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## OPTIMIZATION OF OPERATING PARAMETERS FOR GLASS CAPILLARY COLUMN GAS CHROMATOGRAPHY

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### SUMMARY

The relationship between analysis time and separation with glass capillary columns was studied. Optimal operating parameters for achieving the shortest analysis times consistent with degree of separation were determined experimentally. It was found that the optimum column temperature is governed by retention characteristics of the solutes and the optimum column length by the required magnitude of separation. The optimum carrier gas flow-rate was found to be a function of the column length. Emphasis is placed on using capillary column length as an operating parameter.

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### INTRODUCTION

The obvious advantage of open tubular columns in comparison with packed columns is their extremely high resolution. Analyses involving compounds of similar retention times require high resolution. This in turn requires a long analysis time. Another important but less apparent advantage is that open tubular columns require shorter analysis times than packed columns to achieve given separations. Faster analysis is by no means less important than greater resolving power. In order to achieve the fastest analysis, all the operating parameters must be optimized with respect to the time of analysis. It is a formidable task to establish the optimum conditions when all operating parameters are considered. This is not necessary, as we are concerned here with column performance under nearly optimum conditions. This would still result in considerable time saving relative to other arbitrarily chosen conditions. The purpose of this study has been to improve our understanding of the relationship of the numerous operating parameters with respect to the analysis time.

The effect of chromatographic conditions upon retention time and resolution has been studied by a number of workers. The Van Deemter equation in which HETP is expressed as a function of the carrier gas velocity is widely accepted and serves as a basis for further development of chromatographic theory. Most of the parameters have been, therefore, studied in light of the theoretical plate model<sup>1</sup>.

Purnell and Quinn<sup>2</sup> explored the best means for achieving fast analysis. Gid-

dings<sup>1</sup> examined the validity of the theory and derived an approach to rapid analysis. Open tubular columns were also studied; the absence of "multi-path effect" of the solid support (or eddy diffusion) made the use of these columns ideal for such study<sup>3</sup>.

From Golay's equation for open tubular columns (see Fig. 1), it can be seen that the highest number of theoretical plates obtained at the optimum average linear velocity (where the height equivalent to a theoretical plate (HETP) is minimum) is not the maximum attainable when the analysis time is concerned. For the same given period, a column with increased length at proportionally increased gas velocity would produce more theoretical plates. Based on the assumption that Golay's equation is dependent on column length, increases of the two would result in ever increasing theoretical plates. However, the increase must be finite in reality (as discussed later). Thus by incorporating both column length and average linear velocity simultaneously into the operating parameters, the column efficiency can be maximized. This gas velocity is greater than the optimum average linear velocity and is usually referred to as "optimum practical gas velocity" (OPGV). This concept is very valuable for the pursuit of fast analysis. Scott and Hazeldean<sup>4</sup> originally defined the OPGV as "the linear velocity at which the HETP curve tends to become linear" (see Fig. 1).

#### Van Deemter Plot for Open Tubular Column

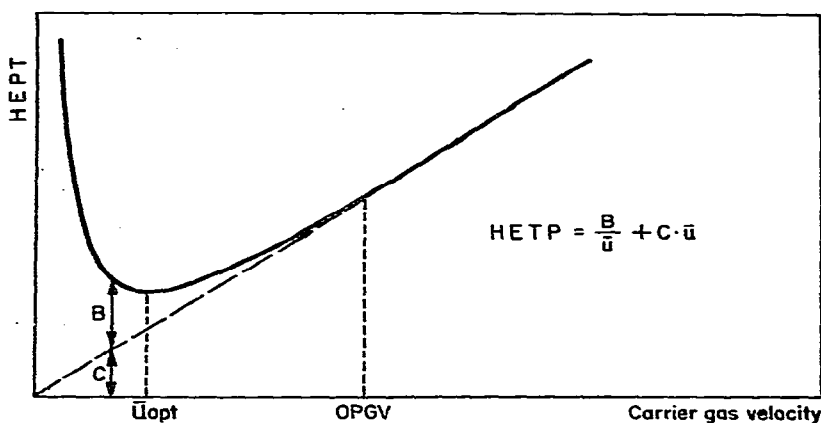


Fig. 1. Plot of HETP vs. carrier gas velocity for open tubular columns based on the given equation. Optimum average linear velocity ( $\bar{u}_{opt}$ ) and optimum practical gas velocity (OPGV) are indicated.

