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A NEW VARIABLE PATH LENGTH COLUMN FOR GAS CHROMATOGRAPHY

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SUMMARY

The design features and performance characteristics of a new type of gas chromatographic column, whose effective length can be varied externally during analysis, are described. The column, though of comparatively small dimensions is shown to have a very large number of theoretical plates compared to those of very long capillary columns. It can easily be dismantled, cleaned and recoated with another stationary phase when required.

INTRODUCTION

The operating conditions for gas chromatographic analysis have to be varied greatly to meet the requirements of individual analyses. Even when a suitable stationary phase is found, several columns of different lengths and coatings of the support are often necessary in order to have the required efficiency, reasonably short analysis time and sufficient sample capacity. The requirements for these conditions are generally contradictory and sometimes the analysis has to be repeated a number of times to suit each of these requirements in turn. Therefore, there has been, since the beginning, a search for a universal column in which the column dimensions and stationary phase could be changed at will during analysis, but with little success. The present paper describes a column in which the effective dimensions can easily be changed from the outside during analysis without any need to open connections and which can easily be dismantled for cleaning and recoating with another stationary phase. This new type of column is of cylindrical design, though of physically small dimensions, permits a very large number of theoretical plates to be obtained, comparable to that of long capillary columns.

Capillary columns which are capable of achieving a very large number of theoretical plates, can only tolerate very small amounts of sample and invariably call for the use of sample splitters and very sensitive detectors. Moreover, coating is a tricky affair and recoating frequently with a different phase is not possible in routine practice. On the other hand, packed columns of normal dimensions, though easy to prepare and capable of tolerating much larger sample quantities, generally have low

efficiencies. The new column combines to some extent the advantages of both. Its design features and performance are described below.

COLUMN DESIGN

Fig. 1 illustrates the simplified principle of the working of such a column without any provision for varying the path length. It consists of two separate sets of hollow concentric cylinders fixed hermetically into two discs A and B (Fig. 1), in such a way that the cylinders of one fit into the spaces of the other leaving a uniform narrow

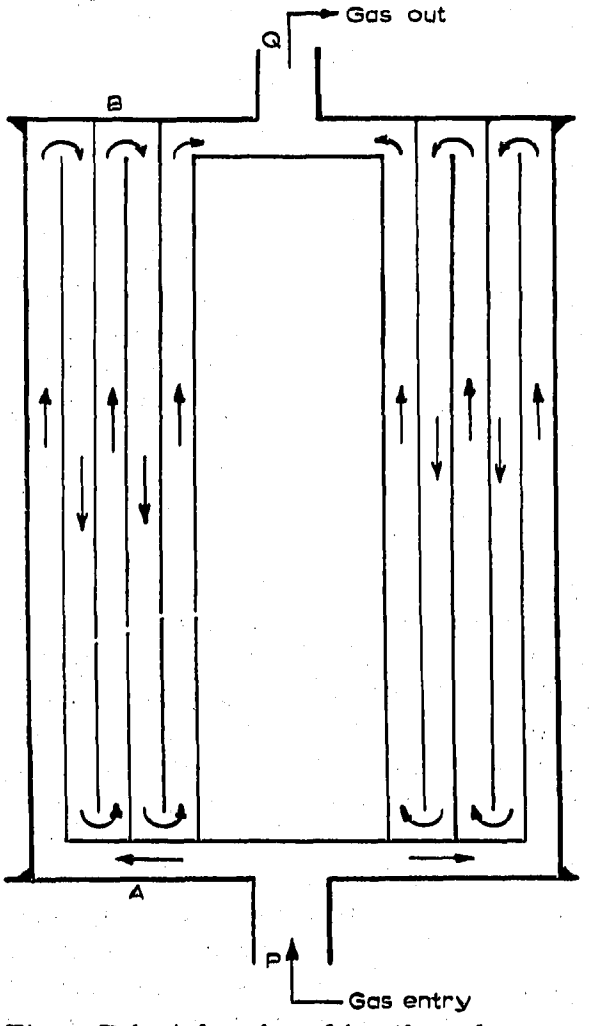

Fig. 1. Principles of working the column.

clearance throughout. Thus the carrier gas entering from P through the outermost cylinder has to follow the path as per clearance between the various cylinders and will ultimately come out as shown through Q. The stationary phase must be coated on both the inside and outside of each cylinder so that the clearance between the cylinders in their assembled positions, works like a large number of open tubular capillaries packed together. As will be shown subsequently the separating efficiency of such a column can be varied greatly by changing the length, diameter, and number of these cylinders and distance of the clearance.

