COLUMN DEVELOPMENT AND TECHNOLOGY IN GAS CHROMATOGRAPHY

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SUMMARY

The highlights of column development in gas chromatography have been reviewed from a kinetic rather than a thermodynamic stand-point. Thus, the introduction of the various column types and the controversies which stimulated the early rapid progress in the field have been considered against a background of the prevailing theory. The theoretical and practical performances of columns are compared in relation to liquid phase distribution and loading, and efficiency characteristics are discussed with particular reference to the different types of diffusion process. The paper concludes by considering the optimization of column parameters to achieve minimum analysis time and the feasibility of achieving this in packed and open tubular columns.

INTRODUCTION

It is now 25 years since the classic paper by James and Martin[1] introduced the technique of gas–liquid partition chromatography, and it is 20 years since the then newly formed Gas Chromatography Discussion Group organized its first international symposium in London under the auspices of The Hydrocarbon Research Group of the Institute of Petroleum. During this period the technique has advanced through many phases of development and today occupies a unique position in the field of analytical chemistry. In more recent years the appearance of fundamentally new column technology has naturally dwindled as the theoretical possibilities become exhausted and attention has now tended to turn to more fruitful areas of research such as high-performance liquid-chromatography (HPLC).

The modern art of gas chromatography (GC) can be said to date from the paper by James and Martin, although other pioneers such as Turner[2], Claesson[3], Glueckauf et al.[4], Phillips[5], and Turkel'taub[6] had all used a gaseous mobile phase in adsorption chromatography for the analysis of hydrocarbon gases and other materials. Appropriately, James and Martin not only described the fundamental theory of their new method but they also exemplified the application by successfully separating fatty acids, which even now is recognized as one of the more difficult types of analysis to

perform. Even more surprising perhaps is that a quarter of a century later we are still using very similar columns and packing material for most routine purpos s.

This 20-year anniversary is a convenient vantage point from which to review the highlights of column development. It is not intended to be a comprehensive review and attention has been restricted to the development and comparison of different types of column rather than to attempt to include retention behaviour and selectivity. The latter subject has progressed independently of column development and deserves separate treatment, of which one could not possibly hope to do justice to in a limited space.

The properties which are used to identify a particular type of column depend on whether physical properties or performance define the uniqueness of the column. In the author's opinion it is not only irrelevant but misleading to attempt any classification of columns, except for the purposes of nomenclature, because we now know that there is no theoretical boundary between the levels of performance of different types of column. Classification tends to imply that this boundary exists and gives rise to misconceptions such as that "capillary columns are faster than packed columns". One may enquire then why have new types of column been developed if there is no theoretical difference between attainable performances? The answer, very simply, is that new types of column have made it easier to achieve higher levels of performance within the practical limitations of the apparatus.

This paper will consider that all gas chromatographic columns fall into one of four categories, viz., packed, wall-coated open tubular (WCOT, or "capillary"), porous layer open tubular (PLOT), or packed capillary columns.

PACKED COLUMNS

Undoubtedly the most satisfactory way to appreciate the reasons for the development of new types of column is on the basis of theory as the early understanding of the chromatographic process and the effects of the operative variables and column parameters soon resulted in improved performance. The theoretical scene in partition GC was originally set by Martin and Synge[7] with their plate theory, which showed that elution peaks were gaussian in shape and so their widths could be defined in gaussian parameters. Hence they showed that the number of theoretical plates was a simple function of the standard deviation. It followed that the degree of quantitative separation between components could also be measured in gaussian terms, as described by Glueckauf[8] in the case of unequal peak areas, and by Golay[9] for equal peak areas. The definition of resolution which is now universally accepted, viz., that of the ratio of the distance between the two peak maxima to the mean peak width (see Appendix, eqn. 1) was originally proposed by a special committee set up during the First International Symposium[10].

The introduction of the rate theory by Van Deemter et al.[11] initiated a phase of rapid development in column technology. The theory was based on an evaluation of the effects of diffusion processes in packed columns and the balance between these diffusion processes and the carrier gas flow. The theory, usually referred to as the Van Deemter theory, considered that the main diffusion processes were "eddy diffusion", which arises from the multiplicity of different paths taken by solute molecules through the packing; molecular diffusion, which describes the tendency of

solute molecules in a discrete concentration zone to diffuse longitudinally in the carrier gas, and lastly transverse diffusion in the stationary liquid, the slowness of which causes instantaneous non-equilibrium between solute molecules in the gas phase in relation to those in the liquid phase. The equation (see Appendix, eqn. 2) was soon to be vigorously tested in practice by Keulemans and Kwantes[12], who showed it to be valid in a semiquantitative way. These authors tested columns packed with 20–30 and 30–50 mesh "Sterchamol", a proprietory brand of crushed firebrick, coated with different amounts of hexadecane. The effects of stationary phase loading, nature of carrier gas, and support particle diameter on column efficiency were studied. For example, the effects of liquid phase loading on the HETP for the two compounds propane and n-butane are shown in Fig. 1, reproduced from the original paper.

As predicted by the Van Deemter theory, the minimum plate height and the slopes of the curves in the mass transfer region both decrease markedly with decreasing stationary phase loading. Also the optimum gas velocity increases with decreasing loading, again conforming with the theory and suggesting that faster analysis would be possible by the use of lightly loaded columns.
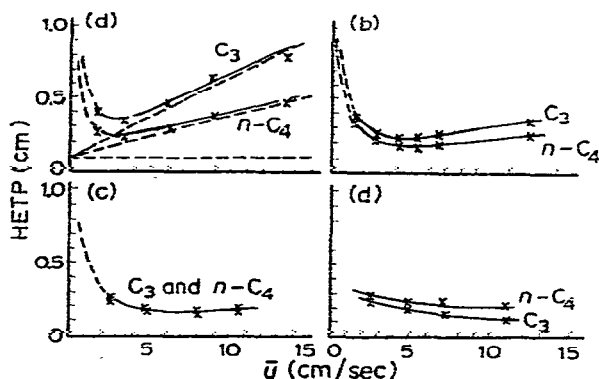

Fig. 1. Curves of H against $\bar{u}$ for various ratios of hexadecane to 30–50 BSS support: (a) 45:100, (b) 30:100, (c) 15:100, (d) 5:100. Solutes, propane and n-butane; carrier gas, hydrogen. [Reproduced from A. I. M. Keulemans and A. Kwantes, in D. H. Desty (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 15.]

