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CONTINUOUS CHROMATOGRAPHY ON A PACKING OF PLASTIC FIBRES

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SUMMARY

Continuous chromatography has been studied on a bunch of plastic fibres used as mobile stationary phase. The effect of fibre velocity on peak velocity was determined by elution chromatograms. The relation obtained can be used for continuous separations.

It was demonstrated that the decreasing theoretical plate numbers of peaks coming from moving fibre are due to the decreasing peak velocities. In spite of this the resolution increases.

INTRODUCTION

The first continuous chromatograph was made by Berg for the separation of light hydrocarbons from natural gas[1]. Several continuous chromatographs have been constructed with the application of the so-called "moving bed" counter-current technique, but only for preparative purposes[2,3]. The porous material (*e.g.* active carbon) constituting the packing gravitates downwards while the carrier fed in at the bottom streams upwards. A multicomponent mixture fed in continuously at the middle of the column separates into two fractions. The weakly sorbed components move upwards with the carrier, the strongly sorbed ones move downwards with the moving bed. In case of two components a complete separation can be obtained by choosing appropriate speeds of the packing and the carrier. The "light" component may be obtained pure and continuously at the upper end, and the "heavy" component at the lower end of the column. The effective separation depends partly on the sorption properties of the components on the stationary phase and partly on diffusion and mass transfer. The inhomogenities caused by the motion of the packing also influence (worsen) the separation. A major disadvantage of this system is the abrasion of the packing owing to continuous motion[2,4]. To eliminate these disadvantages a bunch of polymer fibres has been selected for column packing.

APPARATUS

Our apparatus incorporates the counter-current moving bed technique. The main part of the chromatograph, the column with the moving fibre, is shown in Fig.

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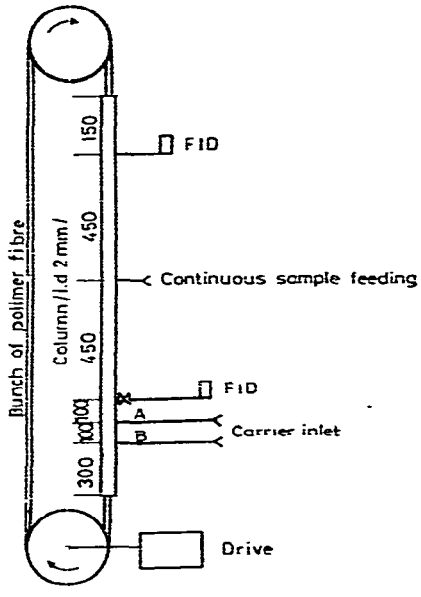

Fig. 1. apparatus for continuous chromatography. A, Carrier gas inlet; B, gas seal.

1. The fibre bunch is made of a plastic filament by the rotation of pulleys. Carrier is fed into the column at point A. As it was impossible to make the fibre packing perfectly homogenous, its flow resistance may change considerably during the motion. In spite of this the carrier flow-rate must be kept constant. This is achieved by another gas stream fed in at point B. The pressure at B is automatically regulated to be identical with the pressure at A. As a result, the carrier fed in at A flows exclusively upwards.

The fibre is moved by a high-powered stepping motor. The pilot frequency determines the fibre velocity, which can thus be changed within wide limits. Sample feeding is at the middle of the column. The flame ionisation detectors (FIDs) enable sensitive detection of the components.

EXPERIMENTAL

The first problem was to find a convenient fibre for chromatographic use. There are two main requirements: the fibre must act satisfactorially as a chromatographic stationary phase, and it must have a low coefficient of friction.

Polyester, nylon, viscose and polyacrylonitrile fibres have been tested, and viscose has been found the most suitable for our purposes. Using this fibre we could easily separate hydrocarbon mixtures without partition liquid. This filament is cylindrical and has a diameter of 15–20 μm. The internal diameter of the column is 2 mm. A good tight fit was achieved with a bunch of 6500–9500 filaments. To realise effective continuous separation, the influence of the velocity of the fibre on separation of the mixture has to be determined. As a model, a mixture of *n*-hexane and *n*-heptane vapours was used. Elution chromatograms were studied, because this is the simplest

way of determining peak velocities (ratio of column length to retention time). The sample was 10–50 mm^3 of air, saturated with *n*-hexane and *n*-heptane and containing *ca.* 1 mm^3 of methane to produce an air peak. Chromatograms were produced with different fibre velocities at a constant carrier flow-rate. These chromatograms are shown in Fig. 2. The velocity of the fibre varied from 0 to 64.5 cm/min. As fibre velocity increases so the peaks separate better and the resolution improves. On chromatogram (e) in Fig. 2 the *n*-heptane peak "disappears" from the upper detector and can be found at lower detector. At higher velocities of fibre (i and j in Fig. 2) *n*-hexane "disappears" at the top and appears at the bottom. So in this case at the lower detector the first peak is *n*-heptane and the second one is *n*-hexane.