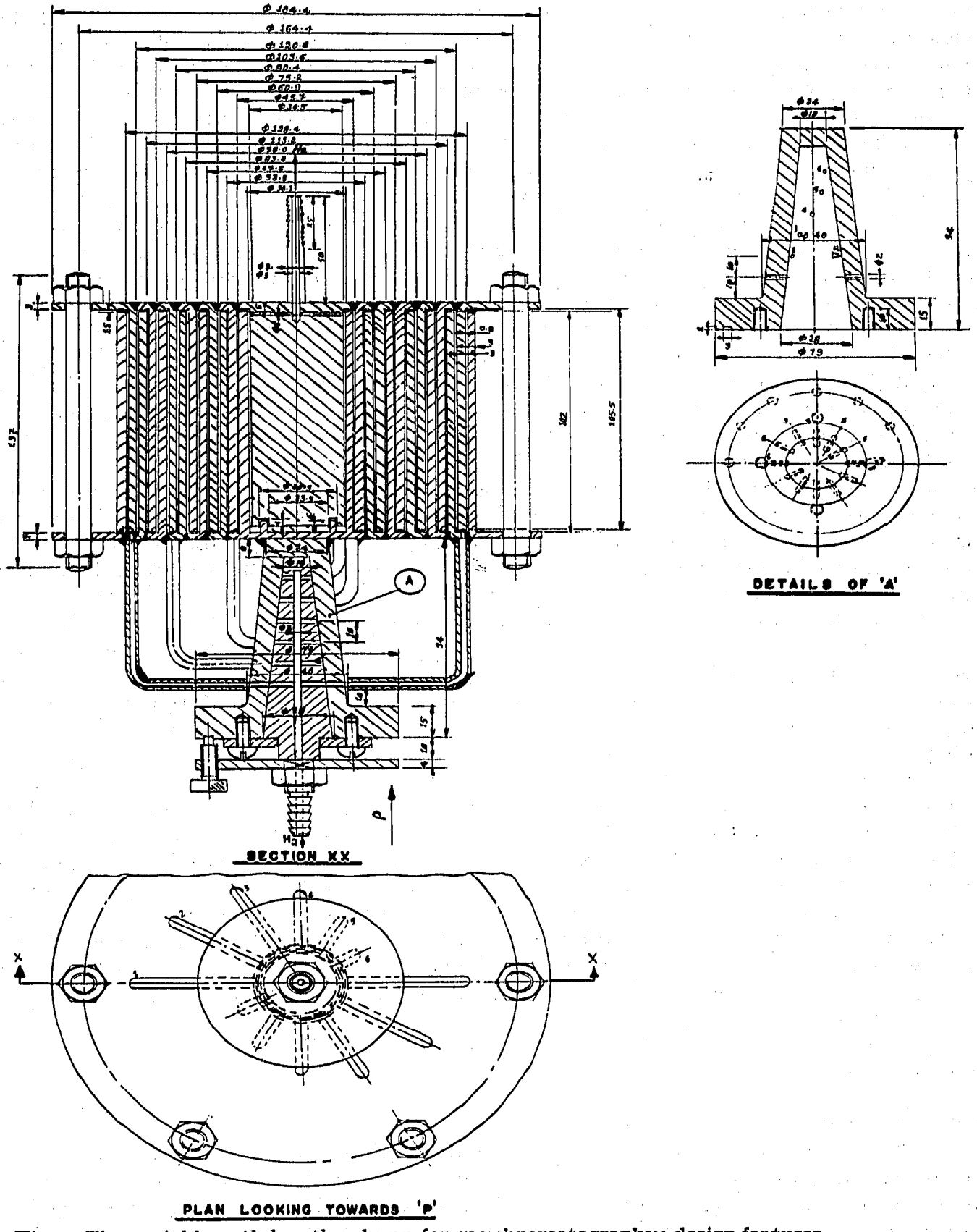

Fig. 2. The variable path length column for gas chromatography: design features.