The eddy diffusion term A caused some early controversy. Golay[13] preferred to call this the multipath term because the type of diffusion it represented was not strictly analogous to the well-known eddy diffusion in turbulent flow. The experimental work of Keulemans and Kwantes indicated that the quantities λ and d_p tended to act in opposition to each other. Large particles seemed to pack more easily than small particles and gave λ values in the region of unity. The smaller particles gave λ values as high as 8 and this was attributed to channelling of the packing, particularly with the relatively heavy liquid phase loadings that were used. Nowadays, with the much lower loadings that are normal in GC the λ values can be expected to be very much lower for fine supports.

The efforts being made to significantly improve column performance following the publication of the Van Deemter theory were one of the prominent features of

the second International Symposium held in Amsterdam in 1958. Littlewood[14] was the first to report the use of wetted glass beads as column packings. Because of their well defined regular shape these had better packing characteristics and λ values of about unity were claimed. It is interesting to examine the experimental C terms obtained by Littlewood. For a column packed with 150–200 mesh beads (0.074–0.1 mm diameter) loaded with about 3 % of tri-o-tolyl phosphate, C values for well retained components were in the region 0.05–0.07 sec at 28.5°, *viz.*, somewhat higher than the values reported by Keulemans and Kwantes for their heavily loaded columns. Littlewood's C values decreased sharply, however, with increasing temperature, reaching values of less than 0.01 sec at 100°. This was attributed to an improvement in the distribution of the liquid phase over the bead surface resulting from the decrease in the interfacial surface tension of the liquid at the higher temperature. Thus it seemed that the use of regularly shaped supports such as glass beads could have advantages over irregular porous supports, particularly if stable uniform layers of stationary phase could be achieved. The permeability of glass bead columns to the carrier gas flow is certainly better than that of columns packed with diatomaceous earth or firebrick because in practice the latter invariably contain fines. Also the much lower permissible liquid phase loading on glass beads should be advantageous from the viewpoint of fast analysis (see the section *Minimum analysis time*).

One of the difficulties with the Van Deemter theory is the precise interpretation of the mean film thickness d_f, which depends critically on the way in which the liquid phase is distributed on the support. The remarkable series of scanning electron micrographs shown by Drew and Bens[15] at the 1968 symposium in Copenhagen revealed many of the structural properties of the commonly used supports. Unfortunately attempts to examine the distribution of phases such as Carbowax and silicone gum rubber were not very conclusive although the results did indicate that in a support such as Chromosorb P, holes having a diameter of equal to, or less than twice the mean film thickness were not in fact filled with liquid. Thus a calculation of d_f from the surface area would hardly be valid. On glass beads, however, a calculation of d_f should be possible provided that the liquid phase is distributed as a uniform film. Littlewood did not calculate the film thickness from his data but a rough calculation shows that C should be at least two orders of magnitude less than the values he reported if the Van Deemter theory is correct. The reason for the discrepancy was probably the fact that with the relatively low loadings used, the liquid phase mass transfer term is no longer rate limiting and that transverse gas phase mass transfer is a significant contribution to non-equilibrium.

Giddings[16] has discussed the performance of glass bead columns in connection with non-equilibrium theory in which the effects of various modes of diffusion were considered from perhaps a more realistic basis. The treatment was continued in a later publication[17] which, it was claimed, more accurately represented the role of the liquid phase. Giddings pointed out that previous concepts of the liquid phase distribution were over-simplified and a new theory was presented. Subsequently, a comparison[18] of experimental efficiencies with theoretical values for a glass bead column coated with tri-o-tolyl phosphate showed good agreement, as did the variation of plate height with the particle size.

Recently, the present author[19] has used glass beads coated with a thin layer of stationary phase stabilized by the addition of the organoclay "Bentone 34", with

which it forms a solid or semi-solid gel. Fig. 2 shows the effect of using a combination of silicone OV-17 and Bentone 34. This is a set of HETP *versus* gas velocity curves for columns packed with 100-mesh glass beads which have been coated with a constant 0.08% loading of stationary phase containing increasing amounts of the Bentone 34. Curve a, which corresponds to a zero addition of the clay, gives a high C term and the effect of increasing the clay content is clearly to decrease the C value to a minimum level of about 4×10^{-3} sec.
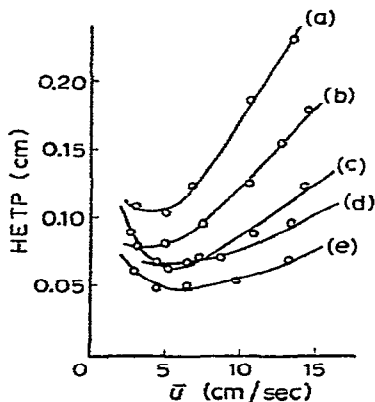

Fig. 2. Effect of adding Bentone 34 to stationary liquid phase on plate characteristics of glass bead columns, packed with 0.08% (w/w) (Bentone 34 + OV-17) on 100 BSS glass beads. Solute, naphthalene; carrier gas, nitrogen. (a) 100% OV-17; (b) 25% Bentone 34; (c) 100% Bentone 34; (d) 50% Bentone 34; (e) 75% Bentone 34.

At the Amsterdam meeting in 1958 it seemed that the Van Deemter equation could be used as a basis for the design of high-efficiency packed columns. Papers by Scott[20], and by Bohemen and Purnell[21] discussed this aspect and reported the fabrication of columns which gave efficiencies of up to 20,000–30,000 theoretical plates. In Scott's work narrow-sieve fractions of finely divided support were loaded with as little as 2.5% of liquid phase and used to pack columns of up to 50 ft. in length. High gas pressures were employed amounting to several hundred p.s.i., and a capillary constriction was placed at the column exit to avoid the steep flow gradient which would otherwise occur in the column. In this way a linear relationship was obtained between the number of theoretical plates and the column length. Scott noted that the low liquid phase loading could cause some peak tailing with polar solutes because of adsorption effects on uncovered active sites on the support surface. This problem was overcome in a unique manner by coating the support surface with a layer of silver.

