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MANUFACTURE OF GLASS OPEN-TUBULAR COLUMNS BY DEHYDRATION OF THE SURFACE

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SUMMARY

Methods are described for the preparation and coating of glass open-tubular columns. By dehydration of the inner surface during the drawing operation, an oxide-type glass surface can be obtained which is completely wettable by non-polar and most polar liquid phases without further treatment. For coating the columns, a modified dynamic method was used. Squalane and OV-101 were used as non-polar phases and Ucon LB, Carbowax 20M and OV-17 as polar phases. Our procedure resulted in open-tubular columns of high efficiency, having a thin uniform film (0.03–0.1 μm) and possessing 3000–10 000 theoretical plates per metre. In order to decrease the phase ratio, small-diameter columns (0.1–0.15 mm) were used. Several of these columns have been in routine daily use for nearly 1 year without any decline in efficiency.

INTRODUCTION

During the last few years, there has been a general trend towards the use of glass open-tubular columns, and many methods have been suggested for their manufacture and preparation. In order to allow proper film formation, the properties of the glass surface have to be altered. This can be accomplished in different ways: (a) by adding a surfactant to the liquid[1], (b) by roughening of the surface[2–5], (c) by chemical modification of the surface[6–8], and (d) by covering the surface with a different solid layer[9–12].

The concepts and data published in the literature are often contradictory and there are discrepancies between the qualities of columns obtained by the different methods.

In order to obtain a better insight into the problems involved, we started our investigation by studying the chemistry and characteristics of glass surfaces.

SURFACE CHARACTERISTICS

When a liquid droplet is placed on a solid surface, it may spread to cover the surface or it may remain as a stable drop. The angle between the tangent to the liquid

drop and the solid surface is known as the contact angle, and the higher its value the poorer is the spreading of the liquid or the wettability of the solid surface.

The correlation between the forces that act between the liquid and solid surface is described by the well known Young equation, which illustrates that the wettability is a function of the equilibrium between the cohesion forces inside the liquid and the energy of the solid surface in the presence of the vapour of the liquid and/or its solvent. The cohesion forces inside the liquid are characterized by the surface tension, and the energetic characteristics of the solid surface by the surface free energy.

Regarding the wettability of a solid surface, there are three questions to be answered: (a) has the solid surface a high enough energy to overcome the cohesion forces inside the liquid; (b) has the liquid low enough cohesion forces to be able to cover a solid surface of given energy with a monomolecular layer; and (c) is the liquid able to spread on its own monomolecular layer.

There are surfaces of high, medium and low surface free energy[13]. Surface energies ranging from 5000 to 500 dyne/cm are characteristic of the so-called high-energy surfaces such as metals, metal oxides, nitrides and sulphides; from about 1000 to 100 dyne/cm of medium-energy surfaces such as glass, silica, ruby and diamond; and below 100 dyne/cm of low-energy surfaces such as waxes, solid organic polymers and most organic compounds.

In Table I[14], the wettabilities of a high- and a medium-energy surface with organic liquids of different types are given. It seems that up to 35 dyne/cm, the metal and glass surfaces are equally wettable with different organic liquids, except aliphatic mono- and diesters. This phenomenon will be discussed later.

In Table II[15], the contact angles of water and tricresyl phosphate measured on an uncovered surface and on a platinum surface covered with different liquids are presented. While the contact angles on uncovered platimun are nearly zero, on the covered surface high contact angles can be measured.

TABLE I

WETTING CHARACTERISTICS OF DIFFERENT ORGANIC LIQUIDS[14]

The + sign indicates wetting and the − sign non-wetting of the solid surface.