The vertical cross section and other views of the column in its assembled position, fitted with the arrangement for varying the gas path length, are shown in Fig. 2. By means of knob D located outside, the carrier gas can be made to enter the outermost or any of the intermediate cylinder junctions, when either the whole or a part of the path length is traversed; thus the column works as if it were of variable path length. The dimensions shown in Fig. 2 are not those that would give the maximum performance but are those that we have chosen for the fabrication of the prototype in which ease of fabrication has been given due consideration.

The working of the variable path length arrangement will be clear from Fig. 2. In the female part shown, there are as many sets of holes as there are cylinders (6 in the figure) arranged along a helical path with a constant distance of separation. These holes are joined respectively to the outermost, next... etc., and innermost cylindrical space each by one set of two capillary tubes fixed diametrically opposite to each other. The male part, which fits hermetically, has a set of thin horizontal channels along its length connecting the main carrier gas stream, and spaced with such accuracy that in one position of the knob connection is only possible with one set of holes in the female part. By turning the male part, by means of the knob clockwise, connection can be made to the 1st, 2nd... set of holes and thus to the outermost, next... innermost clearances—the channel connected being known by the position of the knob. Thus the path which the carrier gas traverses inside the column, can be made shorter or longer depending upon whether the carrier gas enters the innermost, intermediate or outermost cylinder, the exit always being through Q. The effective path length of the column therefore can easily be varied in terms of the annular space between one set of cylinders, and since the moving mechanism is operated through the knob D from outside, the change of path length can be brought about during analysis even when the column is enclosed in an oven and heated to a high temperature. The outer dimensions of the column are sufficiently short to be accommodated in most GC apparatus. However, because of its heavy weight, the column has to be supported adequately.

For coating the column, it would perhaps be better to dip separately, for a short period, the two sets of the concentric cylinders into the stationary phase suitably diluted with a volatile solvent, so that the cylinders are entirely submerged in the solution. After draining off the excess solvent, the two halves can be left open to evaporate off the solvent. This procedure may initially need somewhat larger volumes of the solution but leaves a considerable part of it for use later. The usual methods of coating a capillary can also be applied in this case with suitable precautions. Since the two halves of the column can be easily separated (by opening the screws F and pulling), cleaning of the column and recoating with another stationary phase is comparatively easy.

PERFORMANCE

Effective dimensions

The small space between two consecutive cylinders coated with the stationary phase, can be considered to operate as if a very large number of coated capillaries of diameter d open at both ends are packed together side by side. Assuming that the carrier gas only passes to the next imagined capillary after traversing the earlier

capillary completely, the effective length of the equivalent capillary column is easily calculated. Referring to Fig. 3, if R is the radius of the innermost cylinder, t the metal thickness, d the uniform clearance between any two consecutive cylinders, assumed to be uniform throughout, and l is the constant length of all the cylinders, then the

