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TAPEWORM COLUMNS IN GAS CHROMATOGRAPHY

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SUMMARY

Some theoretical work has been carried out in order to evaluate the potentialities of rectangular capillary columns for gas chromatography. A flattening device for capillaries is described and experience in preparing rectangular columns with this device is discussed. Preliminary results showed an improvement in the column performance of a macrocapillary after flattening to a wall-to-wall distance of 0.2 mm.

INTRODUCTION

In gas chromatography, capillary columns with inner diameters of 0.2–0.3 mm have the great separation power that is usually required combined with the disadvantage of low loads. The latter effect results in poor overall sensitivity. Several proposals have been made for increasing the limits of detection in order to permit the use of capillaries for trace analyses. SCOT and PLOT columns[1,2] and irregularly packed capillaries[3] increase the amount of stationary phase, and trapping techniques[4] and splitless injection[5] enrich the components in question. All these methods are laborious, either in preparing the columns or in applying them. Hence Golay's proposal[6], made in 1958, to use rectangular capillaries was reconsidered. It should result in high-capacity columns with the separation efficiency of microcapillaries (*i.e.*, capillaries with I.D. 0.25–0.30 mm, in contrast to macrocapillaries with I.D. 0.5–1.0 mm), if sufficiently flat capillaries could be made.

Three reasons were decisive in formulating the experiments:

(1) By means of a "micro-mangle" (see Experimental), the preparation of such capillaries is technically feasible.

(2) In his paper, Golay derived equations for rectangular capillaries and proved that, for separation efficiency, the smaller wall-to-wall distance corresponds to the diameter of circular capillaries.

(3) Whereas the gas flow through normal capillaries is proportional to the fourth power of the radius (r^4), that of rectangular tubes is proportional to the third power of half the smaller wall-to-wall distance times the larger (z^3b). Hence a capillary of I.D. 0.25 mm has about the same permeability as a rectangular capillary measuring 0.10 × 1.5 mm. The corresponding cross-sectional areas are 0.05 and 0.15 mm^2 respectively.

This investigation was carried out in order to show that, according to theory,

rectangular capillaries should combine high separation power with high capacity. Preliminary experiments have indicated the potentialities but also the difficulties of this concept.

THEORETICAL

In this work we have assumed that Golay's equations[6] are valid, as they are generally accepted[7]. We first present some calculations that have been made with these equations and conclusions derived from them, and then we discuss some advantages and disadvantages based on a more practical approach.

Conclusions derived from Golay's equations

Golay[6] derived equations for both circular and rectangular capillaries, the latter being valid only for a large ratio of width to thickness:

$$H_{\text{circular}} = 2\frac{D}{U} + \frac{1 + 6k + 11k^2}{24\,(1 + k)^2} \cdot \frac{U r_0^2}{D} + \frac{k^3}{6\,(1 + k)^2} \cdot \frac{U r_0^2}{c^2 D_L} \qquad (1)$$

$$H_{\text{rectang.}} = 2\frac{D}{U} + \frac{4\,(1 + 9k + 25.5k^2)}{105\,(1 + k)^2} \cdot \frac{U z_0^2}{D} + \frac{2k^3}{3\,(1 + k)^2} \cdot \frac{U z_0^2}{c^2 D_L} \qquad (2)$$

where

H = effective height equivalent to a theoretical plate;
U = average velocity of carrier gas;
D = diffusion coefficient of sample in gas phase;
D_L = diffusion coefficient of sample in liquid phase;
k = ratio of fixed to moving capacity for component of sample;
c = partition coefficient;
r_0 = radius of circular tube;
z_0 = half inside thickness of flat tube.

A comparison of these two equations shows a similar pattern, using for circular columns the radius, r_0, and for rectangular columns half the smaller wall-to-wall distance, z_0. The scalar factors differ, however, with the effect that as k increases $H_{\text{rectang.}}$ increases more rapidly than H_{circular}. At first sight, the apparent lack of the film thickness looks astonishing, but this is accounted for by the k values: the capacity ratio, for a given capillary and at constant partition coefficient, depends on the film thickness only.