Class of liquid	Surface tension at 20° (dyne/cm)	Metals	Glass
Open-chain aliphatic hydrocarbons	27–31	+	+
Open-chain methylsilicones	19–20	+	+
Open-chain ethers	28–30	+	+
Open-chain aliphatic monoesters	27–29	+	+, (−)
Open-chain aliphatic diesters	28–34	+	−
Cyclic, saturated hydrocarbons	26–35	+	+
Aromatic–aliphatic hydrocarbons	28–38	+	+, (−)
Cyclic esters (dumb-bell)	36–42	−	−
Cyclic esters (one ring)	30–35	−, (+)	−
Cyclic esters	33–44	−	−, (+)
Phosphate esters (aromatic)	44–40	−	−
Phosphate esters (chlorinated aromatic)	44–46	−	−
Polychlorobiphenyls	42–46	−	−

TABLE II

CONTACT ANGLES OF LIQUIDS AT 20° ON PLATINUM AND ON THIN FILMS ADSORBED ON PLATINUM[15]

Liquid	Surface tension (dyne/cm)	Film on platinum				
		2-Ethyl-hexyl-amine	Sebacic acid	Aniline	n-Hexa-decane	Uncovered platinum
Water	72.8	77	54	55	79	7
Tricresyl phosphate	40.9	40	22	20	31	2

Liquids that are unable to spread on their own layer are called autophobic, and the phenomenon is known as autophoby. Liquids that are not autophobic should have surface tensions that are lower than the critical surface tension (γ_c) of wetting of their adsorbed monolayers. For example, polymethylsiloxane liquids will spread on all high-energy surfaces because the surface tensions of 19–20 dyne/cm are always lower than the critical surface tensions of their own adsorbed films. A closely packed adsorbed monolayer of such silicone molecules has an outermost surface of methyl groups that are less closely packed than those in a single crystal of a paraffin. The γ_c value for the silicone monolayer is 24 dyne/cm or more, depending on the packing density, and because the surface tension of this class of silicones is less than 21 dyne/cm, these silicones cannot be autophobic.

Similarly, hydrocarbons with surface tensions below 30 dyne/cm are never autophobic because the critical surface tension of a typical hydrocarbon surface containing mainly methylene groups, such as polyethylene, is 31 dyne/cm.

The non-spreading behaviour of several ester-type compounds on glass, fused silica and alumina can be explained as follows. Bis(2-ethylhexyl) sebacate is able to spread freely on metals and is unable to cover the above three surfaces. Contrary to metal surfaces, the above three surfaces are hydrated and the diester hydrolyzes on them to form 2-ethylhexanoic acid. The critical surface tension of a closely packed monolayer of 2-ethylhexanoic acid is about 28 dyne/cm. For this reason, the diester, which has a surface tension of 31.1 dyne/cm, cannot spread on the film of its hydrolyzed product.

Table III[15] gives the critical surface tensions of low-energy surfaces of different chemical structures, i.e., liquid surface tensions below which liquids will spread on a given surface.

The following conclusions can be drawn: (1) from the point of view of wettability, there are no significant differences between the properties of metals and glasses; (2) the wettability of surfaces after modification changes significantly; and (3) the further wetting of any surface covered with a monolayer of liquid is possible only if the critical surface tension of the liquid is lower than its actual surface tension. Having drawn these conclusions, we have to search for other reasons to explain the difference in wettability of metal and glass surfaces.

Glass, in a dry atmosphere, is in the so-called hydrogen form (Table IV)[16]. This hydrogen-form glass has a high affinity to sorb water and/or other polar organic compounds and is transformed in a few minutes into another form called the hydrate form (Table IV)[16]. In this form, its surface free energy is decreased significantly and
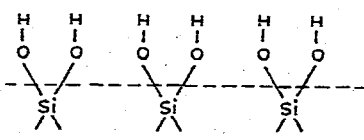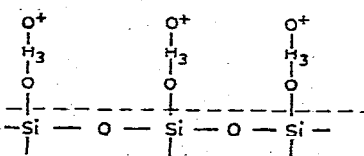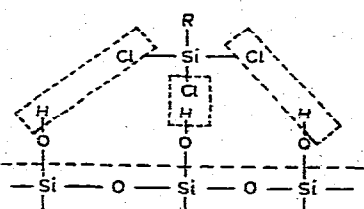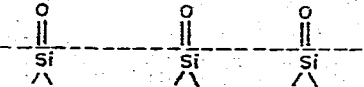
TABLE III

