

# ROTATING UNIT FOR PREPARATIVE-SCALE GAS CHROMATOGRAPHY

## PART II. THEORETICAL ASPECTS

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### INTRODUCTION

The main problem in preparative scale gas chromatography is the separation of the greatest possible amount of substance of the desired purity in the shortest time.

As far as the rotating unit previously described<sup>1</sup> is concerned, the problem of maximum feed rate can be dealt within the following three ways:

- (1) establish the maximum feed per column,
- (2) establish the maximum number of revolutions,
- (3) find out conditions under which the time required for the separation is the shortest one.

By making simplifying assumptions the problem may be solved analytically in a rather simple manner. The results, even approximate ones, can then be used to design a larger scale apparatus.

Furthermore, one of our aims was to find out whether there are any critical dimensions, *e.g.* column length, which may limit the applications of the apparatus within the limits of design. This has been achieved by studying a particular mathematical model of our apparatus. A result of some interest—limited to this particular choice of the model—is the relation existing between the retention times of the components when the model is optimized.

Furthermore, some practical hints are given that make it possible to predict some quantities useful for designing apparatus.

To find out the necessary parameters it is sufficient to carry out experiments on a pilot column (fixed) of any convenient length.

### THEORY

In the case of the separation of a mixture of two components 1 and 2, let

$t_1, t_2$  be the retention times ( $t_2 > t_1$ )

$q$  the amount of mixture injected per column

$\nu$  the number of revolutions per unit of time

$N$  the number of columns

$Q$  the total feed rate.

The quantity  $Q$  is defined by:  $Q = q \nu N$ .

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In this relation  $N$  may be neglected,  $Q$  being an increasing function of  $N$ ; on the other hand the total number of columns in the set should be fixed on the basis of other considerations (feed rate, etc.); for simplicity we put  $N = 1$ .

It is necessary to associate the maximum value of  $Q$  with the condition of minimum residence time, that is of obtaining the separation in the shortest time; therefore the function of which one has to find the maximum is

$$f(t) = \frac{Q}{t_2}$$

Let  $\Delta_1$ , and  $\Delta_2$  be the peak widths (measured between the points of intersection of the tangents with the base line), then  $\nu$  is expressed by the relation:

$$\nu = \frac{1}{t_2 + \frac{1}{2}\Delta_2 - (t_1 - \frac{1}{2}\Delta_1)} = \frac{2}{2(t_2 - t_1) + \Delta_1 + \Delta_2},$$

$t_2 + \frac{1}{2}\Delta_2$  is the total time required for the separation.

From the plate theory of chromatographic columns<sup>2,3</sup> it follows that for rather large amounts the peak width changes linearly with the quantity  $q$  of mixture injected per column (Fig. 1), as given by

$$\Delta_1 = K_1 q + b_1; \quad \Delta_2 = K_2 q + b_2$$

where we suppose that  $K_1$  and  $K_2$  are constants independent of retention time and column length, and therefore under the same conditions we may assume:

$$K_1 \simeq K_2 (\mu l^{-1} \text{sec})$$

$K$  may be considered as a "dilution factor" of the samples in the carrier gas, essentially depending on the evaporation rate of the sample (see also experimental part).

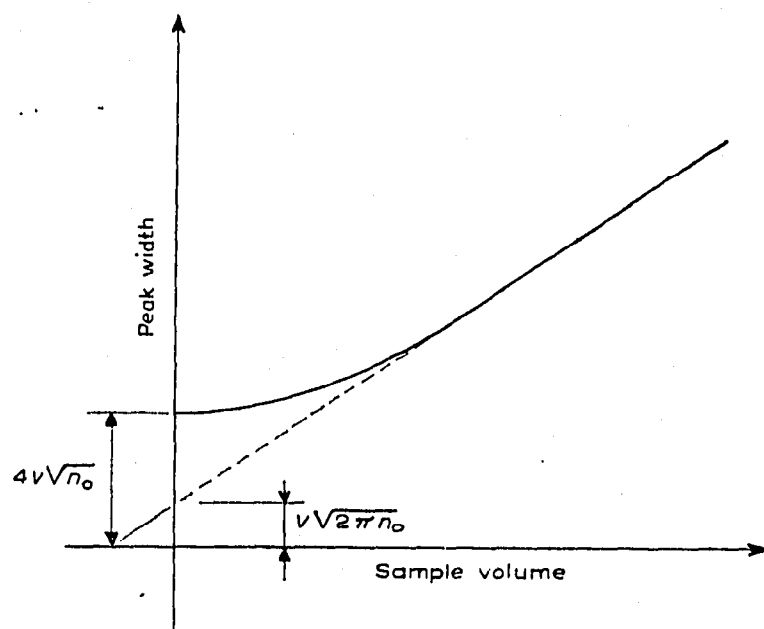


Fig. 1. Plot of peak width against amount of mixture injected.