Bohemen and Purnell found in their experiments that the eddy diffusion term A sometimes appeared to be negative in value, particularly with finely graded supports. They suggested that the modified general equation

$$H = \frac{A + B}{u} + Cu$$

applied more accurately to their results than the Van Deemter equation. Like Scott these authors predicted that high column efficiencies would require the use of small

sample sizes, with columns lightly loaded with stationary liquid, and operated at elevated outlet pressures. This trend was extended considerably some ten years later by the work of Myers and Giddings[22]. These authors employed small-diameter columns packed with particles of less than 1 μm in diameter and operated at gas pressures of up to 2500 p.s.i. In this way they achieved plate heights as low as 0.08 mm.

In retrospect it was already apparent by 1958 that the practical limitations of packed columns had been approached for the average user, at least from the standpoint of column efficiency. Thus it was necessary to use high pressures for high plate numbers, and this involved the use of specially designed equipment that was not available from the commercial suppliers. A normal level of efficiency for packed columns for the vast majority of routine applications may therefore be regarded as one ranging from 10^3–10^4 theoretical plates. This situation has not changed significantly in the intervening years.

There have been a countless number of publications describing new developments in column packings, including low activity supports for polar materials[23-25], bonded phase packings[26], polymeric packings which are formed *in situ* in the column[27], etc. Many of these developments have been invaluable within their respective spheres but the author would select the introduction of porous polymer packings by Hollis[28] as one of the more important advances in practical GC. These materials considerably facilitated the separation of very polar compounds which had previously given trouble as a result of adsorption problems on the support. For example, even water can be separated and determined quantitatively by this means[29].

The development of a generalised theory of chromatography by Giddings and his colleagues was a significant feature of the decade following the Amsterdam meeting. This has helped to elucidate the various mechanisms of the chromatographic process and to evaluate the different types of diffusion that occur in the column. This work culminated in a generalised plate height equation[30-33] which used reduced parameters (see Appendix, eqn. 3) and which could be used to correlate the behaviour and performance of any chromatographic system. Perhaps one of the most distinguishing features of the Giddings theory is the nature of the eddy diffusion term. Unlike the Van Deemter theory, and later the Golay theory, Giddings did not regard the terms describing different diffusion processes as being additive. In particular, the terms representing eddy diffusion and lateral gas phase diffusion are coupled non-additively, as shown in the Appendix.

OPEN TUBULAR COLUMNS

The introduction of capillary columns by Golay remains as one of the most significant advances in chromatography and was to have a tremendous effect on the subsequent utilization of the technique. The term "capillary column" is used for convenience to describe all wall-coated open tubular columns, largely because this nomenclature has become common usage. We should remember, however, that the essential features of this type of column are embodied in the expression "open tubular", and also that packed columns can be of capillary dimensions but are not, by the above definition, "capillary columns". This is clearly confusing to the newcomer to the technique, who would be advised to refer to a comprehensive glossary of terms such as that published by the British Standards Institution[34].

Capillary columns, then, differ from packed columns by virtue of their unrestricted axial gas path and, consequently, exhibit a resistance to the carrier gas flow which is some two orders of magnitude lower. Thus, whatever other theoretical or practical differences exist between the two types of column the essential practical difference is that several hundreds of metres of column can be operated at the same level of pressure as that necessary for the operation of only a few metres of conventional packed column. This, of course, is a very general and over-simplified statement which does contain an element of inaccuracy. Thus, Knox has shown on theoretical grounds that similar plate performances should be attainable from either packed or capillary columns, at the same pressure drop, provided the support particle size and column length are optimized. For high efficiencies at relatively low pressure drops, however, a packed column would have to be packed with very large particles and impractically long columns would be necessary. This aspect will be dealt with later under *Minimum analysis time*.

Golay presented his first paper on the theory and practice of capillary columns at the first GC symposium of the Instrument Society of America, held at East Lancing, Michigan, in 1957[35]. This was followed by a second paper presented to the 1958 Amsterdam Symposium[36]. The theory which Golay advanced, although ultimately similar in form to the Van Deemter theory, had two essential differences, *viz.*, the omission of the eddy diffusion term A because of the absence of packing and the inclusion of an additional mass transfer term representing transverse non-equilibrium in the gas phase (see Appendix, eqn. 4). In his paper Golay ventured the belief that the Van Deemter C term, describing liquid phase non-equilibrium, was in fact less important than the gas phase term in Celite or firebrick packed columns, whereas the opposite should be true in open tubular columns. This was rather surprising in view of the earlier studies of Keulemans and Kwantes[12], and Boheman and Purnell[21], all of whom had reported results which seemed to support the Van Deemter theory in this respect. However, as mentioned earlier, Littlewood's results with glass bead columns, and also the author's own results with gel-coated beads did suggest that there was a transverse non-equilibrium term which remained unaffected by the liquid phase content. This did not appear to be predominant until the liquid phase loading became rather lower than Golay had supposed.

Two years later at the 1960 Edinburgh Symposium there were several papers describing the operation of capillary columns. Desty and Goldup[37], using glass and metal columns coated with squalane, and normal paraffins as test solutes, showed that the effects of liquid phase loading, choice of carrier gas, column temperature, capillary diameter, and the k values were all qualitatively in agreement with the Golay theory but that the quantitative agreement was less satisfactory. For instance a comparison of calculated and experimental C terms showed that the latter were between two and six times greater than the values calculated from terms in the Golay equation. During the course of discussion on their paper Desty pointed out that when practical values were substituted into the terms of the Golay equation the gas phase non-equilibrium term C_g was about ten times greater in value than the liquid phase term C_l for all of the capillaries they had used. This also contrasted with Golay's view that the presence of the retentive layer in such columns should be the rate limiting factor. Desty drew attention to the critical effect of k on resolution (this is clear from eqn. 1, Appendix). In packed columns, where values are usually $\gg 1$, the effect on resolution

is only slight but with capillary columns the k values are often lower than unity as a result of higher phase ratios and so the higher efficiency necessary to effect a resolution must be considered. Nevertheless, lower k values usually enable faster analyses to be performed. These authors illustrated their paper by showing some very impressive chromatograms which demonstrated two of the immense practical advantages of these columns, *viz.*, high resolution and high speed. One example showed the separation of seventeen octane isomers on a 600-ft. × 0.01-in.-diameter glass capillary column with a reported efficiency of 300,000 theoretical plates.

