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MASS TRANSFER IN IDEAL AND GEOMETRICALLY DEFORMED OPEN TUBES

III. DEFORMED METAL AND PLASTIC TUBES

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SUMMARY

Dispersions (h values) in deformed tubes are much better than those in coiled ideal tubes, even at lower velocities ($u < 50$ cm/sec). Such tubes are of interest as connecting pipes, heat exchangers, reaction detectors, liquid chromatographic (LC) separation columns and possibly in catalysis. No theory exists for deformed tubes and hence improvements must be made by trial and error. Squeezed, twisted and coiled tubes are much better than ideal tubes, but they are complicated to make, their geometry is difficult to optimize and is dependent on the kinematic viscosity of the eluent. Coiled wavy tubes, having a circular cross-section, are easy to prepare, and have an efficiency that is relatively insensitive to the diameter of the tube, its exact geometry, the kinematic viscosity of the eluent and the ability of the eluent to wet the tube. Wavy tubes can be prepared from glass, metal or plastic. In all deformed tubes the laminar region is extended to unusually high flow velocities, because of secondary flow. The transition from laminar to turbulent flow is gradual and continuous. These effects are strongest in wavy tubes. For example, in a 2-mm I.D. tube h decreases almost linearly from 2.6 to 1 cm as the linear velocity is increased from 3 to 130 cm/sec, *i.e.*, comparable h values are obtained at low velocities and in the turbulent region. Up to 70 theoretical plates per second can be generated for an inert sample. If this column were 100 m long, then with *n*-heptane as the eluent more than 7000 theoretical plates would be generated for an inert sample at $u = 100$ cm/sec at the cost of a pressure drop of only 7 bar. At high velocities the loss in permeability is only about 50% of that of an ideal tube. Efficient wavy tubes of large diameter (1-4 mm) can be produced, which would have advantages as LC columns and as reaction detectors, because their loadability would be high. Because of the low pressure drop and large peak volume, simple equipment could be used.

INTRODUCTION

In earlier papers, mass transfer in ideal and coiled tubes with circular cross-

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section¹ and their potential application in liquid chromatography (LC)² were described and discussed. The cross-sectionally averaged linear velocity, u , for laminar flow in ideal tubes¹ can be described for non-compressible media by means of the Hagen–Poiseuille equation^{3,4}:

$$u = \frac{K\Delta p}{\eta L} = \frac{r^2\Delta p}{8\eta L} \quad (1)$$

(for definitions, see the list of symbols at the end of the paper). The specific permeability, K , is henceforth abbreviated to permeability.

Carman⁵ calculated the permeabilities for tubes with (a) rectangular, (b) equilaterally triangular and (c) elliptical cross-sections. The flow profiles were calculated for (a) by Golay⁶, for (b) by Gütlich⁷ and for (c) (oval tubes) by Aris⁸. All these equations are special solutions for the well known Navier–Stokes differential equations. No theoretical treatment exists for tubes that are not straight.

The band broadening in ideal tubes can be described with the help of the equations of Taylor^{9–11}, Aris⁸ or Golay^{6,12,13}. The theory has been extended by Golay for rectangular tubes⁶. Theoretical treatments of band broadening exist only for straight tubes.

It has been shown experimentally by Koutsky and Adler¹⁴, Horvath *et al.*¹⁵, Walkling¹⁶ and Hofmann and Halász¹ that secondary flow can be practically neglected in coiled tubes with circular cross-section. At linear velocities less than 50 cm/sec the coiling of an ideal tube will not reduce band broadening appreciably in comparison with that in straight (ideal) tubes. Consequently, these tubes will hardly be of interest in routine LC.

The advantage of deformed tubes^{7,16–24} over ideal open tubes stems primarily from the more rapid radial mass transfer (mixing) within them, which is due to secondary flow^{25,26}. This is not only essential in liquid chromatographic separation tubes, but is also desirable for heat exchangers²¹, mixing tubes (including reaction detectors), connecting tubing between the sampling device and the column and between the column and detector in high-performance liquid chromatography (HPLC).

Deininger²³ extended the definition of laminar flow in an incompressible medium to include the case where the axial velocity in any given layer can be a function of the column length. When this is true it applies to any layer parallel to the axis. "Laminar flow" according to the conventional definition occurs only in an ideal tube. The new definition also includes the case of secondary flow.

Secondary flow occurs in a non-ideal tube, when at Reynolds numbers of less than 2000–2400 for an incompressible medium the permeability decreases with increasing linear velocity. The definition of secondary flow for a gas is more complicated. Secondary flow was first described by Dean^{25,26} for coiled tubes, where centrifugal force causes the flow path of the medium to be larger than the length of the pipe. The longer flow path also occurs in all types of deformed tubes. No theoretical treatment exists for secondary flow, in spite of many efforts to produce one.

Rough-walled tubes

Secondary flow is easily produced in a straight tube if the roughness of the wall is not negligible compared with its diameter, for instance "low quality" stainless-steel

tubing having an inner diameter of 0.25 or 0.5 mm. Commercially available "precision bore tubing" has a precise outer diameter, but the internal walls are often rough, which makes it ideal for use as connecting tubing in LC. It has been shown^{1,18} that the band dispersion (h value) in rough-walled stainless-steel tubes of I.D. 0.25 mm is much less than that for an ideal tube. The decrease in permeability is modest.

Increased radial mass transfer

If it is desired to increase the radial mass transfer above the level obtainable with rough-walled tubes, this can be achieved by deforming the tubes in a suitable manner; that is, variation of the free cross-section of the tube by changing its size and/or its shape and/or its position relative to the axis of flow causes a secondary flow, which increases radial mass transfer. A simple way to achieve this is to squeeze the tube.

Squeezed tubes

If the tube is merely squeezed to give it an oval cross-section, which remains constant along its length, then the effect is not very large. However, if the long axis of the oval is abruptly rotated through 90° every 1 or 2 cm, then the effect is increased considerably. By this means a discontinuous rotation of the axis of symmetry of the cross-section as a function of the distance travelled along the column is achieved. Consequently, the flow profile is discontinuously disturbed. The effect of increased radial mass transfer exhibited by such tubes on their heat exchange properties²¹ and their efficiency as connecting tubes¹⁸ has been demonstrated experimentally.

Squeezed, twisted and coiled tubes

The discontinuous disturbance of the cross-section, described above, can be achieved by disturbing a tube with an oval cross-section, so that the oval shape describes a spiral as it passes along the tube. In such tubes the continuous disturbance of the flow profile can be augmented by coiling them. The effects of such deformations for tubes having an original diameter of 1 mm and for a single ratio of the large to the small axis of the oval have been studied experimentally by Halász and Walking²⁰. At linear velocities above 5 cm/sec the h values decreased about 10-fold with only about a 20% decrease in permeability.

In this paper such tubes of various diameters and also the effect of varying the ratio of the large to the small axis are described. Further, a new and simpler deformation, which we describe as a "wavy tube", is introduced. All of the tubes mentioned above are metallic. Lastly, deformed tubes made of polytetrafluoroethylene (PTFE) are described.

Only the dispersions of inert samples at room temperature were measured. The nomenclature and symbols as used in an earlier study¹, where a summary of the hydrodynamics relevant to open tubes was presented, are employed. For complex geometrical forms the relevant Navier-Stokes differential equations have not been solved. Consequently, it is not possible to give an explicit mathematical description of the flow profile or of the mass transfer phenomena. Here only experimental results are presented, as systematically as possible.

EXPERIMENTAL

Chromatographic equipment

The measurements were made with a home-made apparatus, the dead volumes and detector response time of which were minimized¹.

