QUESTIONS RELATED TO GAS CHROMATOGRAPHIC SYSTEMS WITH GLASS OPEN-TUBULAR COLUMNS

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(Received October 9th, 1975)

SUMMARY

Questions related to the sample introduction system, the column system including its connecting lines, and glass open-tubular columns are discussed. An injector using a pre-column and a pneumatically controlled split point is described. The role of the connecting lines and fittings on column performance is demonstrated. The characteristics of the glass open-tubular columns are illustrated, and the column-to-column consistency and reproducibility of columns produced under industrial manufacturing conditions are investigated.

INTRODUCTION

Glass open-tubular columns do not represent a new innovation. They were used by Golay[1,2] and by Dijkstra and De Goey[3] during the basic development work on open-tubular (capillary) columns. Soon afterwards simple devices for the laboratory preparation of glass capillary tubing were developed by Desty *et al.*[4-6] and Kreyenbuhl[7]. However, these columns had many drawbacks related mainly to their short life, difficulty in handling and restrictions on the applicable liquid phase. For example, in an informal discussion at the 1961 Lansing Symposium[8], Halász pointed out that the lifetime of glass open-tubular columns coated with squalane was only 2–3 days, whereas metal columns coated with the same liquid phase lasted for at least seven months; and Desty emphasized the difficulty of preparing glass open-tubular columns with a polar liquid phase. Bruner *et al.*[9] also discussed the limitations of such columns. Owing to these problems, glass open-tubular columns have found only limited application as compared with metal columns.

In the last ten years extensive development work has been carried out both in Europe and in the United States to overcome the difficulties encountered in the preparation and use of glass open-tubular columns*. As a result of this activity, we

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* It is not our purpose to review the literature of this development. Results before 1971 were summarized by Novotný and Zlatkis[10]. Activities of the last five years are reported in a large number of papers published in journals dealing with chromatographic techniques. Papers presented at the First International Symposium on Glass Capillary Chromatography held May 4–7, 1975, in Hindelang (G.F.R.)[11] present a fair picture of the state-of-the-art.

are now at the stage where the full capabilities of these columns can be exploited: it is possible to consistently prepare columns with uniform and stable liquid phase coatings in a variety of liquid phases. Systems permitting their optimal use are also available.

Since 1972, detailed investigations have been carried out in our laboratories on the preparation and use of glass open-tubular columns, the aims being the production of high-performance columns with consistent characteristics and reproducible performance, and the development of a gas chromatographic system in which the potential of these columns can be fully utilized. In this paper, three aspects of our activities are discussed: the sample introduction system, the column system including its connections to the sample introduction system and the detector, and the consistency and reproducibility of the glass open-tubular columns prepared in a manufacturing group under industrial conditions.

Our discussion concerns *wall-coated* open-tubular columns, *i.e.* columns in which the liquid phase is directly coated on the inside surface of the glass capillary tubing and where surface treatment before coating is used only to prepare a surface with controlled properties permitting the formation of a thin, uniform and stable liquid phase film. Other possibilities would include, *e.g.*, building up an adsorbent layer or a porous layer to be coated. We shall not deal here with these types of column.

THE SAMPLE INTRODUCTION SYSTEM

Since glass open-tubular columns have a small internal diameter and thus small sample capacity —a general characteristic of open-tubular columns— the usual split sampling[12-14] is the most convenient way for sample introduction. Naturally, however, in keeping with the all-glass concept, sample contact during evaporation and splitting should be confined to glass surfaces. Owing to the nature of many of the samples analyzed by glass open-tubular columns, the conventional design of such split sampling systems with a simple evaporation chamber is not always adequate. The system developed by us is essentially based on the work of German and Horning[15,16] and uses a small pre-column and pneumatically controlled split ratios. Fig. 1 shows the schematic of the sample introduction system and Fig. 2 presents the functional schematic of this system incorporated in the whole gas chromatographic system.

As shown in Fig. 1, the injector of our system has an exchangeable glass liner which can be packed to provide a pre-column in front of the analytical column. The pre-column is made of Pyrex glass and is about 13.5 cm × 4 mm I.D.; the part which may contain the packing is 7 cm long but it need not be filled completely. Depending on the type of sample, this pre-column can be used in two different ways.

For complex, high-boiling samples of natural or biological origin, a 3.5–5.0 cm long packing with high liquid phase loading, *e.g.* 15–20% SE-30 silicone gum rubber on 100–120 mesh Chromosorb W HP, is used. Such a pre-column will prevent undesirable and uninformative material from reaching the open-tubular column, such as the non-volatile substances often present in derivatized biochemical samples. Furthermore, the pre-column, while also acting as the evaporation chamber, provides a tortuous path for the sample so as to ensure complete vaporization and mixing with the carrier gas before splitting.
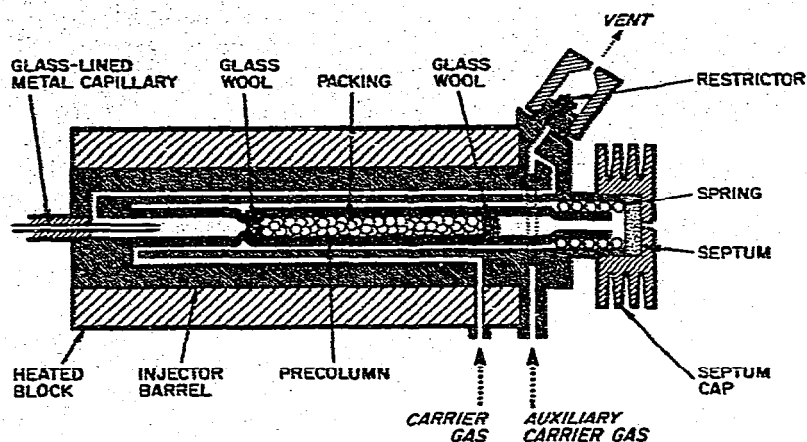
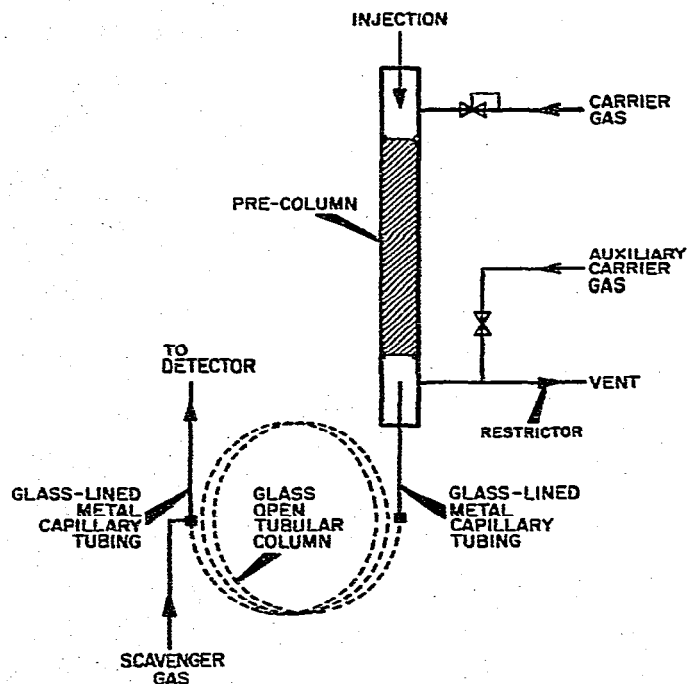Fig. 1. Schematic diagram of the all-glass injector/splitter system.