The theoretical expression of constants  $b_1$  and  $b_2$  is<sup>2</sup>:

$$b_1 = v_1 \sqrt{2\pi n_0}; \quad b_2 = v_2 \sqrt{2\pi n_0}$$

where

$v_1$  ( $v_2$ ) is the effective volume of a theoretical plate given by:  $V_{g1} + V_{l1} k_1$  ( $V_{g1}$  = volume of gas in one theoretical plate;  $V_{l1}$  = volume of stationary phase in one theoretical plate;  $k_1$  = partition coefficient)

$n_0$  is the effective number of theoretical plates for infinitesimally small samples.

The constant  $b_1$  may be expressed as follows:

$$b_1 = v_1 n_0 \sqrt{\frac{2\pi}{n_0}} = V_{R_1} \sqrt{\frac{2\pi}{n_0}}$$

or

$$\bar{b}_1 = t_1 \sqrt{\frac{2\pi}{n_0}} = ct_1$$

where  $V_{R_1} \circ = V_g + V_l k_1$  is the retention volume (measured at the maximum of the peak for infinitesimally small samples), and, for brevity,

$$c = \sqrt{\frac{2\pi}{n_0}}$$

Consequently the expressions for the peak widths, appropriate for our aim, are:

$$\Delta_1 = K_1 q + ct_1; \quad \Delta_2 = K_2 q + ct_2$$

The total width  $\Delta_t$  is (putting  $K = K_1 + K_2$ )

$$\Delta_t = Kq + c(t_1 + t_2)$$

From the definition<sup>4</sup> of "Resolution"  $S_{12}$

$$S_{12} = 2 \frac{t_2 - t_1}{\Delta_t}$$

it immediately follows that:

$$q = (\alpha - \eta)t_2 - (\alpha + \eta)t_1$$

putting, for brevity,

$$\alpha = \frac{2}{KS_{12}}; \quad \eta = \frac{c}{K}$$

Further, the number of revolutions is given by:

$$r = \frac{S_{12}}{1 + S_{12}} \cdot \frac{1}{t_2 - t_1}$$

From the above considerations it follows that the function to study is:

$$f(t) = \frac{Q}{t_2} = \frac{S_{12}}{1 + S_{12}} \cdot \frac{(\alpha - \eta)t_2 - (\alpha + \eta)t_1}{t_2(t_2 - t_1)}$$

The maximum value with respect to  $t_2$  is reached when

$$t_2 = \frac{\alpha + \eta}{\alpha - \eta} t_1 + t_1 \sqrt{\left(\frac{\alpha + \eta}{\alpha - \eta}\right)^2 - \frac{\alpha + \eta}{\alpha - \eta}} \quad (1)$$

With respect to  $t_1$  the behavior of  $f(t_1)$  is monotonic; a three-dimensional representation of the function  $f(t_1, t_2)$  is given in Fig. 2.

As may easily be noted, among the different pairs of values of  $t_1$  and  $t_2$  which satisfy the relation (1) one has to choose the pair having the lowest value of  $t_1$ . This means that in order to obtain the optimum conditions, it is better to employ short columns in spite of the fact that the amount of sample to be injected is low.