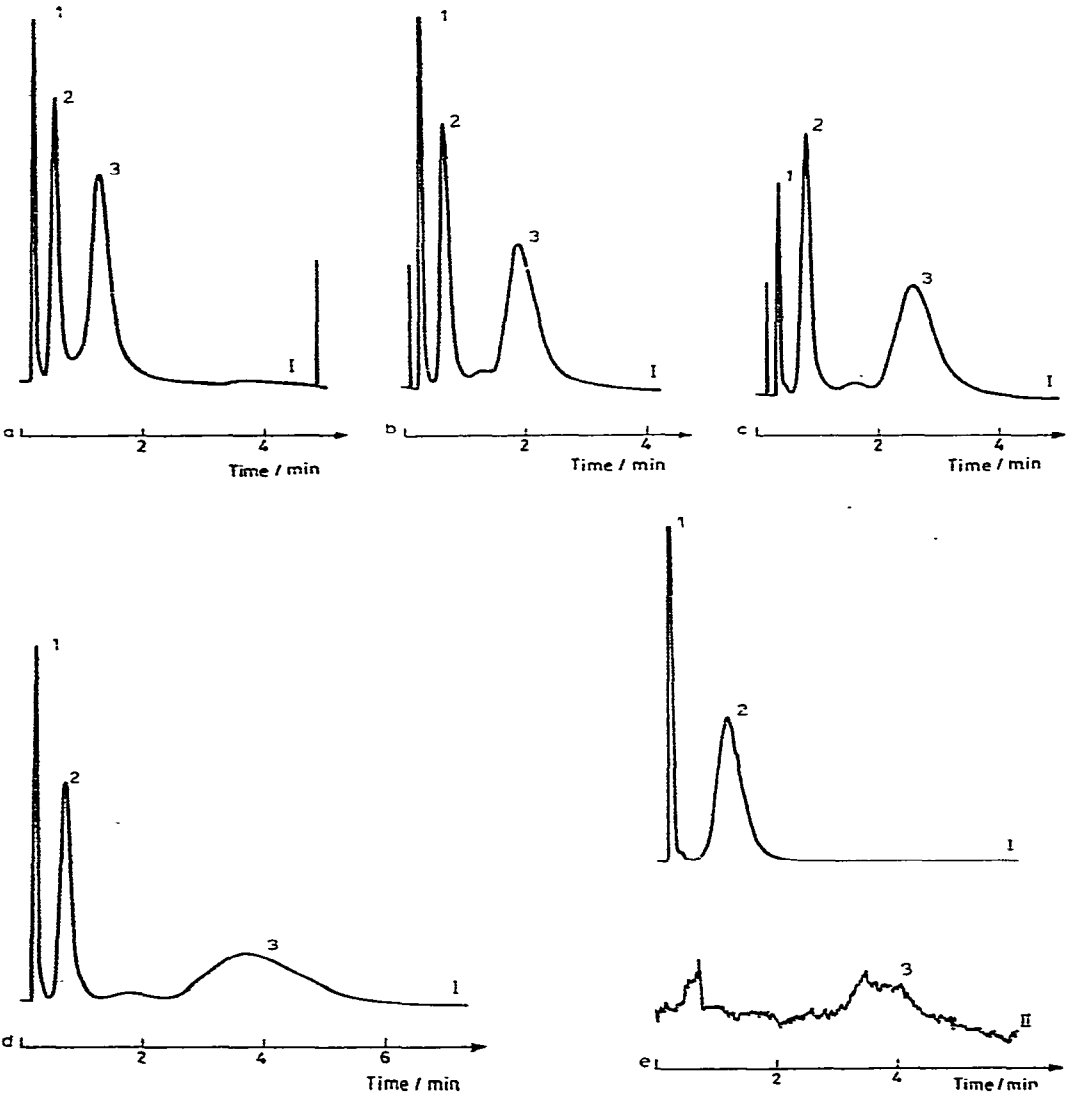

Fig. 2.