Preparation of the metal tubes

The copper capillary tubing was obtained from Schoeller Werk (Hellenthal/Eifel, G.F.R.) and the aluminium tubing from Cochius (Frankfurt/Main, G.F.R.) The metal tubes had more or less smooth inner surfaces and they were cleaned and prepared for use as described previously¹.

Squeezed tubes were flattened by passing them through a goldsmith's rolling mill (Dinkel, Esslingen, G.F.R.). The tubes were characterized by the inner diameter of the original tube, d , and by the sizes of the major axis, a , and the minor axis, b , of the internal cross-section after squeezing. The dimensions were determined by using a measuring magnifier having 0.1-mm scale divisions.

Twisted tubes were produced using a hand-drill (larger tubes required a variable-speed electric drill). One end of the tube was clamped in the drill chuck and the other end was immobilized in a vice. The drill was then rotated in order to give the required number of twists to the tube. The distance in which the tube rotated through 180° (the intermodal distance) was chosen as 26 ± 1 mm; no problems were encountered even with bigger tubes.

Coiled tubes were made by winding the tubes, which may or may not have been squeezed and twisted, around an 11-cm diameter cylinder.

Wavy tubes, having circular or oval cross-sections, were formed by hand bending the tube over the inside of the thumb. Care was taken to avoid kinking, which would have changed the cross-section and formed edges. It was not considered important to make the bends precisely regular. The radius of a bend was 2–3 cm. A straight portion of tube with a length of 6 ± 2 cm remained between each bend, as shown in Fig. 1. When the wavy tube was coiled around a cylinder, then the waves were sometimes on edge and sometimes laid flat.

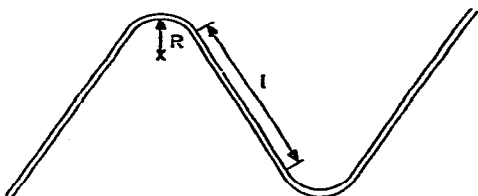


Fig. 1. Shape of a wavy tube. $R = 2-3$ cm, $l = 6 \pm 2$ cm.

Preparation of glass tubes

A complex apparatus was developed by means of which even glass tubes with an oval cross-section could be twisted reproducibly and then coiled.

Preparation of plastic tubes

PTFE tubes are flexible and springy and, if they are to be deformed into a

wavy shape, they must be held in place. They were therefore wound on to an 11-cm diameter sphere and held in place on it by means of ten pegs set radially into the surface of the sphere (see Fig. 2). The pegs were arranged at 60° intervals, about two perpendicular great circles on the sphere, two pegs being common to both great circles. The pegs were oval in cross-section and staggered with respect to the great circle, so that waves of sufficient amplitude could be obtained. The tubing was wound through 360° alternately around each great circle.

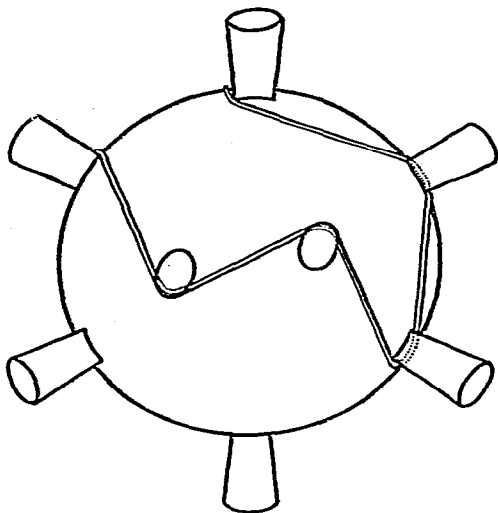


Fig. 2. Ball-shaped form on which wavy plastic tubes were wound. Ball diameter = 11 cm.

Mobile phase and samples

The following eluent-sample systems were used: (a) *n*-heptane-1 vol.-% benzene in *n*-heptane; (b) methylene chloride-1 vol.-% benzene in methylene chloride; and (c) water-5 vol.-% acetone in water.

The amounts of sample varied between 2 and 10 μ l, depending on the tube diameter.

The method of calculation of the Reynolds numbers, relative band broadenings (h values) and permeabilities (K) have been described previously¹.

RESULTS AND DISCUSSION

Comparison of deformed glass and metal tubes

Copper and glass twisted and coiled oval tubes were prepared, which were as nearly as possible identical with each other. The dispersions of benzene in *n*-heptane (h vs. u curves) were measured and are shown in Fig. 3. In Fig. 3 and in the others which follow, the dimensions of the axes of the oval internal cross-section are indicated diagrammatically in the top right-hand corner. In this case the intermodal distance was 8 mm. Although the coiling diameter was large (12 cm) in comparison with that used by Halász and Walkling²⁰, the decrease in h , with increasing linear velocity u , to a more or less constant level at high velocities was also observed.

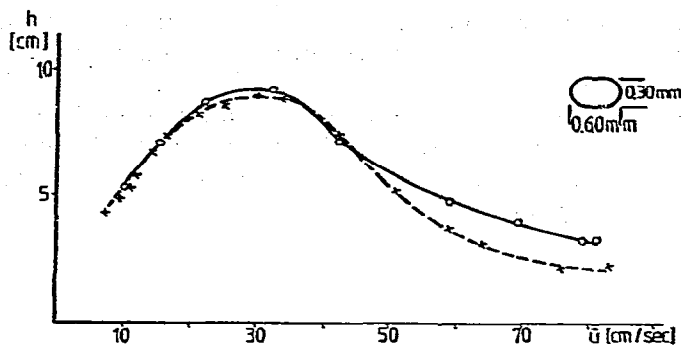


Fig. 3. Comparison of h vs. u curves in copper (solid line) and glass (dashed line) "twisted" tubes of identical dimensions. Twisted and coiled oval tubes ("twisted"); $L = 10$ m; coiling diameter = 12 cm; intermodal distance, exceptionally 8 mm; eluent, n -heptane; sample, benzene.

As can be seen in Fig. 3, the dispersions obtained with glass and copper tubes are very similar. This means that the wall roughness of the copper tubes can hardly be greater than that of the glass. When copper and glass oval, twisted and coiled tubes with various intermodal distances (10 and 1.5 mm) were compared, the dispersions obtained in glass tubes were, for a given geometry, also very similar to those obtained in copper tubes²⁴. The band broadenings obtained here at linear velocities of less than 30 m/sec are, of course, intolerably large, although they are smaller than in ideal tubes.

Consequently, further studies were undertaken only with copper tubes, because they are easier to manipulate. Further, no attempt was made to coil the tubes very tightly. A coiling diameter of 12 cm was chosen as standard.

Choice of optimal intermodal distance

The following measurements were made with stainless-steel tubes, for which the wall roughness is negligible when they have an I.D. > 0.5 mm. Tubes having the same oval cross-section as in Fig. 3, but having different intermodal distances (1.5, 15, 25 and 30 mm) were compared. As can be seen from Fig. 4, at high velocities a 1.5-mm intermodal distance is the best. When the ratio of the axes of the oval tube was changed, the same results were obtained.

At lower linear velocities the picture becomes more complicated and a 25-mm intermodal distance seems to be the best compromise. The mixing properties of such a tube at $u = 20$ cm/sec are definitely better than those of an ideal tube. It is assumed that this will also be true for other degrees of flattening of the oval and for eluents other than the n -heptane used in these experiments.

Dispersion in twisted and coiled oval tubes

In the following experiments n -heptane was the mobile phase. When a tube of circular cross-section is squeezed, then the length of the short axis, b , can be related to the original inner diameter of the tube by $b = \alpha \cdot d$, where $\alpha < 1$. The band dispersion is a function of α . Measurement of the dispersion and of permeability are presented for α values of 0.5, 0.55, 0.6, 0.65, 0.7 and 0.9²⁴. The radial mixing effect was greatest, for n -heptane, at $\alpha = 0.6$.

