CHROM. 10,319

NON-CIRCULAR CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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SUMMARY

The potentialities of capillary columns of non-circular cross-section have been investigated using the gas path efficiency as the diagnostic.

Results indicate that coated non-circular capillary columns can offer a small increment in column efficiency compared with columns of circular cross-section.

Methods of coating non-circular capillary columns are being explored.

INTRODUCTION

In his outstanding paper presented at the Symposium held in Amsterdam in 1958, Golay[1] originated both the theoretical and practical basis of capillary column gas chromatography.

The equation relating height equivalent to a theoretical plate (HETP) and linear gas velocity, which bears his name along with those of Glueckauf and Van Deemter, allowed these fascinating high-performance columns to be designed, constructed and used for a new wide range of analytical problems, particularly associated with complex mixtures.

Over the succeeding two decades capillary columns have become steadily consolidated as the preferred form of gas chromatography, but it is surprising that only circular cross-section tubes have been employed in spite of the fact that Golay showed in his original paper that the performance of flat columns having a high aspect ratio was theoretically better by a factor of as much as 3 when k' is small.

The senior author has been intrigued by the potentialities of non-circular columns for many years, and at the First Symposium on Glass Capillaries in Hindelang during 1975 he discussed at some length the attributes of a number of new column forms. Among these were the flat glass capillaries and an unusual "crinkled" form which had been made by modifications of the original glass capillary-drawing machine. The latter had been conceived with the aim of disturbing the laminar gas flow through the tube so that enhanced transverse mixing would occur by a convected mechanism without causing significant additional longitudinal band broadening. Samples of these non-circular capillaries were distributed at the meeting but, surprisingly enough, no work was published on these or any other unconventional column forms.

In the autumn of 1976 therefore, it was decided to do some exploratory work on this topic by a simple study of the HETP *versus* $\bar{u}$ curves for a non-absorbed solute,

methane, and thus gain an immediate knowledge of the gas path efficiency of both flat and crinkled capillaries. The first results were presented at the Second Symposium on Glass Capillaries at Hindelang in the spring of this year[2], and these showed clearly that flat tubes had a lower minimum HETP than circular tubes of the same cross sectional area at slightly lower linear gas velocities. Perhaps, surprisingly it seemed that the only significant effect was to reduce the longitudinal diffusion term, B, of the Golay equation without any marked change in the slope of the curve at higher velocities or reduction in the C_G term. On the other hand, crinkled tubes, again with the same cross-sectional area, showed some marginal drop in the B term, but, most strikingly, a considerably lower C_G term. These resulted in an even lower minimum HETP, but, more importantly, this minimum was at a linear gas velocity of the order of twice those for both circular and flat columns.

The possibility appeared real of columns of average capacity having an elution time of approximately one quarter of that of similar circular columns at the same total plate numbers. However, since then extension of the work has shown that the preliminary results were distorted by an aberration in the apparatus, and the real gain is not as large as previously suggested.

The coating of such non-circular tubes is bound to be more difficult than that of round tubes and a study of the use of the established techniques of coating became the next stage in the investigation. Most emphasis was given to Dijkstra and De Goey's dynamic method[3] and the mercury pellet method of Schomburg[4] with smooth untreated Pyrex tubes as drawn.

THEORETICAL

In the investigation it was necessary to find a method of comparing the efficiencies of the different types of geometrically differing columns.

A method became apparent when the Golay equation relating the height equivalent to a theoretical plate, H, to column parameters was considered.

This equation for circular capillary columns is of the form:

$$H = \frac{2\,D_G}{\bar{u}} + \frac{1 + 6\,k' + 11\,(k')^2}{24\,(1 + k')^2}\,\frac{r^2}{D_G}\,\bar{u} + \frac{(k')^3}{6\,(1 + k')^2}\,\frac{r^2}{K^2\,D_L}\,\bar{u} \tag{1}$$

where:

- $\bar{u}$ = average linear gas velocity;
- r = column radius;
- D_G = diffusion coefficient of the solute in the gas phase;
- D_L = diffusion coefficient of the solute in the liquid phase;
- K = partition coefficient;
- k' = ratio of the liquid phase capacity to the gas phase capacity.

or

$$H = \frac{B}{\bar{u}} + C_G\,\bar{u} + C_L\,\bar{u} \tag{2}$$

The three terms account, respectively, for longitudinal gaseous diffusion $(B/\bar{u})$, resistance to mass transfer in the gas phase $(C_G\,\bar{u})$, and resistance to mass

transfer in the liquid phase ($C_L \bar{u}$). In eqn. 1 if the column in uncoated, then $k' = 0$. Thus it follows that for an uncoated circular column the Golay equation reduces to:

$$H = \frac{2\,D_G}{\bar{u}} + \frac{1}{24}\,\frac{r^2}{D_G}\,\bar{u} \tag{3}$$

or

$$H = \frac{B}{\bar{u}} + C_G^0\,\bar{u} \tag{4}$$

The C_L term, of course, vanishes but the C_G term does not, and it is this term that is of interest and shall be denoted by C_G^0 (C_G when $k' = 0$).

C_G^0, being a function of the column radius for circular columns, can be extended to a consideration of non-circular columns where it will be a function of some equivalent dimension.

It was decided, therefore, to determine the C_G^0 term for columns of various cross-section as this relates resistance to mass transfer in the gas phase to the column geometry. A reduction in the value of C_G^0 gives rise to a corresponding reduction in C_G for a coated column and is manifested in a lower HETP.

EXPERIMENTAL AND APPARATUS

Chromatographic apparatus

In order to conduct the work on gas path efficiencies with comparatively short columns (*i.e.* 13 m) it was necessary to build a high-speed apparatus similar to that developed by Desty *et al.*[5] in 1960.

The contemporary version of the apparatus comprised of a similar hydrogen flame detector and sample entry system with a division factor (*ca.* 10,000:1) into which gaseous and vapour samples were rapidly introduced by hammering down the plunger of a Hamilton gas-tight syringe.