Scott and Hazeldean[38] at the same meeting described experiments carried out on nylon capillary columns and concluded that their results generally supported the Golay equation both in form and, to a large extent, in the numerical values of the constants. They, like Desty and Goldup, concluded that slowness of diffusion in the gas phase played a significant part in determining the efficiency, particularly at high capacity ratios.

On reflection it seems that the disparity between Golay's comments on the relative importance of the mass transfer terms and the experimental results were caused by the idealistic assumptions relating to the distribution of the liquid phase in both types of column, and also the fact that a clear distinction was drawn between the columns. Experience shows that it is disadvantageous to draw this kind of distinction because it indicates that there are different theoretical boundaries to the performances of the two types of column.

Capillary materials

Capillary columns have been made from stainless steel[37], copper[39,40] aluminium[41], nickel[42], gold[39], glass[37] and plastic materials[38]. Generally the objective is to produce a non-adsorptive surface with favourable coating characteristics. Austenitic stainless steel is used for the majority of applications these days since it is available commercially in almost any continuous length. Glass columns, which are made by the process described by Desty *et al.*[42], are also commercially available and are sometimes preferred for the separation of polar or reactive compounds. Capillary column internal diameters are usually in the range 0.2–0.5 mm and lengths of up to about 100 m may be employed for difficult separations.

Coating of columns

There are two basic methods for the coating of capillary columns, *viz.*, the dynamic method first described by Dijkstra and De Goey[43], and the static method which was used originally by Golay[36]. Both of these methods are too well known to require further elaboration. The dynamic method is the easier of the two methods and is certainly the more widely used but the reproducibility of the coating is open to doubt. Novotny *et al.*[44] have studied the variables which affect the coating of glass columns using the dynamic method. They report that the Fairbrother–Stubbs relation is applicable provided that the surface possesses enough capacity for the spreading of the wetting liquid. Thus the film thickness is given by

$$d_f = \frac{rc}{200} \left(\frac{u\eta}{\gamma}\right)^{\pm}$$

where c is the concentration by volume of the stationary phase in the coating solvent,

u is the linear velocity of the coating plug, η is the viscosity, and γ the surface tension of the coating liquid.

The static method for the coating of capillary columns requires more elaborate equipment but is more controllable with regard to the amount of liquid phase deposited in the column and, consequently, it is more reproducible.

The disposition of the liquid phase on the capillary wall is obviously a crucial factor in determining the chromatographic performance. The formation of a uniform film will depend very critically on such factors as the nature and quantity of the liquid and the physical and chemical characteristics of the inner wall of the capillary. Very smooth surfaces such as are experienced with glass columns do not appear to be satisfactory because liquid films tend to break up to form minute droplets on repeated heating and cooling. Thus considerable efforts have been made to find ways of stabilising the film. Grob[45] has produced excellent columns by first coating the surface with a layer of graphitized carbon black to a thickness of about 10^{-7} cm. The columns are then coated normally with stable films of both polar and non-polar liquids. Vollmin[46] successfully employed 20-m "Grob" columns coated with silicones OV-17 and SF-96 for the separation of urinary steroids after derivatization to the trimethylsilyl ethers. Novotny and Tesarik[47] have prepared thermally stable glass columns by etching the inner surface with HCl and HF. The surface is then silanized in the gas phase using a mixture of trimethylchlorosilane and hexamethyldisilazane. The columns are subsequently coated with stationary phases such as dibutyl phthalate, UCON 55-XB, triethanolamine, and silicone SE-30. In a later publication Bartle and Novotny[48] correlated surface measurements with chromatographic performance after "tailoring" the glass surface by permanent bonding of selective monolayers of silicones of different structures and then coating the columns with liquids of different polarities. They concluded that it was important to achieve a chemical similarity between the surface and the wetting liquid for the preparation of homogeneous films, and a mechanism for compatibility was discussed in terms of the surface phenomena and a molecular model of the modified surface.

Another interesting method of producing thermally stable and efficient glass capillary columns was proposed by German and Horning[49] and involves the addition of silanized silica particles to the liquid phase before coating. The columns, which are about 60 m in length and 0.3 mm I.D., are coated by the dynamic method using a suspension of "Silanox Grade 101" in carbon tetrachloride. The liquid phase is subsequently applied as a separate step using the same coating technique. Column efficiencies of 1700 plates per metre were obtained by this method. An investigation of the surface characteristics of these and other types of treated glass capillary columns has recently been carried out by Schieke et al.[50] using scanning electron microscopy (SEM) and also energy dispersive X-ray analysis. The paper is well illustrated with examples which exemplify the great utility of these techniques for studying methods of treatment.

The papers referred to above are just a few of the many that have dealt with the subject of capillary pretreatment. Mostly the purpose of the treatment has been to produce better and more consistent plate efficiencies but other reasons for pretreatment have been to reduce peak tailing for polar compounds and to increase the capacity of the column for liquid phase loading. Blomberg[51] claims that silanization and etching of glass capillaries with hydrogen fluoride or chloride reduces the column

activity only slightly and that a better method is to coat the surface with a layer of non-extractable Carbowax 20M before applying the stationary phase. The Silanox columns, referred to earlier, would tend to have a higher liquid capacity by virtue of the greater surface area and strictly these are a type of porous layer open tubular column.

POROUS LAYER OPEN TUBULAR COLUMNS

Golay, during his presentation of the theory of open tubular columns, suggested that the C_l term arising from tranverse diffusion in the liquid phase would be substantially reduced by replacing the smooth inner wall by a roughened surface or porous layer. While summarising the state of theoretical development at the 1960 Edinburgh Symposium he showed a practical example of how a marked improvement could be obtained by depositing a layer of colloidal clay on the inner surface of a metal capillary, firing it *in situ* and then impregnating the layer with liquid phase[13]. A fourfold reduction in HETP was apparently achieved compared with a smooth-walled column of similar dimensions. Golay had earlier considered the effect of increasing the effective surface area in this way by introducing a roughness factor F in his original theory. This is the factor by which the effective surface area is increased by the presence of a porous layer compared to an equivalent smooth-walled column. In a later revision of the theory to deal with this type of column it was assumed that the C_l term would be negligible and it was consequently omitted from the plate equation[52]. Also, C_g was modified to include a term a, the ratio of the thickness of the porous layer to the internal column radius (see Appendix, eqn. 5). Later, at the 4th International Symposium on Separation Methods in Heidelberg[53] held in 1967, Golay presented a further revision of his theory, this time to include a modified C_l term which included the factor F and two new terms, expressed in the equations (see Appendix, eqn. 6) as a_1 and a_2. These terms are descriptive of the porous layer, *i.e.*, a_1 represents the mean length of the tortuous path through the layer and a_2 represents the thickness of the mean free gas volume. These factors are difficult to measure from performance data and so the theory remains largely unsubstantiated. The author believes that a better practical approach for assessing the improvements generated by the presence of the porous layer is to compare phase ratios and HETP values at gas velocities beyond the optimum so that the total mass transfer effects may be compared.