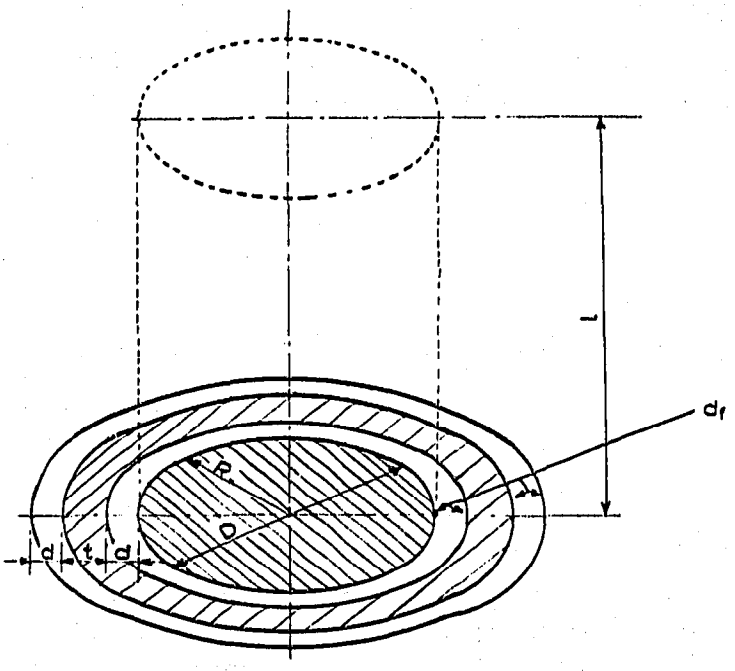

Fig. 3. Simplified section of the top.

number (N) of imaginary capillaries of length l each, packed in the first (innermost) annular space circumference $2\pi R$, and the path length equivalent (L_1) are:

$$N = \frac{2\pi R}{d}$$

$$L_1 = \frac{2\pi R l}{d}$$

Similarly the path length equivalent of the capillaries supposed to be packed in the second annular space (L_2), third annular space (L_3) and the nth (outermost) annular space (L_n) are:

$$L_2 = \frac{2\pi(R + d + t)l}{d}$$

$$L_3 = \frac{2\pi\{R + 2(d + t)\}l}{d}$$

$$L_n = \frac{2\pi\{R + (n - 1)(d + t)\}l}{d}$$

Total length:

$$L = L_1 + L_2 + L_3 + \ldots . L_n$$

$$= \frac{\pi l\{2nR + n(n - 1)a\}}{d}$$

where

$$a = d + t$$

The same results will follow if, in place of vertical capillaries, circular capillaries packed from top to bottom are considered.

Since, however, the imagined capillaries are open from the sides, and in the space there will not be any stationary phase coating, the effective length calculated above should be halved.

Hence the total effective length

$$L = \frac{\pi l}{d}\left\{nR + \frac{n(n-1)a}{2}\right\} \qquad (1)$$

For a typical case, taking the dimensions shown in Fig. 2, the total effective length L

$$= \frac{\pi \times 100}{0.8}\left\{11 \times \frac{(35.6 + 0.8 + 7.6)}{2} + \frac{11 \times 10}{2}(0.8 + 7.6)\right\} \text{ mm}$$

$$= 266.5 \text{ m approx.}$$

Thus the path length provided by the above column of rather small dimensions is seen to be equivalent to that of an unusually long capillary column. (The length of present common capillary columns rarely exceeds 100 m.) From equation (1) it is also evident that the effective length L can be increased by increasing l, R, n and decreasing d. Thus by taking a very large number of long and wide cylinders with extremely narrow clearances between them, it should be possible to make such columns attain efficiencies comparable to thousands of meters of capillary columns. The number of theoretical plates obtainable thus can perhaps be pushed to the billion range—higher by several orders than the present.

Height equivalent to a theoretical plate (HETP)

The VAN DEEMTER–GOLAY equation for coated open tubular columns[1] for HETP is in the form:

$$\text{HETP} = B/\bar{u} + C_G\bar{u} + C_L\bar{u}$$

Where B stands for the longitudinal gaseous diffusion term; C_G and C_L represent the resistance to mass transfer in the gas and liquid phases respectively, and $\bar{u}$ is the average linear gas velocity. This equation can be applied to the present column as well. Certain modifications in the coefficients, however, will be required in view of its changed geometry. The principal change is likely to be in the diffusion term, the resistance to mass transfer terms applying without any modification. The suggested changes are discussed below.

Changes in the molecular diffusion term B

In the usual capillary columns, there is only a single gas path possible; in the present case multiple paths can be taken by the moving carrier gas, also it probably

has differing velocities, and both longitudinal and lateral diffusions are equally probable. The total diffusion can be represented as taking place along three mutually perpendicular directions in the column space: radially across the clearance, tangentially along the periphery, and longitudinally along the length of the annular space. The first part is similar to that in normal capillary columns; its magnitude should vary inversely with the diameter d of the clearance, and the influence of the various parameters on its magnitude is interpreted in the usual way. The diffusions in the other two directions, particularly that along the periphery of the annular space, are rather new, and these may become quite important depending on the working dimensions of the column.