No attempt was made to thermostat the column as the precise temperature of operation was in no sense critical. The coiled column therefore just hung in the laboratory environment at temperatures around 15°.

Recording system

The 1960 high-speed amplifier was re-designed to incorporate superior modern electronic components. A schematic diagram of the amplifier is shown in Fig. 1. The sensitivity of the amplifier is 10^{-12} A for a full scale deflection with a time constant of around 5 msec.

In this it had a similar performance to that of the original amplifier, a sensitivity with a rapid response time being limited only by the Johnson noise in the feedback resistor and the input capacity. This performance was achieved by mounting the first stage of amplification (a shielded F.E.T. analog device Type 42) directly on top of the flame ionization detector by a coaxial connector so as to minimize stray capacity, which would otherwise reduce the frequency response of the amplifier.

The chromatograms were recorded, as in 1960, using a fast UV recorder with simultaneous recordings being made over a range of sensitivities.

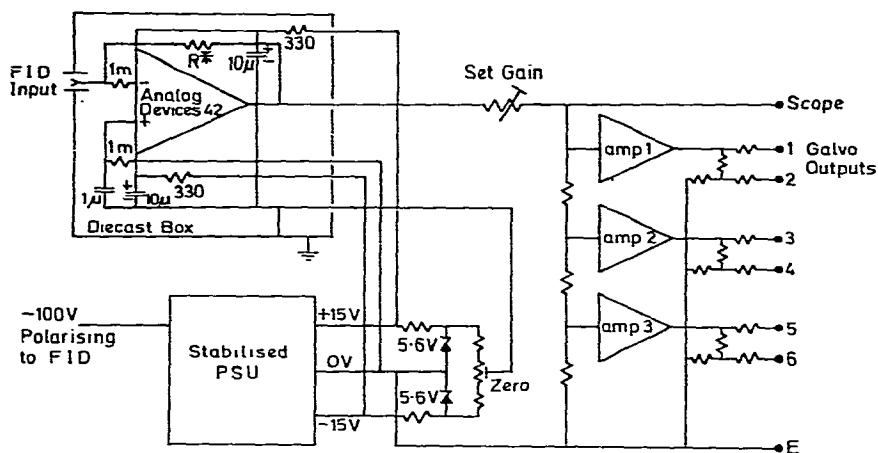Total elution times were of the order of a few seconds.

Fig. 1. Schematic diagram of the amplifier.

A timer was in-built into the amplifier to start the recording paper moving just before the emergence of the peak and to stop it after a pre-set duration. This allowed the recording paper to be conserved. The timer also served to put timing marks on the paper so that elution times and peak widths could be accurately measured and to this end paper speeds were chosen to give peak widths of 2 cm or more. A schematic diagram of the timer is shown in Fig. 2.

Columns

The columns used in this investigation were all Pyrex glass capillary columns drawn on a contemporary version of the glass-drawing machine developed by Desty et al.[6] in 1960.

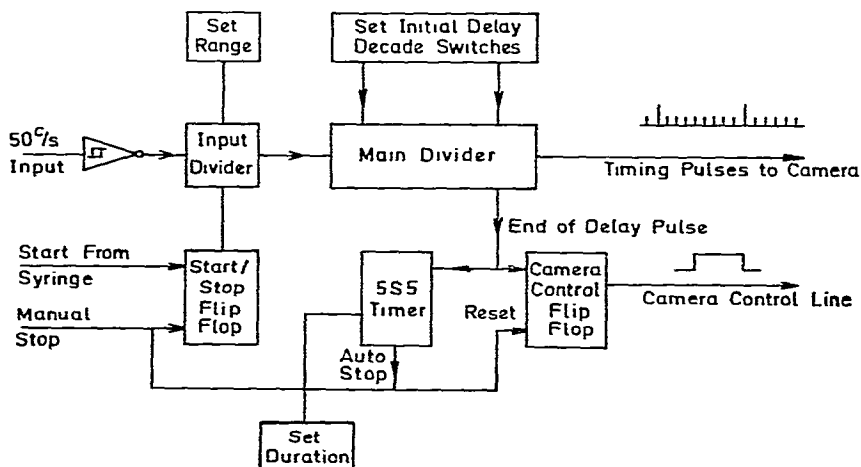Four types of column have so far been considered.

Fig. 2. Schematic diagram of the timer.

Circular capillary columns. Circular capillary was drawn in the conventional manner.

Flat capillary columns. Flat capillary was fabricated by flattening circular glass capillary while it was still soft. This was achieved by placing a pair of brass rollers just downstream of the heater of the drawing machine. The distance between the rollers was altered to achieve different aspect ratios. It was not found necessary to drive the rollers.

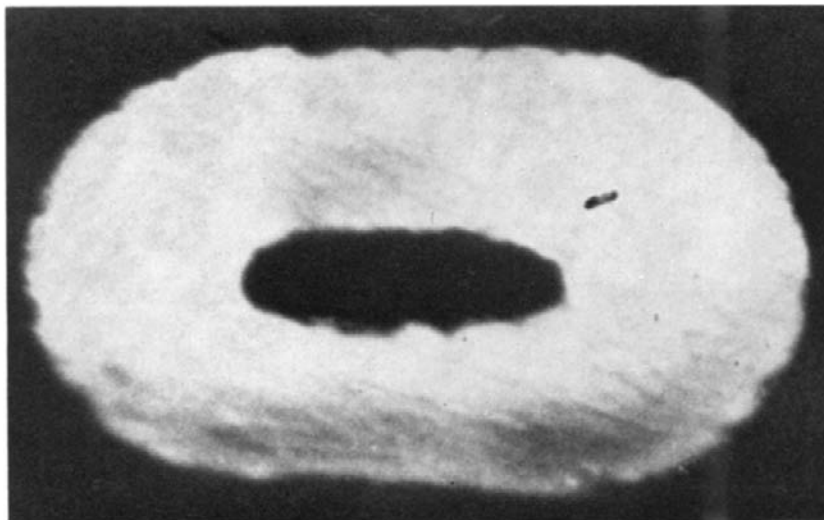A transverse section of this type of capillary is shown in Fig. 3.