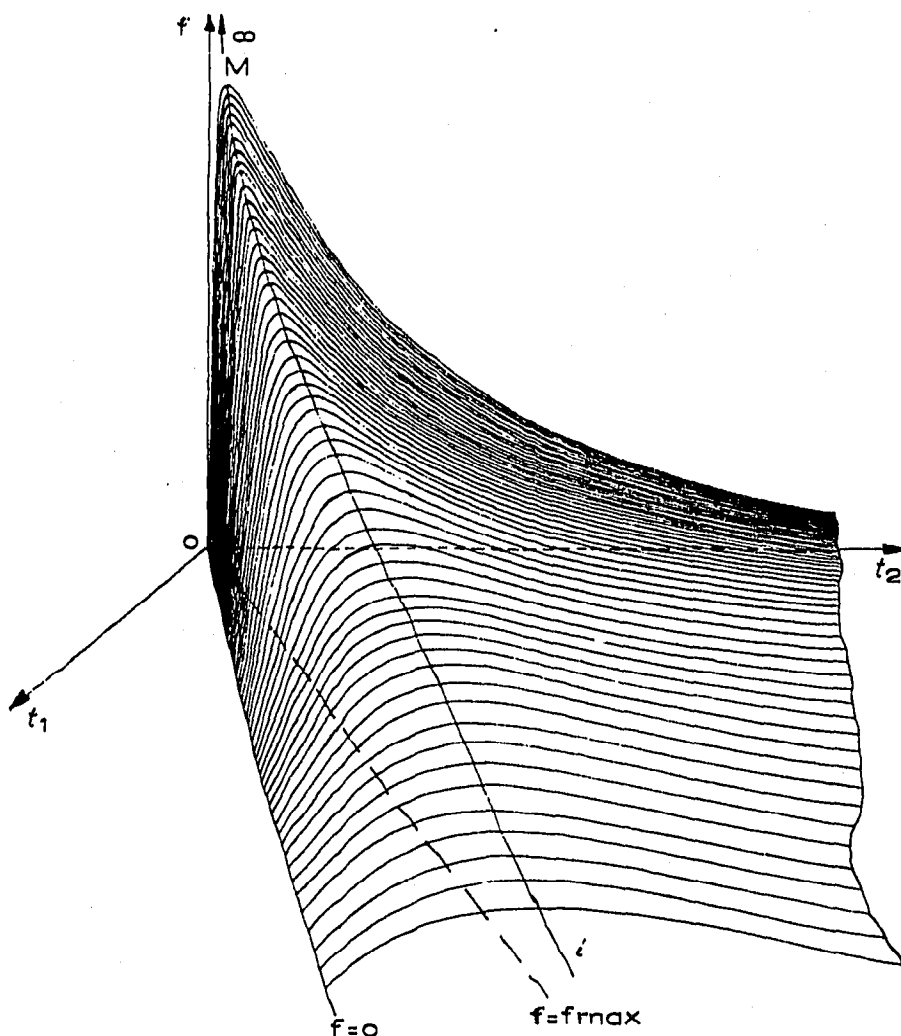


Fig. 2. Three-dimensional representation of the function  $f(t_1, t_2)$ .

Another interesting parameter is the number of plates  $n_0$  corresponding to the maximum condition; according to eqn. (1), this is given by:

$$n_0 = \frac{\pi}{2} \left\{ \frac{(\alpha_{12} + 1)^2 - 2}{(\alpha_{12} - 1)^2} S_{12} \right\}^2 \quad (2)$$

having introduced the "separation factor"

$$\alpha_{12} = \frac{t_2}{t_1} \approx \frac{K_2}{K_1}$$

This expression should be compared with the equation

$$\bar{n}_0 = 4 \left( \frac{\alpha_{12} + 1}{\alpha_{12} - 1} S_{12} \right)^2 \quad (3)$$

which gives the minimum number of plates required for a specific resolution  $S_{12}$ . In Fig. 3 the functions  $n_0$  and  $\bar{n}_0$  are plotted against  $\alpha_{12}$  for  $S_{12} = 1.5$  and  $S_{12} = 1.2$ .

The above theory is presented as a guide for the optimum performance of the rotating unit. However, for practical preparative purposes, instead of requiring

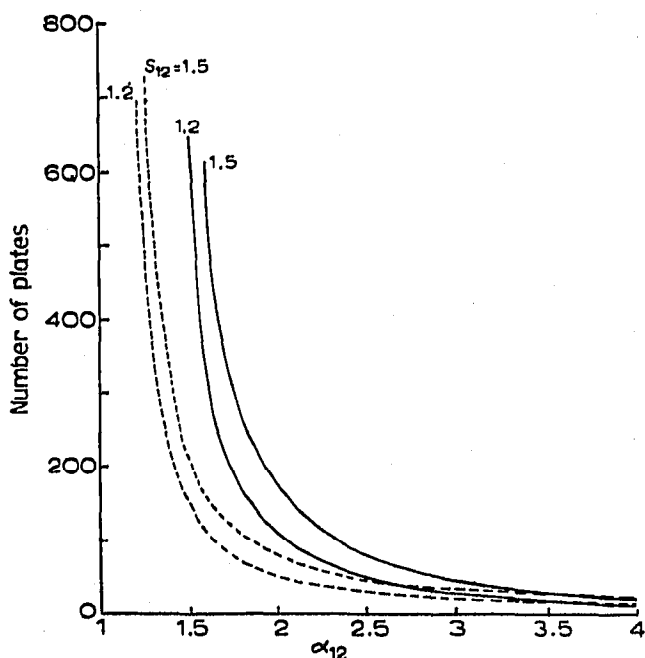


Fig. 3. Plot of the functions  $n_0$  (—) and  $\bar{n}_0$  (----) against  $\alpha_{12}$  for  $S_{12} = 1.5$  and  $S_{12} = 1.2$

