinated hydrocarbons with their standard deviations. The V_R values were obtained from isorheic separations and from five differently flow-programmed experiments. Programming rates between 0.04 and 0.32 min^{-1}, and starting flow-rates between 0.2 and 1 ml/min, were used. The largest final flow-rate was 5 ml/min. The difference between the two sets of retention volumes is small and indicates that calculation of V_R from eqn. 8 leads to negligible errors. It is also noteworthy that the two sets of standard deviations are very close, given that the values reported for the flow-programmed runs are based on retention volumes obtained with five different flow programmes. Further experimentation is needed to confirm the small, non-zero values of ΔV_R and their possible trend with V_R.

Fig. 1 shows retention data for the homologous series decane to octadecane. The straight line represents the relationship between V_R and t_R at a constant flow-rate of 1.2 ml/min. The filled circles designate the observed retention times when the hydrocarbons are separated at this flow-rate (Fig. 2). The exponentially rising line has been calculated from eqn. 8 with $Q_0 = 0.5$ ml/min, $Q_c = 0$ ml/min, and $k_q = 0.26$ min^{-1}. These programming parameters were used in the separation shown in Fig. 3. The retention volumes in the isorheic experiment, $V_{R,I}$, were obtained from the corresponding retention times and the constant flow-rate. The experimental points ($V_{R,I}$, $t_{R,Fp}$) designated by open circles in Fig. 1 are seen to fall on the calculated line. Thus, these measurements also indicate that the corrected retention volume is virtually independent of the flow programme.

The flow function

The extended form of the flow function, eqn. 7, offers improved possibilities to adapt the flow to a certain separation problem. With three adjustable parameters the dispersion of the peaks in a chromatogram can be chosen within very wide ranges. Fig. 4 presents some flow profiles, which can be generated by the present flow function. The values of the flow function parameters Q_c, Q_0 and k_q are selected so that the retention volume is 20 ml when the retention time is 10 min. The flow-rate is allowed to increase to 10 ml/min. The initial flow-rate which can be measured in the column is Q_s. The individual values of Q_c and Q_0 can be chosen freely under the condition that Q_s is relatively close to the optimal flow-rate. For $Q_c = 0$ the flow profile is fixed for a certain choice of V_R, k_q, and Q_0 (curve 1). Introducing Q_c leads to increased possibilities for choosing different flow profiles. Curves 2–5 show changes

TABLE I

COMPARISON OF CORRECTED RETENTION VOLUMES DETERMINED FROM ISORHEIC AND FLOW-PROGRAMMED ELUTIONS

Column, 25 m SE 30; carrier gas, nitrogen; column temperature, 190°C; $V_{R,I}^0$ = isorheic retention volume; $\sigma(V_{R,I}^0)$ = standard deviation of $V_{R,I}^0$; $V_{R,Fp}^0$ = average of the flow-programmed retention volumes; $\sigma(V_{R,Fp}^0)$ = standard deviation of $V_{R,I}^0$ and $V_{R,Fp}^0$.

| No.	Compound	Concn. (ng/μl)	$V_{R,I}^0$ (ml)	$\sigma(V_{R,I}^0)$ (ml)	$V_{R,Fp}^0$ (ml)	$\sigma(V_{R,Fp}^0)$ (ml)	ΔV_R^0 (ml)
1	Pentachlorobenzene	3.0	3.94	0.05	4.05	0.06	0.11
2	Technazene	1.5	5.05	0.05	5.19	0.04	0.14
3	α-HCH	2.0	5.53	0.04	5.65	0.03	0.12
4	β-HCH	4.0	5.99	0.06	6.11	0.05	0.12
5	γ-HCH (lindane)	2.5	6.39	0.06	6.52	0.05	0.12
6	Pyrazon	2.0	8.29	0.08	8.38	0.03	0.09
7	Heptachlor	2.0	9.83	0.10	9.91	0.06	0.08
8	Aldrin	2.0	12.03	0.10	12.06	0.03	0.04
9	Heptachlorepoxide	2.0	15.04	0.11	14.98	0.03	-0.06
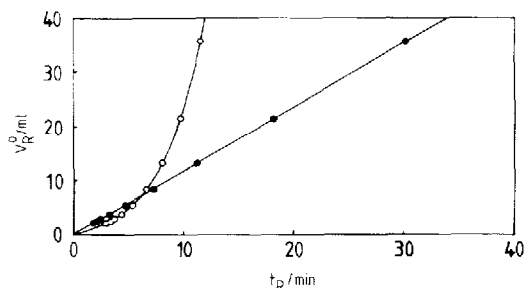
Fig. 1. Corrected retention volume, V_R^0 (ml), as a function of retention time, t_R (min), calculated for the constant flow (straight line) and the programmed flow (curved line) used in the separations shown in Figs. 2 and 3. The circles designate the observed retention times of the separated alkanes.