Desty *et al.*<sup>5</sup> attempted to express the column performance as the ratio of the number of effective theoretical plates to the analysis time ( $N/t_R$ ). Since most chromatographic analyses deal with resolution of more than one component, the effective theoretical plates are more expressive of the degree of separation than the values related to theoretical plates. They<sup>5</sup> defined the OPGV more explicitly as the velocity for the maximum of  $N/t_R$ . Ettre and March<sup>6</sup> suggested a plot of resolution vs. analysis time for comparison of column performance. It is also our belief that the actual measurement of the resolution of a pair of selected solutes will permit direct comparison of various columns and valid evaluation of parameters within a column, if experimental conditions are carefully controlled.

The usefulness of relatively short capillary columns for rapid analysis was advocated by Gouw *et al.*<sup>7</sup>. Previously developed theories are helpful in studying this fast analysis problem. However, one of the most critical restrictions on the use of HETP and its related variables (*e.g.*, Golay equation, etc.) for this problem is that the relationship of HETP *vs.* average linear velocity is considerably affected by the pressure gradient (*i.e.*, by column length) (discussed later in detail). Indeed, Desty *et al.*<sup>5</sup> warned of the error in assuming that the Van Deemter plot is little affected by column length.

While most of the parameters concerning both the column design and its operation influence performance, three of the most conveniently variable parameters were chosen for study. Unlike packed columns, the glass capillary or wall-coated open tubular columns (WCOT) can be trimmed to any desired length with little effort. The column length was, therefore, considered as an operational parameter rather than a column design parameter even though this is not yet commonly practiced. Moreover, this is imperative for approaching the optimum conditions necessary for rapid analysis.

The other two parameters chosen, carrier gas velocity and column temperature, are the commonly changed operational parameters. Previous work on this subject did not treat the effect of temperature as an interrelating variable with respect to other parameters. The column temperature does affect not only the retention times but also the relative retention which makes the mathematical treatment cumbersome, but it cannot be ignored or set constant to evaluate the true column performance; it must be treated as one dimension of the interrelating parameter matrix.

The rest of the parameters, such as column diameter and the stationary phase film thickness, were considered as part of the column design, hence not constituting additional dimensions in this study. From the practical point of view, the emphasis should be placed on the above three parameters.

## EXPERIMENTAL

### *Column coating*

Coiled glass capillary tubing (0.50 mm O.D., 0.25 mm I.D.  $\times$  over 80 m) was drawn from flint glass by a modified Shimadzu glass drawing machine Model GDM-1. The capillary tubing was coated with the liquid phase by thermostatic method. The tubing was filled with SE-30 solution in pentane (4 mg/ml) and one end flame-sealed. The glass capillary was then driven into a specially designed heated oven (200°) at constant speed (2 cm/sec) starting from the open end. At the entrance of the oven, an additional stainless-steel tube was installed and heated to 250° for instant heat transfer to the capillary. Evaporated solvent vapor was forced to escape through the open end of the capillary tubing into the oven. After completion of the drying step, the solvent vapor remaining in the column was removed by vacuum. The detailed procedure is reported by Jennings *et al.*<sup>8</sup>. This coating method is quite reproducible in achieving uniform liquid phase film thickness and satisfactory separation efficiency. The column was cut to desired length and both ends straightened by microflame.

### *Instrumentation*

A Hewlett-Packard Model 5731A gas chromatograph with dual-flame ionization detector was used. Variable-ratio inlet splitters were installed and the detector

TABLE I  
GAS CHROMATOGRAPHIC CONDITIONS

<i>Parameter</i>	<i>Value</i>
Inlet split ratio	80-100:1
Carrier gas flow	0.1-2.0 ml/min
Detector make-up gas flow	30 ml/min
Hydrogen flow	30 ml/min
Air flow	240 ml/min
Inlet temperature	250°
Column temperature	115-160°
Detector temperature	250°

slightly modified so that the column effluent entered the flame tip directly. Conditions were adjusted as shown in Table I. All gases were supplied through pressure regulators.

#### *Parameters examined*

**Column length.** Four column lengths were chosen for study. To minimize variation of column efficiency resulting from variations in the coating procedure, 7.5-m and 40-m columns were made from one long column. The other two columns (15 m and 25 m) were made from the 40-m column after experiments using that length column were completed. The efficiency and liquid phase loading did not change during this study.