Fig. 3. Transverse section of a flat capillary column.

Crinkled capillary columns. The concept of crinkled capillary was conceived of by the senior author and was described at the First International Symposium on Glass Capillary Chromatography in 1975[7].

It was thought that the geometry of the capillary would produce convective mixing in the transverse direction without significantly increasing the longitudinal band broadening.

The capillary was fabricated by placing a pair of cogs just downstream of the heater of the glass-drawing machine. Early attempts to make crinkled capillary were unsuccessful as the cogs were operated in mesh producing a sinusoidal capillary without altering the cross-section. This was overcome by adding a pair of gear wheels to the shafts of the cogs and orientating them such that they allowed the cogs to rotate in synchronization and not in mesh, thus producing a glass capillary of crimped longitudinal section.

A longitudinal sectional of such capillary is shown in Fig. 4.

Orthogonally crinkled capillary columns. An obvious extension to the work on capillary crinkled in one plane was to investigate the concept of capillary crinkled in two planes. The form chosen was a longitudinal cycle of circular, crimped horizontally, circular, crimped vertically, thus producing an orthogonally crinkled capillary.
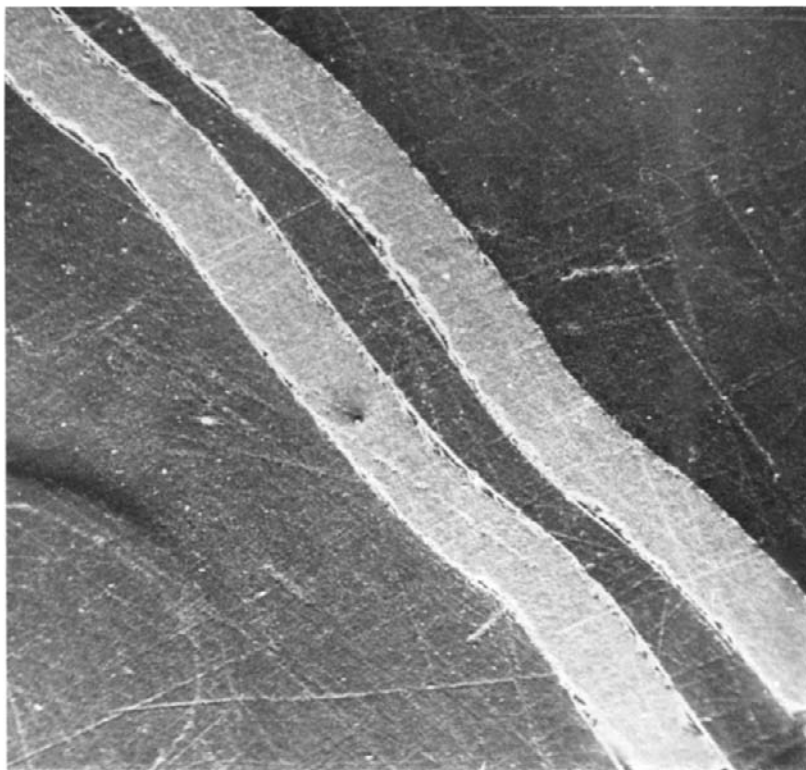
Fig. 4. Longitudinal section of a crinkled capillary column.

The capillary was fabricated by a special design of toothed roller arrangement again placed just downstream of the heater on the glass-drawing machine. The teeth on the rollers were such that two apertures consisting of two opposite sides of a square were alternately presented to the still soft circular capillary as it emerged from the heater.

It was found necessary to raise the heater temperature when drawing this type of capillary so that the glass was still soft on reaching the rollers. A powered drive for the toothed rollers was again not necessary.

Mounting columns

It was considered undesirable to leave lengths of capillary of circular cross-section at the ends of the non-circular columns to allow conventional mounting in the chromatographic apparatus as this could give distorted results, especially in the case of short columns.

The method of mounting decided upon was to use a silicone rubber septum in an adapted compression fitting so that the silicone rubber was compressed around the column forming a gas-tight seal regardless of the external geometry of the column.

Coating apparatus

The apparatus for coating columns with both the dynamic procedure and the

mercury pellet method was conventional with a constant flow helium supply obtained with a precision Negretti and Zambra pressure regulator forcing the driver gas through a long length of steel capillary tube (*ca.* 100 ft.) in parallel with a low-impedance bleed. This provided a constant flow of dry gas with which to push the pellets of coating solution (followed by a mercury pellet in the case of the Schomburg method) at uniform velocity along the tube.

Determination of the gas path efficiencies

The gas path efficiencies were determined by injecting 10-μl samples of methane into a splitting ratio of about 10,000:1 for each of the uncoated columns. From the eluted peaks HETP *versus* $\bar{u}$ curves were plotted.

The HETP was found using the relation

$$\text{HETP} = l \left(\frac{\Delta t}{4\,t} \right)^2 \tag{4}$$

where:

l = length of the column;
Δt = peak width at the tangent intercept;
t = elution time measured from the start.

The H *vs.* $\bar{u}$ curves were compared to determine the relative efficiencies of the different column geometries.

GAS PATH EFFICIENCY DETERMINATION

Procedure

The results described earlier at Hindelang for circular, flat and crinkled columns were confirmed and extended as the first part of the experimental work conducted, the use of helium as carrier gas being maintained. HETP *vs.* average linear gas velocity curves for groups of flat and crinkled columns with a range of degree of flattening were compared with that for a circular column drawn with a similar draw ratio. The cross section ratios between the reference circular column and the group of flat columns having a range of aspect ratios are given in Table I together with other dimensional data and the system diffusivity. Groups of crinkled columns, of the 180° type, are compared in a similar way with the reference circular column in Table II. In this case, the aspect ratio of the flat section of the columns is given together with crinkling pitch.

TABLE I

DIMENSIONAL DATA FOR COLUMNS USED IN METHANE–HELIUM SYSTEM
Diffusivity = 0.62 cm^2/sec.