As indicated earlier, the presence of a porous layer will increase the liquid phase loading capacity of the column. This is advantageous from the viewpoints of increased sample capacity and of increased k values. This makes it easier to achieve optimum values for minimum time of analysis, and of course reduces the plate efficiency required for resolution.

Practical methods for producing a porous layer

There are two fundamentally different ways to produce a porous layer on the inner wall of a capillary tube, *viz.*, by the addition of a separate porous material or by forming it *in situ* by chemical treatment of the wall. Aspects of the latter have been dealt with in the last section, where the resulting columns cannot be regarded strictly as porous layer columns, although this is largely a question of definition. Mohnke and Saffert[54] were the first to report the effects of using etched glass capillaries in gas–

solid chromatography when they successfully separated hydrogen isotopes and their nuclear spin isomers. The columns were prepared by filling the capillary with 17% aqueous ammonia solution, sealing both ends, and then heating to 170° for 70 h. The tube was opened, the ammonia solution removed by air pressure, and the temperature raised to 190°. Bruner and Cartoni[55] used a solution of 20% caustic soda to etch glass capillaries, which were subsequently used either as adsorption columns or coated with squalane for use as partition columns. Excellent performances were reported for these columns for separations of low-boiling hydrocarbons and of deuterocarbons from hydrocarbons. Columns coated with squalane were shown to behave partly as adsorption columns and partly as partition columns, with the proportion of adsorption decreasing with increasing liquid phase loading. Table I summarises some of the essential features of these columns.

TABLE I

CHARACTERISTICS OF ETCHED GLASS CAPILLARY COLUMNS COATED WITH SQUALANE

(Reproduced from the data of Bruner and Cartoni, *Anal. Chem.*, 36 (1964) 1522.)
Column length, 38 m; internal radius (r), 0.22 mm.

Column characteristic	Column No.				
	1	*2*	*3*	*4*	*5*
Weight liquid phase deposited (mg)	0	3.14	11.2	35.1	55.6
Film thickness d_f (μm)	0	0.01	0.04	0.12	0.18
Percentage adsorption	100	87	61	25	6
Phase ratio (β)	0	1471	410	131	92
$H_{min.}$ (mm)*	0.45	0.42	0.85	0.88	0.95
Total mass transfer coefficient C ($\times 10^2$ sec)	0.52	0.55	1.20	1.25	1.25

* $H_{min.}$ = minimum plate height.

The effect of increasing the liquid phase loading obviously increases the minimum plate heights and mass transfer C terms initially but the values become more or less constant at about the 11% level. After this level, where partition is the major contributing process, the values are comparable with typical values for wall-coated columns although the phase ratios are very much lower (*viz.*, loadings much higher) than can normally be achieved in such columns. In fact, the two lowest values can be approached in modern lightly loaded packed columns, thus illustrating the overlap between the two basic column types.

Columns prepared by the deposition of a separate porous layer on the inner wall are probably the more representative of the class of column visualized by Golay. Halász and Horvath[56,57] realized the potentialities of such columns and soon published papers which described the preparation and properties of columns coated either with adsorbent material or finely powdered support impregnated with liquid phase. A procedure was employed in which the finely ground solid plus the requisite amount of stationary liquid is suspended in a mixture of high-density solvents. The suspension is then used to coat the column in much the same way as is used for wall-coated columns

using the static coating procedure. Columns of this type have been studied in detail by Ettre and his colleagues, who prefer to call them "support-coated open tubular" (SCOT) columns[58-61]. Ettre, in collaboration with Purcell, has also written an authoritative review of PLOT columns as a contribution to a recent volume in the well-known series *Advances in Chromatography*[62].

Table II shows the effect of the presence of the support layer on the phase ratio for different SCOT columns compared with a typical WCOT column having the same dimensions.

TABLE II

CHARACTERISTIC VALUES OF SUPPORT-COATED OPEN TUBULAR COLUMNS
(Reproduced from *Separ. Sci.*, 1 (1966) 781.)

	*SCOT columns**				*Capillary column*
	1	*2*	*3*	*4*	*5*
Tube I.D. (min)	0.5	0.5	0.5	0.5	0.5
Geometric surface area of wall (cm²/m)	15.7	15.7	15.7	15.7	15.7
Weight solid support in column (mg/m)	8.75	8.75	8.75	8.75	0
Weight liquid phase deposited (mg/m)	8.2	4.1	2.6	0.51	0.15
Phase ratio, β	22	50	67	360	320

* Perkin-Elmer, Beaconsfield, Great Britain.

Phase ratios as low as 22 are achieved without difficulty on the SCOT columns and these values are typical of the level normally experienced with packed columns. Thus such a column would allow an approximate tenfold increase in sample size while maintaining the same degree of resolution as the capillary column, a considerable advantage when fractions need to be collected for spectroscopic examination.

In 1968 the present author[63] described another method for the preparation of PLOT columns in which a glass tube loosely packed with diatomaceous earth is drawn down to capillary dimensions using the apparatus of Desty *et al.* Thus, the method is similar to that used by Halász and Heine[64] for their so-called "packed capillary" columns, except that a stationary wire is inserted through the open end of the tube, through the loose packing, and terminates in the hot zone where the tube narrows. This causes the support particles to be trapped between the wire and the tube wall and hence to become partially embedded in the wall. This leaves an unrestricted axial path through the column. The stationary liquid is applied from solution using the dynamic plug method, except that the plug length must be somewhat longer than is used for wall-coated columns. Also, unlike the coating of wall-coated columns, the loading is reproducible and depends only on the concentration of the liquid phase. Lithium chloride was added to the support in early columns to help bond the particles to the glass wall but this was later found to be unnecessary. Similar methods for the preparation of PLOT columns have been described by Cronin[65], who employed glass powder as a bonding agent, and Goretti *et al.*[66], who coated columns with graphitized carbon black for adsorption chromatography.