Calculation of the equations for circular and rectangular columns with squalane as stationary phase for *n*-heptane is illustrated in Table I and Fig. 1. Assuming the validity of both equations within the calculated range, one can draw the following conclusions:

(1) H is smaller for circular columns than for rectangular columns with equal wall-to-wall distances ($r_0 = z_0$). This difference increases with increasing film thickness.

(2) The height equivalent to a theoretical plate decreases with decreasing r_0 or z_0 and the dependence on film thickness becomes smaller. This first term, which holds for the velocity- and hence time-determined gas diffusion, influences the H of macro-

TABLE I

DEPENDENCE OF EFFECTIVE HEIGHT EQUIVALENT TO A THEORETICAL PLATE (H) ON RADIUS (r_0) OR HALF THE SMALLER WALL-TO-WALL DISTANCE (z_0) FOR CIRCULAR AND RECTANGULAR CAPILLARIES, RESPECTIVELY

The calculation was made for squalane as stationary phase, *n*-heptane as solute and nitrogen as carrier gas with an average linear velocity of $\bar{u} = 20$ cm/sec. The gas diffusion coefficient $D_{g\ 25°C} = 0.064$ cm²/sec; the liquid diffusion coefficient $D_{L\ 25°C} = 1.0 \cdot 10^{-6}$ cm²/sec. The variation of k was calculated via the film thickness; variation of stationary phase film thickness $d_f = 0.02$–$5\ \mu$m.

r_0 (mm)	z_0 (mm)	H (cm)				
		$k = 0.5$	$k = 1.0$	$k = 2.0$	$k = 4.0$	$k = 10.0$
0.5		0.109	0.167	0.256	0.389	0.701
	0.5	0.176	0.320	0.574	1.013	2.183
0.25		0.034	0.048	0.071	0.104	0.182
	0.25	0.051	0.086	0.150	0.259	0.552
0.125		0.013	0.017	0.024	0.033	0.052
	0.125	0.017	0.026	0.044	0.071	0.145
	0.0625	0.009	0.012	0.016	0.024	0.043
	0.03125	0.007	0.008	0.009	0.011	0.015
	0.0156	0.007	0.007	0.007	0.008	0.009

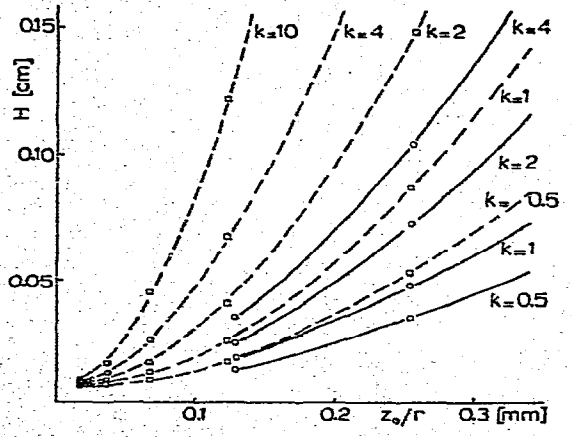

Fig. 1. Dependence of plate height (H) on radius (r_0) or half the smaller wall-to-wall distance (z_0) for circular (solid line) and rectangular (broken line) capillaries, respectively, with squalane as stationary phase and *n*-heptane as solute (for further details, see Table I).

capillaries only slightly (a few per cent), but becomes the governing factor for wall-to-wall distances of less than 0.03 mm.

(3) As the capacity ratio is shifted in favour of the stationary phase by flattening the capillary (the gas volume decreases whereas the volume of stationary phase remains constant), at first a decrease in resolution occurs (Fig. 2). For smaller wall-to-wall distances, however, the resolution increases.

(4) From eqn. 2, a rapidly decreasing peak broadening with increasing film thickness can be predicted for rectangular capillaries with $z_0 \leqslant 0.02$ mm. If this holds true in practice, the possibility arises of preparing capillaries with high resolution and good capacity.