**Temperature.** Chromatographic data were collected under isothermal conditions at four different temperatures (115°, 130°, 145° and 160°) with all four columns.

**Carrier gas flow.** Carrier gas flow was varied by regulating the inlet pressure. Flow condition was expressed in terms of average linear velocity measured by the retention time of methane. For each set of condition (column length and temperature) the average gas velocity was varied from *ca.* 20 cm/sec to 100 cm/sec for at least six data points.

**Retention time range of solutes.** The test mixture for the measurement of column efficiency was composed of a series of straight-chain hydrocarbons (C<sub>11</sub>-C<sub>16</sub>) dissolved in heptane. This mixture allowed examination of theoretical plates and resolution of hydrocarbon pairs at wide ranges of the partition ratio. In order to express the physical properties of the solutes for further generalization, their retention behaviour was expressed in terms of Kováts' retention indices, *I*<sup>9</sup>. The retention property range examined in this experiment was, therefore, from *I* = 1100 to *I* = 1600. Each injection included a small amount of methane.

#### *Measurement*

Retention times and widths at half peak height of all peaks were measured. Column performance at each set of operating condition was evaluated by resolution of neighboring hydrocarbon peaks, theoretical plates and effective theoretical plates. The equations used are given below:

$$R = \frac{1.18 (t_{R2} - t_{R1})}{(W_{h2} + W_{h1})}$$

$$n = 5.54 \times \left( \frac{t_R}{W_h} \right)^2$$

$$N = 5.54 \times \left( \frac{t'_R}{W_h} \right)^2$$

where  $R$  is resolution\*,  $n$  number of theoretical plates,  $N$  number of effective theoretical plates,  $t_R$  retention time,  $t'_R$  adjusted retention time,  $W_h$  peak widths at half height.