in the flow profile produced by increased programming rates. Note that Q_0 must be correspondingly reduced in order to keep the final flow-rate below 10 ml/min. Changed signs of Q_0 and k_q (curves 6 and 7) can result in almost linear or even convex forms, but with very limited practical use.

Graphical aids for selecting the parameters of the flow programme

The dispersion of the peaks in a flow-programmed chromatogram can be strongly influenced by the choice of the parameters Q_0, Q_c, and k_q in eqn. 7. Fig. 5 shows simulated separations of nine members of a homologous series in order to demonstrate the effects of changes in the values of the parameters. In the calculations the retention volume of the last eluted component was set to 50 ml, and the adjusted retention volumes were assumed to be exponentially distributed. A time limit of 40 min and a final flow-rate of 20 ml/min were set for each run.

The first two runs are isorheic and the nine components are eluted in 40 min
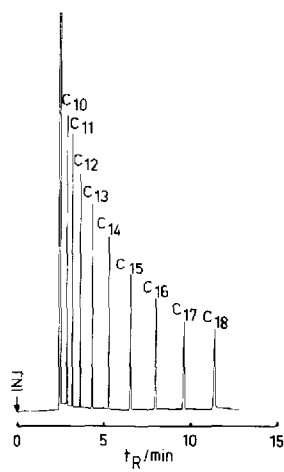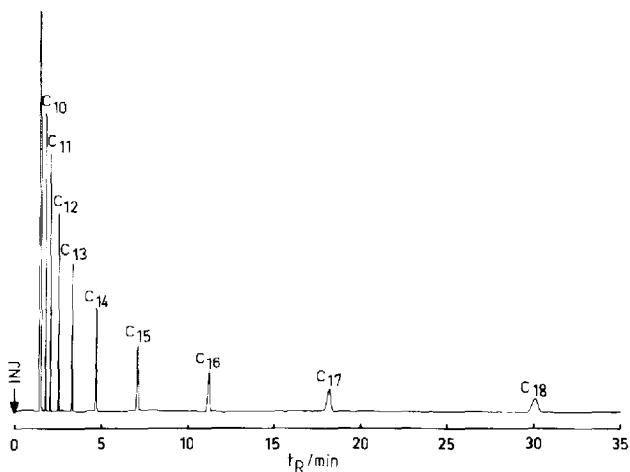

Fig. 2. An isorheic and isothermal separation of a mixture of alkanes, decane to octadecane, with helium as the carrier gas on a 25 m Apiezon L column. Flow-rate, 1.2 ml/min; column temperature, 120°C.

Fig. 3. A flow-programmed separation under the same conditions as in Fig. 2 except for the flow-rate, which was exponentially programmed at the rate $k_q = 0.26$ min^{-1}, from 0.5 to 10 ml/min.
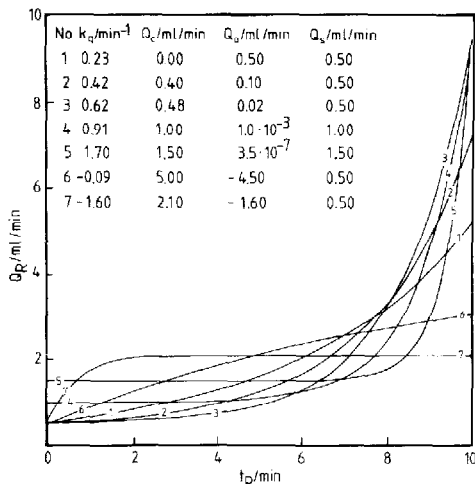
Fig. 4. The retention flow-rate, Q_R, plotted as a function of retention time, t_R. Q_R was calculated from eqn. 7 with the parameters in the inset. These were constrained to give a retention volume of 20 ml for $t_R = 10$ min at a final flow-rate less than 10 ml/min.