CRITICAL SURFACE TENSIONS OF LOW-ENERGY SOLID SURFACES[15]

Surface	Chemical structure	Critical surface tension (dyne/cm)
Perfluorolauric acid, monolayer	CF_3, closely packed	5.6
Perfluorobutyric acid, monolayer	CF_3, less closely packed	9.2
Perfluorokerosene, thin liquid film	CF_2, some CF_3	17.0
Polytetrafluoroethylene, solid	CF_2	18.2
Octadecylamine, monolayer	CH_3, closely packed	22
α-Amylmyristic acid, monolayer	CH_3 and CH_2	26
2-Ethylhexylamine, monolayer	CH_3 and CH_2	29
n-Hexadecane, crystal	CH_2, some CH_3	29
Polyethylene, solid	CH_2	31
Naphthalene, crystal	C_6H_6, edge only	25
Benzoic acid, monolayer	C_6H_6, edges and faces	53
2-Naphthoic acid, monolayer	C_6H_6, edges and faces	58
Polystyrene, solid	CH_2, some C_6H_6	32.8–43.3
Polyethylene terephthalate, solid	C_6H_6, CH_2, ester	43
Nylon, solid	CH_2, amide	42.5–46.0

TABLE IV

SURFACE CONSTITUTION OF GLASSES[16]

Structure	Form
	Hydrogen
	Hydrate
	Silanized
	Oxide

the surface becomes autophobic against most organic compounds and cannot support organic layers.

On reacting the glass with, *e.g.*, chlorosilanes (Table IV)[16], alkyl groups are formed on the surface whose critical surface tension is high enough to support layers of several organic compounds (Table III)[15], which explains the usefulness of silanization as regards the wettability of glass surfaces.

It is probable that the treatment of glass surfaces with dry hydrogen chloride gas results not only in roughening of the surface by formation of sodium chloride crystals, but also in the removal of the bonded water. This can be confirmed by the fact that treatment with hydrochloric acid is never as effective as that with dry hydrogen chloride.

Glasses kept above 350° in a stream of dry insert gas lose their hydrogen-form properties and form a so-called oxide-type glass (Table IV)[16] and are able to support layers of organic compounds in a similar manner to metal surfaces[15].

MANUFACTURE OF COLUMNS

We manufactured the tubes for our columns with a home-made drawing apparatus. The apparatus is suitable for drawing glass tubes made of soda-lime, borosilicate or any sort of glasses with an outside diameter between 6 and 12 mm. The drawing factor, *i.e.*, the ratio of the diameter of original tube to that of the capillary tube, can vary between 10 and 500. The rate of drawing can be adjusted between 10 and 25 m/h relative to the capillary tube.

During the drawing procedure, a stream of very dry argon was introduced into the glass tube by means of a PTFE tube up to the point where the glass began to melt. At this point, the purging gas turned back, carrying the impurities of the glass surface, leaving a clean and smooth glass surface.

The coating was carried out as follows. The capillary tube was quickly filled with a solution of the liquid phase and closed for 24–100 h. The solution was free from water and other polar compounds and contained 10–30% of the liquid phase. During the time of contact with the glass wall, the large molecules of the liquid phase have sufficient time to diffuse and adsorb on the active sites of the wall. After this period, the solution was removed relatively quickly (0.5–1 m/sec) by the introduction of a stream of dry argon and the column was stabilized, first by purging with the carrier gas at room temperature for several hours, then with a slow temperature programme up to the maximum temperature of later application.

For manufacturing open-tubular columns, we used borosilicate glass (Pyrex type) of French origin. We chose Pyrex glass because it is a well defined, reproducible three-component system and we found no differences in different batches.

We used squalane and OV-101 as non-polar phases and OV-17, Ucon LB and Carbowax 20M as polar phases. As regards the stability of our columns, several have been in routine daily use for several months without any decline in efficiency or resolution.

TESTING OF COLUMNS

The testing of the columns was carried out with Carlo Erba Model 2300 and

Pye Model 104 gas chromatographs using flame ionization detectors. Silicone–rubber discs were used for fitting the columns into the oven. The apparatus had metal splitting devices and we generally applied splitting ratio s of 1:100 to 1:200.