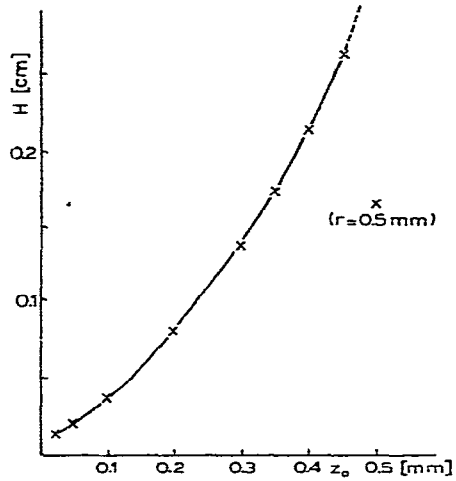

Fig. 2. Variation of the effective height equivalent to a theoretical plate during flattening of a macrocapillary of 1 mm I.D. (for further details, see Table I).

All of these conclusions lead to the assumption that, according to eqn. 2, rectangular columns with very small wall-to-wall distances should have distinct advantages in comparison with microcapillaries.

General consideration of rectangular columns

A general discussion of the potentialities and limitations of rectangular columns must take into account the following aspects.

Distortion of velocity profile. An important point, which could make the whole concept questionable, is the actual shape of the cross-sectional velocity distribution. A column design with plane-parallel walls and semicircular sides provides optimal flow conditions, but nevertheless the wall effects are much greater than with circular columns and hence there is a larger amount of gas phase with a zero or very small linear velocity. Correspondingly, the gas velocity of the centre part of the capillary must be higher, which causes a more distorted velocity profile than in circular columns. The separating power depends on the actual shape of this profile and the *H versus U* graph should be much steeper than with circular columns.

Uneven cross-section along the column. The flattening must be performed with high uniformity. Buckling of the tube will result in very small deviations from the mean wall-to-wall distance, but an alteration of that distance by only $\pm$ 0.01 mm produces a variation in the free cross-section of $\pm$ 20% and hence a change in the permeability of + 73 to — 49%. The overall result would be an uneven velocity distribution and perhaps a greater pressure drop.

Short gas paths that reduce peak broadening. A shorter wall-to-wall distance causes shorter times between the sorption steps, and therefore more sorption/desorption steps occur per unit time than in a microcapillary. This in turn results in a better statistical distribution of the total sorption times of the individual molecules of one component and consequently in a reduction in peak broadening. This holds true also,

if greater film thicknesses are used to increase the capacity. Under this aspect the diminished influence of the film-thickness predicted by equation (2) is understandable.

Optimum column profile. The "rectangular column", owing to the manner of manufacture, is not exactly rectangular (see Fig. 3). Although the condition of two plane-parallel walls is achieved, the smaller sides have semicircular profiles of radius z_0. That is the ideal shape for rectangular columns, as it permits the most uniform coating and effects an optimum velocity profile under these circumstances (see above). As the column is coated before flattening the film thickness is uniform, even in places of greater curvature. For a ratio of half the smaller side to the film thickness (z_0/d_f) of more than 100:1, no redistribution should occur on flattening. However, if a true rectangular column were coated, then of necessity patches of stationary phase would be formed in the corners.