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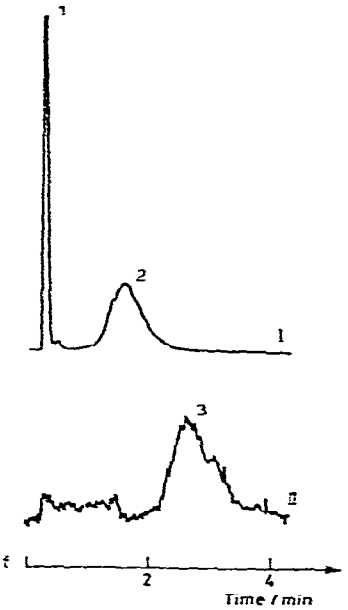
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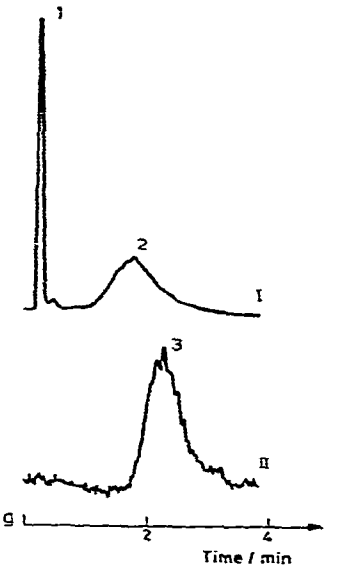
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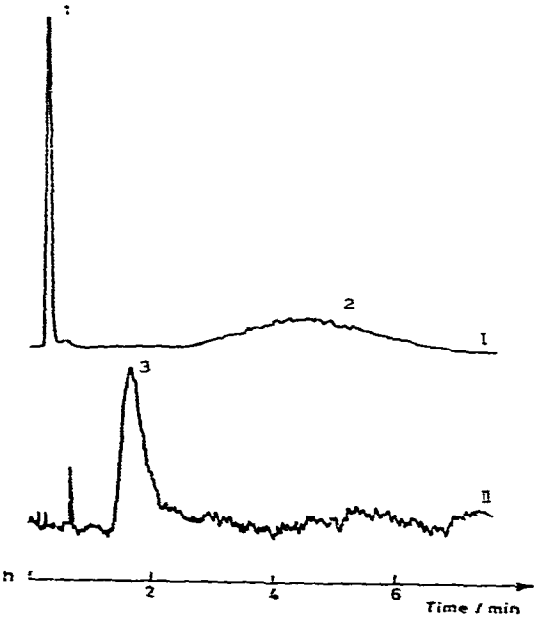
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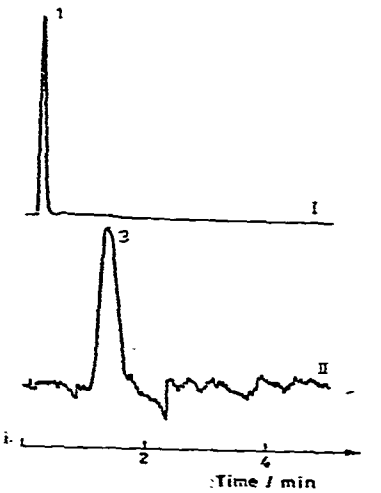
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Fig. 2.

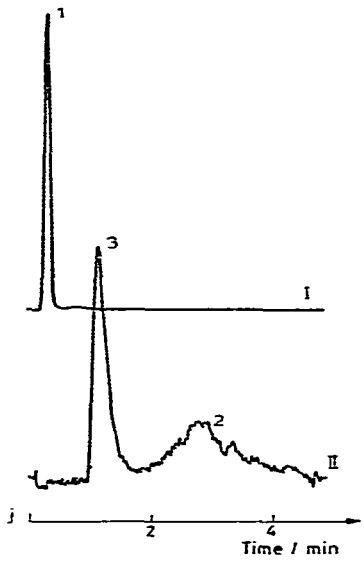


Fig. 2. Chromatograms of mixtures of *n*-hexane and *n*-heptane on stationary and moving fibre. 1 = Air peak; 2 = *n*-hexane peak; 3 = *n*-heptane peak; I = signal of upper detector; II = signal of lower detector. a–j, see Table I.