Inset parameters for Fig. 4:

No	k_q/min⁻¹	Q_c/ml/min	Q_o/ml/min	Q_s/ml/min
1	0.23	0.00	0.50	0.50
2	0.42	0.40	0.10	0.50
3	0.62	0.48	0.02	0.50
4	0.91	1.00	$1.0 \cdot 10^{-3}$	1.00
5	1.70	1.50	$3.5 \cdot 10^{-7}$	1.50
6	-0.09	5.00	-4.50	0.50
7	-1.60	2.10	-1.60	0.50

Parameters for Fig. 5:

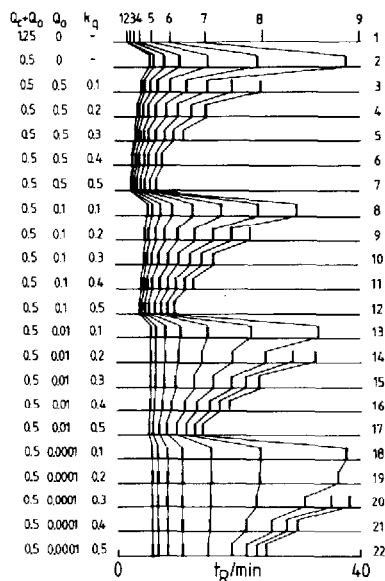| Q_c+Q_o	Q_o	k_q	Run
1.25	0	-	1
0.5	0	-	2
0.5	0.5	0.1	3
0.5	0.5	0.2	4
0.5	0.5	0.3	5
0.5	0.5	0.4	6
0.5	0.5	0.5	7
0.5	0.1	0.1	8
0.5	0.1	0.2	9
0.5	0.1	0.3	10
0.5	0.1	0.4	11
0.5	0.1	0.5	12
0.5	0.01	0.1	13
0.5	0.01	0.2	14
0.5	0.01	0.3	15
0.5	0.01	0.4	16
0.5	0.01	0.5	17
0.5	0.0001	0.1	18
0.5	0.0001	0.2	19
0.5	0.0001	0.3	20
0.5	0.0001	0.4	21
0.5	0.0001	0.5	22

Fig. 5. Different distributions of the peaks in flow-programmed chromatograms illustrated by 22 simulated separations of a homologous series. The nine peaks are exponentially distributed in time when separated isorheically, and the retention volume of the last eluted component is 50 ml. The total time of a run is 40 min, and it is interrupted if the flow-rate exceeds 20 ml/min. The retention data were calculated from eqn. 8 with Q_c and Q_o expressed in ml/min and k_q in min⁻¹.

when Q_s is 1.25 ml/min, whereas at $Q_s = 0.5$ ml/min only seven components will be eluted during the same period, (run 2). The succeeding runs are flow-programmed and they all have a starting flow-rate of 0.5 ml/min. In runs 3–7 Q_c is zero, whereas in runs 8–22 Q_c has a non-zero value and Q_0 is reduced correspondingly. Flow programming results in shorter retention times and in more evenly spaced peaks. In some separations, e.g. runs 16 and 17, the peaks are dispersed at an almost constant interval. A small value of Q_0 will make the separation almost isorheic in the initial stage. Hence the early peaks are almost exponentially dispersed (runs 18–22). As k_q is increased, the last few peaks will have more and more reduced retention times.

The separation of a polychlorobiphenyl sample (Fig. 6) further illustrates some basic features of flow programming. Fig. 6A shows the chromatogram from a non-programmed run with $Q = 0.95$ ml/min. The peak distribution resembles that of a homologous series (cf. Fig. 3 and Fig. 5, run 1). The chromatogram in Fig. 6B was obtained when the flow of the carrier gas was programmed with $k_q = 0.125$ min⁻¹, $Q_0 = 0.5$ and $Q_c = 0$ ml/min. The retention times of late peaks are almost halved compared with those in the isorheic run. Thereby the peak heights are increased and late components more easily detected (cf. Fig. 5, run 3). The peaks in the first parts of the two chromatograms are close together. This can be remedied by decreasing the flow-rate during the initial stages by putting $Q_c = 0.49$ ml/min and, at the same

time, reducing Q_0 to 0.01 ml/min in order to keep the initial flow-rate at 0.5 ml/min. The value of k_q was 0.180 min^{-1}. The result is shown in Fig. 6C. The separation is improved for early peaks, and the rapid increase in the flow-rate at the end of the run compresses the range of the late peaks so that the analysis time is about the same as for the non-programmed run (*cf.* Fig. 5, run 14).