HETP vs Average Linear Velocity

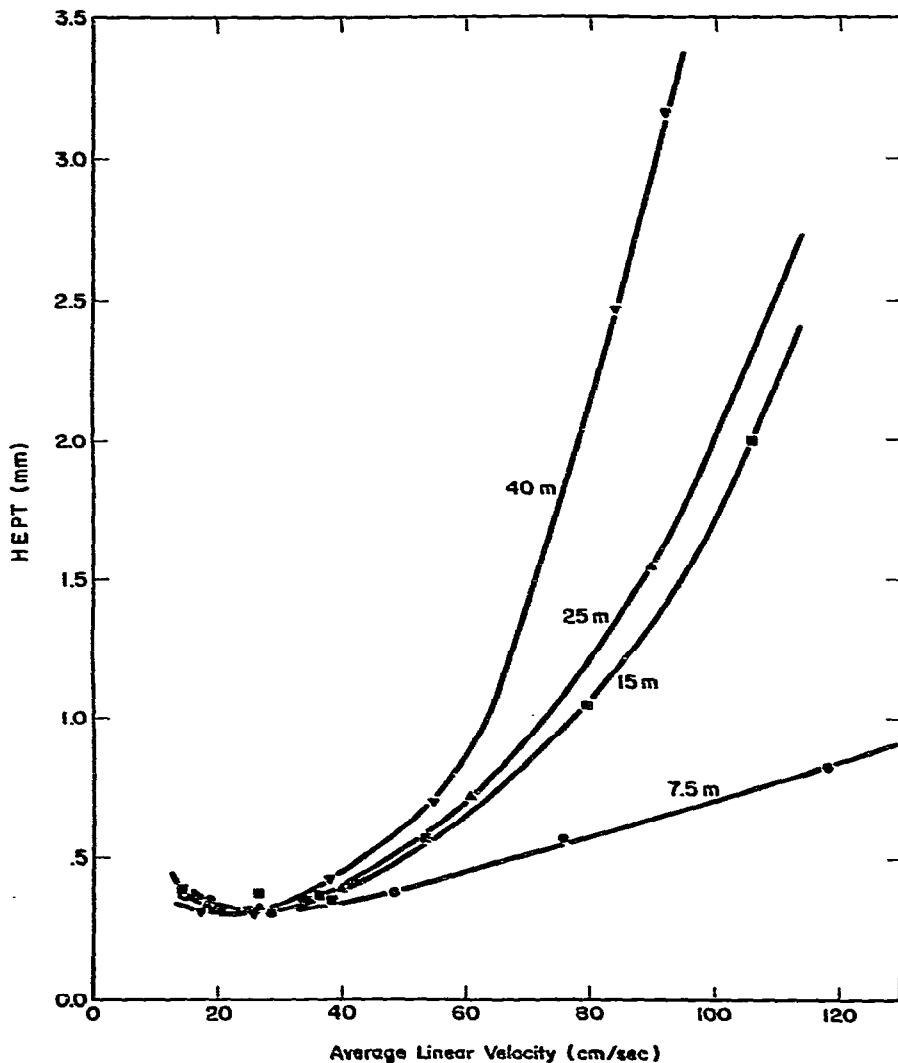


Fig. 2. Plot of HETP vs. average linear velocity measured by tetradecane peak at 130° on 0.25 mm I.D. SE-30 columns.

\* The equation is equivalent to the commonly used expression,  $R = 2(t_{R2} - t_{R1})/(W_2 + W_1)$ . The factor is adjusted for the peak width measured at half peak height of a gaussian curve.

## RESULTS AND DISCUSSION

Because of the compressibility of carrier gas, a gas chromatographic (GC) column always exhibits a pressure gradient. Hence, a uniform linear velocity can never exist. Moreover, when column length is changed, the linear velocity profile throughout the column will be affected. Since the band broadening process is a function of carrier gas linear velocity at a particular position in the column, most conventionally used terms such as the number of theoretical plates or HETP value are of limited validity. Fig. 2 shows the relationship of average linear velocity to HETP.

Variation in column length has little effect upon HETP when the average linear velocity is near the optimum. However, at increased flow the longer columns have much greater HETP value than the shorter ones. The 40-m column exhibits little greater resolution than the shorter columns at an average linear velocity of 80 cm/sec or above. This is perhaps because with a longer column, there is a greater spread of linear velocities than with a shorter column.

It follows that carrier gas flows expressed as average linear velocity are of limited validity when variations in column lengths are concerned, as are equations using these values. For the same reason, the curve shown in Fig. 1 has large deviation from actually measured values (Fig. 2). Since the Van Deemter curve shifts with increase in column length, the value of OPGV cannot be a constant value.

*Choice of carrier gas*

Helium is a commonly used carrier gas primarily because of its high diffusivity, allowing faster analysis with only slightly greater HETP compared to nitrogen. Fig. 3 shows that analysis using helium as carrier allows a significant reduction of the analy-

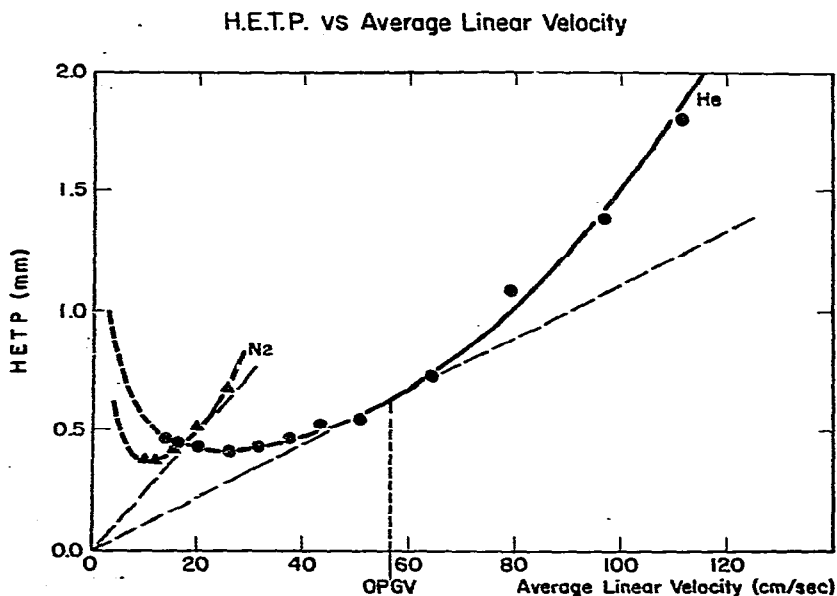


Fig. 3. Effect of carrier gas on HETP at various velocities. Measured by tricosane peak at 230° on 20 m × 0.28 mm I.D. SE-30 column.

sis time at increased flow compared to use of nitrogen. Hydrogen has been demonstrated to be an even better carrier gas for fast analyses; however, it was not examined in this study.