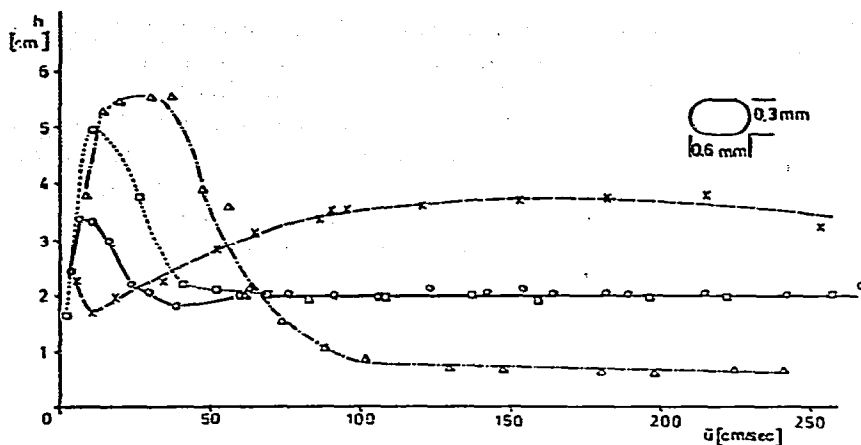


Fig. 4. Influence of intermodal distance on dispersion. Stainless-steel "twisted" tubes; $d = 0.5$ (1.0) mm; $L = 10$ m; coiling diameter = 12 cm. Intermodal distances: 30 mm (x); 25 mm (o); 15 mm (□) and 1.5 mm (△). Eluent, *n*-heptane; sample, benzene.

It has been found by experiment that the wall thickness of the tube can be of some consequence and this is always quoted, e.g., $d = 0.5$ (1.5) mm means that inner diameter of the original tube was 0.5 mm and the outer diameter was 1.5 mm. The dimensions of the oval cross-section will be designated as, e.g., $b/a = 0.3/0.65$ mm.

The results depicted in Fig. 5 were obtained using an aluminium tube with $b/a = 0.3/0.65$ mm. The solid line represents h vs. u , the dashed line K vs. u and the alternating dots and dashes the theoretical K vs. u values⁵. At linear velocities greater than 10 cm/sec the dispersion ($h = 3$ cm) is independent of u up to at least $u = 120$ cm/sec, in contrast to an ideal tube, where h is a linear function of u . At higher veloci-

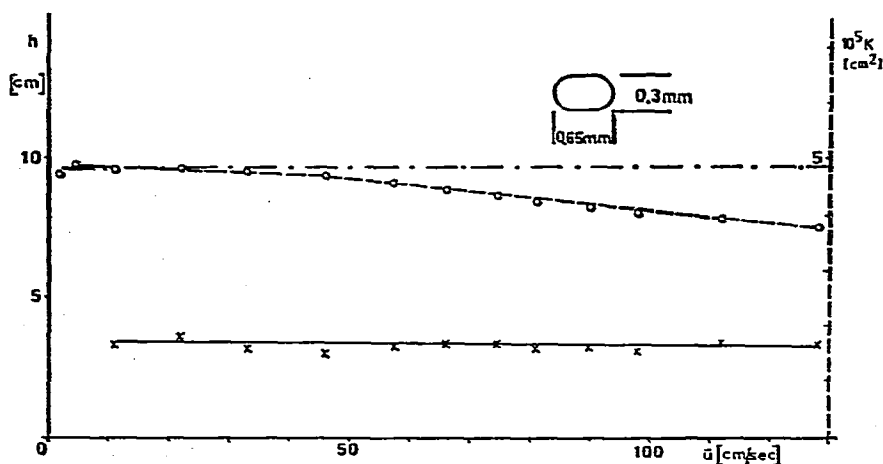


Fig. 5. h vs. u and K vs. u curves for an aluminium "twisted" tube with *n*-heptane as eluent. h vs. u curve, solid line (x); K vs. u curve, dashed line (o); K vs. u curve as calculated by Carman's method⁵ ($K_{theoret.}$), dotted and dashed line. $d = 0.5$ (1.5) mm; $\alpha = 0.6$; $L = 10$ m; coiling diameter = 12 cm; intermodal distance = 25 mm; sample, benzene.

ties the permeability decreases monotonically. However, the decrease in permeability is less than 30% of that of the theoretical value, as calculated by Carman⁵. Almost identical results were obtained with a copper tube of the same dimensions.

When comparing the results shown in Fig. 4, where the intermodal distance was also 25 mm, and the results in Fig. 5, the trends of the h vs. u curves are similar, except that (1) the horizontal part starts for the stainless-steel tube at around 20 cm/sec, instead of at 10 cm/sec for the aluminium tube, and (2) the constant h value for the stainless-steel tube is 1 cm less than that for the aluminium or copper tube.

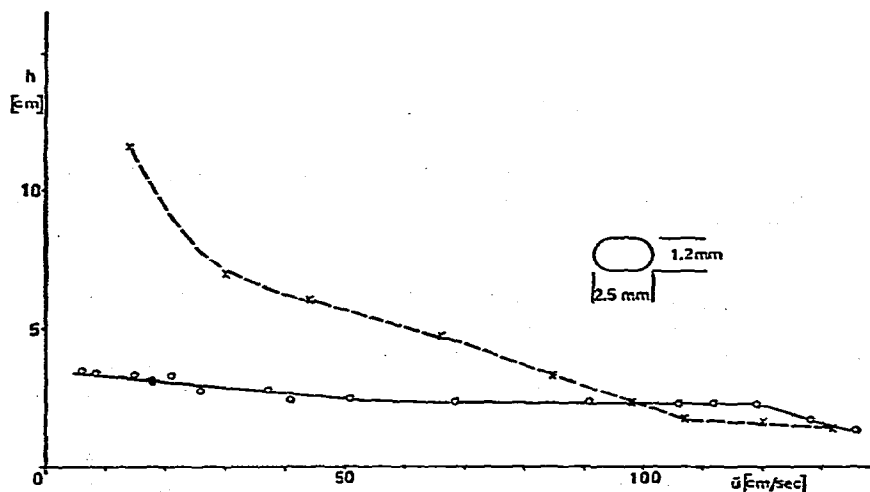


Fig. 6. Dispersion in copper "twisted" tubes with different coiling diameters. 12-cm coil diameter, solid line (○); 60-cm coil diameter, dashed line (×). Parameters as in Fig. 5, except that $d = 2.0$ (3.2) mm, α again being 0.6.

The h vs. u curves in Fig. 6 were obtained using copper tubes, where $b/a = 1.2/2.5$ mm. The solid line was obtained using the usual coiling diameter of 12 cm and the dashed line was obtained using a coiling diameter of 60 cm. For the 12-cm coil, although both axes of the oval are about four times greater than those in Fig. 5, the value of h at lower velocities is about the same (3 cm). The h values fall gradually to 2 cm for $u = 120$ cm/sec, where turbulence begins. In the early turbulent region h drops to 1.5 cm. Thus, for deformed tubes, in the velocity range of interest to chromatographers ($u < 50$ cm/sec), the dispersion is only twice as great as it is in the early turbulent region. Hence, it does not seem sensible to attempt to use coiled ideal tubes in the turbulent range, where the pressure drop is high, the permeability is low and the linear velocities are so high as to prohibit efficient mass transfer. Further, it would be especially difficult to maintain a thin layer of stationary phase on the wall of the tube when the flow is turbulent. However, it remains a fact that twisted and coiled oval tubes are only half as efficient in a non-turbulent range as in the turbulent range.