The author notes that this process, in principle, was described some years earlier than his own publication by Jentzsch[67] and Ness[68] in separate patent applications and related to metal columns. As far as is known, the latter have not been widely applied in GC.

The performance of PLOT columns produced in the author's laboratory using the "drawing-down" method can be judged from the HETP *versus* gas velocity plots given in Fig. 2 of the author's original publication[63].

These show the effect of capacity ratio k for naphthalene on the shape of the resulting curve. The position of the minimum occurs at increasing velocity as k decreases, and the minimum becomes more diffuse hence increasing the range of gas velocities for which the minimum remains near optimum. The minimum HETP is obviously not critically affected by liquid phase loading and the slopes of the curves in the mass transfer region are very similar, suggesting that C_l in the Golay equation is less effective than C_g. This contrasts with the situation shown earlier in Fig. 1 for packed columns where liquid phase loading clearly had a very marked effect.

Table III shows computed values of C_g and C_l for n-paraffins on a squalane PLOT column of phase ratio 140. These values were determined by a method[69] which involves running the column with the two carrier gases helium and nitrogen and determining the values of B and $(C_g + C_l)$ from the plate height *versus* gas velocity curves.

TABLE III

EXPERIMENTAL NON-EQUILIBRIUM TERMS FOR A SQUALANE-COATED PLOT COLUMN PRODUCED BY THE DRAWING-DOWN PROCESS

Solute	k	Helium		Nitrogen		C_l (sec)
		$(C_g + C_l)$ (sec)	C_g (sec)	$(C_g + C_l)$ (sec)	C_g (sec)	
n-Hexane	0.17	0.00189	0.00139	0.00418	0.00368	0.0005
n-Heptane	0.38	0.00341	0.00135	0.00565	0.00359	0.0021
n-Octane	0.80	0.00435	0.00290	0.00893	0.00748	0.0015
n-Nonane	1.68	0.00633	0.00553	0.0135	0.0127	0.0008

Since C_g values for the two carrier gases are related by $C_g(\text{He}) = C_g(\text{N}_2) \cdot B(\text{He})/B(\text{N}_2)$ simultaneous equations can be formulated which contain C_g and C_l for one carrier gas only and C_l is obtained effectively by difference between $(C_g + C_l)$ and C_g.

Broadly speaking, the results support the contention that liquid phase mass transfer is the lesser of the two contributions to mass transfer resistance with both carrier gases. The variation of the C_g and C_l terms with k also tends to follow that predicted by the Golay equation, *viz.*, that C_g would be expected to increase with increasing k while C_l would decrease continuously after reaching an early maximum value. Ettre and Purcell, in their monograph on PLOT columns[62] criticized this method for the determination of C_l on the basis of an assumption that it is two orders of magnitude smaller in numerical value than C_g according to purely theoretical arguments. If this is the case, then of course the method is invalid because the result will merely be a reflection of the error of determining $(C_g + C_l)$ and C_g. However, the

numerical values shown in Table III for the compounds heptane and octane are sufficiently far apart for us to have some degree of confidence in the result. In the author's view it is highly questionable whether C_i values calculated from the Golay theory, which involves assumed values of a_2 and F, have any practical validity. Thus, the experimental evidence suggests that there is a large discrepancy between the theoretical and practical levels of F, which reflects the fact that, as with packed columns, the liquid phase does not form a uniform layer but that its configuration is far more complex. In this respect, it seems that all the theoretical advantages of PLOT columns have not yet been realized and that their major practical benefit is the greater permissible capacity and the attendant lowering of phase ratio values.

TABLE IV

COMPARISON OF PROPERTIES AND PERFORMANCE OF VARIOUS TYPES OF OPEN TUBULAR COLUMNS

Carrier gas: N_2; solute: n-heptane; liquid phase: squalane.

Property measured	Column type				
	WCOT (stainless steel)[37]	WCOT (glass)[37]	PLOT[69]	SCOT[62]	Etched[55]
Temperature (°C)	75	25	100	81	40
I.D. (mm)	0.24	0.12	0.50	0.50	0.44
Length (m)	13	4.6	20	15	38
Phase ratio, β	100	385	150	76	131
k (heptane)	1.73	3.1	0.38	1.99	5.90
Efficiency, N	37,000	15,000	23,800	32,000	43,000
$H_{min.}$ (mm)	0.35	0.30	0.84	0.47	0.88
$\bar{u}_{opt}$ (cm/s) *	8	10	6	7.2	3.5
$(C_a + C_i)$ (sec)	0.0015	0.0015	0.0057	0.0032	0.0125
F	—	—	5–10**	30***	7.15***

  * $\bar{u}_{opt}$ = the gas velocity giving $H_{min.}$.
 ** Experimental value.
*** Calculated from geometric data.

Table IV gives a rough comparison of the performances of columns selected from four different sources, viz., a PLOT column prepared in the author's laboratory[69], WCOT stainless-steel and glass columns prepared by Desty and Goldup[37], a SCOT column prepared by Ettre and Purcell[62], and an etched column prepared by Bruner and Cartoni[55]. All the columns have squalane as liquid phase and n-heptane as the solute. Obviously, a strict comparison is not possible but the data does reflect in a general way the relative properties of typical columns of different types, i.e., that wall-coated columns tend to give the best plate performance and, even at a phase ratio as low as 100, the total mass transfer coefficient is considerably lower than that for the other columns. Also, the optimum gas velocity is rather higher, which suggests the possibility of faster analysis.

There have been a number of attempts to produce capillaries coated with colloidal silica or alumina, using the dynamic coating procedure. Kirkland[70] coated stainless-steel tubing with 4–7% of an aqueous solution of Baymal*, a fibrillar col-

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  * A colloidal brand of alumina marketed by DuPont (Hitchin, Great Britain).

loidal boehmite, and obtained an effective sixfold increase in wall area. Colloidal silica was used in a paper published by Schwartz *et al.*[71] and Purcell[72] described the use of columns coated with molecular sieve for gas analysis. More recently Kaiser[73] has described the preparation of partition type PLOT columns using a dynamic procedure. Nikelly[74] reported a similar method for preparing columns with a 30-40 μm layer thickness in 0.5-mm- and 0.75-mm-diameter columns.