The dead volume of the columns and the linear carrier gas velocity were determined by the injection of methane as a non-retained component.

For testing the columns, we used n-C_6–n-C_7, and n-C_{11}–n-C_{12} alkanes, an aromatic hydrocarbon mixture and the so-called Averill mixture containing cyclohexane, benzene, methyl ethyl ketone and ethanol. For the characterization of the columns, we obtained the chromatograms of these mixtures at different temperatures and carrier gas velocities. From the chromatograms, we determined the retentions and peak widths of the components and calculated the Van Deemter constants, the k', N, N_{eff}, H, R and d_f values. The most important data for different columns measured with the n-alkane test mixtures are summarized in Table V. In order to determine the

TABLE V

CHARACTERISTICS OF THIN-FILM SMALL-DIAMETER OPEN-TUBULAR COLUMNS

Stationary phase	L (m)	d (mm)	d_f (μm)	u (cm/sec)	t (°C)	Component	k'	N/m	$R/\sqrt{L}$
Squalane	110	0.27	0.04	16.0	50	n-C_6	0.04	5661	1.81
						n-C_7	0.10	3941	
	42	0.14	0.02	14.7	50	n-C_6	0.04	5762	1.85
						n-C_7	0.10	4776	
	50	0.14	0.02	14.4	50	n-C_6	0.03	6079	1.84
						n-C_7	0.09	6798	
	55	0.11	0.03	9.9	50	n-C_6	0.09	9856	4.85
						n-C_7	0.23	7710	
OV-101	50	0.11	—	5.5	90	n-C_{11}	0.16	5454	3.25
						n-C_{12}	0.29	4355	
OV-17	32	0.11	—	6.4	90	n-C_{11}	0.16	2585	1.59
						n-C_{12}	0.26	2523	
Carbowax 20M	29	0.11	—	7.9	90	n-C_{11}	0.36	4331	4.82
						n-C_{12}	0.64	3091	
Ucon LB (Máfki)	22	0.14	—	14.1	50	n-C_{11}	0.12	2007	1.81
						n-C_{12}	0.22	2638	
Ucon LB (Grob)	20	0.30	—	16.1	50	n-C_{11}	1.32	1862	9.4
						n-C_{12}	2.68	2660	

optimal operating conditions, experiments were carried out using temperature programming. The optimal operating conditions for the aromatic hydrocarbon mixture on the squalane column are: length, 55 m; I.D., 0.11 mm; starting temperature, 7°; temperature gradient, 2.7°/min; final temperature, 93°; carrier gas velocity, 7.7 cm/sec; inlet pressure of the carrier gas, 3 atm; carrier gas, argon. The results of this measurement are summarized in Table VI.

In Table VII, column characteristics are given for some components of the above mixture measured isothermally at 50° and 70°.

In Figs. 1 and 2, typical chromatograms for the Averill mixture on non-polar and polar columns are shown. Fig. 3 shows the chromatogram of a gasoline fraction.

TABLE VI

CHARACTERISTICS OF A SQUALANE COLUMN WITH TEMPERATURE PROGRAM-MING

Component	N/m	N_{eff}/m	k'	$R/\sqrt{L}$
$n\text{-}C_6$	15,066	973	0.34	18.3
Benzene	10,276	1211	0.52	
$n\text{-}C_7$	10,820	2674	0.99	18.7
Toluene	7,326	2572	1.45	
$n\text{-}C_8$	12,139	5411	2.00	
o-Xylene	16,382	8672	2.67	13.3
Styrene	18,512	9889	2.72	
$n\text{-}C_9$	15,365	8686	2.93	10.4
$n\text{-}C_{10}$	18,157	11,359	3.78	
Indene	22,584	14,560	3.95	11.0
$n\text{-}C_{11}$	11,220	7752	4.93	

TABLE VII

CHARACTERISTICS OF A SQUALANE COLUMN DETERMINED ISOTHERMALLY AT 50° AND 70° AND BY TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHY FROM 7° TO 93°