The interdependence of V_R, t_R and the flow function parameters is further illustrated in Fig. 7. The parameters of the flow function have been assigned the same values as in Fig. 5 and the curves have been calculated from eqns. 8 and 9. The derivative dQ_R/dV_R is found from eqns. 7 and 8 to be

$$\frac{dQ_R}{dV_R} = \frac{Q_0 k_q e^{k_q t_R}}{Q_c + Q_0 e^{k_q t_R}} \tag{15}$$

For $Q_c = 0$, Q_R will increase linearly with V_R as in Fig. 7A and the slope of the line equals k_q (*cf.* eqn. 10). When $Q_c \neq 0$, eqn. 15 shows that for small values of Q_0 and k_q the initial slope of the function $Q_R = f(V_R)$ approximates $Q_0 k_q Q_c^{-1}$ (Fig. 7C and D). After a transition range in V_R, the function will tend to be linear for large V_R with slope k_q. In practice Q_R has an upper limit, which has been set equal to 20 ml/min in Fig. 7. As can be seen, for instance, in Fig. 7A the upper limit for Q_R may be reached before all components have been eluted if k_q is assigned a large value. Compare also the number of analytes eluted in runs 3–7 in Fig. 5. The slope of the curves showing t_R as a function of V_R is given by

$$\frac{dt_R}{dV_R} = \frac{1}{Q_R} = \frac{1}{Q_c + Q_0 e^{k_q t}} \tag{16}$$

The initial slope is seen to be Q_s^{-1}. Hence there is an initial period, the length of which depends on the values of Q_c, Q_0 and k_q, when the elution is more or less isorheic (Fig. 7C and D). The retention times are then governed by Q_s. The t_R values of the first few peaks in Fig. 5 are seen to be quite similar. This is due to the fact that Q_s has the same value in runs 2–22. At large retention volumes (dt_R/dV_R) is approximately equal to $(Q_0 e^{k_q t_R})^{-1}$. Analytes with exponentially distributed retention volumes will then yield equally spaced peaks (cf. runs 2, 17 and 22 in Fig. 5). The dispersion of these peaks can be effected mainly by k_q, whereas the influence of Q_0 is small, as can be deduced from Fig. 5.