Fig. 2. Functional schematic of the split flow sample introduction system for glass open-tubular columns.

For samples that contain only volatile components, the screening effect of the pre-column is not necessary. Silanized glass beads can then be used as the packing; they provide the tortuous path needed for complete evaporation and mixing.

The pre-column can be easily removed by simply unscrewing the septum cap. This permits rapid replacement of a "dirty" pre-column with a new one.

In the lower part of the pre-column, a glass-lined metal capillary tubing (GLT; Scientific Glass Engineering, Melbourne, Australia) of 1.6 mm O.D. and 0.4 mm I.D. is inserted to provide the conventional concentric tube split design. The sample and carrier gas mixture entering this tube does not make contact with any metal, but only with glass.

Two carrier gas flows are connected to the inlet system (cf. Fig. 2). The main supply of carrier gas enters the system in the usual way, sweeping the septum area and flowing through the pre-column. It mixes with the sample vapor and is then split. A small part of the flow enters the column through the GLT while the rest is vented. This carrier gas stream is flow-controlled upstream of the inlet system.

The second or auxiliary carrier gas flow is conducted to the vent line and joined with it just before the vent restriction. This stream is pressure controlled and provides the inlet pressure for the open-tubular column. This inlet pressure is independent of the pre-column flow and, therefore, can be kept constant to maintain the optimal flow to the analytical column even when the pre-column flow is varied. Since the sample split is determined by the ratio of the pre-column flow-rate to the analytical column flow-rate, this feature makes it possible to vary the split over a wide range by adjusting the pre-column flow without disturbing the flow conditions of the analytical column. This is illustrated in Table I.

TABLE I

THE INFLUENCE OF THE PRE-COLUMN FLOW-RATE AND AUXILIARY CARRIER GAS PRESSURE ON COLUMN FLOW-RATE, VELOCITY AND SPLIT RATIO IN THE ALL-GLASS SAMPLE INTRODUCTION SYSTEM FOR OPEN-TUBULAR COLUMNS

Inlet pressure of aux. carrier gas (p.s.i.g.)	Variable*	Pre-column flow-rate (ml/min)		
		60	80	120
10	Column flow-rate (ml/min)	0.24	0.24	0.23
	Average linear carrier gas velocity (cm/sec)	5.26	5.15	5.10
	Split ratio	250/1	333/1	522/1
20	Column flow-rate (ml/min)	0.50	0.48	0.49
	Average linear carrier gas velocity (cm/sec)	10.74	10.47	10.56
	Split ratio	120/1	167/1	245/1
30	Column flow-rate (ml/min)	0.74	0.73	0.76
	Average linear carrier gas velocity (cm/sec)	15.86	15.70	16.33
	Split ratio	81/1	110/1	158/1

* The column flow-rate was measured at the end of a 150 ft. × 0.25 mm I.D. open-tubular column. The average linear carrier gas velocity ($\bar{u}$) was calculated from the retention time of methane (t_M) and the column length (L): $\bar{u} = L/t_M$. Split ratio was calculated as (pre-column flow-rate)/(column flow-rate).

This sample introduction system is capable of linear splitting over a wide range of split ratios and sample sizes. This splitting is demonstrated by two series of measurements. In the first, a C_{11}–C_{16} hydrocarbon sample representing a boiling range of about 100° (195.9°–287°) was analyzed by keeping the sample size injected constant at 0.2 μl while adjusting the pre-column flow to vary the split from 10:1 up to 150:1.

TABLE II

LINEARITY OF THE ALL-GLASS SAMPLE INTRODUCTION SYSTEM WITH INCREAS-ING SPLIT RATIO

Sample size: 0.2 μl. A 150 ft. × 0.25 mm I.D. open-tubular column coated with Apiezon L grease liquid phase was used.

Sample component	Relative peak area (%)					Average deviation	Relative deviation (%)
	Split ratio				Mean		
	150/1	100/1	50/1	10/1			
n-Undecane	19.00	19.01	19.16	18.91	19.020	0.070	0.37
n-Dodecane	20.59	20.72	20.74	20.59	20.660	0.070	0.34
n-Tetradecane	18.49	18.79	18.81	18.89	18.745	0.128	0.68
n-Pentadecane	21.11	21.05	21.02	20.97	21.038	0.058	0.28
n-Hexadecane	20.81	20.43	20.27	20.64	20.537	0.187	0.91

Table II lists the results obtained; the normalized peak areas for the five components were within 1 % relative deviation from the average at every split ratio tested.

The second, more complex, sample contained all the n-paraffins from n-nonane (b.p. 150.8°) to n-heneicosane (b.p. 356.7°) representing a boiling range of over 200°; the concentration range of the n-paraffins varied from 0.3 % to about 10 %, a factor of 30. For this test the split ratio was held constant at 20:1 while the injected sample size varied from 0.1 to 5 μl, a factor of 50. The data are shown in Table III. As seen, the relative deviation of the normalized peak areas for each component (except n-nonane, which is present in very small concentrations) was less than 1.5 % with the

TABLE III

LINEARITY OF THE ALL-GLASS SAMPLE INTRODUCTION SYSTEM WITH INCREAS-ING SAMPLE SIZE

Split ratio: 20/1. A 150 ft. × 0.25 mm I.D. open-tubular column coated with Apiezon L grease liquid phase was used. The sample also contained isomeric paraffins in small concentrations. This is the reason that the vertical columns do not add up to 100%.

Sample component	Relative peak area (%)					Average deviation	Relative deviation (%)
	Sample size (μl)				Mean		
	0.1	0.5	1.0	5.0			
n-Nonane	0.35	0.32	0.32	0.33	0.330	0.010	3.03
n-Decane	3.53	3.45	3.49	3.43	3.475	0.035	1.01
n-Undecane	8.63	8.47	8.56	8.26	8.480	0.115	1.36
n-Dodecane	10.56	10.36	10.49	10.13	10.385	0.140	1.35
n-Tridecane	11.16	10.98	11.09	10.74	10.993	0.133	1.21
n-Tetradecane	10.70	10.60	10.76	10.44	10.625	0.105	0.99
n-Pentadecane	10.20	10.11	10.28	9.91	10.125	0.115	1.14
n-Hexadecane	9.55	9.45	9.62	9.57	9.548	0.049	0.51
n-Heptadecane	8.53	8.42	8.56	8.57	8.520	0.055	0.65
n-Octadecane	7.08	7.06	7.19	7.27	7.150	0.080	1.12
n-Nonadecane	5.80	5.81	5.88	6.05	5.885	0.083	1.41
n-Eicosane	4.72	4.79	4.81	4.93	4.813	0.065	1.35
n-Heneicosane	3.61	3.72	3.64	3.93	3.725	0.102	2.74

single exception of the C_{21} peak in the 5.0-μl injection. If this last point were omitted, the relative deviation for n-heneicosane would also be less than 1.5%.