Column	Length (m)	Aspect ratio	Cross-sectional area ratio
Circular	12.6	1:1	1.0
Flat A	12.6	1.4:1	1.0
Flat B	12.6	3.3:1	0.7
Flat C	12.6	4.1:1	0.57
Flat D	12.6	6.2:1	0.41

TABLE II

DIMENSIONAL DATA FOR CRINKLED COLUMNS USED IN METHANE–HELIUM SYSTEM

Diffusivity = 0.62 cm²/sec.

Column	Length (m)	Pitch of crinkling (mm)	Aspect ratio at flat section
Circular	12.6	—	—
Crinkled A	12.6	2.3	1.7:1
Crinkled B	12.6	2.3	2.2:1
Crinkled C	12.6	2.3	2.8:1

It is clear that the act of flattening glass capillary causes a substantial loss of cross sectional area as might have been expected and subsequent performance comparison made between circular–flat and circular–crinkled must take account of this feature.

HETP vs. $\bar{u}$ curves obtained supported well the original hypothesis that substantial reductions in the C_G term of the Golay equation could be effected by flattening or crinkling, with the best results being obtained with the latter column as suggested in our earlier paper and explained on the basis of a new convection term. Final assessment of the results, however, exposed the fact that the reference circular column had a minimum HETP value that was about twice the value predicted by the Golay equation and caused considerable concern, at a late stage, in respect of the splitter performance.

The metal splitter employed was replaced with a simple all glass design manufactured by SGE (North Melbourne, Australia) and the HETP vs. $\bar{u}$ curve for the reference circular column was hastily redetermined. It became immediately apparent that the minimum HETP value was now much closer to that predicted by the Golay equation and that the HETP data determined earlier with the metal splitter were markedly distorted by band broadening effects in the metal design, particularly at linear gas velocities above 30 cm/sec.

The confusion caused by this unexpected poor performance of a well-proven splitter design caused a re-assessment of the response time of the detector and the time constant of the amplifier and recording system as these could well have been contributing additional band broadening effects at the highest linear velocities when peak widths were a fraction of a second.

The time constant of the amplifier and recording system was therefore determined by injecting a step function voltage change into the input of the FET preamplifier. A value of 6.6 msec was obtained, and on Schmauch's criteria[8] by which the time constant should be less than a twentieth of the peak width for faithful peak reproduction, it became clear that this constrained the minimum width for methane peaks emerging from the column to above 140 msec.

Similarly the response time of the detector was measured by injecting a long, box car-type peak, with a flat top, directly into the detector entry using a very short connector and a very dilute methane–helium mixture. The additional band broadening effect of the detector was shown, in this way, to be about 4 msec, presumably owing to the ion transit time across the jet–collector gap. The apparatus in this form

was therefore limited by these two factors, to the passage of methane peaks with widths not less than 150 msec.

This background enabled the performance of the two splitters to be directly determined by injecting 10-μl methane samples into each, in the manner described earlier, with the shortest possible connection to the detector. The metal design produced a minimum peak width of 90 msec whereas the all glass SGE design allowed peaks of about half the value, 40 msec, to be produced.

It would have been possible to make a substantial improvement in the time constant of the amplifier–recording system to achieve the 1-msec time constant originally projected, and similarly a new detector design with a smaller interelectrode distance might well have produced a significant reduction in the detector response. Time, however, did not permit this development work, which would undoubtedly had to have included an improved splitter design to match this performance.

In the event it was decided to adopt two changes in the operational procedure to make further work compatible with the constraints of the equipment as then defined. The first was to use columns with a somewhat wider bore to manifest larger C_G^0 values and so make comparison of the performance of the three column forms more apparent. The second involved a choice of sample–carrier gas system which would have a lower diffusivity and thus give minimum HETP values at substantially lower gas velocities. In this way the peak width, even at the higher flow-rate end of the HETP *vs.* $\bar{u}$ curves, would be never less than 200 msec. The vapour of *n*-heptane was first substituted for methane with helium as carrier gas, but slight skewness of the peaks was noticed, presumably owing to adsorption on the glass wall of the capillary of the heavy vapour.

The substitution of carbon dioxide for helium using again methane as sample was more successful, and the final assessment of column form performance was made using this combination. For comparison with the original experiments using methane–helium, dimensional values for the wider column are given in Tables III and IV again with the system diffusivity (methane–helium 0.62 cm²/sec, methane–carbon dioxide 0.17 cm²/sec).

Fig. 5 shows the HETP *vs.* $\bar{u}$ curves for the methane–helium system with a circular (0.025 cm diameter) column using the original metal splitter and the glass SGE splitter. The high linear gas velocities necessary to complete the curves at the

TABLE III

DATA FOR FLAT COLUMNS FOR METHANE–CARBON DIOXIDE SYSTEM

Diffusivity = 0.17 cm²/sec.

Column	Length (m)	Cross-section dimensions (mm)	Aspect ratio	$H_{min.}$ (cm)	Specific pressure drop at 50 cm/sec (mm Hg/m)	$C_G^0 \times 10^4$ (sec)	Specific rate of plate production (sec⁻¹·m⁻¹)
Circular 1	12.6	0.5	1:1	0.0145	0.10	1.7	230
Flat 2	12.6	0.18 × 0.57	3.2:1	0.0125	0.25	1.5	330
Flat 3	12.6	0.10 × 0.61	6.1:1	0.011	0.75	1.2	400
Flat 4	12.6	0.07 × 0.66	9.4:1	0.0155	2.25	3.7	160

TABLE IV

DATA FOR CRINKLED COLUMNS FOR METHANE–CARBON DIOXIDE SYSTEM

Diffusivity = 0.17 cm²/sec.