As can be seen from Fig. 6, turbulent flow for the 60-cm coil starts at around $u = 100$ cm/sec ($Re = 2760$), and for the 12-cm coil at $u = 120$ cm/sec ($Re = 3310$). Thus, increasing deformation stabilizes the laminar flow, *i.e.*, turbulent flow starts at

higher Reynolds numbers, that is if Reynolds numbers have any meaning for non-ideal tubes.

The onset of turbulent flow can be clearly seen in Fig. 6. Consequently, it is reasonable to define laminar flow to include the case of even strong secondary flow.

In Fig. 7 the permeabilities for the tubes described in Fig. 6 are shown as a function of the linear velocity. The onset of turbulence cannot be detected in these curves. At the highest velocities approximately 60% of the theoretical permeability is lost. The results shown in Figs. 6 and 7 could be reproduced using aluminium tubes.

As has been mentioned previously, the optimal α value for *n*-heptane is 0.6, *i.e.*, $b = 0.6d$. When α is reduced to less than 0.5, the efficiency of radial mixing decreases rapidly.

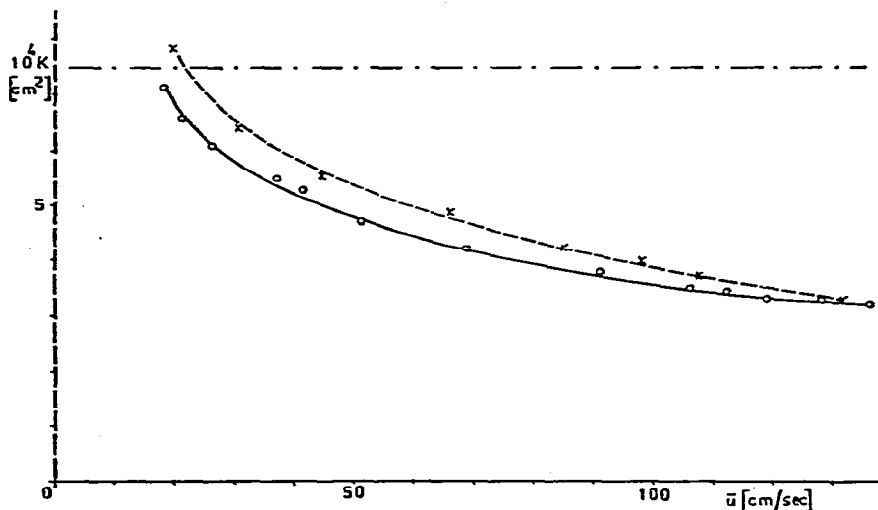


Fig. 7. Permeabilities of the copper tubes described in Fig. 5. 12-cm coil diameter, solid line (O); 60-cm coil diameter, dashed line (X); $K_{\text{theoret.}}$, dotted and dashed line.

Surprisingly, when the deformation of the circular cross-section of the tubes is minimal, *e.g.*, $\alpha = 0.9$, the mixing effects are not small, even for larger diameter tubes. These tubes and those shown in Figs. 6 and 7 were prepared from circular cross-section tubes of identical I.D. [*i.e.*, $d = 2.0$ (3.2) mm]. In Fig. 8 the dispersion in a loosely coiled (60-cm diameter) copper tube with $b/a = 1.8/2.2$ mm is shown. The dispersion, h , decreases continuously with increasing velocity, from 7.5 cm at $u = 30$ cm/sec to 5.5 cm at the onset of the turbulence, $u = 78$ cm/sec. As the speed is further increased the h value suddenly decreases to 2.5 cm and decreases further with increasing velocity, reaching 1.5 cm at $u = 110$ cm/sec. The dashed line in Fig. 8 is an impressive demonstration of the fact that the h vs. u curve is sensitive to the onset of turbulence.

The usual 12-cm coil diameter gives, when $u = 30$ cm/sec, an h value of 4 cm, which is virtually half that of the 60-cm coil. Once again it is demonstrated that the effect of coiling is much greater on deformed tubes than on ideal tubes.

Very similar radial mixing effects were achieved with larger tubes, *e.g.*, a copper

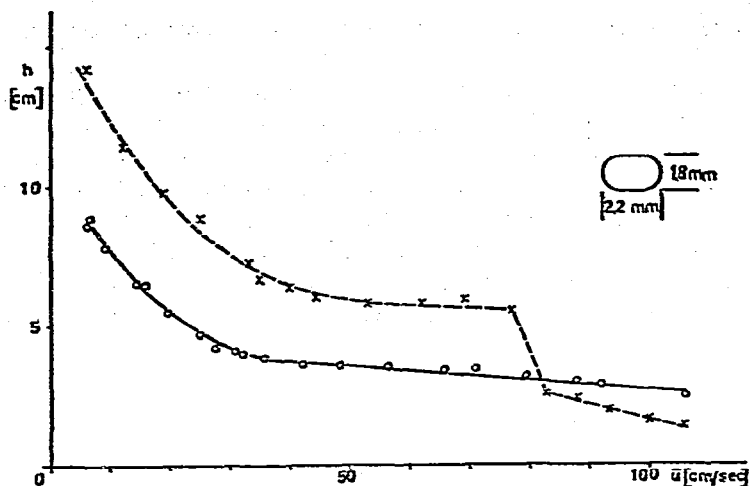


Fig. 8. Dispersion in scarcely deformed copper "twisted" tubes. 12-cm coil diameter, solid line (O); 60-cm coil diameter, dashed line (x). Parameters as in Fig. 6, except that $\alpha = 0.9$.

tube with $b/a = 3.6/4.6$ mm. Whereas in ideal tubes the dispersion is proportional to the second power of the tube diameter, for deformed tubes the dispersion varies much more gradually with increasing "bore".

The only eluent so far described has been *n*-heptane, where $\alpha = 0.6$ proved to be optimal. However, when water used as the eluent, the picture is completely changed. The optimal α value becomes 0.7 and the dispersion of an inert sample becomes greater.

Fig. 9 shows the results obtained with water as eluent, using a copper tube with $b/a = 0.35/0.6$ mm. This tube was made from a tube of the same original cross-

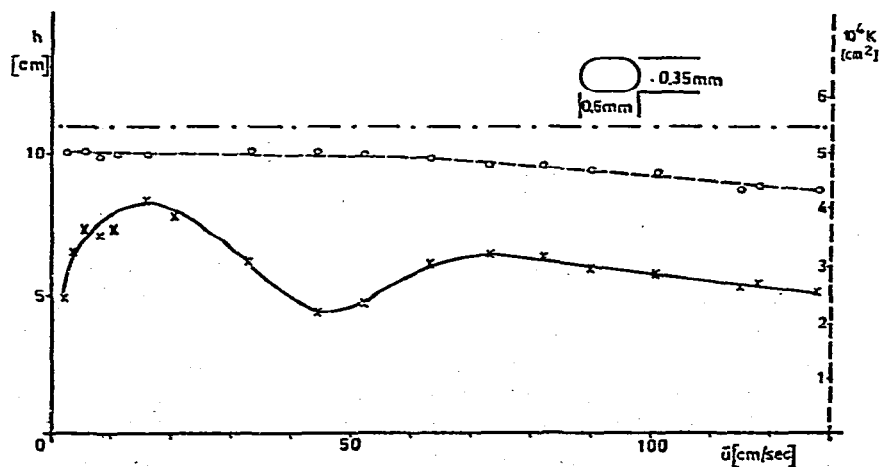


Fig. 9. h vs. u and K vs. u curves for a copper "twisted" tube with water as eluent. h vs. u curve, solid line (x); K vs. u curve, dashed line (O); $K_{\text{theoret.}}$ vs. u , dotted and dashed line. Parameters as in Fig. 5, except that $\alpha = 0.7$ and the sample was acetone.

section, $d = 0.5$ (1.5) mm, as that shown in Fig. 5. The h values obtained with water are much worse than those obtained with n -heptane. The h vs. u curve shows both a maximum and a minimum. It is reproducible however, and such curves are not uncommon when water is used as the eluent. Such a geometry cannot be used with water.