PACKED CAPILLARY COLUMNS

The term "packed capillary column" is by convention reserved to describe the type of column originally prepared by Halász and Heine[64] by drawing down a larger-diameter tube filled with support material or solid adsorbent. Thus the drawn-down tube contains packing which is more tenuously distributed than in conventionally packed columns and consequently we can expect the permeability to gas flow to be somewhat higher. The columns made by Halász and Heine were prepared from glass tubes packed with support material and the liquid phase was applied after the drawing-down procedure by using the dynamic plug method. Partition columns of a similar type have also been studied by Landault and Guiochon[75]. Adsorption type packed capillary columns, packed with graphitized carbon black, have been employed by Schneider *et al.*[76] for the separation of C_1 and C_8 hydrocarbons by carbon number. The latter is an outstanding example of how adsorption chromatography can be applied to give symmetrical peaks with good resolution, and to solve an otherwise difficult problem. Surprizingly, packed capillary columns have not become popular, possibly because of the difficulty of manufacturing them commercially.

GENERAL COMPARISON OF COLUMN TYPES

It will be apparent from my earlier comments that there remains some considerable controversy with regard to the relative magnitudes of mass transfer contributions to the plate heights of different types of column. To the practicing chromatographer this is of marginal interest and the most important properties governing his choice of column for a particular purpose are:

(a) Permeability, which governs the maximum length he can use within the practical restrictions of his apparatus.

(b) Phase ratio, β, which affects the sample capacity, the resolution, and the analysis time.

A comparison of different column types is illustrated in Table V, which shows the conditions that were used to resolve 1- and 2-methylnaphthalenes in practice. These are not optimized conditions, but merely practical ones selected over a period of time from work carried out in the author's laboratory.

The efficiency values in parentheses are the minimum values that would have been required for the relevant column to produce a unit resolution, the minimum that could be tolerated for quantitative analysis using conventional techniques for peak measurement. The permeability constant K_p is seen to increase in the order packed <packed capillary<PLOT<WCOT. The phase ratios are fairly typical of the range of values associated with each column type, being lowest for the packed column and highest for the WCOT column.

TABLE V

EXPERIMENTAL COLUMNS USED TO PRODUCE A RESOLUTION OF $R > 1$ BETWEEN 1- AND 2-METHYLNAPHTHALENES

k is measured on 2-methylnaphthalene; Δp is the pressure drop across the column; t_r is the retention time for 2-methylnaphthalene; K_p is the permeability constant, viz. $K_p = \bar{u}\eta L/\Delta p$ ($= r^2/8$ for an ideal capillary) ($\eta =$ viscosity of carrier gas).

Column type	Temperature (°C)	Description	Efficiency (theoretical plates)	k	β	Exptl. R	Δp (p.s.i.)	K_p ($\times 10^{-7}$ cm²)	t_r (min)
Packed	150	2 m packed with 72–85 mesh Celite coated with 5% silicone SE-52	2800 (1321)	5.4	30	1.45	6.5	3.1	7.9
WCOT	150	25 m × 0.25 mm I.D. coated with 16 mg SE-52	13000 (6183)	0.64	253	1.45	6.5	243	4
PLOT	150	6 m × 0.5 mm I.D. coated with a 0.1-mm layer of 150–200 mesh Celite and a 0.5% solution of SE-52 in diethyl ether	5000 (2373)	1.7	95	1.45	1.0	102	3
Packed capillary	150	3 m × 0.38 mm I.D. containing 2% SE-52 on 85–90 mesh Celite	3500 (2118)	2.0	80	1.3	2.6	21.4	3

Minimum analysis time

In the early days of the technique it was rather arbitrarily considered that capillary columns were intrinsically faster than packed columns. However, Knox[77] has shown this to be fallacious on theoretical grounds, although it is probably easier to achieve faster analysis on capillary columns because of the normally lower k values.

There have been two fundamentally different approaches to the optimization of variables to achieve minimum analysis time, both based on the formula

$$t_r = \frac{H}{\bar{u}} \frac{16R^2}{(\alpha - 1)^2} \frac{(1 + k_B)^3}{k_B^2}$$

where t_r is the minimum time necessary to achieve a resolution of R between the two components (see Appendix, eqn. 1). The approach adopted by Desty and Goldup[37], Scott and Hazeldean[38], and Purnell and Quinn[78] was to operate at a mean carrier gas velocity above the optimum value at a point were the ratio $H/\bar{u}$ become virtually constant, i.e., where mass transfer non-equilibrium terms of the various rate theories become predominant. This velocity Scott and Hazeldean called the "optimum practical gas velocity" or the "OPGV". Thus, the fastest analysis possible will always be at the OPGV provided that the column length is increased to compensate for the theoretical plate loss and that there is always sufficient pressure capability to attain the OPGV.

Knox pointed out, however, that pressure is nearly always the limiting factor in practice and that under these circumstances the fastest possible analysis time is obtained when the maximum permissible pressure is applied to a column designed to give the true optimum gas velocity. The Knox theory, although aesthetically more satisfying than the "OPGV" theory, is based on a strict interpretation of the Golay theory and has also been criticized on the basis that operating the column exit at the optimum velocity with a high pressure drop would be disadvantageous because a large fraction of the column would then be operating in the molecular diffusion region. The latter objection is easily overcome by ensuring that the mean velocity in the column corresponds to the theoretical optimum value. As pointed out earlier, however, the Golay equation has not been unequivocably demonstrated to be sufficiently accurate to apply to practical optimization, whereas the OPGV method is an expedient method for real situations. Nevertheless, it is of interest to examine the results of the Knox theory reproduced from his original publication in Tables VI and VII.

TABLE VI

CAPILLARY COLUMN PARAMETERS FOR MINIMUM TIME ANALYSIS

(Reproduced from J. H. Knox, *J. Chem. Soc.*, (1961) 433.)

Carrier gas, nitrogen. Data are calculated using assumed typical values for variables in the theory.

Separation factor, S	Elution time (sec)	Column diameter (mm)	Column length (cm)	Gas velocity (cm/sec)
100	7×10^{-4}	0.0065	0.10	650
1,000	7×10^{-2}	0.020	3.20	200
10,000	7	0.065	100	65
100,000	700	0.20	3200	20
1,000,000	70,000	0.65	100,000	6.5

TABLE VII

PACKED COLUMN PARAMETERS FOR MINIMUM TIME ANALYSIS

(Reproduced from J. H. Knox, *J. Chem. Soc.*, (1961) 433.)