Column	Length (m)	Max. diameter (mm)	Min. diameter (mm)	$H_{min.}$ (cm)	Specific pressure drop at 50 cm/sec (mm Hg/m)	$C^0_G \times 10^4$ (sec)	Specific rate of plate production ($sec^{-1} \cdot m^{-1}$)
Circular 1	12.6	0.5	—	0.0145	0.1	1.7	230
Crinkled 2	12.6	0.5	0.1	0.0135	0.15	1.6	260
Crinkled 3	12.6	0.5	0.07	0.0125	0.2	1.5	300
Crinkled 4	12.6	0.5	0.03	0.0175	0.35	2.5	170

upper flow-rate end should be noted in the context of the associated sample peak widths, which are indicated on the plot for three linear gas velocity values. It is obviously impossible to obtain the true curve shape with the apparatus constraint of 150 msec.

In contrast Fig. 6 shows the predicted curves for methane–carbon dioxide with the larger bore columns (round diameter 0.05 cm) which demonstrate that the upper linear gas velocities required are a fifth of those for helium. Peak widths are well above
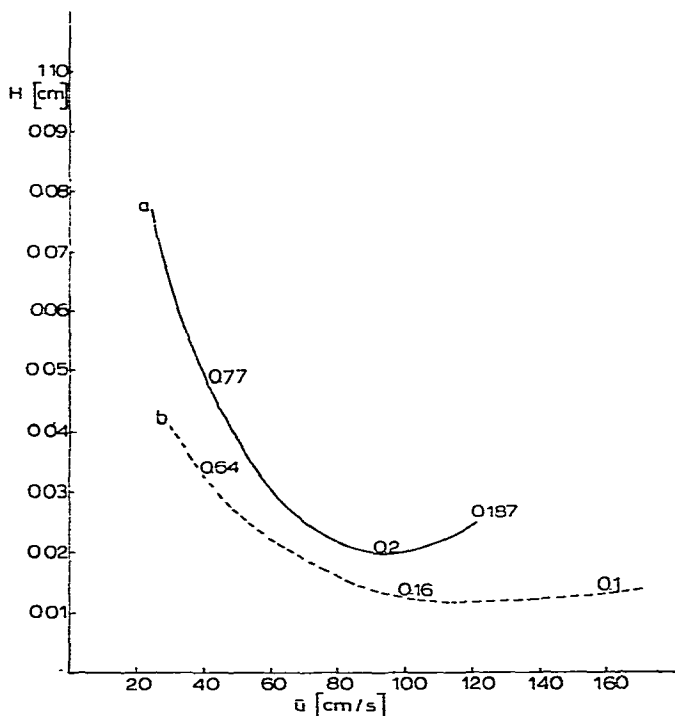

Fig. 5. Comparison of the HETP *vs.* *ū* curves obtained for a circular (0.25 mm diameter) column with a metal splitter (a) and with a glass splitter (b).
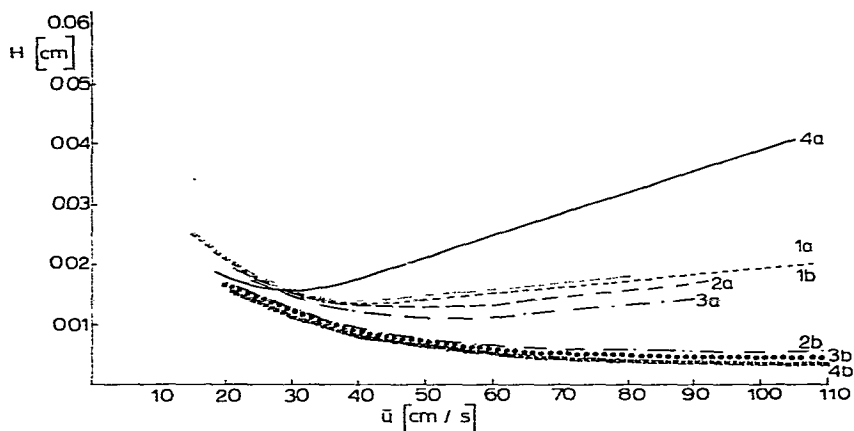
Fig. 6. Experimental and predicted HETP *vs.* $\bar{u}$ curves for flat glass capillaries (uncoated). Carrier gas, carbon dioxide. 1a = Experimental circular 1; 1b = predicted circular 1; 2a = experimental flat 2; 2b = predicted flat 2; 3a = experimental flat 3; 3b = predicted flat 3; 4a = experimental flat 4; 4b = predicted flat 4.

the 150 msec limit over the complete range of $\bar{u}$. Experimental curves for circular and flat columns are shown on the plot, and it is clear that these are true curves not distorted by band broadening effects either in the sample splitter, detector or amplifier recording system.

It therefore became possible to conduct a systematic examination of the dimensional parameters of the various column forms with complete reality and to compare and contrast their performance both with non-absorbed methane peaks and as projected coated columns.
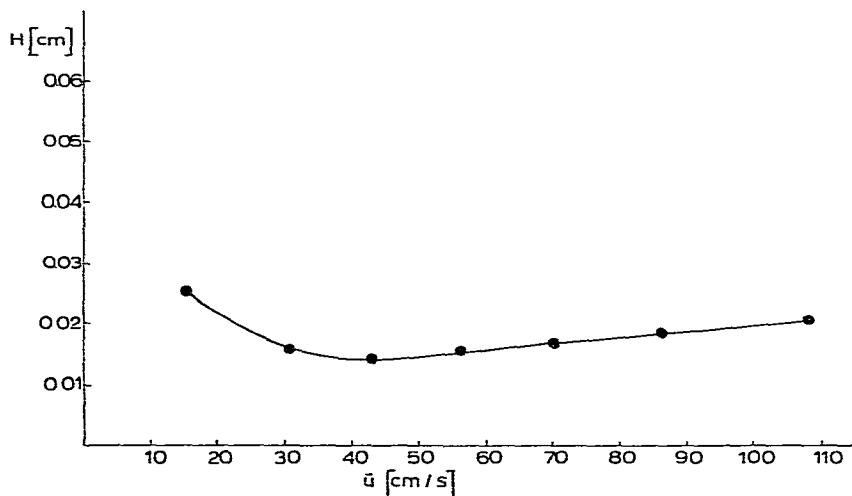

Fig. 7. HETP *vs.* $\bar{u}$ curve for a circular uncoated column showing the accuracy of the gas path efficiency determination. Carrier gas, carbon dioxide; column diameter, 0.05 cm.