minimum residence time in the stationary phase, it may be more profitable to examine the behaviour of feed rate when, for instance, the column length is changed. The explicit expressions of load per column  $q$ , number of revolutions  $\nu$  and load per unit of time  $Q$  are respectively (putting for brevity  $x = c S_{12}$ ):

$$q = (\alpha - \eta)\alpha_{12}t_1 - (\alpha + \eta)t_1 = \frac{t_1}{KS_{12}} [(2 - x)\alpha_{12} - (2 + x)] \quad (\mu\text{l per column}) \quad (4)$$

$$\nu = \frac{S_{12}}{1 + S_{12}} \frac{1}{\alpha_{12} - 1} \frac{1}{t_1} \quad (\text{sec}^{-1}) \quad (5)$$

$$Q = q\nu = \frac{(2 - x)\alpha_{12} - (2 + x)}{K(1 + S_{12})(\alpha_{12} - 1)} \quad (\mu\text{l}\cdot\text{sec}^{-1} \text{ per column}) \quad (6)$$

From eqn. (6), assuming that  $n_0 = l/h_0$ , it is found that

$$Q(l) = \frac{S_{12}}{K(1 + S_{12})} \left( \frac{2}{S_{12}} - \sqrt{2\pi h_0} \frac{\alpha_{12} + 1}{\alpha_{12} - 1} \frac{1}{\sqrt{l}} \right) \quad (6')$$

The plot of this relation is given in Fig. 4.

This function has no maximum and for  $l \rightarrow \infty$ ,

$$Q \rightarrow \frac{2}{(1 + S_{12})K}$$

This equation shows that larger values of  $\alpha_{1,2}$  and  $h_0$  lead to a larger value of  $Q$ .

Other authors<sup>5</sup> have also reached these same conclusions when dealing with high speed gas chromatography in packed columns. Of course, the conditions of temperature, pressure, etc. to obtain the best values of  $\alpha_{1,2}$  and  $h_0$  must be found experimentally.

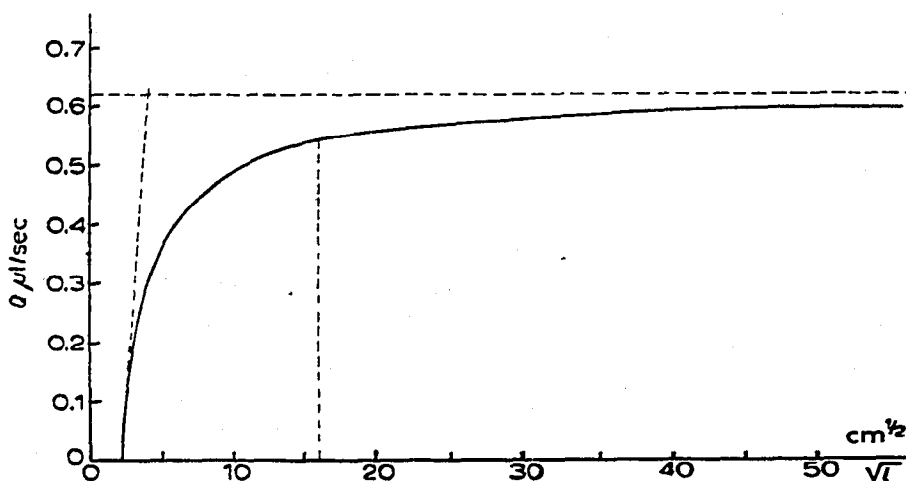


Fig. 4. Relationship between total feed rate and column length.

#### EXPERIMENTAL

In this section we summarize briefly the experimental work performed in order to test some of the statements made in the previous section and to work out from experimental data the parameters required for applications of relations (5) and (6').