Much better results are obtained, with water as the eluent, by using a tube having the same α value (0.7), but a larger cross-section, $b/a = 0.98/1.6$ mm, as is shown in Fig. 10. Between 20 and 70 cm/sec the h values decrease from 4 to 3 cm, and decrease to 2.6 cm at $u = 120$ cm/sec.

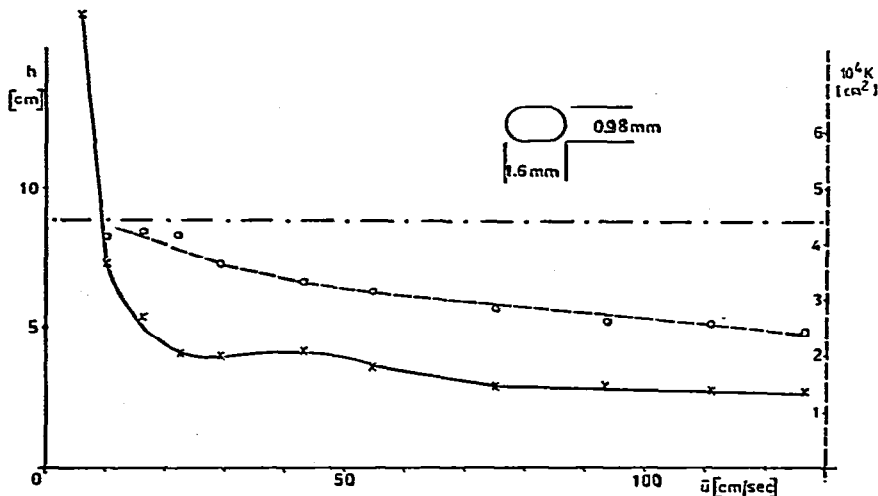


Fig. 10. Dispersion and permeability for a larger copper "twisted" tube. h vs. u curve, solid line (\times); K vs. u curve, dashed line (\circ); $K_{\text{theoret.}}$ vs. u , dotted and dashed line. Parameters as in Fig. 9, except that $d = 1.4$ (2.0) mm.

As can be seen in Fig. 11, the band broadening of an inert peak is a function of the kinematic viscosity of the eluent. Three eluents were used, methylene chloride ($3.8 \cdot 10^{-3}$ St), n -heptane ($5.8 \cdot 10^{-3}$ St) and water ($10 \cdot 10^{-3}$ St), all at 22°C . As demonstrated in Fig. 11, the lower the kinematic viscosity the smaller is h and the stronger the secondary flow.

Dispersion in metal wavy tubes with circular cross-section

The wavy tubes with circular cross-section described in this section are simple to prepare, simple in geometry and highly efficient. The preparation of such tubes has been described above (Fig. 1). It is not necessary to define the geometry exactly. Tubes bent to this prescription behave reproducibly, independent of whether they are made of glass, copper, aluminium or stainless steel. Further, the wall roughness is of only small importance.

The shape shown in Fig. 1, with a bending diameter of 2–3 cm and a distance between the bends of 6 ± 2 cm, was found by trial and error. If the distance between the bends was reduced to less than 1 cm, then the tubes were less efficient, although the dispersion properties were still acceptable. It is important that the circular cross-

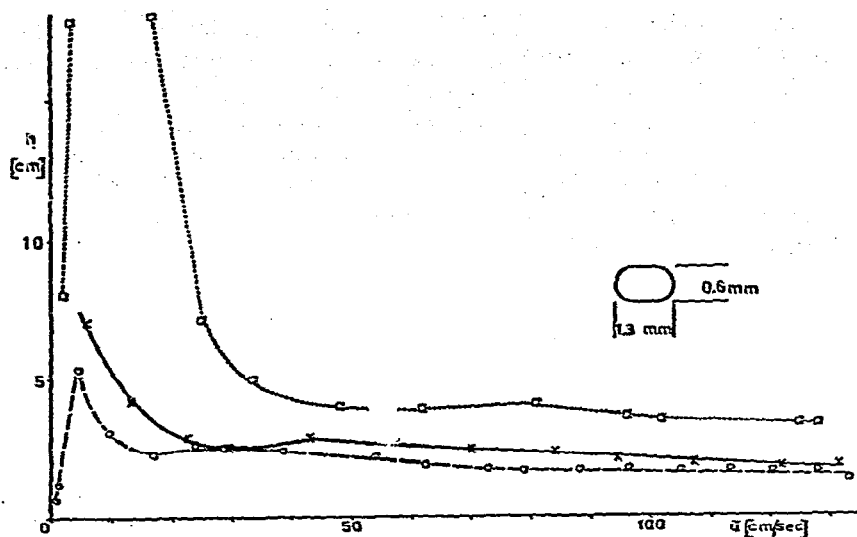


Fig. 11. Band broadening for three different eluents in the same "twisted" copper tube. Dotted line: eluent, water (\square); sample, benzene. Solid line: eluent, *n*-heptane (\times); sample, benzene. Dashed line: eluent, methylene chloride (\circ); sample, acetone. $d = 1.0$ (2.0) mm; $\alpha = 0.6$; $L = 10$ m; coiling diameter = 12 cm; intermodal distance = 25 mm.

section of the tube be maintained relatively unchanged, otherwise dead spaces may be formed. Zig-zag tubes with sharp bends do not have comparable properties. As far as we know the dispersion properties of wavy tubes have never before been described.

Radial mixing in a wavy tube can be explained as shown in Fig. 1. As the liquid flows round the bend, centrifugal force causes secondary flow. When the liquid reaches the next bend, the direction of the centrifugal force is reversed and hence so is the direction of the secondary flow. A certain distance is required between the bends for this process to be at its most efficient. Eddies will occur in the straight portion of the tube. This effect is similar to turbulent flow, however, at much lower flow velocities and with much better permeabilities.

When wavy tubes are coiled, desirable dispersion properties are obtained at much lower linear velocities. Hence, only wavy tubes coiled around a 12-cm diameter form will be discussed here. Small h values are obtained with these tubes at low linear velocities ($u < 50$ cm/sec).

A further surprising advantage of wavy tubes is that the h values obtained are more or less independent of the inner diameter of the tube, when this lies between 0.25 and 4 mm. The h values are also rather insensitive to the viscosity of the eluent. The h vs. u curves of an ideal tube and of a wavy tube, made of the same material are compared in Fig. 12 with *n*-heptane as eluent. In this example extremely thick-walled tubing was used [$d = 0.5$ (3.2) mm]; however, identical results were obtained with $d = 0.5$ (1.5) mm tubing. As has been described previously¹, in the velocity range 50–140 cm/sec the ideal tube yielded deformed peaks, which could not be evaluated. The onset of turbulence occurs in the ideal tube at $u = 220$ cm/sec ($Re = 1870$) when $h = 12$ cm, as is also shown in Fig. 13. Perfect turbulence is achieved at $u = 245$ cm/sec when $h = 1.75$ cm.