#### Velocity and length

Fig. 4 shows the effect of the carrier gas flow on the analysis time and resolution for four columns at 130°. The solid curves were obtained when the column length was fixed to the four values. The tangential broken line (maximum resolution curve) was drawn to facilitate estimating the resolution attainable for continually changed column length.

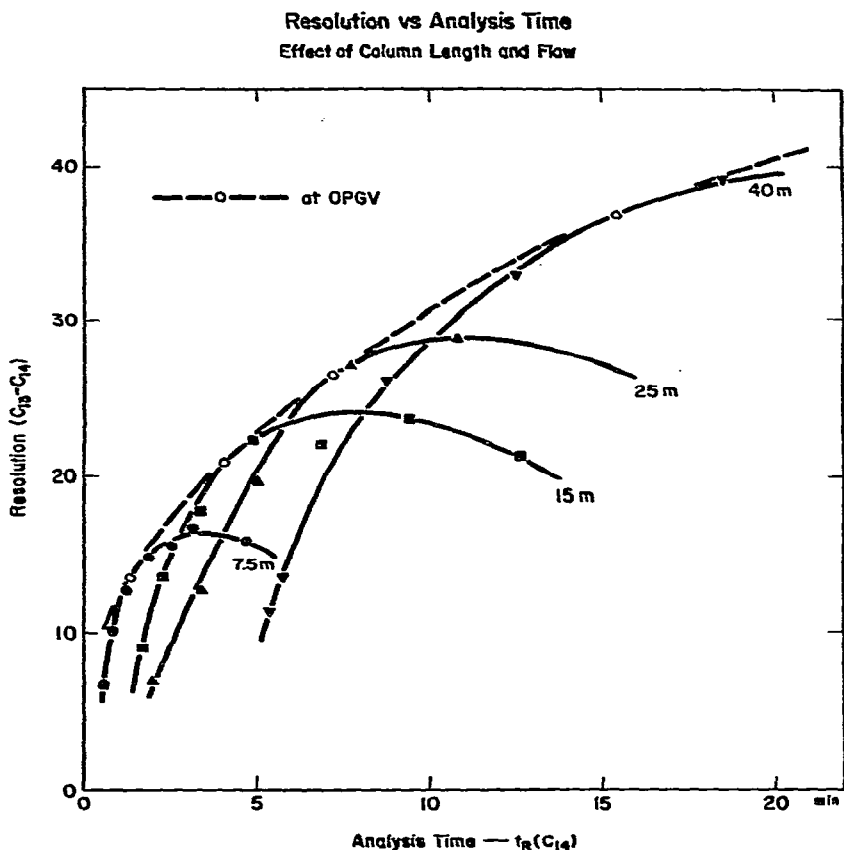


Fig. 4. Effect of column length and carrier gas flow on resolution and analysis time. Measured by tridecane and tetradecane peaks at 130° on 0.25 mm I.D. SE-30 columns. The broken curve (maximum resolution curve) indicates the highest resolution attainable from the capillary column of 0.25 mm I.D.

The maximum resolution curve can be drawn for each set of temperature and the retention property (retention index of the peak). It is apparent that the highest resolution from a given column is not the optimum with respect to analysis time. Also, the condition which results in the maximum value of  $R/t_R$  for the given column can be

outperformed by shorter columns. It can be noted from the graph that each column length has only one average linear velocity at which the column is used optimally when the column length is allowed to be an operating parameter. At the temperatures other than 130°, the same effects were observed. Measurement of the other pair of hydrocarbon peaks also showed a similar trend.

#### Temperature and retention character

The maximum resolution attainable for each pair of peaks for various temperatures were examined with the aid of graphs similar to Fig. 4. Among the four temperatures examined, the temperature of 130° showed more resolution than others for the C<sub>13</sub> and C<sub>14</sub> hydrocarbons. Similarly, for the C<sub>15</sub>/C<sub>16</sub> pair, a temperature of 160° exhibited higher resolution for analysis time than the other three temperatures. As already reported in 1960<sup>4</sup>, there is an optimum temperature for a pair of solutes at which the highest resolution can be obtained for a given analysis period. Fig. 5 was plotted in order to generalize this temperature-retention relationship. The partition ratio was chosen for the horizontal axis. As the partition ratio of a solute is independent of either column length or flow condition (as the phase ratio was kept constant in this study) the plot is valid to examine the maximum resolution curve where both length and the flow were variables.