THE COLUMN SYSTEM

In the utilization of glass open-tubular columns in a gas chromatographic system three questions must be considered: (a) one should protect the fragile glass column during storage and use; (b) the connections to and from the column should also be glass; and (c) connection should not represent any difficulty or necessitate considerable skill.

These requirements are somewhat conflicting. For example, a number of users of glass open-tubular columns advocate the absolute necessity of bringing the column ends into the inlet system and the (flame ionization) detector. However, this necessitates straightening of the column ends by the user with the help of a small Bunsen flame, and this certainly cannot be considered a manipulation that can be carried out by unskilled persons.

We solved these problems by the design of a protective cage-like enclosure, using glass-lined metal tubing for connections and the development of special no-volume fittings.

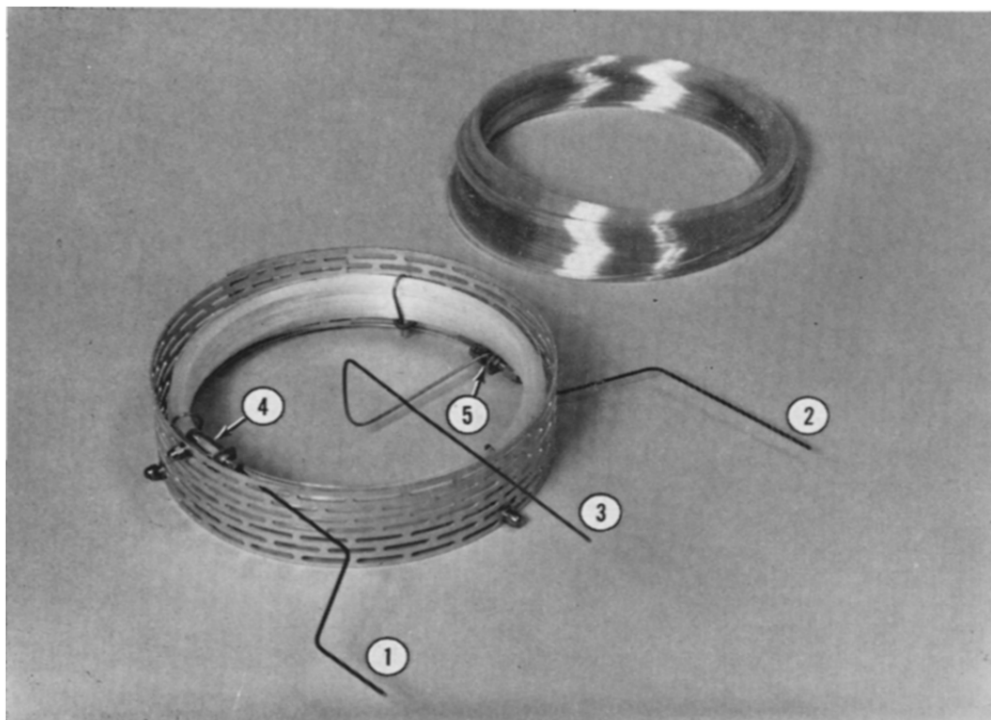The protective cage with the connecting lines and fittings is shown in Fig. 3.

Fig. 3. Glass open tubular column enclosure with the connecting lines. Both the installed and the separate columns are 100 m long. 1 and 2 are glass-lined metal tubes for connection to the inlet system and the detector respectively; 3 is the line bringing the scavenger gas to the column exit; 4 and 5 are the respective special inlet and outlet fittings.

A 100-m long glass open-tubular column is installed in the cage; a loose, unprotected column of the same length is placed alongside in the figure. The GLT has an O.D. of 1/16 in. and thus can be connected directly, with the usual fittings, to the injector and the detector. Since the outside of this tubing is metal, little precaution is necessary in connecting the column system to the other parts of the gas chromatograph. Glass-to-GLT connections are made only once when the column is placed in the protective cage. The special fittings (see below) are designed so that the column ends need not be straightened, thereby eliminating the continual use of a small Bunsen flame. These fittings are fixed to the cage, and the column ends are inserted via ferrules made of Vespel® (a DuPont polyimide). In this way the fragile glass has a rigid connection and will not break even if the GLT is manipulated. The only requirement in the connection of the glass open-tubular columns is that they should meet the fitting properly. This usually requires breaking off a few centimeters at one of the column ends. ·

The fitting at the column exit allows the addition of flow-controlled scavenger gas to the column effluent. This simplifies the optimization of detector flow-rates and eliminates the effect of any extra-column volume in the detector connection line.

The influence of the connecting lines and fittings

In the past, there has been a number of discussions on the influence of connecting lines and/or fittings on the apparent column performance. Kaiser and Rieder, in a recent article[17], expressed the opinion that a small addition to the column length should not cause any trouble if that addition is also of "capillary chromatography quality". This, of course, is only true if one disregards the volume of the commercially available fittings and provides a sufficiently high velocity in the connecting line(s) to prevent band spreading.

During the development of our system various constructions were tested and, in each case, the overall performance was carefully evaluated. Here, we illustrate the performance with various set-ups. Four cases were investigated; these are summarized in Table IV. For all experiments, a 25-m long glass open-tubular column with Carbowax 20M poly(ethylene glycol) liquid phase was used; the operating con-

TABLE IV

THE FOUR MODES OF GLASS OPEN-TUBULAR COLUMN CONNECTIONS INVESTI-GATED

Mode No.	Front (injector to column)	End (column to FID)
1	Column inserted directly into the injector, acting as the split point	Conventional low-volume fitting and GLT*
2	Column inserted directly into the injector, acting as the split point	Specially designed fitting (Fig. 4B) and scavenger gas; GLT
3	GLT inserted into the injector; connection with the glass open tubular column with conventional low-volume fitting	Specially designed fitting (Fig. 4B) and scavenger gas; GLT
4	As above but using a specially designed fitting (Fig. 4A)	Specially designed fitting (Fig. 4B) and scavenger gas; GLT

* Glass-lined metal tubing, 1/16 in. (1.59 mm) O.D., 0.40 mm I.D.

ditions are listed in Table V. This short column was selected because, owing to its low volume, it should represent the worst example of the effect of extra-column and unswept "dead" volumes. Isothermal operating conditions were used for the same reason since temperature programming can mask the effect of poor connections.

