Journal of Chromatography, 158 (1978) 73–82

CHROM. 11,025

STUDY OF NEW COLUMN FORMS IN GAS CHROMATOGRAPHY

D. H. DESTY and A. A. DOUGLAS

The British Petroleum Company Limited, BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex (Great Britain)

SUMMARY

After the authors' previous study of non-circular capillaries for gas chromatography (GC) showed that only a small increase in efficiency could be effected by these columns, further column forms have been assessed with a view to reducing the resistance to mass transfer in the gas phase.

Using the gas path efficiency as the diagnostic different column forms have been assessed, such as static mixer columns, helically coiled open-tube (HOT) columns which Tijssen has considered for liquid chromatography and spinning band columns taken from distillation technology.

Results so far obtained show that HOT columns could have potential in GC whilst static mixer and spinning band columns offer no advantage.

INTRODUCTION

In 1958 Golay originated both the practical and theoretical bases of capillary column gas chromatography[1]. The equation which bears his name allowed high-performance columns to be "designed".

Since then, however, although capillary column techniques, sampling and detection systems have been greatly advanced there has been no major improvement in the efficiency attainable from capillary columns although there is an increasing requirement for such in the medical and biochemical fields, where complex stereoisomers have to be separated.

It was for this reason that the authors decided to reconsider the implications of the Golay equation to assess the possibilities of increasing the efficiency of capillary columns. In abbreviated form the Golay equation is (see List of symbols):

$$H = \frac{B}{\bar{u}} + C_G\bar{u} + C_L\bar{u} \qquad (1)$$

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 ($C_L\bar{u}$).

Longitudinal diffusion is small at high gas velocities. Resistance to mass transfer in the liquid phase is usually quite small, the largest contribution to the height equivalent to a theoretical plate (HETP) coming from the resistance to mass transfer in the gas phase. It was therefore decided to try to reduce this term by attempting to introduce a convective mixing phenomenon producing radial mixing without significant axial mixing.

Initial attempts to achieve this consisted of changing the geometry of the capillary column, but the results presented at Amsterdam[2] showed only a slight advantage in terms of efficiency which was outweighed by the disadvantage of coating difficulties. It was also clear that the slight decrease in HETP was due to a decrease in the characteristic dimensions of the capillaries rather than due to a mixing effect.

The second stage of the investigation consisted of an appraisal of helically coiled open-tube (HOT) columns wherein the centrifugal forces[3] give rise to a distortion of the Taylor profile[4] to produce a Dean-like profile[5], a characteristic of which is a secondary radial flow.

Most effort, however, was concentrated on the addition of various elements (both static and moving) to the inside of the columns designed to impart a radial velocity to the carrier gas.

In this way it was aimed to produce a gas path efficient column leaving the introduction of a stationary phase to a further investigation.

THEORETICAL

In assessment of the columns our previous method of determining the gas path efficiency[2] was employed.

Methane was injected into the uncoated columns which allowed HETP *versus* $\bar{u}$ curves to be plotted.

As k' is zero the Golay equation reduces to

$$H = \frac{B}{\bar{u}} + C^0_G \bar{u}$$

where C^0_G is the resistance to mass transfer in the gas phase when $k' = 0$. A column form which manifests a lower C^0_G term than the corresponding open-tube column can be expected to manifest a lower C_G term when a stationary phase is introduced.

EXPERIMENTAL

Chromatographic apparatus

The chromatographic assembly was a very simple arrangement comprising of a glass sampling system manufactured by Scientific Glass Engineering (SGE, North Melbourne, Australia) and a hydrogen flame ionisation unit. The carrier gas was carbon dioxide.

Recording system

The amplifier was a fast-response amplifier with a time constant of around 6 msec and a full-scale deflection of 10^{-12} A. The output was fed to a fast ultraviolet (UV) recorder over a range of sensitivities simultaneously.

Columns

HOT columns. These were made by winding copper or stainless-steel capillary around suitable-diameter metal rods as formers. All metal columns were washed through with toluene followed by trichloroethane followed by acetone in order to remove any hydrocarbons present.

Static mixer columns. These columns consists of alternate right- and left-handed twisted metal elements inserted into a glass column. The twists are orientated at 90° to each other. The columns are similar in form to the static mixers manufactured by Kenics (Danvers, Mass., U.S.A.). The mixing action is a double effect of the elements inducing a radial velocity and also stratifying the flow by flow division at each element.

The smallest commercially available mixer is 7 mm I.D. Our work necessitated much smaller diameter columns to be made and after much perseverence 1.5 mm I.D. columns were constructed in lengths up to 1.65 m. The method of construction was to take two lengths of Ni-chrome tape and to twist them tightly in a drill, one right handed and the other left handed.