Minimum Analysis Time vs Partition Ratio For Fixed Resolution

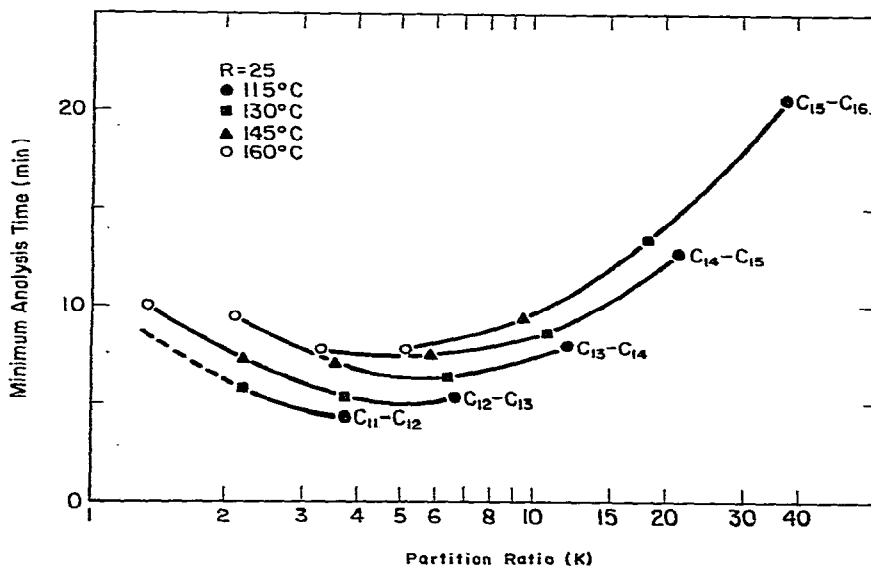


Fig. 5. Minimum analysis time required to produce a fixed resolution ( $R = 25$ ) of the hydrocarbon pairs vs. partition ratio ( $k$ ) measured at the second peak of each pair. Minimum analysis time was obtained from maximum resolution curve at  $R = 25$  in each condition.

In Fig. 5, the minimum analysis time was determined as the analysis time required to achieve the resolution of 25 (an arbitrarily chosen value) along the maximum resolution curve (Fig. 4). In other words, each data point in Fig. 5 represents the



shortest analysis time for the pair of hydrocarbons by allowing the length and flow to be optimal. It is noted from the graph that the partition ratio of about 6 results in the shortest analysis time for the desired resolution regardless of the retention behavior. Since in the range from 3.5 to 8 the curves are flat, the temperature is not critical; *i.e.*, as long as the temperature was set to give the partition ratio of the solutes from 3.5 to 8 (in terms of temperature, *ca.*  $\pm 8^\circ$  from the optimum), the maximum resolution curve will be similar and all very close to the optimum. However, greater departure from that optimum range (either very large or very small partition ratio) causes the required analysis time to be much longer.

It is interesting to note that a hydrocarbon pair of longer chain length (*e.g.*,  $C_{15}/C_{16}$ ) requires a longer analysis time to achieve the same degree of resolution in comparison with a solute pair of smaller retention indices (*e.g.*,  $C_{14}/C_{15}$ ). By generalizing the statement, for the same difference in retention indices for two solutes, the pair with larger retention indices requires longer analysis time than a pair of smaller retention. As an example, the pair of methyl decanoate ( $I = 1368$ ) and methyl 1-decenoate ( $I = 1338$ ) will require a longer retention time for complete separation than the pair of methyl hexanoate ( $I = 869$ ) and methyl 1-hexenoate ( $I = 839$ ). This is so even though in both cases the structural difference within the pair is saturated/mono-unsaturated and  $\Delta I$  for both pairs is 30. This can be accounted for by the relative retention decrease with increased temperature. For the pair with larger retention indices, temperature must be elevated to put the partition ratio in the suitable range; therefore, the relative retention becomes closer to unity which in turn results in complete separation becoming more difficult.