The test mixture for the experiments consisted of n-nonane, isopropylbenzene, cyclohexanone and hexanol-1. This mixture is useful in pointing up dead-volume problems via the hydrocarbon peak shape and active surfaces by the alcohol and ketone peak shape. Any tailing evident in the chromatogram can be identified to its source with this sample.

TABLE V
ANALYTICAL CONDITIONS OF THE INVESTIGATIONS SHOWN IN FIG. 5–10

Column	25 m × 0.27 mm I.D. glass open tubular
Liquid phase	Carbowax 20M poly(ethylene glycol)
Temperature of	
sample inlet system	250°
column	105°
detector	250°
Carrier gas	helium
Pre-column flow-rate*	100 ml/min
Column flow-rate*	0.45 ml/min
Split ratio	222/1
Sample volume	0.2 µl
Detector	flame ionization
Attenuation	× 256 (1 mV recorder)

* Measured at outlet and ambient temperature with a soap bubble flow meter. Corrected to column temperature and dry gas conditions, the column flow-rate would correspond to 0.56 ml/min.

In the first mode, the column was inserted directly into the injector acting as the split point while its end was connected to the detector via a conventional low-volume fitting and GLT. Fig. 5 shows a chromatogram obtained in this system. There was some tailing on all peaks, which was evidence of an unswept dead volume in the fitting connecting the glass column to the GLT. This tailing was completely eliminated in the second mode when the connection at the column end was made with a specially designed "T" fitting (see Fig. 4B) allowing the addition of a scavenger ("make-up") gas to the column effluent. This make-up gas sweeps the end of the column eliminating the dead volume of the connection and also any effect of the volume of the connecting glass-lined tubing. Fig. 6 shows the resulting chromatogram.

The position of the column end with respect to the entrance of the make-up gas into the fitting is important: if it is too close to it, turbulence at the exit point may give completely unacceptable results. Fig. 4B illustrates the proper positioning.

The disadvantage of the system corresponding to the second mode is that the insertion of the column end into the injector is a delicate operation necessitating some straining of the column's front end and can easily result in breakage. For this reason, the aim was to use the GLT at this point also. However, when this tubing was connected to the column's front end via the usual low-volume fitting (third mode), column efficiency and peak shape suffered drastically. This is illustrated by the chro-
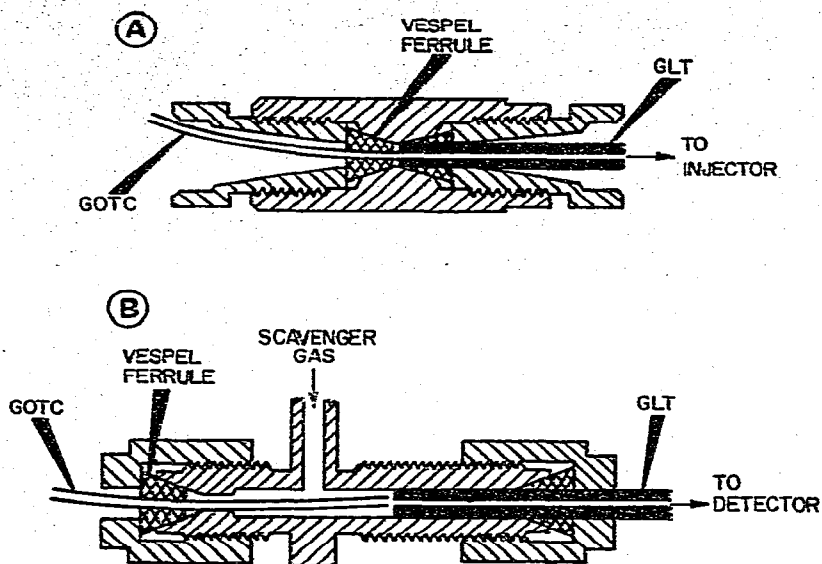
Fig. 4. Schematic diagram of the special inlet (A) and outlet (B) fittings. GLT = glass-lined metal tubing; GOTC = glass open-tubular column.
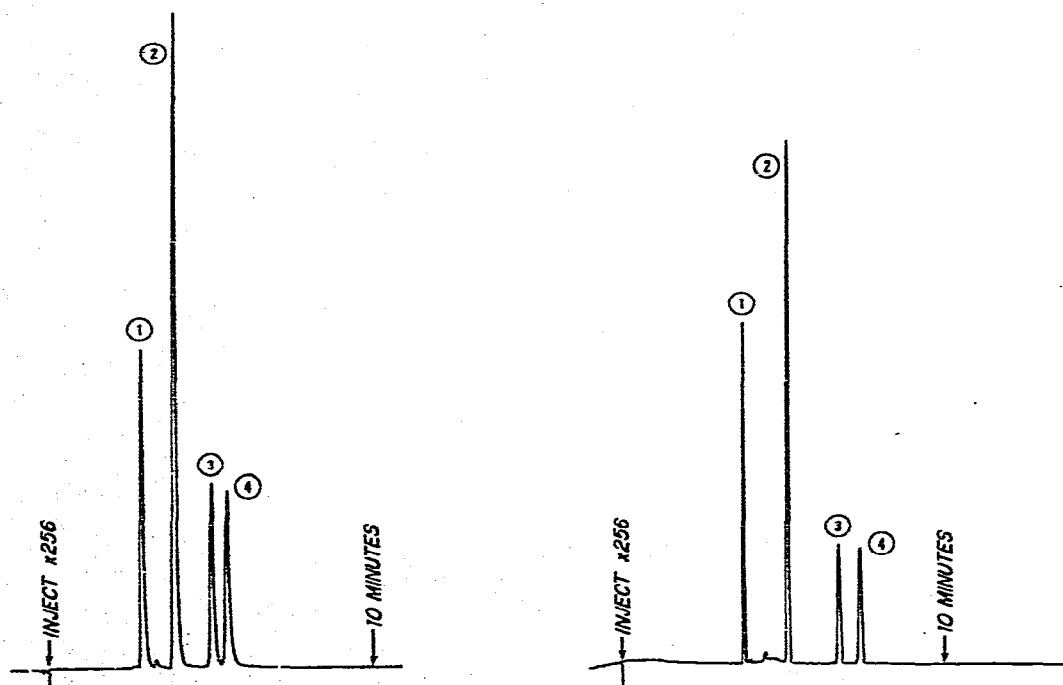

Fig. 5. Chromatogram obtained in mode No. 1 (Table IV). For conditions see Table V. Peaks: 1, n-nonane; 2, isopropylbenzene; 3, cyclohexanone; 4, hexanol-1.

Fig. 6. Chromatogram obtained in mode No. 2 (Table IV). For conditions see Table V. Peaks as in Fig. 5.

matogram in Fig. 7. It was obvious that the classical "zero dead volume" connection would not suffice for this application.