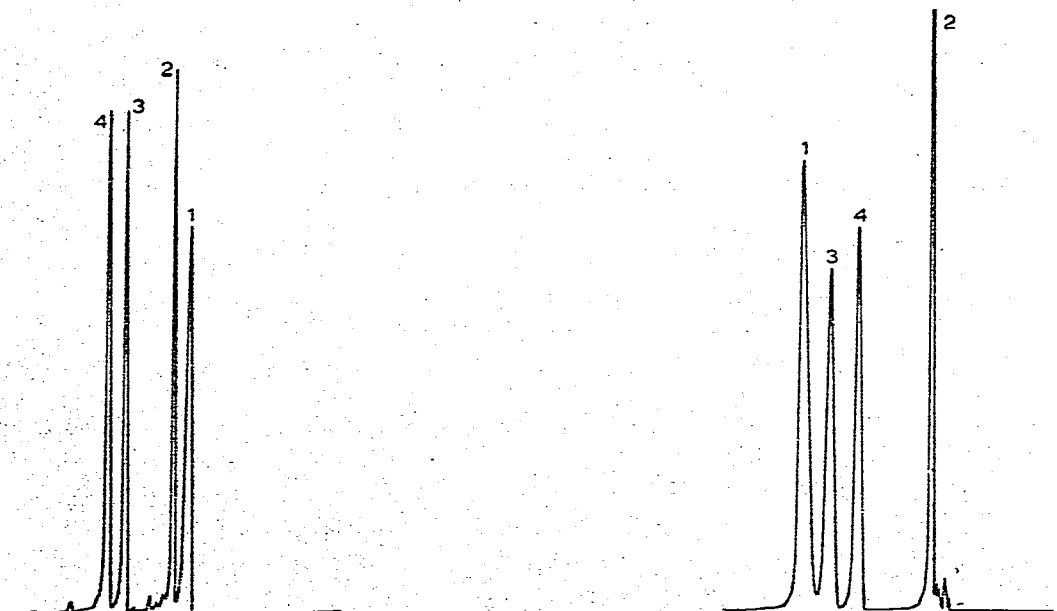| Component	N/m			N_{eff}/m			k'			$R/\sqrt{L}$	
	50°	70°	7–93°	50°	70°	7–93°	50°	70°	7–93°	50°	7–93°
$n\text{-}C_7$	9708	8686	10 820	234	100	2674	0.18	0.12	0.99	11.7	31.6 ($n\text{-}C_7$ — styrene)
Styrene	1880	—	18 512	464	—	9889	0.98	—	2.72	24.0	48.6 ($n\text{-}C_7$ — indene)
Indene	1800	3530	22 584	1100	1490	14 560	3.58	1.86	3.95	14.1	17.5 (styrene — indene)

Fig. 1. Chromatogram of the Averill mixture on a squalane column. Column length, 40 m; I.D., 0.20 mm. Components: 1, methanol; 2, cyclohexane; 3, methyl ethyl ketone; 4, benzene.

Fig. 2. Chromatogram of the Averill mixture on a Ucon LB column. Column length, 30 m; I.D., 0.20 mm. Components as in Fig. 1.
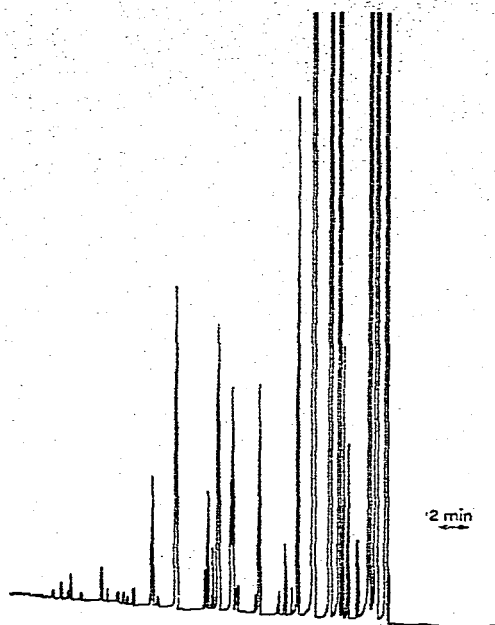
Fig. 3. Chromatogram of a gasoline fraction on a squalane column. Column length, 50 m; I.D., 0.11 mm. Starting temperature, 7°; final temperature, 43°; temperature gradient, 2.7°/min. Carrier gas, argon; flow-rate, 7.7 cm/sec. Sample size, 0.2 μl split in the ratio 1:200.