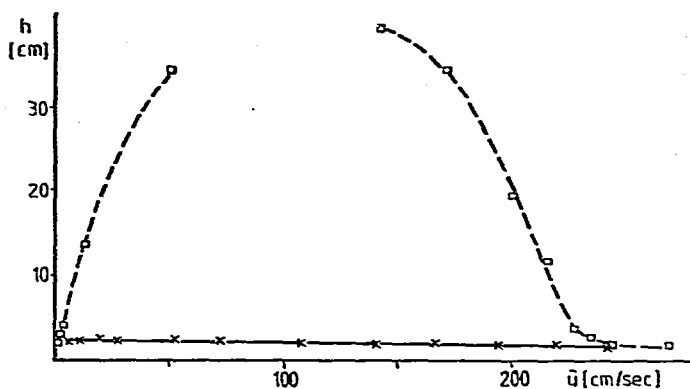


Fig. 12. Band broadening in an ideal tube and in a circular cross-section, coiled wavy tube ($d = 0.5$ mm). Dashed line, ideal (straight); solid line, "wavy". $d = 0.5$ (3.2) mm; $L = 10$ m; coiling diameter = 12 cm; eluent, *n*-heptane; sample, benzene.

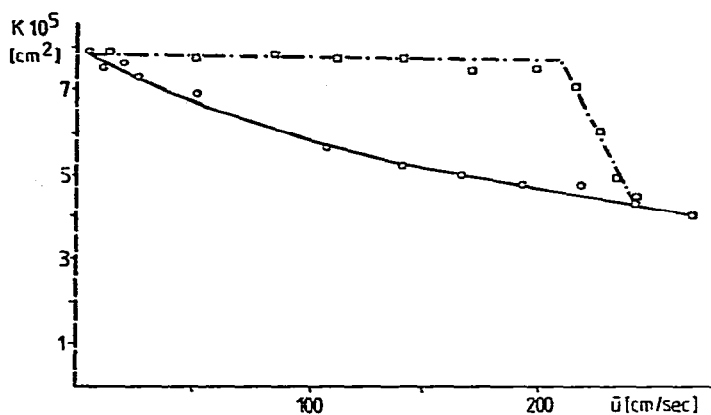


Fig. 13. Permeabilities of the ideal and "wavy" tubes described in Fig. 12. Dotted and dashed line, ideal tube (measured); solid line, "wavy" tube.

In contrast, the h values obtained in the wavy tubes are very small and gradually decrease monotonically with velocity in the range 5–245 cm/sec, the h values decreasing from 2.8 to 1.8 cm.

As can be seen from Fig. 12 the h values and from Fig. 13 the permeabilities of the ideal and wavy tubes are identical in the region of complete turbulence. However, the h values of the wavy tubes at low velocities ($u = 5$ cm/sec) are comparable to those obtained in the ideal tube in the complete turbulent region.

The onset of turbulence cannot be determined for wavy tubes from either the h vs. u curve or the K vs. u curve (Fig. 13). Both h and K decrease monotonically. These curves are consistent with the model proposed for the flow in such tubes.

Very similar results were obtained using 1- and 2-mm I.D. tubes. The results obtained with *n*-heptane for $d = 1.0$ (2.0) mm are shown in Fig. 14. The h values in the wavy tube again fell monotonically from 2.5 to 0.9 cm as u was increased from 10 to 238 cm/sec. Complete turbulence was achieved in the ideal tube at $u = 140$ cm/sec

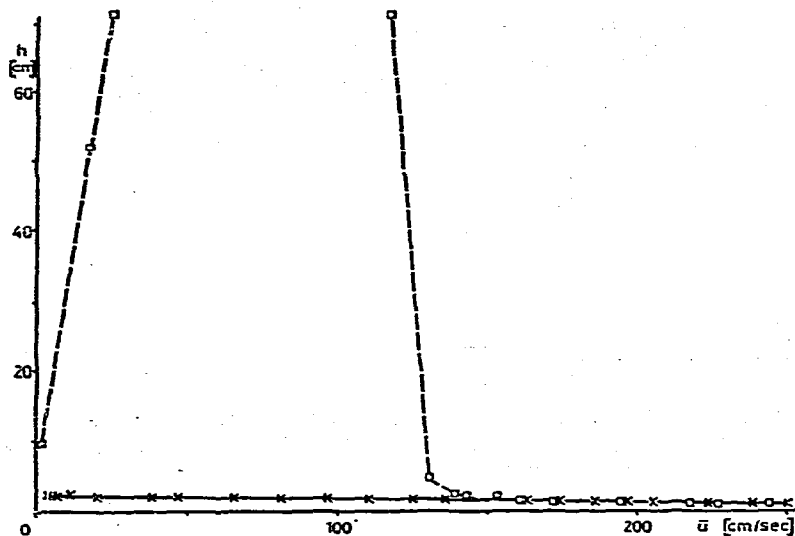


Fig. 14. Band broadening in an ideal and in a "wavy" tube ($d = 1.0$ mm). Solid line, "wavy"; dashed line, ideal tube. Parameters as in Fig. 12, except that $d = 1.0$ (2.0) mm.

($Re = 2210$). Above this velocity the dispersions for the wavy and for the ideal tube are identical. Although the inner diameter of the tube is twice that in Fig. 12, the h values here are slightly better.

The results obtained with $d = 2.0$ (3.2) mm tubes, again using n -heptane, are illustrated in Fig. 15. In this instance the h values for the wavy tube decrease from 2.6 cm at $u = 3$ cm/sec to 1 cm at $u = 131$ cm/sec. Although the tube diameter in

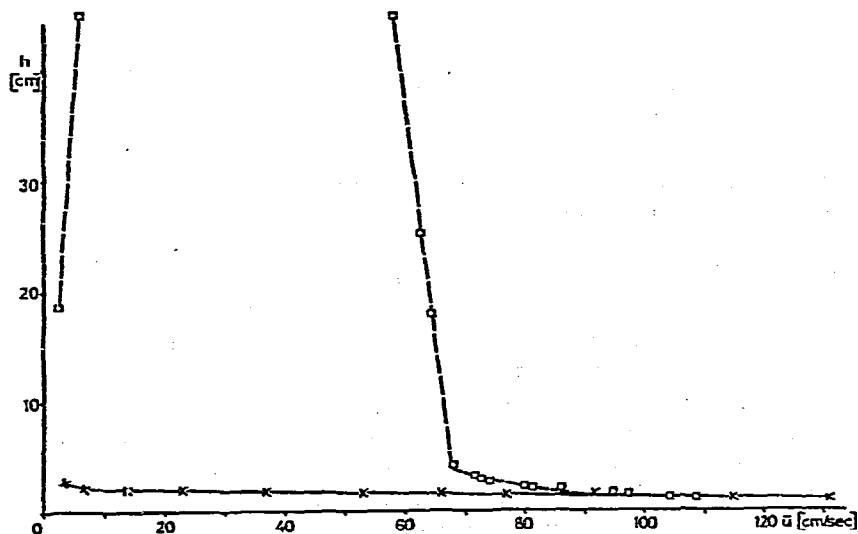


Fig. 15. Band broadening in an ideal and in a "wavy" tube ($d = 2.0$ mm). Solid line, "wavy"; dashed line, ideal tube. Parameters as in Fig. 12, except that $d = 2.0$ (3.2) mm.

this instance is four times greater than that in Fig. 12, the h values are still very similar. Capillary wavy tubes are not suitable in LC. Their dispersions are worse than those for wider tubes ($d = 2-4$ mm) and the loadability increases with the square of d .

When a tube $d = 4.0$ (6.0) mm was used it had to be coiled to a diameter of 30 cm, instead of the usual 12 cm. The h values obtained in this wavy tube with n -heptane eluent decreased from 4.5 to 2 cm as u was increased from 3 to 42 cm/sec.

The dispersion in a capillary wavy tube, $d = 0.25$ (0.5) mm, with water as eluent is shown in Fig. 16, in order to illustrate the fact that changing from n -heptane to water has no fundamental effect in wavy tubes. This is true for tubes with an I.D. up to 4 mm. In the tube illustrated the h values decreased from 4 to 3 cm as u was increased from 10 to 263 cm/sec. This capillary wavy tube was little better with n -heptane as eluent.