RESULTS

The virtual velocity of peaks can be determined from the chromatograms. Table I contains these values (v_v) for *n*-hexane and *n*-heptane as a function of fibre velocity (v_f). Fig. 3 shows a plot of v_v against v_f. The points lie on straight lines with the same slope for both components. The lines are described by the common equation

$$v_v = c_1 v_0 - c_2 v_f$$

where v_0 is the peak velocity on stationary fibre, and c_1 and c_2 are empirical constants; in our case $c_1 = 1.06$ $c_2 = 0.82$. This is not valid at $v_f = 0$ owing to deformation of the fibre caused by friction between the packing and the column wall. In the case of a two-component mixture, optimal separation is achieved when the "light" component moves upwards with the same velocity as the "heavy" one moves downwards, so that $v_{v1} = v_{v2}$. In this case the optimal fibre velocity is $v_f = \frac{c_1}{2c_2}(v_{o1} + v_{o2})$. Knowing c_1 and c_2 for a fibre bunch and using the data obtained on stationary fibre, we can determine the fibre velocity optimal for continuous separation. For example, if the peak velocity of *n*-hexane on stationary fibre is $v_{o1} = 38.9$ cm/min, and of *n*-heptane is $v_{o2} = 16.6$ cm/min, then for $c_1 = 1.06$ and $c_2 = 0.82$, we have $v_f = 35.9$ cm/min. The values of c_1 and c_2 depend only on the fibre bunch. So if c_1 and c_2 are known, the optimal fibre velocity can be calculated for any other mixture, by measuring only v_0 on stationary fibre.

Fig. 4 shows the chromatogram of the continuous separation of mixture of *n*-hexane and *n*-heptane. A continuous stream of nitrogen saturated with vapours of

TABLE I

VARIATION OF VIRTUAL PEAK VELOCITY WITH FIBRE VELOCITY

Mixture, *n*-hexane and *n*-heptane; packing, viscose fibre, 9500 filaments diameter 15 μm; column diameter, 2 mm; column length, 45 cm; carrier, nitrogen at 2.8 cm^3/min; temperature, 25°C.

	Fibre velocity (v_f/cm/min)	*n-Hexane*				*n-Heptane*			
		Virtual velocity (v_v/cm/min)	*Velocity calculated* (v_{vc}/cm/min)	*Theoretical plate number, N*	*Theoretical plate number calculated, N_c*	*Virtual velocity* (v_v/cm/min)	*Velocity calculated* (v_{vc}/cm/min)	*Theoretical plate number, N*	*Theoretical plate number calculated, N_c*
a	0	38.9	–	92	92	16.6	–	90	90
	3.6	38.1	38.3	80	91	14.3	14.6	74	77
b	7.2	35.1	35.3	76	84	11.7	11.7	63	63
c	10.8	32.1	32.4	75	77	8.8	8.7	61	48
d	14.4	29.9	29.4	75	71	5.8	5.8	23	31
	18.3	26.1	26.2	66	62	–	2.6	–	–
	22.4	23.5	22.8	58	56	–	– 0.8	–	–
e	29.4	18.2	17.1	38	43	– 7.7	– 6.5	–	–
f	33.4	13.8	13.8	37	33	–11.4	– 9.8	30	–
g	36.7	11.9	11.1	23	28	–13.2	–12.5	43	–
h	43.6	4.7	5.5	18	11	–21.2	–18.2	38	–
i	51.1	–	– 0.7	–	–	–23.2	–24.3	57	–
	57.0	– 9.1	– 5.5	–	–	–28.6	–29.1	67	–
j	64.5	–13.8	–11.6	–	–	–33.8	–35.3	–	–

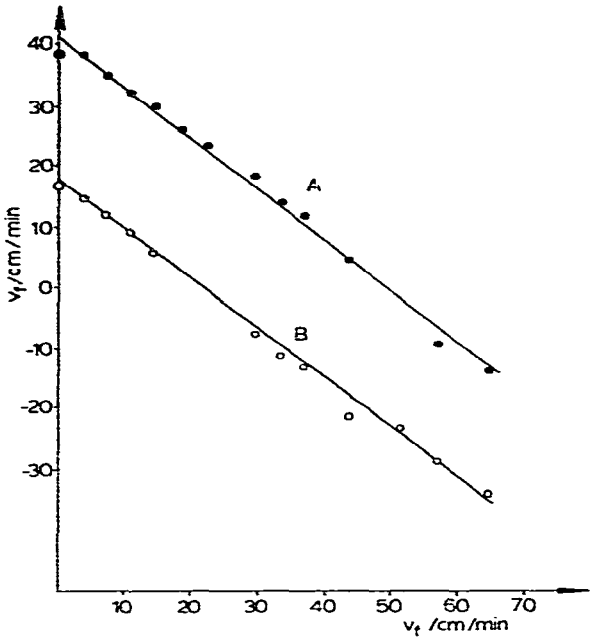


Fig. 3. Plot of virtual peak velocity against fibre velocity for *n*-hexane (A) and *n*-heptane (B).