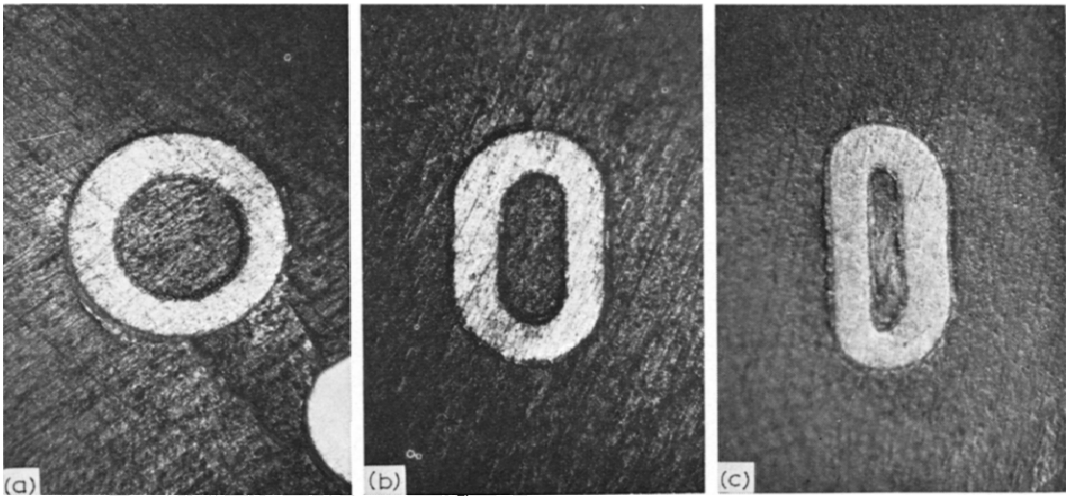

Fig. 3. Microphotographs of the cross-sections of the initial capillary (a) and of two flattened capillaries (b and c).

A critical assessment of all considerations regarding rectangular columns with relatively small wall-to-wall distances indicates a good performance for this type of column. The distorted velocity profile with the increased proportion of "stationary" gas phase should not be too harmful for separation, as this phenomenon is inherent in all packed columns with porous supports. Also, the unevenness of the wall-to-wall distance seems to be negligible as judged by the good agreement between calculated and measured gas flows. The predicted good properties should therefore more than compensate for the possible drawbacks.

EXPERIMENTAL

Theory predicts that the favourable effects of rectangular capillaries will be greatest with the smallest possible small-side distances and the greatest feasible widths. Therefore, one should flatten columns of large internal diameter to be as

narrow as possible. For practical reasons of availability, we started with a tube of 1 mm I.D.

After cleaning, we coated this macrocapillary in the usual manner. The subsequent flattening was carried out with a device (Fig. 4) developed in our laboratory to produce by-pass capillaries of minimum dead volume with high reproducibility for the INTEX Standard proposed by Rohrschneider and Jaeschke[8]. This device, which we call a "micro-mangle", consists essentially of two rollers made of tempered steel, the distance between which can be adjusted very precisely and reproducibly with a precision screw. Both copper and steel capillaries were flattened with the micro-mangle. After sawing off and careful filing they showed profiles of the desired type (Fig. 3), with plane-parallel middle sections and semicircular sides.

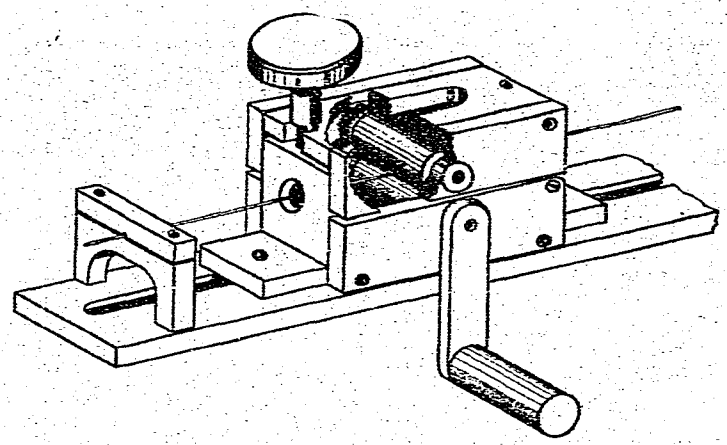

Fig. 4. Flattening device or "micro-mangle".

The evolution of heat during flattening gave more trouble than expected. The heat evolved with copper, and even more with steel capillaries was so great that the coating (squalane) was completely destroyed in the first trials. Air cooling was applied in further flattening trials. As this precaution was inadequate, the air stream directed at the rollers was pre-cooled with liquid nitrogen. Moreover, the flattening was performed slowly and gradually and, in addition, we used a more thermostable stationary phase (silicone oil). These precautions gave successful results.