For the production of 180° static mixer columns the tapes were cut up at intervals of 180°, for the 90° static mixer columns the tapes were cut at 90° intervals. The twists thus formed were approximately 3 mm in length. The twists were spot-welded together (alternately left- and right-handed twists) by means of a small piece of stainless-steel wire. The chain thus formed was then drawn into glass capillary by feeding it down the glass tube from which the capillary was being drawn.

As mentioned above two types of mixer were produced, one comprised of 180° twists, the other 90° twists. Figs. 1 and 2 show close-up pictures of a section of the 180° Kenics-type column produced.

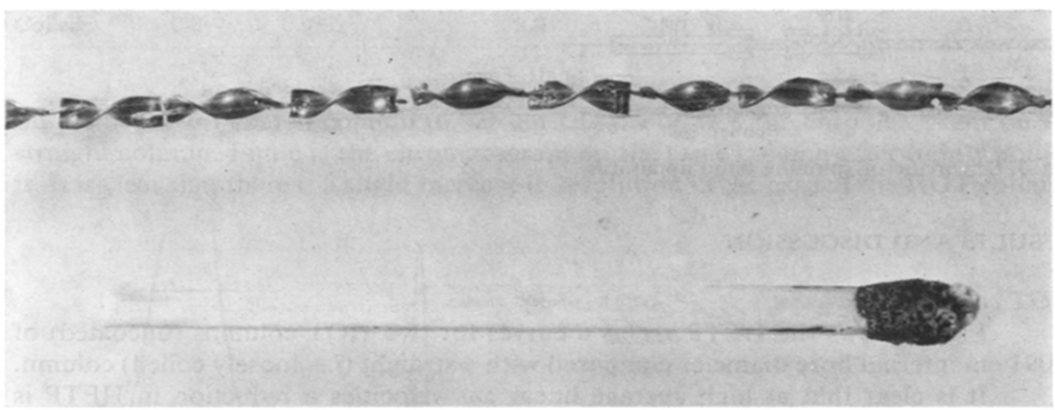

Fig. 1. Static mixer (section). (A match is shown to indicate the scale.)

Spinning band columns. Spinning band columns were designed to produce a mechanical mixing independent of the average linear gas velocity.

The columns consisted of 1.6 mm I.D. copper tube 1.65 m in length. Inside the column bands of different types could be inserted. Two types of band were used, the first was a tightly twisted length of Ni-chrome tape (closed-structure band), the second was a flattened copper wire helix (open-structure band).

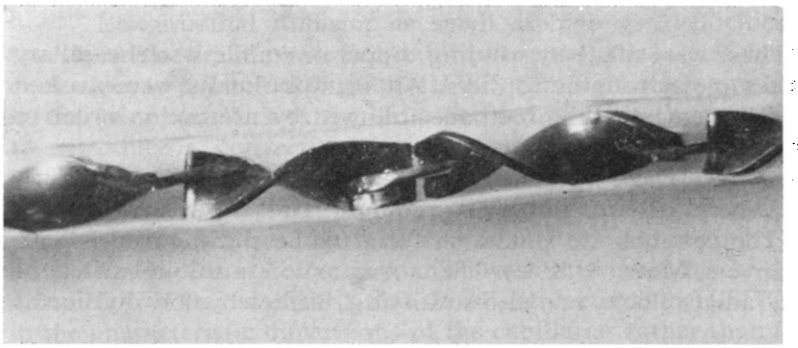

Fig. 2. Static mixer (section).

Spinning band column apparatus

The bands employed were hard soldered to a thin stainless-steel shaft which entered the column through a lubricated glass gland. The gland being sealed to the copper column by means of a compressed rubber seal. There was a deliberate bleed rate of carrier gas through the gland to provide a constant purge. The band was driven by means of a DC model motor connected to the shaft soldered to it. By supplying a range of voltages speeds up to 7500 rpm could be achieved. Fig. 3 shows a schematic of the spinning band arrangement.

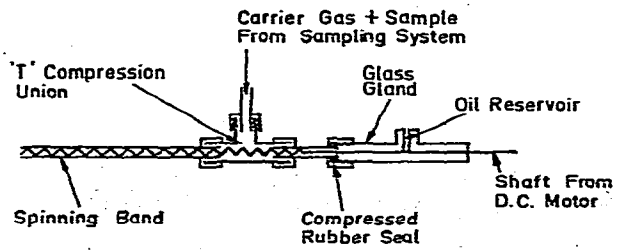

Fig. 3. Schematic of spinning band apparatus.