Carrier gas, nitrogen. Data are calculated using assumed typical values for variables in the theory.

Separation factor, S	Elution time (sec)	Particle diameter (mm)	BSS mesh	Column length (cm)	Gas velocity (cm/sec)
100	0.0013	0.03	420	0.15	600
1,000	0.13	0.09	130	5.0	190
10,000	13	0.3	42	155	60
100,000	1300	0.9	13	5000	19
1,000,000	130,000	3.0	4.2	155,000	6

Here the "separation factor" S is defined by

$$S = N \left(\frac{k}{1+k} \right)^2$$

and is related to R by

$$R^2 = \frac{S}{16} (\alpha - 1)^2$$

i.e., a separation factor $S = 10,000$ corresponds to a resolution of $R = 1$ for $\alpha = 1.04$. The separation factor becomes equal to the plate number for high values of k.

A comparison of these tables shows that there is little to choose between the speeds of packed and capilllary columns. Knox also pointed out that the liquid film thickness was about the same for the coatings on capillary and equivalent packed columns and obviously this indicates the need for very inert supports if equivalent performances are to be achieved in practice. The discrepancy between theoretical performance and practical feasibility is demonstrated clearly here. For instance, for $S = 1000$ a capillary column diameter would have to be 0.02 mm and its length 3.2 cm. This would require the use of an extremely small effective detector volume having ultra-high sensitivity, and injection techniques which are at present beyond present technology. This level of performance would be more easily achieved with a packed column with its intrinsically higher volume. Alternatively, while it is theoretically possible to achieve very high separation factors in a packed column operated at limited pressure drop, it would be necessary to use impracticably long columns packed with very large particles. Knox concluded that for S values of up to 10,000 packed columns are the more convenient, while for higher values capillary columns are to be preferred.

APPENDIX

1. Resolution between two components A and B

$$R = \frac{\text{distance between peak maxima}}{\text{average peak width}} \simeq \frac{N}{4}(\alpha - 1)\left[\frac{k_B}{1 + k_B}\right]^2$$

where

N = number of theoretical plates

α = relative retention volume of component B to component A

k_B = capacity ratio of component B

$$= \frac{\text{mass B in liquid phase per unit of column length}}{\text{mass B in gas phase per unit of column length}}$$

$= K_B/\beta$, where K_B = thermodynamic partition coefficient of B and β = column phase ratio (ratio of gas volume to liquid phase volume in the column)

2. Van Deemter's equation

$$H = 2\lambda d_p + \frac{2\gamma D_g}{\bar{u}} + \frac{8}{\pi^2}\frac{k d_f^2}{(1 + k)^2 D_l}\bar{u}$$

where

H = theoretical plate height (= column length L/N)

λ = multipath constant

d_p = mean particle diameter

γ = tortuosity constant

D_g = diffusion coefficient of solute in gas phase

D_i = diffusion coefficient of solute in liquid phase
d_f = mean liquid phase film thickness
$\bar{u}$ = mean gas velocity
= column length L/retention time for "air peak"

This equation can be put in the form

$$H = A + \frac{B}{\bar{u}} + C\bar{u}$$

where

A = eddy diffusion term (multipath term)
B = longitudinal molecular diffusion coefficient
C = "resistance to mass transfer" coefficient in the liquid phase (liquid phase non-equilibrium coefficient)

3. Gidding's generalized plate equation

$$h = \frac{2\gamma}{v} + \frac{2\gamma\beta_1}{v} + \Omega v + \sum \frac{1}{\dfrac{1}{2\lambda_i} + \dfrac{1}{w_i v}}$$

where

h = reduced plate height = H/d_p

v = reduced gas velocity = $\dfrac{\bar{u}d_p}{D_i}$

β_1 = $\dfrac{(1 - R)\,\gamma_1 D_i}{R\gamma D_g}$

Ω = CD_g/d_p^2
λ_i = a configurational parameter describing any one of a number of possible modes of eddy diffusion
w_i = the mass transfer parameter for the mobile phase corresponding to λ_i
γ,γ_1 = longitudinal diffusion parameters for the mobile and stationary phases, respectively

R $\approx R_F$, the retention factor $\left(= \dfrac{1}{1 + k}\right)$

C = a mass transfer term representing the finite rate of adsorption–desorption in adsorption chromatography, and the finite rate of diffusion in the stationary phase in a partition column. This parameter represents the rate effects of the stationary phase

4. Golay's equation for round WCOT columns

$$H = \frac{2D_g}{\bar{u}} + \left[\frac{2kd_f^2}{3\,(1 + k)^2\, D_i} + \frac{(1 + 6k + 11k^2)\,r^2}{24\,(1 + k)^2\, D}\right]\bar{u}$$

where

r = internal capillary radius

$$H = \frac{B}{\bar{u}} + (C_l + C_g)\,\bar{u}$$

C_l = non-equilibrium coefficient due to transverse liquid phase mass transfer resistance

C_g = non-equilibrium coefficient due to transverse gas phase mass transfer resistance

5. Golay's equation for PLOT columns (first modification)

Eqn. 4 applies except that the gas phase non-equilibrium coefficient, C_g, is

$$C_g = \left[\frac{1 + 6k + 11k^2}{(1 + k)^2} + 8a + \frac{16ka}{(1 + k)^2}\right]\frac{r^2}{24D_g}$$

where

a = ratio of porous layer thickness to internal column radius

6. Golay's equation for PLOT columns (second modification)

The C_g and C_l terms become

$$C_g = \left[\frac{1 + 6k + 11k^2}{(1 + k)^2} + \frac{8 + 32k}{(1 + k)^2}\cdot a_2 + \frac{8k^2}{(1 + k)^2}\cdot\frac{a_1{}^2}{a_2}\right]\frac{r^2}{24D_g}$$

and

$$C_l = \left(\frac{1 + 2a_2}{F}\right)\left(\frac{k^3}{6(1 + k)^2}\right)\frac{r^2}{K^2 D_l}$$

where

F = roughness factor = factor by which the liquid phase surface area has been increased by the presence of the porous layer compared with an equivalent smooth walled column

a_1, a_2 = configurational factors describing the tortuosity and free gas volumes of the porous layer

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