The dispersion of the chromatographic peaks can also be discussed in terms of the pseudo capacity factor, k'_{Fp}, defined by eqn. 12. An explicit relationship between k'_{Fp} and k' can be found only when $Q_c = 0$ (eqn. 13). The relationship is shown for $Q_0 = 0.5$ ml/min and $V_m = 1.8$ ml in Fig. 8. The difference between the two capacity factors is moderate at values less than 2, particularly at small values of k_q. Hence the appearance of the isorheic and flow-programmed chromatograms will be similar. For components with large capacity factors (10–20) the corresponding pseudo capacity factors only reach values in the range 2–6. Thus late peaks, which tend to be more and more dispersed in a non-programmed chromatogram, will appear at more regular intervals with an exponentially programmed flow. In other words, exponential flow programming is a technique that partly solves the general elution problem.[12]
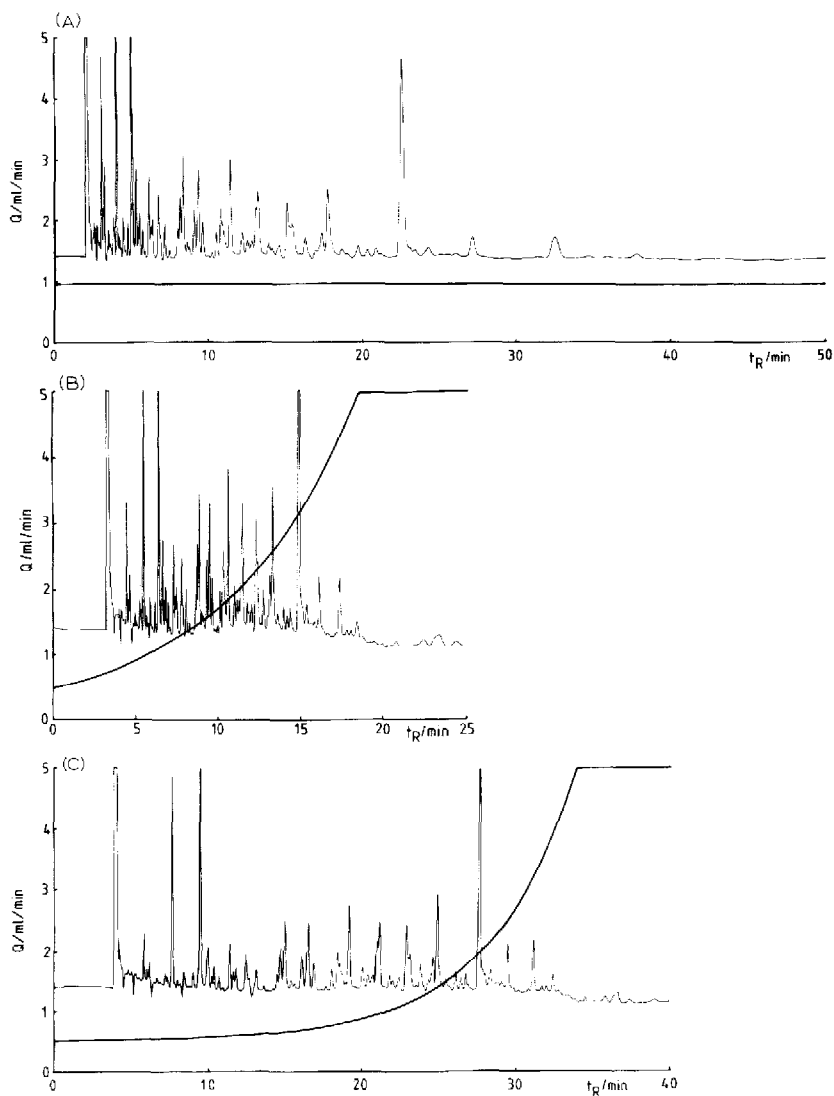
Fig. 6. Separation of a polychlorobiphenyl sample on a 25 m SE 30 column at 180°C. (A) Isorheic with $Q = 0.95$ ml/min; (B) flow-programmed with $k_q = 0.125$ min^{-1}, $Q_0 = 0.5$ and $Q_c = 0$ ml/min; (C) flow-programmed with $k_q = 0.180$ min^{-1}, $Q_0 = 0.01$ and $Q_c = 0.49$ ml/min.

As discussed in the preceding paragraphs, the retention times of components with small retention volumes will largely be governed by the initial flow-rate. The t_R values of late peaks, on the other hand, will increasingly be determined by Q_0 and k_q. It is then of interest to study the relationship between Q_0 and k_q for present values of V_R and t_R. The relationship is found by transforming eqn. 8 to

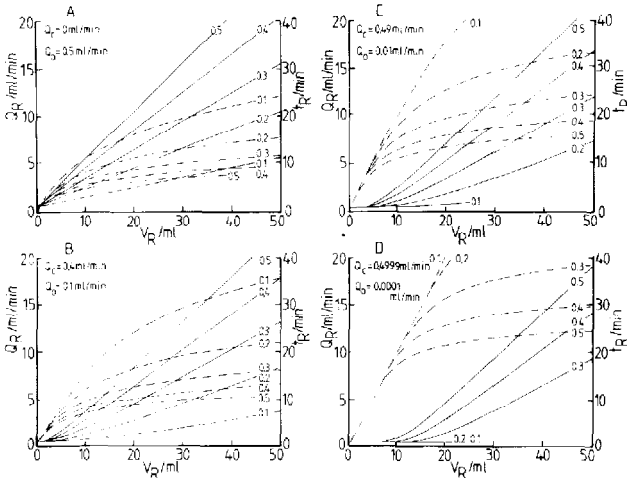$$Q_0 = \frac{(V_R - Q_c t_R)\, k_q}{e^{k_q t_r} - 1} \tag{17}$$