To allow for the multiplicity of the paths, terms analogous to 'eddy diffusion' in normal packed columns and which are omitted in the case of capillary columns, should be added for this new column. In the opinion of the author, however, this term should not be independent of the carrier gas velocity for this new column. The effect, therefore, is better incorporated by modifying the B term. The magnitude of this effect should be a function of the length, peripheral circumference and diameter of of the annular space. If we also consider the two extreme cases when either R or l is zero, the column approaches miniature capillaries (the two cases, however, are not identical), and a coefficient of the form $rR/(R + l)$ is suggested.

The correction factor γ—somewhat analogous to the tortuosity factor for packed columns accounting for the difference in the linear carrier gas velocity and the mean of the different gas velocities that are possible—is also reintroduced for this new column. The complete diffusion term should therefore be of the form:

$$2\{1 + \gamma rR/(R + l)\} Dg/\bar{u}$$

Changes in the mass transfer terms C_G and C_L

No change is envisaged for the terms expressing the resistance to mass transfer as the picture does not essentially change for the new column.

The complete HETP equation

With the modifications suggested above, the complete HETP equation for the present column would be:

$$H = 2\left\{1 + \gamma rR/(R + l)\right\}\frac{Dg}{\bar{u}} + \left\{\left(\frac{1 + 6k + 11k^2}{24(1 + k)^2}\right)\frac{\gamma^2}{Dg} + \frac{k^2}{6(1 + k)^2}\frac{\gamma^2}{K^2DL}\right\}\bar{u} \qquad (2a)$$

or

$$H = 2\left\{1 + \gamma rR/(R + l)\right\}\frac{Dg}{\bar{u}} + \left\{\left(\frac{1 + 6k + 11k^2}{24(1 + k)^2}\right)\frac{\gamma^2}{Dg} + \frac{k}{6(1 + k)^2}\frac{d_f^2}{D_L}\right\}\bar{u}$$

Since for the new column,

$$V_G = \Sigma V_{G_1} = \pi l\{nd + 2nR + n(n - 1)a\}(d - 2d_f) \qquad (3a)$$

and

$$V_L = \Sigma V_{L_1} = 2\pi l d_f\{2nR + n(n - 1)a + n(d - d_f)\} \qquad (3b)$$

Whence

$$\beta = V_G/V_L = \gamma/d_f \text{ } (d_f \text{ being} < d)$$
$$K = \gamma k/d_f \qquad (3c)$$

which is analogous to the extended VAN DEEMTER equation for packed columns[2]. In principle normal packed columns, ordinary capillary columns and this new column can be treated in a similar manner. The influence of the various parameters on column efficiency can thus be easily evaluated as has been discussed by several authors[3–6], and this will not be repeated here. However, attention of the readers is drawn to the points of differences arising out of the changes introduced in the HETP equation.

Optimum linear gas velocity, minimum HETP, and maximum sample size

The minimum value of HETP, $2\sqrt{BC_G}$ is easily seen to be

$$= \gamma \sqrt{\left\{1 + \gamma r R/(R + l)\right\}\left\{\frac{1 + 6k + 11k^2}{3(1 + k)^2}\right\}}$$

$\cong 0.6\,\gamma\sqrt{1 + \gamma\, rR/(R + l)}$ for small values of k which is $\cong 0.6\,\gamma$ when $R = 0$; $\cong 0.6\,\gamma\sqrt{1 + r}$ when $R \gg l$, and $\gamma = 1$; and $\cong 1\sqrt{11/3}\sqrt{1 + \gamma\, rR/(R + l)}$ for large values of k, which will be $\cong 1.92\,r$ when $R = 0$ and $\cong 1.92\,r\sqrt{1 + r}$ when $R \gg l$, and $\gamma = 1$.