Most experiments were performed using a cyclohexane (1)-benzene (2) (1:1 v/v) mixture injected in various amounts under the following conditions

temperature	80°
stationary phase	polyethyleneglycol 400 (30 %) on firebrick
carrier gas	nitrogen
column length	120 cm
	300 cm

From plots of peak widths ( $\Delta_1, \Delta_2$ ) between the tangents against the amount of mixture injected (a typical plot is given in Fig. 5), it is possible to find the constants  $K$ , angular coefficients of the straight lines; the heights  $h_0$  can be obtained from plots of

TABLE I

Column length (cm)	Inlet pressure (atm)	Carrier gas flow rate (cm <sup>3</sup> /min)	Data obtained from plots						Calculated values		Corrected values	
			$K_1$	$K_2$	$b_1$	$b_2$	$h_{01}$	$h_{02}$	$b_1$	$b_2$	$K_1$	$K_2$
120	1.45	103	0.60	0.90	14	59	0.20	0.13	14	52	0.60	0.90
	1.60	109	0.53	0.69	14	45	0.25	0.14	11	42	0.57	0.75
300	2.10	103	0.39	0.57	29	142	0.25	0.14	28	115	0.52	0.75

plate heights by extrapolation. Some results are summarized in Table I ( $K$  has been corrected for mean pressure inside the column<sup>6</sup>).

We see that, at least in the range of interest for practical applications in preparative gas chromatography,  $K$  and  $h_0$  are independent of column length to a sufficient approximation.

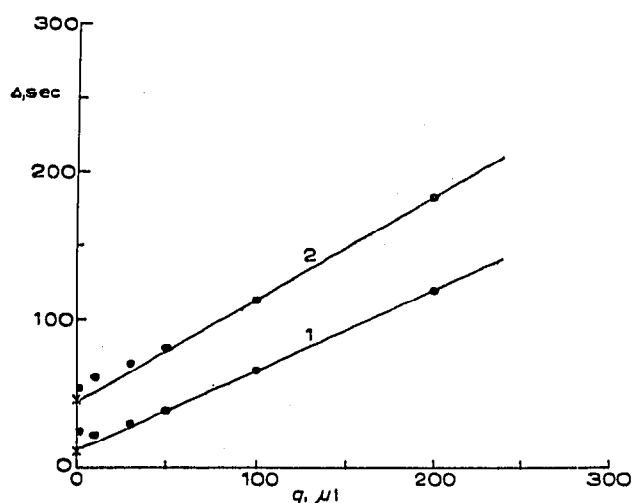


Fig. 5. Plot of peak width against the amount injected. Column length 120 cm;  $\Delta p = 0.6$  atm.

To test the applications of the formulae derived in the preceding section we have chosen the same mixture working under the following conditions

column length 120 cm  
 inlet pressure 1.6 atm  
 temperature 108°  
 stationary phase tricresyl phosphate on firebrick  
 carrier gas nitrogen, 75 c.c./min

Under these conditions the relevant experimental data are

$t_1 = 160$  sec ( $\alpha_{12} = 2.03$ )  
 $t_2 = 325$  sec  
 $K_1 = 0.50 \mu\text{l}^{-1}$  sec ( $b_1 = 17$  sec)  
 $K_2 = 0.83 \mu\text{l}^{-1}$  sec ( $b_2 = 35$  sec)  
 $h_{01} = 0.13$  cm (mean value  $h_0 = 0.145$  cm)  
 $h_{02} = 0.16$  cm

From these data and for  $S_{12} = 1.5$  our formulae (6') and (5) give, respectively,

$$Q = 0.502 \mu\text{l} \cdot \text{sec}^{-1}$$

$$v = 13 \text{ h}^{-1};$$

for the set of 100 columns one obtains a feed rate of 182 ml/h. Working with our rotating unit under these same conditions we were able to use a feed rate of 190 ml/h at 10 revolutions per hour.

It is thus possible to make reasonable predictions about running conditions of the unit from data obtained on a pilot column.

From the expression of  $Q$  as a function of column length  $l$

$$Q(l) = 0.620 - 1.297 \frac{1}{\sqrt{l}} \mu\text{l. sec}^{-1} \text{ per column,}$$

the plot of which is given in Fig. 4, it appears that with a length of 200 cm one should obtain a feed rate improvement up to 200 ml/h.

#### SUMMARY

A two-component mathematical model for the rotating gas chromatography unit previously described is suggested.

From well-known chromatographic relations, an explicit function depending on the retention times is derived. By studying this function an equation can be obtained, which gives the retention times necessary to achieve optimal operating conditions.

Furthermore, in view of practical applications on a preparative scale, the relation between feed rate and some of the column features, such as length, H.E.T.P., etc., is examined.

Experimental results are reported which support some of the assumptions made in the theoretical part.

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