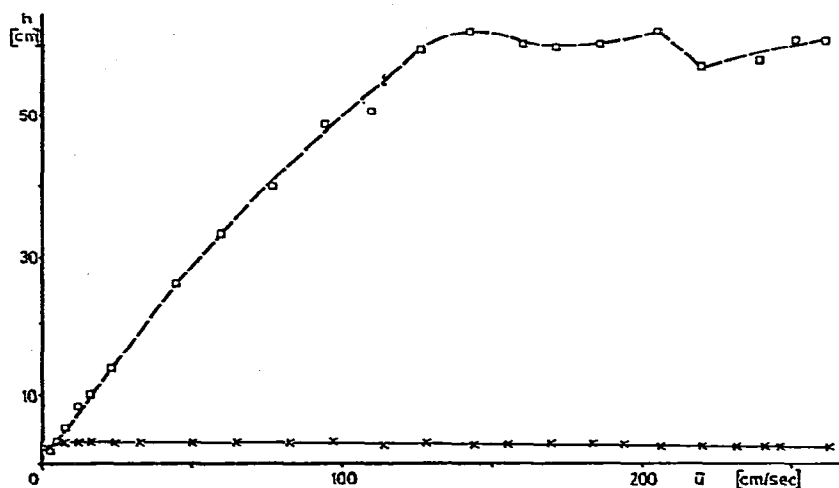


Fig. 16. Band broadening in an ideal and a "wavy" capillary tube ($d = 0.25$ mm) with water as eluent. Solid line, "wavy"; dashed line, ideal tube. $d = 0.25$ (1.5) mm; $L = 10$ m; coiling diameter = 12 cm; eluent, water; sample, acetone.

To summarize, wavy capillary tubes ($d = 0.25-0.5$ mm) result in h values from about 4 cm at $u = 10$ cm/sec to 2.5 cm at $u = 250$ cm/sec. In wider tubes ($d = 0.75-1.4$ mm) the h values decrease from 4 to 1.5 cm as u is increased from 10 to 250 cm/sec. Tolerable dispersions are obtained with 4-mm tubes. However, the optimal diameter for wavy tubes is 2 mm, as demonstrated in Fig. 15. The h values obtained at low velocities in wavy tubes are only slightly worse than those obtained in both ideal and wavy tubes in the fully turbulent region.

The permeability of a wavy tube as a function of u is illustrated in Fig. 13. Similar curves were obtained for all other wavy tubes. If the linear velocities in the wavy tubes are adjusted to $Re = 1000$, then the permeabilities are 50% of those of the corresponding ideal tubes ($K = d^2/32$). At low velocities the permeabilities are identical in ideal and in wavy tubes. The change in K with increasing u is continuous for wavy tubes.

Metal wavy tubes of oval cross-section

Various ways of coiling the oval wavy tubes around the 11-cm diameter form were studied. When the tubes were coiled on to the form either all laid flat or alternately laid flat and on edge, the dispersions obtained were considerably worse than those with circular cross-section tubes.

When the wavy tubes were coiled entirely on edge, the dispersions obtained were better than those in squeezed, twisted and coiled tubes. However, they were not better than those achieved with the simpler to construct circular wavy tubes.

Twisting oval tubes before waving and coiling them brought about a very small increase in efficiency, which was not worth the extra complication. This approach was therefore abandoned.

Applicability of wavy tubes to LC

A 100 m long, 1 mm I.D. wavy tube column will generate, for an inert peak, about 6300 theoretical plates at $u = 100$ cm/sec. The pressure drop over the wavy column will be, for *n*-heptane, about 26 bar and the hold-up time will be 100 sec.

The number of plates generated in an ideal tube of the same length and inner diameter under identical conditions ($Re = 1700$) would be 29 with a pressure drop of 13 bar. That is, making the tube wavy increases the number of plates by a factor of about 220.

If the inner diameter of the wavy tube is increased to 2 mm, while the length and linear velocity remain as before, then more plates (7100) are generated. It is not reasonable to compare this wavy tube with an ideal one under these conditions, because $Re = 3400$ and hence the flow would be turbulent.

Until now narrow capillaries have been used in chromatography, with I.D. 100–500 μm for gas chromatography and 15–100 μm for LC. The wider wavy tubes described above offer several advantages: (a) much simpler apparatus (pump, fittings, detectors); (b) the sample size could be increased by a factor of a 100 or more, *i.e.*, to the "semi-preparative" scale; (c) the time of analysis ought to be dramatically reduced, 60–70 plates/sec being generated for the inert peak. The disadvantage, of course, would be an increased consumption of eluent.

Such wavy tubes would only be useful for LC if a thin, stable and even layer of stationary phase could be deposited reproducibly on their walls. Our experience with ideal and deformed tubes and the experience of other groups with ideal tubes indicate that a satisfactory method of coating the tubes has not yet been found. The efficiency for retained peaks, including those with the smallest capacity ratios, is unfortunately less by a factor of 2–10 than that obtained for the inert peak.

Deformed PTFE tubes

Chemically resistant PTFE tubes could be of interest as reaction detectors or as heat exchangers. The PTFE tubes were wound on to the form described in Fig. 2 to give a slightly modified wavy tube.

The h vs. u curves are shown in Fig. 17 for PTFE and copper tubes ($d = 0.75$ mm), which were wound around the ball-shaped form. The eluent was water. There is little difference between the two curves and they are similar to those achieved with the previously described wavy tubes. This also applies to the K vs. u curve for the PTFE tube, which is also illustrated in Fig. 17. Although our PTFE tube was

not wetted by water, the results were little different than those obtained with a well wetted clean metal tube. In wavy tubes the ability of the eluent to wet the wall evidently has little influence on the dispersion.

The geometry described above for plastic tubes is not optimal. Better geometries will be discussed in a further paper concerned with reaction detectors.

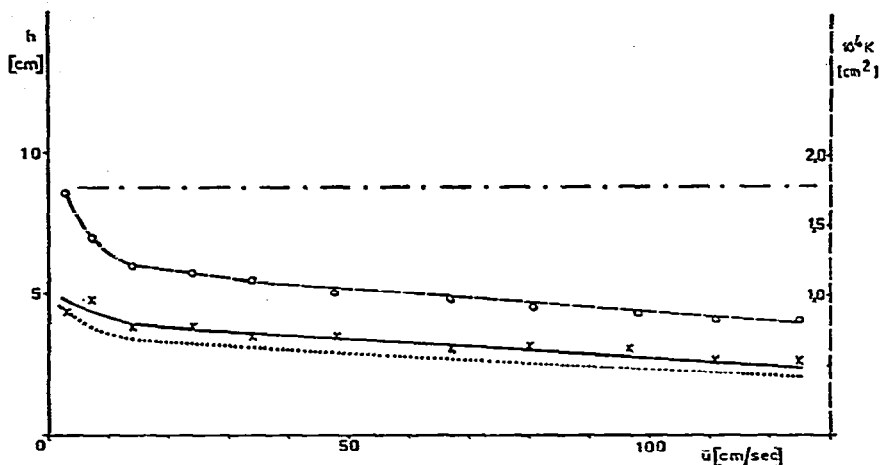


Fig. 17. Comparison of modified copper and PTFE "wavy" tubes. Dashed and dotted line, $K_{\text{theoret.}}$; dashed line, measured permeability of the PTFE tube; solid line, h values in the PTFE tube; dotted line, h values in the copper tube. The circular cross-section tubes were formed as shown in Fig. 2. $d = 0.75$ (2.0) mm; $L = 10$ m; eluent, water; sample, acetone.