Results and discussion

Fig. 5 shows the HETP *versus* $\bar{u}$ plot for the metal and glass sample entry systems. It is clear that the result is distorted in the case of the metal sample entry system owing to severe band broadening whilst the true shape of the curve is given by the SGE glass sample entry system with distortion only apparent at the very high velocity end where the peak widths are limited by the restraints of the amplifier–recording system.

It was for the latter reason that larger bore columns and a carrier gas of lower diffusivity for methane (carbon dioxide) were chosen so that the minimum HETP values occurred at lower average linear gas velocities. Fig. 7 shows the accuracy of the gas path efficiency determination for a circular column (diameter 0.05 cm).

Flat columns. It is clear from the HETP *versus* $\bar{u}$ curves in Fig. 6 and the data in Table III that flattening circular capillary initially produces a lower HETP than that for circular capillary, which is due to a reduction in the resistance to mass transfer in the gas phase as proposed by Golay.

The minimum HETP for the flat 2 and 3 columns occur at higher velocities than the circular column minimum which is in line with a reduction in the C_G^0 value as differentiating eqn. 4 with respect to $\bar{u}$ gives

$$\frac{\mathrm{d}H}{\mathrm{d}\bar{u}} = -\frac{B}{\bar{u}^2} + C_G^0 \tag{5}$$

At the minimum value $\dfrac{\mathrm{d}H}{\mathrm{d}\bar{u}} = 0$

$$\frac{B}{C_G^0} = \bar{u}^2 \tag{6}$$

which shows reducing the C_G^0 value increases the velocity at which the HETP minimum occurs.

Fig. 6 also shows the HETP *versus* $\bar{u}$ curve for flat column 4 which displays a higher minimum HETP than the reference circular column. It is believed that this is because the aspect ratio is so large for this column that, owing to poor uniformity of the bore, the opposing faces of the column actually touch in places along the length. This gives rise to regions of local turbulence, which have the effect of increasing the longitudinal band broadening and this as one would expect is quite marked at high velocities.

The equation linking H and $\bar{u}$ for coated flat columns as derived by Golay is:

$$H = \frac{2 D_G}{\bar{u}} + \frac{4 (1 + 9 k' + 25.5 (k')^2)}{105 (1 + k')^2} \frac{\bar{u}z^2}{D_G} + \frac{2 (k')^3}{3 (1 + k')^2} \frac{\bar{u}z^2}{K^2 D_L} \tag{7}$$

where:

H = effective height equivalent to a theoretical plate;
$\bar{u}$ = average velocity of carrier gas;
D_L = coefficient of diffusion in the liquid phase;
D_G = coefficient of diffusion in the gas phase;
k' = ratio of liquid phase capacity to the gas phase capacity;

K = partition coefficient;
z = half internal thickness of flat tube.

which for uncoated flat columns reduces to:

$$H = \frac{2 D_G}{\bar{u}} + \frac{4}{105} \frac{z^2}{D_G} \bar{u} \tag{8}$$

Using this equation the predicted H–$\bar{u}$ curves were plotted in Fig. 6. Comparing the experimental curves with the predicted curves, it appears the experimental results do not agree with Golay's theory perhaps because the cross section is ellipsoidal rather than flat rectangular.

Fig. 8 shows a comparison of the predicted H–$\bar{u}$ curves for the circular column and flat column 2 ($k' = 2$) assuming Golay's theory to be true. In the light of the gas path efficiency results obtained, however, it seems unlikely that coated flat glass capillary columns, made by this method, will manifest such a large increase in performance.

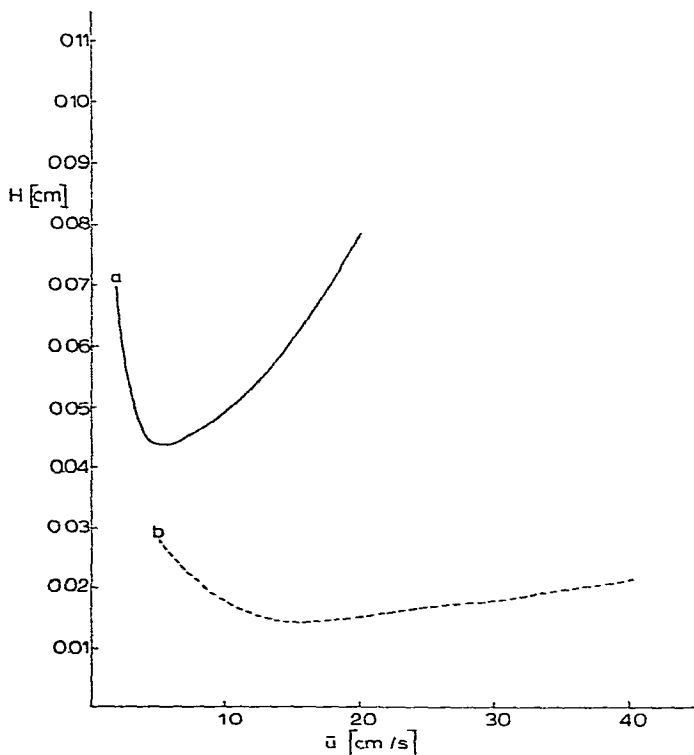As would be expected the pressure drop along the column rises sharply with increasing aspect ratio.

Fig. 8. Predicted HETP vs. $\bar{u}$ curves for coated circular and flat columns. Carrier gas, nitrogen; solute, n-heptane; stationary phase, squalane; $k' = 2$. a, Circular ($r = 0.0254$ cm); b, flat ($z = 0.0089$ cm; aspect ratio 3:1).