liquid mixture was fed into the chromatograph at 22°C. After 40 min the temperature was reduced to 0°C, and after a further 20 min the sample feed was stopped. It can be seen in Fig. 4 that changes in the concentrations of *n*-hexane, appearing pure at the top of the column, and of *n*-heptane coming from the bottom, follow the changes in the concentration of the sample. This shows that the apparatus could be used for continuous analysis.

We were able to determine and registrste concentration profiles along the whole column. If the carrier and sample feeding are stopped simultaneously, and the fibre and registration paper velocities are known, every point of the record can be

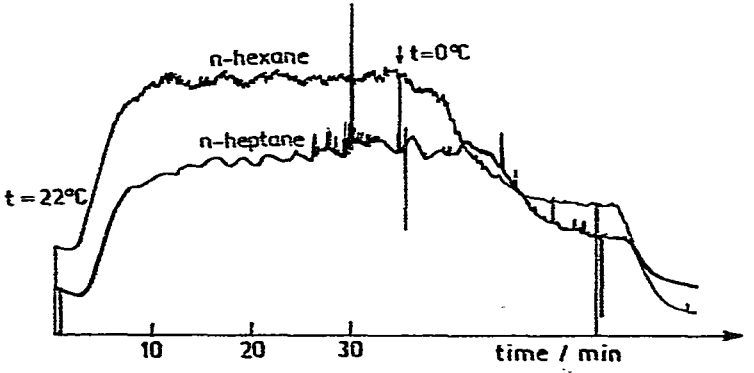
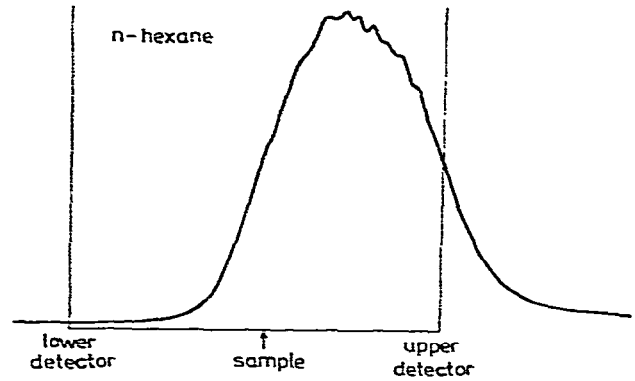
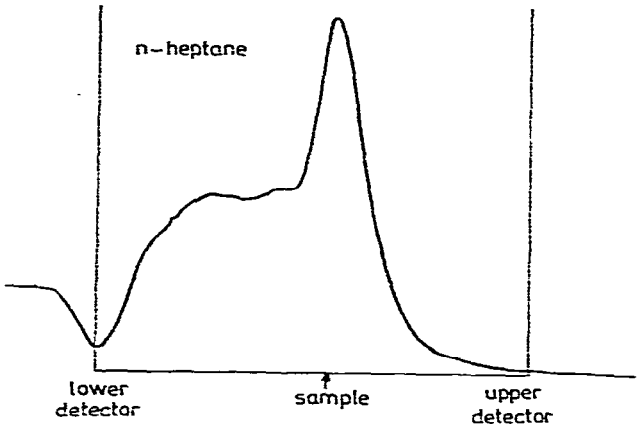


Fig. 4. Chromatograms of pure *n*-hexane and *n*-heptane separated continuously from a mixture of heir vapours.