CONCLUSION

There is no theory of dispersion in deformed tubes, because the necessary Navier-Stokes equations have not yet been solved. Therefore, any attempt to improve the dispersion in open tubes by deforming them must be empirical. We have found it convenient in this work to adapt Deininger's extended definition of laminar flow, which includes the case of very strong secondary flow²³.

Increased speed of radial mass transfer is of interest in heat exchangers, connecting tubing, reaction detectors and in LC. Until now the proposals for LC have been (a) the use of turbulent flow and (b) the use of very narrow ($d < 25 \mu\text{m}$) tubes. The first proposal requires high pressure drops and rapid mass transfer in the stationary phase is required. The second proposal involves enormous instrumental difficulties.

Our intuitive approach was to progress from discontinuously deformed tubes^{18,21} to continuously deformed tubes of a sophisticated nature, extending our previous treatment²⁰ using squeezed, twisted and coiled tubes (here designated "twisted"). Our aim was to produce tubes exhibiting h values at low linear velocities which were as small as those in the turbulent region.

When "twisted" tubes were studied in detail it was found that:

- (1) wall roughness was unimportant;
- (2) the optimal squeezing ratio, $\alpha = b/d$, was 0.6 for *n*-heptane and 0.7 for water; surprisingly, deformations as small as $\alpha = 0.9$ were also effective;

- (3) the optimal intermodal distance was 25 mm;
- (4) on coiling, the dispersion in twisted tubes, as in other deformed tubes, decreased much more than in ideal tubes;
- (5) in coiled twisted tubes, as in other deformed tubes, laminar flow was stabilized and extended to higher linear velocities;
- (6) the optimal coiling diameter was 12 cm;
- (7) the dispersion at velocities of less than 50 cm/sec was much better than in ideal tubes, being about twice that in the turbulent region;
- (8) the dispersion of an inert peak was a function of both the flattening of the tube (α) and the kinematic viscosity of the eluent;
- (9) the permeability, K , at $Re = 1000$ was 50% of that in an ideal tube.

The properties of "twisted" tubes are not perfect and our experience with them led us to the simple geometry of the wavy tubes with circular cross-section, as illustrated in Fig. 1. They are very simple to prepare and, as the exact shape of the waves is unimportant, no detailed description of their preparation is required. It is important, however, not to kink the tube, so that no dead spaces are introduced. Some of the properties of these tubes are:

- (1) the composition of the tube seems unimportant, glass, copper, aluminium, stainless steel and plastic all being suitable;
- (2) it is extremely important that the column be coiled;
- (3) typically $h = 4$ cm when $u = 10$ cm/sec and decrease continuously to the h value obtained for turbulent flow in an ideal tube ($h \approx 1$ cm) as u is increased;
- (4) h varies little with I.D. within the range 0.25–4 mm;
- (5) the dispersions are actually minimal at 2 mm I.D.;
- (6) the dispersion is independent of the kinematic viscosity of the eluent;
- (7) the wettability of the walls of the tube is unimportant;
- (8) the h vs. u and the K vs. u curves are smooth, so there is no transition to a turbulent region;
- (9) as in "twisted" tubes, the permeability is 50% of that of an ideal tube at $Re = 1000$.

With existing techniques an even coating of stationary phase cannot be applied to open tubes, so that the efficiencies for retarded peaks are remarkably low. If this problem were to be solved, then wavy open tubes would have the following advantages:

- (1) a high number of plates would be generated per unit pressure;
- (2) the speed of analysis would be much higher than that achievable in coiled ideal tubes;
- (3) because of the large inner diameters (1–4 mm), larger samples could be separated and instrumental difficulties would be minimized.

Oval wavy tubes offer no advantages.

The dispersion in modified wavy plastic (PTFE) tubes is identical with that in metal tubes. The chemical resistance of such tubes could be of interest for reaction detectors.

This work was necessarily performed by trial and error and hence much more experimental work was required than is described above. This has been reviewed in more detail by Hofmann²⁴.

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LIST OF SYMBOLS

a (cm)	the length of the major axis of an oval tube
b (cm)	the length of the minor axis of an oval tube
d (cm)	inner diameter of the open tube
h (cm)	height equivalent to a theoretical plate
K (cm ²)	specific permeability
$K_{\text{theoret.}}$ (cm ²)	specific permeability as calculated by Carman's method ⁵
L (cm)	column length
l (cm)	distance between the bends of a wavy tube
Δp (dyne/cm ² $\approx 10^{-6}$ bar)	pressure drop over the column
r (cm)	radius of the open tube
R (cm)	radius of the bends of a wavy tube
Re (—)	Reynold's number
St (cm ² /sec)	Stokes
u or \bar{u} (cm/sec)	cross-section averaged linear velocity of the mobile phase
$\alpha = b/d$	
η (g/cm sec or Poise)	dynamic viscosity
ν (cm ² /sec or Stokes)	kinematic viscosity

REFERENCES

- 1 K. Hofmann and I. Halász, *J. Chromatogr.*, 173 (1979) 211.
- 2 I. Halász, *J. Chromatogr.*, 173 (1979) 229.
- 3 G. Hagen, *Poggendorfs Ann.*, 4 b (1839) 423.
- 4 J. L. M. Poiseuille, *C.R. Acad. Sci.*, (1840) 11; (1841) 12; *Mem. Savants Etranges*, (1846) 9.
- 5 P. C. Carman, *Trans. Inst. Chem. Eng.*, 15 (1937) 150.
- 6 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 36.
- 7 K. F. Gütlich, *Ph.D. Thesis*, Johann Wolfgang Goethe Universität, Frankfurt/Main, 1970.
- 8 R. Aris, *Proc. R. Soc. London*, A235 (1956) 67.
- 9 G. J. Taylor, *Proc. R. Soc. London*, A219 (1953) 186.
- 10 G. J. Taylor, *Proc. R. Soc. London*, A223 (1954) 446.
- 11 G. J. Taylor, *Proc. R. Soc. London*, A225 (1954) 473.
- 12 M. J. E. Golay, *Nature (London)*, 180 (1957) 435.
- 13 M. J. E. Golay, *Anal. Chem.*, 29 (1957) 928.
- 14 J. A. Koutsky and R. J. Adler, *Can. J. Chem. Eng.*, 43 (1964) 239.
- 15 C. G. Horvath, B. A. Preiss and S. R. Lipsky, *Anal. Chem.*, 39 (1967) 1422.
- 16 P. Walkling, *Ph.D. Thesis*, Johann Wolfgang Goethe Universität, Frankfurt/Main, 1968.
- 17 K. Hofmann, *Diplomarbeit*, Johann Wolfgang Goethe Universität, Frankfurt/Main, 1966.
- 18 I. Halász, H. O. Gerlach, A. Kroneisen and P. Walkling, *Z. Anal. Chem.*, 234 (1968) 97.
- 19 I. Halász, H. O. Gerlach, K. F. Gütlich and P. Walkling, *Ger. Pat.*, 1,675,313; *U.S. Pat.*, 3,820,660; *Brit. Pat.*, 1,220,552 (1968).
- 20 I. Halász and P. Walkling, *Ber. Bunsenges. Phys. Chem.*, 74 (1970) 66.

- 21 G. Deininger and I. Halász, *J. Chromatogr. Sci.*, 8 (1970) 499.
- 22 I. Halász, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley, New York, 1971, p. 325.
- 23 G. Deininger, *Ber. Bunsenges. Phys. Chem.*, 77 (1973) 145.
- 24 K. Hofmann, *Ph.D. Thesis*, Universität des Saarlandes, Saarbrücken, 1975.
- 25 W. R. Dean, *Philos. Mag.*, 7/4 (1927) 208.
- 26 W. R. Dean, *Philos. Mag.*, 7/5 (1928) 67.