Several attempts were made to modify the front connection to eliminate this unwanted volume. For example, the GLT in the fittings was wrapped with PTFE tape before insertion into the union to fill the volume. This modification helped somewhat as evidenced by the chromatogram in Fig. 8. However, it was difficult to get the proper thickness of tape and, therefore, the result was very dependent on the skill of the operator. Replacement of the Vespel ferrules normally used by graphite ferrules was also tried. The soft graphite deforms under the pressure of tightening and fills the void volume in the union. As shown by the chromatogram in Fig. 9, this improved the system performance considerably; however, the ferrule was destroyed. This would mean that the ferrule could be used only once. Another problem posed by the graphite ferrule was frequent leaking owing to the small diameter (0.75 mm) of the glass capillary tubing.
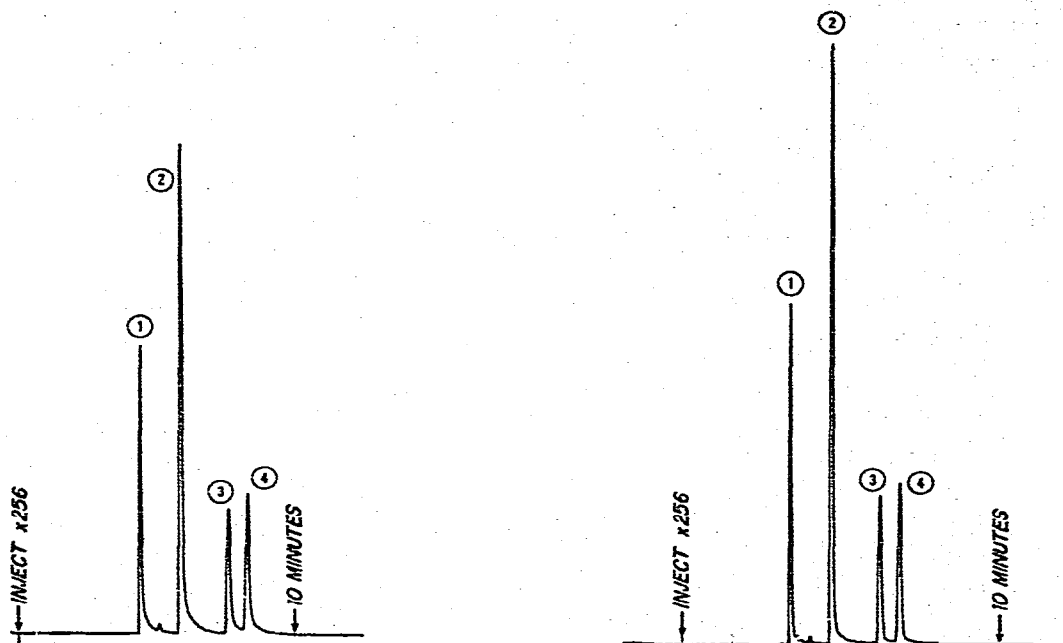

Fig. 7. Chromatogram obtained in mode No. 3 (Table IV). For conditions see Table V. Peaks as in Fig. 5.

Fig. 8. Chromatogram obtained in mode No. 3 (Table IV), wrapping the front of the column with PTFE tape to reduce volume in the fitting. For conditions see Table V. Peaks as in Fig. 5.

Faced with the above problems, we felt that neither solution was routine enough for everyday practical use of the glass open-tubular column system. Therefore, a new fitting was designed; its scheme is shown in Fig. 4A. The new fitting is an internal type with no seat for the tubing. This allows for a butt-to-butt, ferrule-to-ferrule union of the GLT and the glass column. The performance of the system incorporating this fitting is shown in Fig. 10. This chromatogram is practically identical with the
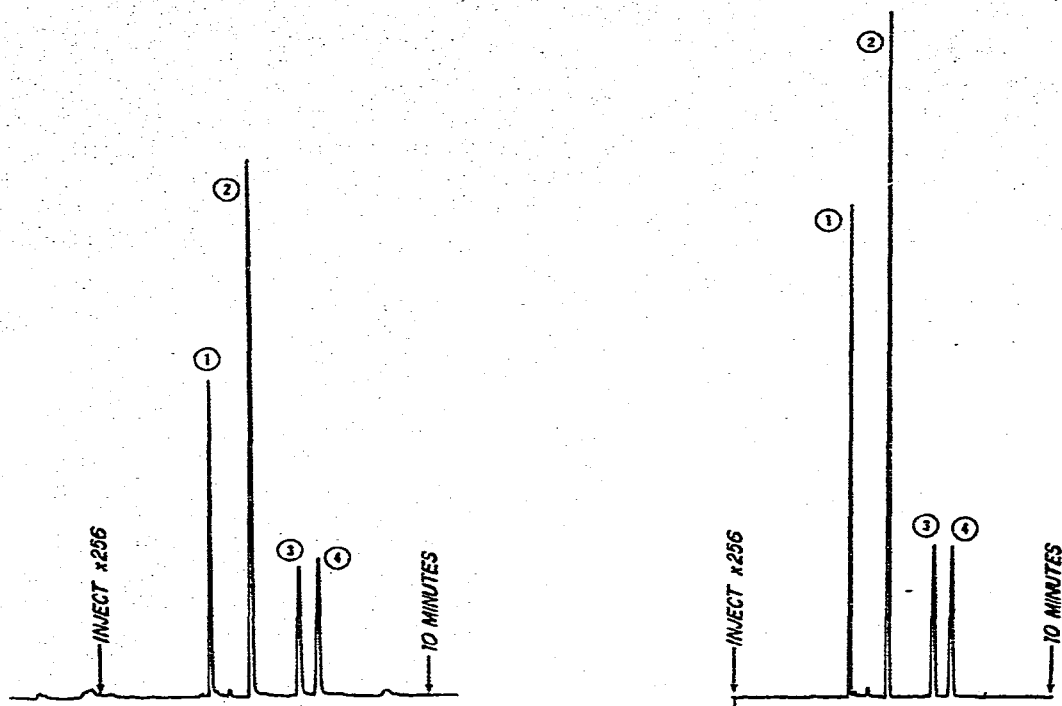
Fig. 9. Chromatogram obtained in mode No. 3 (Table IV), with graphite ferrules substituted for the Vespel ferrules. For conditions see Table V. Peaks as in Fig. 5.

Fig. 10. Chromatogram obtained in mode No. 4 (Table IV). For conditions see Table V. Peaks as in Fig. 5.

chromatogram in Fig. 6 obtained when the column's front end was inserted into the injector. This proves that our column system does not reduce the actual performance of the glass open-tubular column.

THE GLASS OPEN-TUBULAR COLUMNS

Column preparation

The columns used in our system are prepared and coated in lengths of 100 m. The capillary tubing is drawn by the commercially available equipment to coils with 150 mm diameter. The internal diameter of the tubing is 0.27 mm with a tolerance of ± 0.02 mm representing ± 7.4%; the outside diameter of the capillary tubing is 0.75 mm thus giving an average wall thickness of 0.24 mm.