The connection of flattened columns to the splitter and detector was a further problem. In order to make chromatograms after each flattening step, pieces of 0.25-mm I.D. capillaries were inserted in the ends of the macrocapillary, the pieces being connected with the splitter and detector in the usual manner. In order to minimize the dead volume, we tried to apply the flattening as near as possible to the ends. Unfortunately, this resulted in a series of over-flattened capillaries, so that we had to observe a "safety distance" of 1 cm from the ends. This in turn increased the dead volume, which is a disadvantage, especially at higher pressures (*ca.* 5 atm).

In order to circumvent these difficulties and minimize dead volumes, the capillary was soldered directly to the splitter T-piece and the make-up gas T-piece after flattening to a minimal small-side distance. By means of this procedure, dead volumes

were avoided, but the stationary phase was destroyed in the soldered area, a problem which has not yet been overcome.

In spite of the precision and reproducibility available with the micro-mangle, the inner distance cannot be estimated from the outer diameter owing to the relative thickness of the wall. It can be calculated, however, by considering the differences between the k values of individual components and those of the ordinary capillary. The small-side distance as well as the width can easily be calculated from the remaining gas volume under the assumption that the circumference of the capillary does not change on flattening.

The necessary carrier gas pressures increase rapidly on approaching the desired inner distance of 0.05 mm, in spite of the relatively large open cross-section. The permeability of a circular capillary of 0.25 mm I.D. corresponds to that of a rectangular capillary measuring 0.1 × 1.5 mm, but, in order to obtain the same linear carrier gas velocity, the volume velocity must be three times that in a circular capillary of 0.25 mm I.D., since the cross-sectional area of the rectangular capillary is three times as great (0.15 mm^2 *versus* 0.05 mm^2). Consequently, the pressure drop is also threefold.

The permeability of a rectangular capillary, measuring 0.05 × 1.5 mm, decreases to *ca.* 10% of that of a 0.25-mm I.D. circular capillary. In order to obtain equal linear gas velocities, the inlet pressure must be fifteen times greater than that for the 0.25-mm I.D. circular capillary.

The high pressure drop and the shape of the H *versus* U curves, which have a minimum at relatively small carrier gas velocities, suggest rather short columns. Thus the separation times will be as usual and the necessary inlet pressures will remain within reasonable limits. The number of plates attainable, however, is therefore limited.

RESULTS

As we are engaged in routine industrial analyses, we possess neither the equipment nor the time available to research organizations. Our practical work was therefore intended more to show preliminary results in order to stimulate other workers to establish the best conditions and procedures or to prove that there is something wrong with our proposals.

At first, we obtained promising results by using a column coated with silicone oil. When we used wall-to-wall distances of 0.3 and 0.2 mm, the H value for n-heptane decreased from 1.6 to 0.6 and 0.4 cm, showing an overall improvement of 75%. However, the increase in the k value from 0.33 to 0.69 and 1.0, respectively, would itself cause, with no change in separation efficiency, a decrease in H from 1.6 to 0.7 and 0.5 cm, respectively. Hence the real gain was small, but it encouraged us to present this paper and to perform further work.

Unfortunately the column was flattened to destruction when we tried to reduce the small-side distance to about $z_0 = 0.05$ mm, and it was therefore impossible to obtain further chromatograms with this column and to determine its loadability. Since then we have obtained discouraging results, mainly we believe owing to the dead volume at both ends of the columns. In attempting to eliminate this problem, we have destroyed many columns by flattening them to zero permeability, and we therefore tried to solder a flattened column into the T-pieces of the splitter and of the de-

tecting system. However, the heating of the column while soldering most likely destroyed the stationary phase and our latest results did not show any improvement.

In spite of our meagre experimental results, theory supports our optimism in continuing our work on rectangular capillaries, aiming at excellent resolution and high loadability.

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