Fig. 7. Graphical presentation of the relationships between retention flow-rate, Q_R, retention volume, V_R, and retention time, t_R, under different starting conditions and programming rates. The continuous curves represent $Q_R = f(V_R)$ and the dashed curves $t_R = f(V_R)$. The graphs were calculated from eqns. 7 and 8. The numbers, 0.1–0.5, on the curves give the value of k_q in min^{-1}.

and it is shown in Fig. 9 for a wide range of retention volumes and retention times. The influence of Q_c has been neglected ($Q_c = 0$). If, as an example, an analyte with $V_R = 20$ ml is to be eluted in 10 min and Q_0 chosen to 0.5 ml/min, then from Fig. 9 it is found that this choice fixes k_q to be 0.23 min^{-1}. For a lower value of Q_0, say 0.3 ml/min, k_q must be increased, in this case to 0.31 ml/min.

The largest flow-rate, Q_{max}, that can be allowed is dependent on the bore and length of the capillary column as well as the nature of the eluting gas. It is usually in the range 2–10 ml/min. In Fig. 9, corresponding values of Q_0 and k_q yielding certain values of Q_{max} are connected by dashed lines. In the example the retention flow-rates will be ca. 5 and 7 ml/min, respectively.

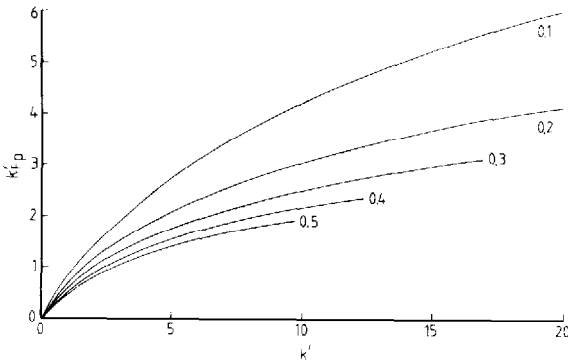Diagrams of the kinds presented in Figs. 7–9 are useful for finding tentative

Fig. 8. The relationship between the capacity factor, k', and the pseudo capacity factor for flow-programmed separations, k'_{Fp}, defined by eqn. 12. The curves were calculated from eqn. 13 with $Q_0 = 0.5$ ml/min and $V_m = 1.8$ ml. The values of k_q in min^{-1} are shown beside the curves. The largest flow-rate was restricted to 10 ml/min, which causes the curves to have different lengths.
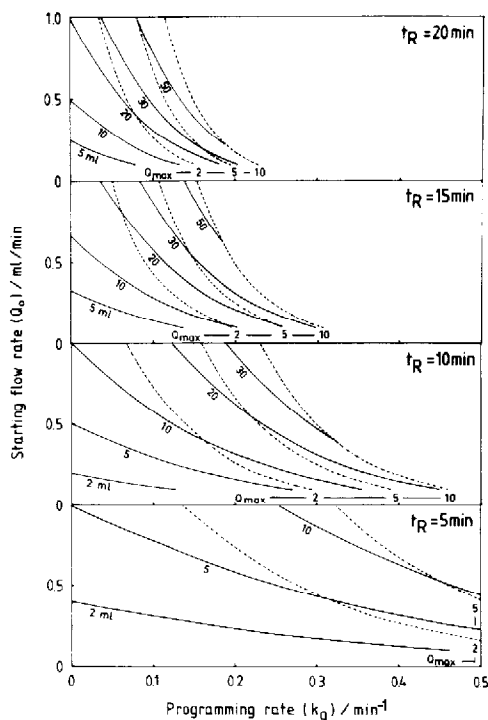
Fig. 9. The pre-exponential factor, Q_0, plotted as a function of the programming rate, k_q, for four constant retention times, t_R, between 5 and 20 min, and constant retention volumes, V_R, in the interval 2–50 ml. The dashed lines show the limits for final flow-rates, Q_{max}, of 2, 5, and 10 ml/min.

values of the parameters in the flow function. The final choice can then be made from simulated chromatograms as presented in Fig. 5.

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