RESULTS AND DISCUSSION

HOT columns

Fig. 4 shows the HETP *versus* $\bar{u}$ curves for two HOT columns (uncoated) of 0.091 cm internal bore diameter compared with a straight (*i.e.* loosely coiled) column.

It is clear that at high average linear gas velocities a reduction in HETP is effected by coiling which causes a reduction in the C^0_G term. The effect seems to increase with tighter coiling. There is only a slight reduction in the HETP values in the velocity region where the minimum HETP occurs for the straight column.

The fascinating feature of the curves for the HOT columns is that they reach HETP maxima at high linear gas velocities. Unfortunately the time constant restraint of the apparatus prevented investigating further into this region. However, at the first available opportunity the necessary modifications to the apparatus will be made in order to perform the work.

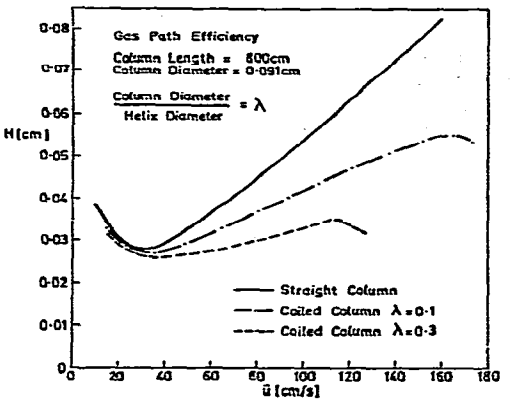

Fig. 4. Comparison of the HETP *versus* $\bar{u}$ curves for straight and tightly coiled uncoated copper columns.

As Tijssen[3] has explained with reference to liquid chromatography (LC) the reduction in HETP produced by coiling is due to centrifugal forces giving rise to a secondary flow phenomenon which can be considered to mix radially in the column. Dimensional data for the uncoated HOT columns are given in Table I.

TABLE I

DATA FOR UNCOATED HOT COLUMNS

Column	λ	*Diameter (cm)*	*Length (m)*	$C^0_G \times 10^4$ *(sec)*	$H_{min.}$ *(cm)*
Straight	—	0.091	8.0	5.0	0.0275
Coiled	0.1	0.091	8.0	3.7	0.027
Coiled	0.3	0.091	8.0	2.6	0.026

Figs. 5 and 6 show the initial peaks of a vapour sample of North Sea crude on a silicone oil coated column (0.025 cm I.D.). Fig. 5 is the chromatogram on the straight column. Fig. 6 is the chromatogram on the same column after tightly coiling it. It is clear that there is a slight increase in resolution in the case of the HOT column.

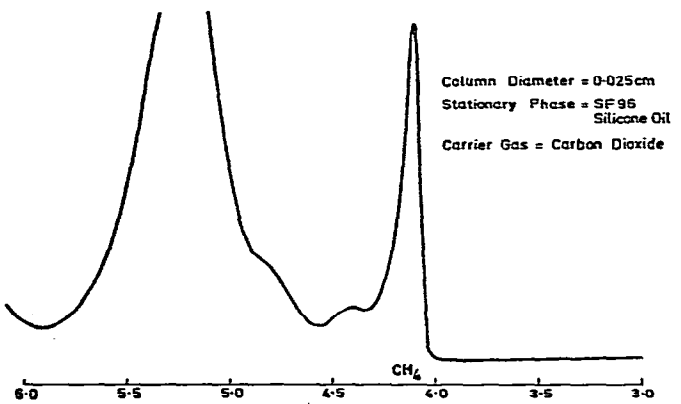

Fig. 5. Initial peaks of vapour sample of North Sea crude on a straight column.

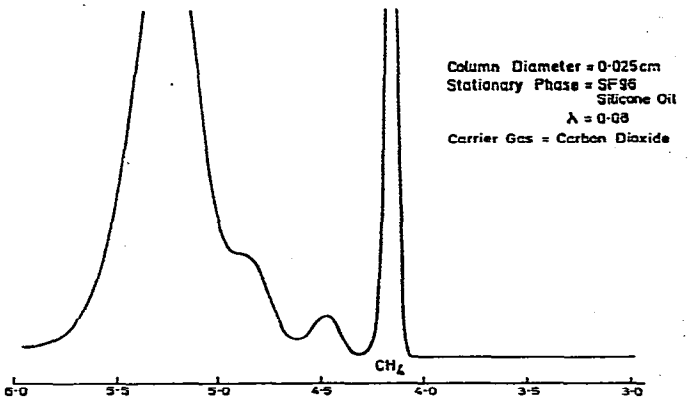

Fig. 6. Initial peaks of vapour sample of north sea crude on tightly coiled column.