#### Overall relationship

Up to this point, the interrelating parameters were discussed while others were set constant. We can summarize as follows:

(1) There is an optimum temperature at which a given pair of solutes can be best separated in the shortest time. The optimum temperature is governed by the retention properties of the solutes regardless of desired resolution. That is, column temperature should be adjusted to obtain a partition ratio of 6 for the later peak.

(2) Once the desired degree of separation is defined, there is only one optimum column length and its corresponding optimum value of average linear velocity. For a given column (fixed diameter, film thickness and coating efficiency), the maximum resolution curve will facilitate estimation of the optimum column length.

Using this approach, one can select the three operating parameters with a minimum of effort at or close to the optimal conditions.

In practice, column length is usually kept constant, and the only operating parameters varied are temperature and carrier gas flow. Let us examine the merit of employing the additional parameter, *i.e.*, varied column length. Fig. 6 shows the degree of time saving by this method. The point where all three curves join indicates the best choice of all the parameters (temperature, length, flow).

The "curve for varied flow" was plotted at various gas velocities while the temperature was set constant to give the partition ratio of 6. The "curve for varied temperature" was obtained by increasing and decreasing temperature for the optimum value while the average linear velocity was kept constant. In both cases the same column was used. In both directions from the original condition point, manipulation by

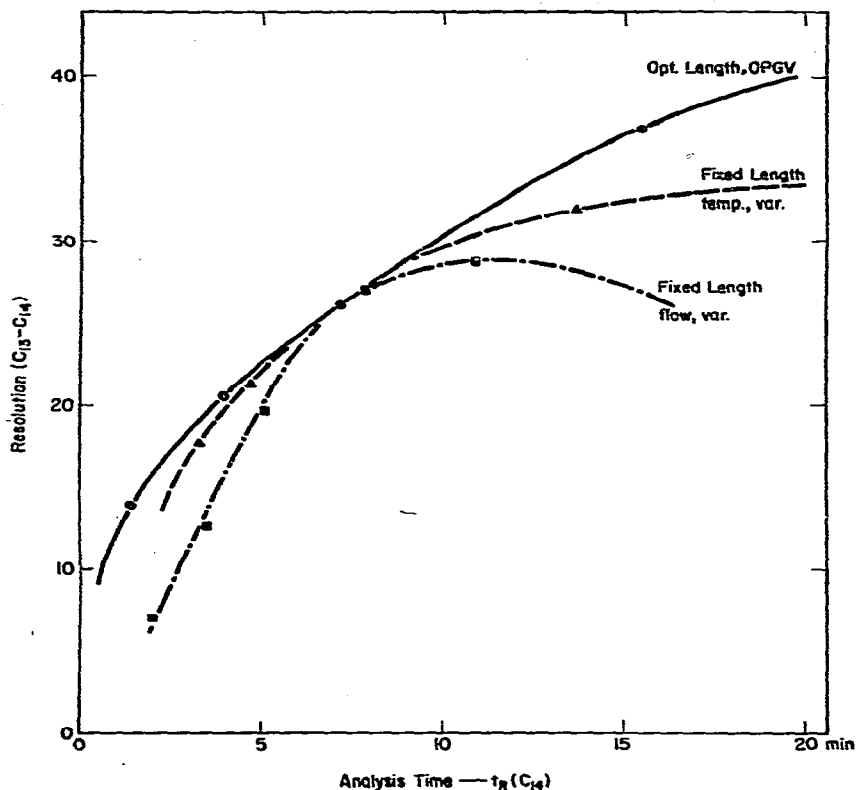


Fig. 6. Effect of varied parameters on resolution and analysis time. Top curve (maximum resolution curve) was obtained at 130° (near optimum) by adjusting the column length and flow. Second curve was obtained by changing only the temperature. The bottom curve was obtained by changing only flow at 130°.

temperature gives higher resolution than by flow. The temperature curve is not significantly remote from the "curve for optimum length and flow" (maximum resolution curve). Therefore, one can simply raise temperature to take advantage of time saving with slight departure from the "maximum resolution curve". On the other hand, in order to achieve greater resolution than the original point, time saving by optimum column length with OPGV (increase in length with concomitant flow adjustment) can be considerable. This is because the slope of the maximum resolution attainable constantly decreases. Therefore, when the relative retention of the solute pair is very close to unity (*i.e.*, difficult to separate), increase of column length and re-adjusting the average linear velocity result in considerably greater time saving than simply lowering temperature with the same column.

#### ACKNOWLEDGEMENT

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