Crinkled capillary. The HETP *versus* $\bar{u}$ curves in Fig. 9 show that crinkling circular capillary does initially produce lower HETP minima which occur at slightly higher average linear gas velocities as compared with the reference circular column. This reduction in the HETP is due to a reduction in the resistance to mass transfer in the gas phase, C_G^0, which also accounts for the increase in the gas velocity at the minimum HETP.
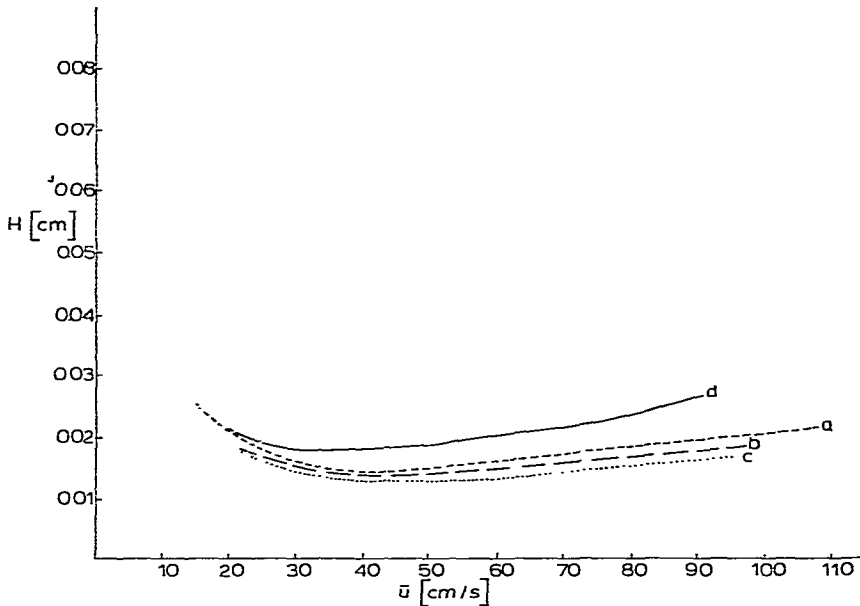

Fig. 9. Experimental HETP *vs.* $\bar{u}$ curves for crinkled (180°) glass capillary columns (uncoated). Carrier gas, carbon dioxide. a, Circular 1; b, crinkled 2; c, crinkled 3; d, crinkled 4.

The reduction in C_G^0 is somewhat less for the crinkled columns than for the flat columns and so it is reasonable to assume that the reduction in C_G^0 for crinkled columns is due only to a reduction in the characteristic dimension of the capillary rather than to a convective mixing phenomenon acting across the column as originally hoped for.

With very heavily crinkled columns an increase in HETP is apparent as is the case with very flat columns. Similarly this probably is due to poor uniformity of the column bore, which leads to opposite faces of the column to touch which again gives rise to local turbulence. This increases the longitudinal band broadening along the column which is marked at high linear gas velocities.

Data for crinkled columns are given in Table IV.

Orthogonally crinkled capillary. The orthogonally crinkled capillary produced results very similar to the 180° crinkled capillary with reduction in the C_G^0 term being due primarily to a reduction in the characteristic dimension rather than being due to a convective mixing phenomenon.

Conclusions

It is concluded that gains in efficiency of capillary columns, particularly in

terms of plate production per second, can be obtained by use of flat or crinkled capillaries whilst the same sample capacity is maintained as compared with circular columns.

The gain in efficiency displayed by flat columns is somewhat smaller than originally predicted by Golay, which may be due to the fact that the columns used in the investigation were elliptical in section rather than rectangular upon which Golay based his predictions.

It may be necessary to achieve very large aspect ratios in order for his theory to apply effectively.

Work in this direction would certainly be worthwhile as Fig. 8 shows that 8,000 theoretical plates per metre could be achieved.

New column forms are still being explored such as the tightly coiled columns Tijssen[10] has considered for liquid chromatography. Also static mixer columns (which consist of right and left handed twisted elements orientated at 90° to each other) have been assessed. Both of these have been considered in an attempt to produce real convective mixing which would decrease the resistance to mass transfer in the gas phase. However, preliminary results indicate that in a tightly coiled column very little reduction in HETP is manifested at the velocities in the area of the optimum average linear gas velocity although reduction in the resistance to mass transfer in the gas phase is apparent at higher velocities.

The static mixer columns display higher HETP values than the corresponding open-tube columns because the mixing elements block the diffusion path but do not produce enough convective mixing to compensate for this.

Results so far indicate that no more than a maximum of about 70 % increase in efficiency can be achieved by column forms designed to produce secondary flow mixing phenomena. This is because such mixing will undoubtedly be velocity-dependent and will not have a significant effect on the HETP at the average linear gas velocities in the region of the optimum value. This is because in capillaries the Reynolds number in this velocity region is too small.

A velocity-independent method of mixing is currently being explored employing the spinning band principle from distillation technology.

Further details of these types of columns will be presented at the symposium.

COLUMN COATING

Procedures

It is considered worthwhile to attempt to coat the non-circular columns that have been explored as a confirmation of the results obtained on gas path efficiencies.

Preliminary attempts have been made employing Dijkstra and De Goey's dynamic method and Schomburg's mercury pellet dynamic method using solutions of squalane in heptane and SF-96 silicone oil in toluene.

The attempts so far have failed, but some hope is still held out that these columns can be coated as watching the coating process under a microscope shows that the film collapse is not instantaneous. Coating of unetched columns only has so far been tried.

Whilst exploring for new thoughts on coating which would work on any geometry of column the method discovered by Blodgett[9] for producing multi-layer mono-

molecular films stimulated some new thoughts. She found that when a microscope slide was pushed through a water–air interface upon which was a condensed mono-layer of stearic acid (a surfactant), a layer of the latter acid, one molecule thick, was deposited on the slide. If the water contained small amounts of barium and copper ions, repeated dipping of the slide produced more layers and up to 3000 on top of each other were produced. The layers consist of stearic acid and barium and copper stearate. The layers are alternately reversed such that carboxylic and hydrocarbon groups alternately face outwards in consecutive layers.