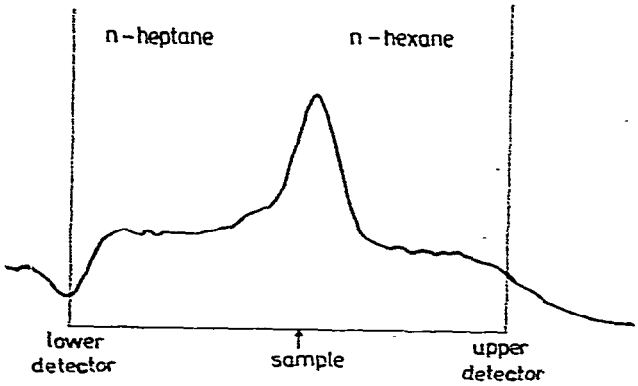


Fig. 5. Stationary concentration profiles on the length of the packing.

correlated to a definite point of the column. Pure *n*-hexane can be found in the upper part of the column (Fig. 5). The concentration of *n*-hexane in the lower part is practically zero. Pure *n*-heptane stays only in the lower part. When a mixture of the two components is fed in, the two previous curves are superimposed. The curves show that the column was long enough for a good separation.

DISCUSSION

Fig. 2 shows that the separation improves with increasing fibre velocity, but visible theoretical plate numbers (N) determined from peak broadening decrease. In the case of *n*-hexane, while the fibre velocity changes from 0 to 43.6 cm/min, N decreases from 90 to 18. For *n*-heptane, N decreases from 90 to 23 while the fibre velocity changes from 0 to 14.4 cm/min.

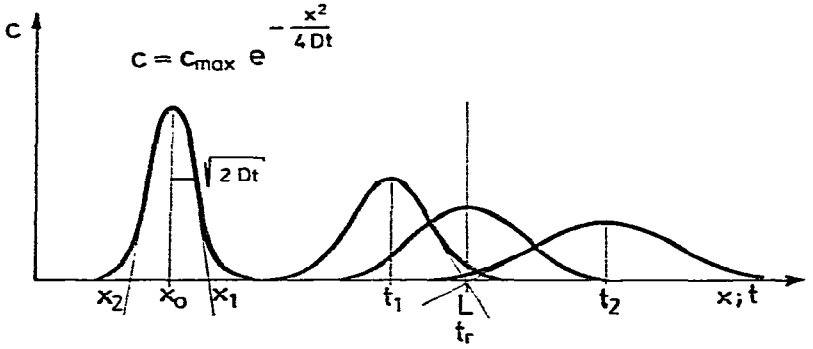


Fig. 6. Distribution of a peak concentration in the column at different lengths and times.

To explain this phenomenon we determined values of N mathematically in the case of moving fibre. Our system of co-ordinates is fixed to detectors in a similar way to chromatograms on recorder papers.

Fig. 6 represents a peak concentration distribution (Gaussian) in the column in function of place (x) and time (t). We determined $x_1 - x_2$ as peak width

$$x_1 = x_0 + 2\sqrt{2Dt}$$

and

$$x_2 = x_0 - 2\sqrt{2Dt}$$

where D is the diffusion coefficient. The peak maximum appears in the detector at time t_r. To determine N we need the peak width in terms of time. Fig. 6 shows that this is the difference between t_2 and t_1; t_1 is the moment at which the sum of the distance of the peak maximum and the peak width is equal to the column length. At time t_2 the difference between the peak maximum and the peak width is equal to the column length:

$$L = v_v t_1 + 2\sqrt{2Dt_1} \text{ and } L = v_v t_2 - 2\sqrt{2Dt_2}$$

Solving the equations one gets:

$$t_2 - t_1 = \frac{\sqrt{8D(8D + 4v_s L)}}{v_s^2}$$

The theoretical plate number is:

$$N = \left(\frac{4t_r}{t_2 - t_1}\right)^2$$

Substituting $t_r = L/v_s$ and $t_2 - t_1$ one obtains:

$$N = \frac{L^2 v_s^2}{4D^2 + 2Dv_s L}$$

In practice, $4D^2$ is less than 1% of the product of $2Dv_s L$, so $4D^2$ can be neglected. Our simplified equation is:

$$N = \frac{Lv_s}{2D}$$

It can be seen that as the virtual peak velocity decreases (as the fibre velocity increases) the "virtual" theoretical plate number necessarily decreases. The value of D can be calculated from the equation $N = \frac{Lv_0}{2D}$, were N is determined graphically from a chromatogram obtained on stationary fibre.

Calculated values of theoretical plate numbers (N_c) on moving fibre from chromatograms of mixtures of *n*-hexane and *n*-heptane are in Table I. They correlate well with the values of N. So we can state that the decreasing plate number is the result of the choice of the system of co-ordinates. The resolution is independent of the co-ordinates; it depends only on the path run by the peak relative to the fibre. This path increases with decreasing virtual velocity of the component.

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