Both Pyrex and soft glass are used to prepare the capillary tubing: Pyrex tube is used for the capillaries to be coated with SF-96 methyl silicone oil and soft glass is used for columns with other liquid phases. The Pyrex capillary tubing is treated with silylation reagents before coating whereas the soft glass tubes are etched with gaseous HCl at elevated temperatures. Coating is done by the dynamic method at room temperature. For highly polar phases the liquid phase film is deposited by more than one coating step and sometimes the glass tube wall is also pre-treated with organic substances. All these procedures are documented in the literature, in the publications of Tesařík, Novotný, Schomburg and coworkers[18-26].

Liquid film thickness and phase ratio

We established these values for the glass open-tubular columns by comparison with support-coated open-tubular (SCOT) columns prepared with the same liquid phase. This comparison is based on the observation that the product of the phase ratio (β) and the capacity ratio (k), which is equal to the partition coefficient (K), is independent of the column type and, at a given temperature, is constant:

$$K = \beta k \tag{1}$$

Thus for two columns prepared with the same liquid phase and operated at the same temperature

$$\beta_1 k_1 = \beta_2 k_2 \tag{2}$$

$$\beta_2 = \beta_1 \frac{k_1}{k_2} \tag{3}$$

where k_1 and k_2 are measured with the same solute.

The SCOT columns are prepared by the static coating technique, by filling the column tubing with a suspension of the support particles in which the liquid phase is dissolved and then evaporating the solvent[27]. It is known[28a] that, if the coating is carried out by the static method, the phase ratio can be approximated as the ratio of the volumes of the solvent and liquid phase in the solution (suspension). Thus, the phase ratio of the SCOT columns can be established to permit calculation of the phase ratio of the corresponding glass open-tubular column, using eqn. 3.

For wall-coated open-tubular columns, the phase ratio can be related to the inside tube radius (r_c) and the average liquid film thickness (d_f) [28b]:

$$\beta = \frac{r_c}{2 d_f} \tag{4}$$

Thus, if the phase ratio is established, the liquid film thickness can be calculated. As an example, Table VI lists data calculated for an OV-17 column. The corresponding SCOT column had a phase ratio $\beta = 94$.

TABLE VI

CALCULATION OF THE PHASE RATIO AND AVERAGE LIQUID FILM THICKNESS OF A GLASS OPEN-TUBULAR COLUMN PREPARED WITH OV-17 PHENYL METHYL SILICONE OIL LIQUID PHASE

SCOT = Support-coated open-tubular; GOT = glass open-tubular.

Sample component	k (at 160°)		β**	d_f**
	SCOT column*	GOT column		(μm)
2-Methylnaphthalene	5.698	1.574	340	0.20
1-Methylnaphthalene	6.406	1.783	338	0.20
Acenaphthene	15.434	4.284	339	0.20

* Value of phase ratio $\beta = 94$.
** Calculated for the GOT column.

In general, the phase ratio of the glass open-tubular columns prepared by us varies between 335 and 670 giving an average liquid film thickness range of 0.1–0.2 μm. This is not the variation of the columns prepared with the same liquid phase —that will be discussed below when we consider the consistency of the capacity ratio values— but represents the range of the columns prepared with different liquid phases.

Relationship between film thickness and coating velocity

There is some controversy about the relationship between the liquid film thickness, the inside tube radius and the coating velocity when the dynamic coating method is used. Kaiser[29] presented the following empirical equation:

$$d_f = \frac{c}{200\, r_c} (a\,u + b) \tag{5}$$

Novotný, Bartle and Blomberg, however, considered that the following equation more accurately described this relationship[21,30].

$$d_f = \frac{c}{200} r_c \left(\frac{\eta\, u}{\gamma} \right)^{1/2} \tag{6}$$

On the other hand, Guiochon[31] has suggested that the following equation should be more applicable:

$$d_f = \frac{2.68\, c}{200} r_c \left(\frac{\eta\, u}{\gamma} \right)^{2/3} \tag{7}$$

In these equations c refers to the concentration of the stationary phase in the coating solution (v/v), η and γ are, respectively, the viscosity and surface tension of the solution, u represents the linear coating velocity, and a and b are constants.

The film thickness can also be related to the capacity ratio (k), by substituting eqn. 4 into eqn. 1:

$$d_f = \frac{r_c}{2\,K} k \tag{8}$$

This means that for the same tubing (r_c constant) and the same liquid phase, the proportionalities expressed in eqns. 5–7 between the coating velocity and the liquid film thickness are also valid for the capacity ratio.

It was not our purpose to investigate which of the three equations corresponds most closely to practice. However, since we have prepared a large number of SF-96 columns closely corresponding to those investigated by Bartle[23], we felt that the publication of our data might represent a further contribution to this question.

Assuming that the concentration of the coating solution is kept constant and the radius of the tube is also constant, eqns. 5–7 can be reduced to the following expressions:

$$k = (\text{const}) (u) + (\text{const}) \tag{9}$$

$$k = (\text{const}) (u)^{1/2} \tag{10}$$

$$k = (\text{const}) (u)^{2/3} \tag{11}$$

Actually, the radius may vary $\pm 7.4\%$ (see above). However, the influence of this variation would be the same for all three equations.

Table VII lists data for sixteen SF-96 columns[*] and Fig. 11 presents the corresponding plots. In each figure the linear plot corresponding to the $y = mx + a$ type equation established by least squares linear regression analysis is shown by a solid line; the values of the slope and the y intercept are listed in Table VII. We also indicated the $\pm 10\%$ envelope around the linear plot. From the figures, it seems that the $k = (\text{const}) (u)^{1/2}$ relationship is the most accurate, for all points are within the $\pm 10\%$ envelope, whereas five points are outside it in Fig. 11A and two in Fig. 11C. However, as indicated in Table VII, statistical evaluation of the data gives practically the same correlation coefficient for all three equations; thus neither relationship can be termed as more applicable to express the relationship between the capacity ratio (and hence, the liquid film thickness) and the coating velocity for these thin-film columns if the radius of the tube is considered to be a constant.

Column testing and efficiency

Routine preparation of gas chromatographic columns is only meaningful if they consistently result in high efficiencies.