It should be noted that the average linear gas velocity is 246 cm/sec although much higher velocities *e.g.* 1000–2000 cm/sec may be very interesting in that if the maxima apparent in the HETP *versus* $\bar{u}$ curves for the uncoated columns occur in the HETP versus $\bar{u}$ curves for the coated column high resolution and efficiencies could well be attainable along with very rapid analyses.

Static (Kenics) mixer columns

Fig. 7 shows the HETP *versus* $\bar{u}$ curves obtained with uncoated static mixer columns. Although the mixer with 180° twists displays much lower HETP values than the mixer with 90° twists both columns are not as good, in HETP terms, as the open-tube column (Table II). The reason is that the twisted elements, by virtue of their presence, form a barrier impeding the normal diffusion mechanism, however, the mixing effect they produce is not efficient enough to compensate.

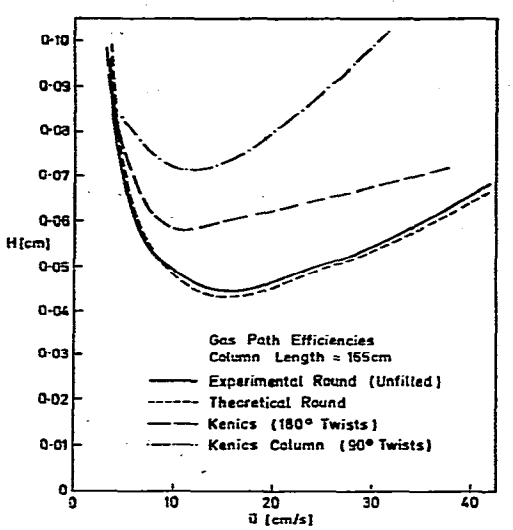

Fig. 7. HETP *versus* $\bar{u}$ curves for 1.5 mm I.D. round (unfilled) and Kenics columns.

TABLE II

DATA FOR KENICS COLUMNS

Column	*Length (m)*	*Diameter (mm)*	$C^0_G \times 10^4$ *(sec)*	$H_{min.}$ *(cm)*
Open-tube	1.65	1.5	13.7	0.0445
Kenics (90°)	1.65	1.5	27.8	0.0715
Kenics (180°)	1.65	1.5	16.8	0.058

It is possible that the static mixer concept could find application in LC where the mixing effect will be the same (the mixing is independent of viscosity) whilst the diffusion coefficients in LC are of the order of 10^4 times smaller. The concept could offer the potential, therefore, of low pressure drop, high-efficiency LC columns.

Spinning band columns

Fig. 8 shows the HETP *versus* $\bar{u}$ curves obtained with the spinning band column where the band was of a closed structure (twisted metal tape). It is clear that

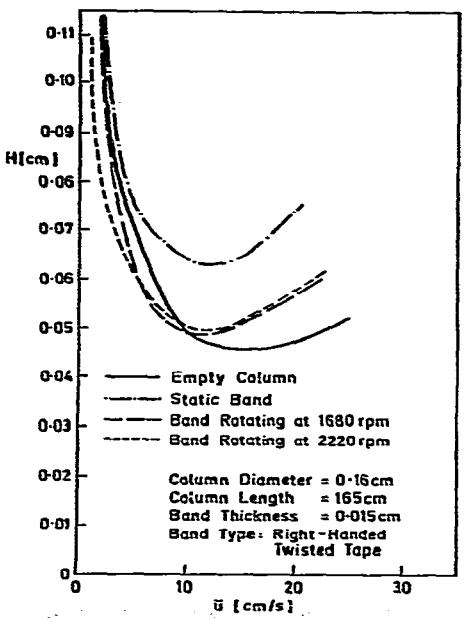

Fig. 8. Comparison of HETP *versus* $\bar{u}$ curves for spinning band columns (closed structure band).

when the band is spinning lower HETP values are manifested over the case where the band is static (Table III). However, the HETP minima are slightly higher for the spinning band cases than for the open-tube column although the spinning bands manifest lower HETP values than the open-tube column at low average linear gas velocities. The reason for the latter fact is not clear at the present time.

It was thought that if a more open band was used, so as to present less impedance to the normal diffusion process, a system could be produced which would

TABLE III

DATA FOR SPINNING BAND COLUMN WITH CLOSED-STRUCTURE BAND

Column	*Spinning speed (rpm)*	*Length (m)*	*Diameter (mm)*	$C^0_G \times 10^4$ *(sec)*	$H_{min.}$ *(cm)*	*Width of band (mm)*
Open tube	—	1.65	1.6	15.7	0.046	—
Static band	0	1.65	1.6	29	0.063	1.5
Spinning band	1680	1.65	1.6	21	0.049	1.5
Spinning band	2220	1.65	1.6	22	0.05	1.5

display lower HETP values than the open-tube column. It was also considered likely that higher speeds of revolution could produce lower HETP values.