This appeared to be an exciting prospect for coating non-circular capillaries as the phenomenon does not seem likely to depend on the geometry factors very much.

It also offered the potentiality of coating circular columns with quantitative amounts of stationary phase and furthermore the characteristic of the coating could be chosen by choosing an odd or even number of layers.

A preliminary investigation was therefore made of the Blodgett technique using circular columns. An aqueous solution of the following concentrations of bar-ium and copper ions was made up (pH 6.8): $0.3 \cdot 10^{-4}\ M\ BaCl_2$, $2.0 \cdot 10^{-4}\ M\ KHCO_3$, $0.02 \cdot 10^{-4}\ M\ CuCl_2$ (or other soluble copper salt).

A burette with a length of rubber tubing attached to the outlet end was used as a variable head device. A compression fitting was attached to the end of the rubber tube and the capillary pushed into it through a rubber septum.

A small crystal of stearic acid was placed into the beginning of the capillary and this was pushed up it by use of the head of solution in the burette. Care was taken to ensure that the crystal of stearic acid remained on the meniscus. The stearic acid spreads directly onto the meniscus of the aqueous solution producing a condensed monolayer. The crystal was pushed through the column at about 1 mm/sec so that the rate of deposition of the monolayer did not exceed the rate of evaporation from the crystal.

When the crystal reached the other end of the capillary it was forced back, again on the meniscus, by helium gas. This was repeated several times. When the desired number of layers had been achieved the column was dried by passing dry helium gas down the column.

Results and discussion

The first Blodgett layer has lyophilic characteristics as the carboxylic groups hydrogen bond to the hydroxyl groups on the glass surface. Therefore, as there is a reversal on every consecutive layer all odd layers should have lyophilic characteristics and even layers should have lyophobic characteristics.

Fig. 10 shows a chromatogram obtained on a column of 896 cm in length with five Blodgett layers.

The order of the components is fascinating in that heptane is eluted before iso-octane, which is opposite to the order obtained on squalane. Also toluene is eluted very early.

Because the stationary phase is crystalline, the peaks are adsorption peaks and this is born out by the fact that the absolute retention increased very little with further layers, indicating that the interaction is with the top monolayer only.

It was noted that on even layers the isooctane peak was skewed whilst that of heptane was only slightly skewed. This is probably due to the carboxylic groups of the
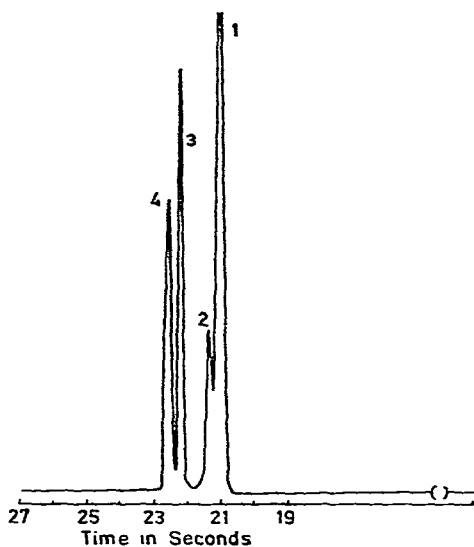
Fig. 10. Chromatogram on column coated with five Blodgett layers. Peaks: 1, methane; 2, toluene; 3, heptane; 4, isooctane.

stearic acid and stearates inducing polarization in the polarizable isooctane molecule and increasing the adsorption.

In her work on surface films Blodgett found that if multiple layers of stearic acid and stearates are built up and the films soaked in benzene, the stearic acid is leached out to leave a skeletal structure of mixed metal stearates. This presents the exciting possibility of producing a stereospecific absorption layer on the capillary wall.

Attempts are being made to produce the new skeletal coating in about 100 layers so that the molecular porosity it potentially exhibits may be exploited for very specific separation.

Conclusions

It is concluded that coating by the Blodgett technique can produce quantitative coating. The multi-layers produced display some interesting characteristics.

The technique offers the potentiality of stereospecific, stationary, phases that could be employed in capillaries of all types, which may particularly solve some of the problems of non-circular columns.

LIST OF SYMBOLS

C_G Resistance to mass transfer in the gas phase.
C_G^0 Resistance to mass transfer in the gas phase when k' is zero.
C_L Resistance to mass transfer in the liquid phase.
D_G Gaseous diffusion coefficient.
D_L Liquid diffusion coefficient.
H Height equivalent to a theoretical plate (HETP).
k' Ratio of liquid phase capacity to gas phase capacity.

K Partition coefficient.
l Column length.
n Number of theoretical plates.
P_i Column inlet pressure.
r Column radius.
t Elution time of component from start.
Δt Peak width at tangent intercept with baseline.
$\bar{u}$ Average linear gas velocity.
z Half the inter-wall distance for flat capillary.

ACKNOWLEDGEMENTS

REFERENCES

1 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958.
2 D. H. Desty and A. A. Douglas. *2nd Internat. Symp. Glass Capillary Chromatogr., Hindelang, 1977*, to be published.
3 G. Dijkstra and J. de Goey, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958.
4 G. Schomburg, *Proceed. First Internat. Symp. Glass Capillary Chromatogr., Hindelang, 1976*, Institut für Chromatographie, Bad Dürkheim, p. 61.
5 D. H. Desty, A. Goldup and W. T. Swanton, in N. Bremner (Editor), *Gas Chromatography*, Academic Press, New York, 1962.
6 D. H. Desty, J. N. Haresnape and B. H. F. Whyman, *Anal. Chem.*, 32 (1960) 302.
7 D. H. Desty, *Chromatographia*, 8 (1975) 452.
8 L. J. Schmauch, *Anal. Chem.*, 31 (1959) 225.
9 K. Blodgett, *Phys. Rev.*, 51 (1937) 964; *J. Amer. Chem. Soc.*, 57 (1935) 1007.
10 R. Tijssen, *12th International Symposium on Advances in Chromatography, Amsterdam, November 7–10, 1977*.