All the columns prepared by us are tested with two test mixtures. The first is the so-called polarity mixture and consists of n-nonane, isopropylbenzene, cyclo-

TABLE VII

CAPACITY RATIO OF n-HEXADECANE (AT 165°) AS A FUNCTION OF THE COATING VELOCITY OF GLASS OPEN-TUBULAR COLUMNS PREPARED WITH SF-96 METHYL SILICONE OIL LIQUID PHASE

Column number	k	u (mm/sec)	$u^{1/2}$ (mm/sec)$^{1/2}$	$u^{2/3}$ (mm/sec)$^{2/3}$
1	2.578	29.8	5.46	9.61
2	2.620	39.8	6.31	11.66
3	2.705	43.4	6.59	12.35
4	2.716	36.7	6.06	11.04
5	2.744	47.7	6.91	13.15
6	2.842	39.8	6.31	11.66
7	2.844	39.8	6.31	11.66
8	2.879	43.4	6.59	12.35
9	2.886	43.4	6.59	12.35
10	2.921	47.7	6.91	13.15
11	2.924	36.7	6.06	11.04
12	2.937	47.7	6.91	13.15
13	2.971	38.2	6.18	11.34
14	3.070	47.7	6.91	13.15
15	3.094	43.4	6.59	12.35
16	3.181	47.7	6.91	13.15
Slope		17.386	1.386	3.398
y Intercept		− 7.833	2.499	2.322
Correlation coefficient		0.563	0.566	0.564

[*] The columns are arbitrarily numbered with increasing capacity ratio values. This numbering is maintained through the other tables.
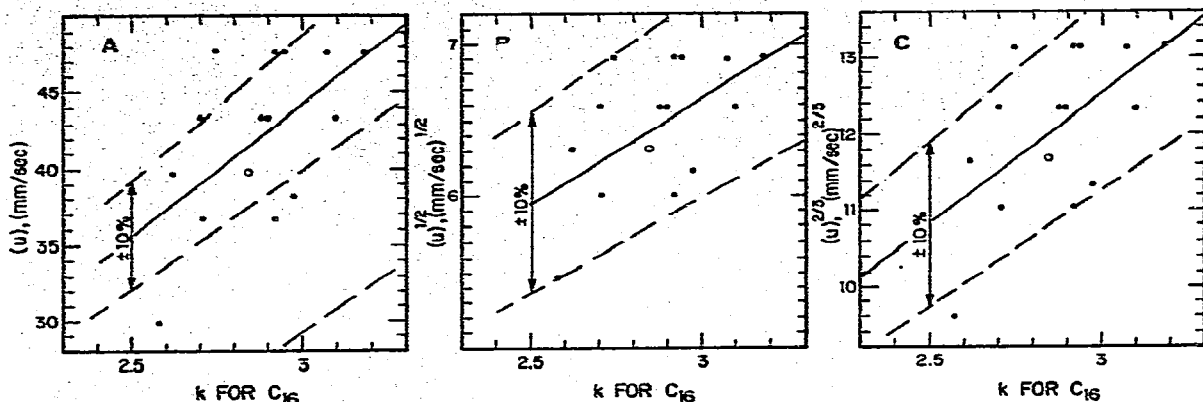
Fig. 11. Plots of the capacity ratio of n-hexadecane against various powers of the linear coating velocity (u), for SF-96 glass open-tubular columns. Column temperature, 165°. Circle refers to two data points. Solid line represents the best fit plot established by least-squares linear regression analysis; the $\pm 10\%$ envelope around this plot is indicated by broken lines. For numerical data see Table VII.

TABLE VIII

CONSISTENCY OF THE GLASS OPEN-TUBULAR COLUMNS PREPARED WITH SF-96 METHYL SILICONE OIL LIQUID PHASE

Column dimensions, 100 m × 0.27 mm I.D.; number of columns prepared, 22; number of columns rejected either due to poor performance or physical problems (breakage), 6; number of columns evaluated, 16; test substance, n-hexadecane; column temperature, 165°; carrier gas (He) velocity during testing (cm/sec), 18.5 ± 2.6.

Column No.	k	HETP (mm)
1	2.578	0.326
2	2.620	0.264
3	2.705	0.301
4	2.716	0.280
5	2.744	0.371
6	2.842	0.337
7	2.844	0.304
8	2.879	0 349
9	2.886	0.374
10	2.921	0.372
11	2.924	0.274
12	2.937	0.384
13	2.971	0.336
14	3.070	0.337
15	3.094	0.299
16	3.181	0.284
Highest value	3.181	0.384
Lowest value	2.578	0.264
Arithmetic mean*	2.8795	0.3240
Range as % of mean	±10.5	±18.5
Ratio highest/lowest value	1.23	1.45

* This is calculated as (max + min)/2. The statistical mean values calculated as Σ/n are $\bar{k} = 2.8695$ and $\overline{\text{HETP}} = 0.3245$ mm.

TABLE IX

CONSISTENCY OF THE GLASS OPEN-TUBULAR COLUMNS PREPARED WITH CARBO-
WAX 20M POLY(ETHYLENE GLYCOL) LIQUID PHASE

Column dimensions, 100 m × 0.27 mm I.D.; number of columns prepared, 11; number of columns
rejected either due to poor performance or physical problems (breakage), 2; number of columns
evaluated, 9; test substance, acenaphthene; column temperature, 165°; carrier gas (He) velocity
during testing (cm/sec), 18.2 ± 1.3.

Column No.	k	HETP (mm)
1	2.141	0.430
2	2.531	0.372
3	2.645	0.313
4	2.711	0.401
5	2.731	0.351
6	2.919	0.357
7	3.150	0.392
8	3.234	0.390
9	3.258	0.371
Highest value	3.248	0.430
Lowest value	2.141	0.313
Arithmetic mean*	2.6995	0.3715
Range as % of mean	±20.7	±15.7
Ratio highest/lowest value	1.52	1.37

* This is calculated as (max + min)/2. The statistical mean values calculated as Σ/n are $\bar{k} = 2.8133$ and $\overline{HETP} = 0.3752$ mm.

TABLE X

CONSISTENCY OF THE GLASS OPEN-TUBULAR COLUMNS PREPARED WITH OV-17
PHENYL METHYL SILICONE OIL LIQUID PHASE

Column dimensions, 100 m × 0.27 mm I.D.; number of columns prepared, 9; number of columns
rejected either due to poor performance or physical problems (breakage), 2; number of columns
evaluated, 7; test substance, acenaphthene; column temperature, 165°; carrier gas (He) velocity
during testing (cm/sec), 16.2 ± 1.5.

Column No.	k	HETP (mm)
1	2.616	0.318
2	2.943	0.352
3	3.203	0.335
4	3.415	0.323
5	3.520	0.379
6	3.565	0.365
7	3.622	0.376
Highest value	3.622	0.379
Lowest value	2.616	0.318
Arithmetic mean*	3.1190	0.3485
Range as % of mean	±16.1	± 8.7
Ratio highest/lowest value	1.38	1.19

* This is calculated as (max + min)/2. The statistical mean values calculated as Σ/n are $\bar{k} = 3.2691$ and $\overline{HETP} = 0.3497$ mm.

hexanone and hexanol-1. As already mentioned above, in a discussion of the investi-
gations related to the column connections, the analysis of such a mixture composed
of components of different polarities and chemical characters can give information
on surface activities and/or extra-column band spreading. The second test mixture is
used to evaluate the efficiency of the column. The composition of this mixture is
chosen according to the nature of the liquid phase, and efficiency is calculated for a
peak having $k > 2$. Furthermore, we also evaluate the capacity ratio, which must be
within a certain range.