Because of the extra term $\gamma rR/(R + l)$, the minimum HETP obtainable in the present case would thus be larger than that possible for normal capillary columns of equivalent lengths.

Similarly, the optimum average linear gas velocity $(U_{opt}) = \sqrt{B/C_G}$ would be $\cong 7\,Dg/\gamma\sqrt{1 + \gamma\, rR/(R + l)}$ or $\cong 2\,Dg/\gamma$ according to whether k is very small or very large. The term $\sqrt{1 + \gamma\, rR/(R + l)}$ will reduce to 1 when $R = 0$, and to $\sqrt{1 + r}$ when $l \ll R$ and $\gamma = 1$.

The effect of the term $\gamma\, rR/(R + l)$ under the square root will be to reduce the dependence of U_{opt} on r. Thus in spite of small values of Dg (ref. 7), much larger carrier gas flow rates can be used in the case of the new column, resulting in shorter analysis time.

Assuming that a relation similar to KEULEMANS equation, giving the maximum amount of a substance injectable for packed columns from considerations of the effective volume of a theoretical plate[8], is applicable to the new column with the changed constant; the maximum sample size S, in ml vapour, would be

$$S = A'(V_G + KV_L)\sqrt{N}$$

where A' is a constant, and N the total number of theoretical plates

$$= A'(1 + k)(\pi l)^{3/2}\left[\left\{nd\sqrt{nR + \frac{n(n-1)a}{2}}\right\} + 2\left\{nR + \frac{n(n-1)a}{2}\right\}^{3/2}\right]$$

using eqns. 3 and 1.

The largest sample size which can be injected into the column is thus seen to be much larger than is usually possible for capillary columns; and this can be further increased by increasing n, R, l and d. For $R = 0$, and $n = 1$, when it approaches the

case of a capillary column, the sample size is found to approach to zero irrespective of the length l. The above equation of KEULEMANS[8], however, was shown to be unapplicable to normal capillary columns by DESTY[9].

Summarising, a column of even moderate dimensions, fabricated on this new design, should show the advantages of very large number of theoretical plates, larger sample capacity, very low column resistance and large permeability, faster analyses; besides permitting a change in its effective length during the analysis and ease of dismantling the column when required.

DISCUSSION

As has been mentioned earlier, the effective length of such a column can be greatly increased by increasing the length l, diameter D, and number of cylinders n, and decreasing the diameter of the clearance, d (eqn. 1). While the proper adjustment of these parameters, to produce columns of very large equivalent capillary length, is mainly limited by the difficulties involved in its manufacture, the increase in the radius R of the innermost cylinder and of the subsequent ones also has other implications. As shown earlier (eqn. 2), the HETP depends on the value of R. Increasing R to increase the effective column length, therefore, also results in a greater HETP. The rate of variation in the latter case, however, is relatively small because of the presence of several other terms also in the equation. R therefore may be made larger with advantage. But increase in the diameter of the cylinders beyond a certain value (perhaps greater than length l), may not be advisable, since in that case the efficiency of the column may not increase further. The other functions H_{min} and U_{opt} are only slightly influenced by the new design. Load capacity and permeability of the new column, however, will be much greater.

Like any other capillary column, the dead volumes have to be reduced to minimum. Besides the injector and detector dead volumes, there are several other design features which may add up to considerable dead volumes, particularly in the arrangement to vary the path length, and the bend over points inside the column. Utmost care is essential to reduce such non-useful volumes to the minimum, which may make the manufacturing requirements still more stringent.

During a change of gas path length various sets of cylinder spaces are bypassed; this is bound to change the column resistance and thereby the carrier gas flow rate. A flow regulator therefore may be very desirable for the circuit. Furthermore, during a decrease in path length, the portion of the carrier gas (along with certain portions of the sample) cut off becomes stagnant. This may slowly diffuse out into the main carrier gas stream with time or in case of a quick subsequent increase in the path length, may even produce a ghost peak and may introduce errors.

In spite of the various limitations and difficulties in fabrication of a column of such design, it is hoped that the concept may perhaps open up a new direction in devising more efficient and versatile columns leading to the realisation of the dream for a universal type of column for gas chromatography.

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