Fig. 9 shows the HETP *versus* $\bar{u}$ curves obtained with a band which took the form of a zig-zag constructed by flattening a copper wire helix between two rollers.

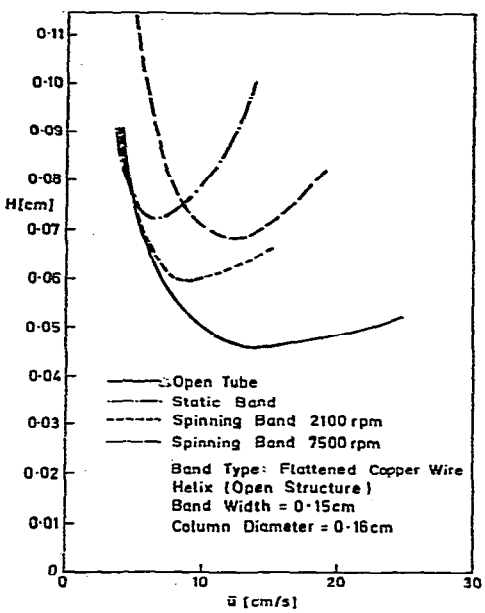

Fig. 9. Comparison of HETP *versus* $\bar{u}$ curves for spinning band columns (open structure band).

In fact it is clear that the more open structure static band (Table IV) displays higher HETP values than the closed-structure band. This is probably due to the fact that the closed-structure band was tightly twisted and thus imparted a radial velocity to the carrier gas hence lowering the HETP over that of the untwisted open-structure band.

Spinning the band at 2100 rpm produces lower HETP values than in the static mode, however, the values are still higher than those for the open-tube column.

When the band is rotated at very high speeds (7500 rpm) the HETP values

TABLE IV

DATA FOR SPINNING BAND COLUMNS WITH OPEN-STRUCTURE BAND

Column	*Spinning speed (rpm)*	*Length (m)*	*Diameter (mm)*	$C^0_G \times 10^4$ *(sec)*	$H_{min.}$ *(cm)*	*Width of band (mm)*
Open-tube	—	1.65	1.6	15.7	0.046	—
Static band	0	1.65	1.6	42	0.0725	1.5
Spinning band	2100	1.65	1.6	31	0.0595	1.5
Spinning band	7500	1.65	1.6	37	0.068	1.5

are higher than those obtained at 2100 rpm especially at low average linear gas velocities. The reasons for this are not clear at the moment but it would appear that the method of using mechanical mixing to produce a lower resistance to mass transfer in the gas phase is not feasible. It would of course be possible to alter the band shape and the rotating speeds but as preliminary results show no advantage it is unlikely changing the parameters will manifest a large reduction in HETP over the open-tube which would make a consideration of ways to introduce a stationary phase worthwhile.

CONCLUSIONS

It is concluded that HOT columns offer only a small increase in efficiency even at gas velocities of up to 250 cm/sec. However, it may be interesting to investigate the effects of very much higher velocities as results on uncoated columns indicate that the HETP could reduce appreciably at even higher average linear gas velocities.

Static mixer columns show no reduction in HETP over the open-tube columns, however, they could find an application in LC (packed or open-tube) where diffusion coefficients are much lower.

Spinning band columns do not offer a way of producing a convective mixing mechanism which is more efficient than normal diffusion.

LIST OF SYMBOLS

H = height equivalent to a theoretical plate (HETP).
B = longitudinal diffusion coefficient.
C_G = resistance to mass transfer in the gas phase.
C^0_G = resistance to mass transfer in the gas phase when $k' = 0$.
C_L = resistance to mass transfer in the liquid phase.
$\bar{u}$ = average linear gas velocity.
k' = ratio of liquid phase capacity to gas phase capacity.
λ = ratio of column diameter to helix diameter.

ACKNOWLEDGEMENTS

The authors wish to thank the Chairman and Directors of the British Petroleum Company Limited for permission to publish this paper.

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, *J. Chromatogr.*, 142 (1977) 39.
3 R. Tijssen, *12th Int. Symp. Advances in Chromatography, Amsterdam, 7–10 Nov. 1977.*
4 G. I. Taylor, *Proc. Roy. Soc., London*, A219 (1953) 186.
5 W. R. Dean, *Phil. Mag.*, 4 (1927) 208; 5 (1928) 682.