Tables VIII–X list data for a number of columns prepared by production
means with three different liquid phases. As seen, columns could be prepared with
consistently good performance, by a yield better than 70%.

In this evaluation, we give the range as % of the arithmetic mean of the
minimum and maximum values and the ratio of the two limiting values rather than the
usual statistical values of the standard deviation and the relative standard deviation
(coefficient of variation). For both HETP and k, users are mainly interested in being
able to obtain columns with consistent performance, and in this respect the range is
more meaningful.

A brief discussion of these data is given below.

Column efficiency. The HETP value of every column tested was better than
0.4 mm, except for one Carbowax 20M column which had an HETP of 0.43 mm.
For a 100-m long column, an HETP of 0.4 mm represents 250,000 theoretical plates.
During testing, the average linear carrier gas velocity is not adjusted to the optimal
value (where the HETP is smallest), but only kept within a range. Actually, if we plot
the individual HETP values against the average linear carrier gas velocities and
reconstruct the respective part of an "average" Van Deemter plot for each column
type (liquid phase), then the deviation of the individual points from this plot would
be less than the deviation from the overall mean value.

Capacity ratio. When evaluating the column-to-column consistency of the
capacity ratio, one must consider the practical limitations. If tested at the same
temperature with the same solute, we can write for two columns prepared with the
same liquid phase (*cf.* eqn. 8):

$$\frac{k_2}{k_1} = \frac{r_{c1}}{r_{c2}} \frac{d_{f2}}{d_{f1}} \tag{12}$$

We have previously mentioned that, by specification, the inside column radius may
vary within $\pm 7.4\%$. If we assume a $\pm 10\%$ variation in the average liquid film
thickness, the worst case would theoretically be represented by

$$\frac{k_2}{k_1} = \frac{1.074}{0.926} \frac{1.1}{0.9} = 1.42$$

Actually the values obtained for the SF-96 and OV-17 columns are better than this
value (1.23 and 1.38 respectively). For the Carbowax 20M columns, the ratio of the
highest and lowest k values is 1.52; however, these columns are prepared by a multi-
step coating procedure where the variation in the final liquid film thickness depends
on the reproducibility of each individual coating step.

TABLE XI

REPRODUCIBILITY OF RELATIVE RETENTION DATA ON GLASS OPEN-TUBULAR COLUMNS PREPARED WITH SF-96 METHYL SILICONE OIL LIQUID PHASE

Column dimensions: 100 m × 0.27 mm I.D.

Column No.	n-Hexadecane	Isopropylbenzene
	n-pentadecane at 165°	n-nonane at 105°
1	1.564	1.132
2	1.562	1.127
3	1.562	1.122
4	1.593	1.126
5	1.559	1.119
6	1.562	1.128
7	1.561	1.129
8	1.559	1.128
9	1.557	1.132
10	1.558	1.133
11	1.566	1.135
12	1.556	1.126
13	1.569	1.126
14	1.563	1.127
15	1.566	1.124
16	1.559	1.132
Mean value	1.5635	1.1279
Standard deviation	0.0086	0.0042
Relative standard deviation, %	0.55	0.38

TABLE XII

REPRODUCIBILITY OF RELATIVE RETENTION DATA ON GLASS OPEN-TUBULAR COLUMNS PREPARED WITH CARBOWAX 20M POLY(ETHYLENE GLYCOL) LIQUID PHASE

Column dimensions: 100 m × 0.27 mm I.D.

Column No.	1-Methylnaphthalene	Acenaphthene
	2-methylnaphthalene at 165°	biphenyl at 165°
1	1.134	1.669
2	1.137	1.683
3	1.132	1.673
4	1.133	1.678
5	1.138	1.673
6	1.137	1.674
7	1.138	1.675
8	1.131	1.680
9	1.138	1.682
Mean value	1.1351	1.6763
Standard deviation	0.0029	0.0047
Relative standard deviation, %	0.26	0.28

Relative retention reproducibility

Theoretically, the relative retention of a peak pair depends only on the liquid phase and the column temperature and is independent of the chromatograph, the carrier gas and its velocity (assuming, naturally, that it is constant during the measurements) and the physical column used. This is the basis of qualitative gas chromatographic analysis and the interchangeability of retention data; without it, relative retention data obtained on instrument A and column X could not be used with instrument B and column Y.

In practice, however, one often finds that relative retention data differ. This may have five causes: (a) poor temperature control and measurement, poor carrier gas regulation; (b) incorrect measurement of the retention time and the gas hold-up time; (c) impure liquid phase, containing impurities with different retention characteristics; (d) column overloading or incomplete peak resolution, both causing shifts in the position of the peak maxima; and (e) influence of the support (packed and SCOT columns) or the inside column wall (wall-coated open-tubular columns).

As to consistency of column performance, the last point is important. If the support is active, it will also contribute to the retardation of the sample molecules and the same is true of the inside wall in wall-coated open-tubular columns. This effect might be particularly critical for glass open-tubular columns prepared with a non-polar phase such as SF-96 methyl silicone oil where the inside column wall is not completely "inert". This is a well-known phenomenon also emphasized, *e.g.* by Schomburg *et al.*[26]. Such columns are quite useful for the separation of non-polar and moderately polar compounds; however, highly polar compounds, such as alcohols, will show peak tailing.

Tables XI–XIII list the statistical evaluation of relative retention measurements on a number of glass open-tubular columns prepared under manufacturing conditions with three liquid phases. As seen, the results are excellent: all relative standard deviation values are well below 1 %. The data compare most favorably with the values published recently on metal wall-coated open-tubular and SCOT columns prepared with squalane liquid phase[32], and actually the data on the glass columns are better than those obtained on the metal and SCOT columns.

TABLE XIII

REPRODUCIBILITY OF RELATIVE RETENTION DATA ON GLASS OPEN-TUBULAR COLUMNS PREPARED WITH OV-17 PHENYL METHYL SILICONE OIL LIQUID PHASE

Column dimensions: 100 m × 0.27 mm I.D.

Column No.	*1-Methylnaphthalene*	*Acenaphthene*
	2-methylnaphthalene at 165°	*biphenyl at 165°*
1	1.132	1.763
2	1.133	1.769
3	1.130	1.763
4	1.135	1.769
5	1.130	1.772
6	1.131	1.765
7	1.131	1.766
Mean value	1.1317	1.7667
Standard deviation	0.0018	0.0034
Relative standard deviation, %	0.16	0.19

We should particularly emphasize the excellent reproducibility of the SF-96 column for the isopropylbenzene–n-nonane pair. As already mentioned, such a column is not entirely "inert". Thus, if the surface treatment does not result in surfaces with identical column-to-column characteristics, the retention of isopropylbenzene (moderately polar) vs. n-nonane (non-polar) will differ from column to column. It is obvious from the data in Table XI that the inside tube surface had consistently identical characteristics evidenced by the excellent reproducibility of the relative retention of this peak pair.

ACKNOWLEDGEMENTS

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