DISCUSSION

An important feature of the untreated glass surface is that, owing to its smooth surface, the amount of stationary phase on it, *i.e.*, the film thickness, is an order of magnitude smaller (0.01–0.1 μm) than that on metal or etched glass surfaces (0.2–1.0 μm). This has an advantageous influence on the efficiency of columns, but on the other hand, the phase ratio (β) is increased. The phase ratio of open-tubular columns can be expressed in terms of the column diameter, d, and film thickness, d_f, by

$$\beta = \frac{d}{4\,d_f} \tag{1}$$

Substituting this expression into the basic equation of resolution, R:

$$R = \sqrt{\frac{L}{4\,H}}\left(1 - \frac{K_1 + \beta}{K_2 + \beta}\right) \tag{2}$$

where L = column length, H = height equivalent to a theoretical plate, and K_1 and K_2 = partition coefficients of components 1 and 2, respectively, it can be demonstrated that by decreasing the film thickness of a column, the resolution decreases considerably (to approximately zero) even for high-efficiency and long columns, because $d \gg d_f$ and

$$R = \sqrt{\frac{L}{4\,H}}\left(1 - \frac{K_1 + \dfrac{d}{4\,d_f}}{K_2 + \dfrac{d}{4\,d_f}}\right) \tag{3}$$

At d/d_f ratios between 100 and 1000, the partition coefficients of solutes should have an order of magnitude of at least hundreds in order to prevent a considerable decrease in resolution. The high value of the d/d_f ratio explains the great difference between N and N_{eff} for columns that have a thin layer of stationary liquid. N_{eff} is the following function of this ratio:

$$N_{eff} = N \left(\frac{K}{K + d/4\,d_f} \right) \tag{4}$$

By beginning the separation at a lower temperature and applying a temperature programme, it is possible to increase the resolution for the weakly soluble components also by increasing the partition coefficient, K. Therefore, temperature programming is of great importance in capillary column gas chromatography.

The d/d_f ratio can be decreased in two other ways. One of these, generally applied with soda-lime glasses, is to increase the internal surface area of the column by roughening its inner wall. By this means, both the holding capacity of the surface for the liquid phase and the wettability of the glass can be improved.

Modification of borosilicate glass surfaces can be achieved by heat treatment followed by dissolution of the superficial layer enriched in boric oxide with acid and enlargement of the pores by subsequent treatment with alkali. This procedure gives a uniform pore diameter distribution. The pore size is determined by the temperature and duration of the heat, acidic and alkali treatments. This procedure has been applied with success to the treatment of glass solid supports for packed gas chromatographic columns[17]. This method is, however, very sophisticated for the treatment of capillary tubes and the reproducibility of the results was therefore very poor, so we discontinued this procedure for increasing the column capacity.

The second possibility is to decrease the d/d_f ratio by decreasing the column diameter to about 0.1 mm, which seems to be the lowest practical value, contrary to the diameters of 0.25–0.50 mm that are generally used. This procedure also decreases the HETP value, because it is proportional to the diameter of the column. This approach resulted in the preparation of high-efficiency columns with 5000–10,000 theoretical plates per metre and also gave a high resolution value, as shown in Table V.

In order to compare the performance of columns with different lengths, the $R/\sqrt{L}$ values are given. As the resolution is proportional to the square root of the column length, any meaningful comparison of different columns can be made only by using the above values[18]. Because the resolution is increased by increasing the capacity ratio, the high $R/\sqrt{L}$ value for the Grob column is self-explanatory.

In our opinion, columns of small diameter with a very thin film of the stationary liquid can be regarded as a special type of open-tubular column. Consequently, if we wish to utilize the whole of their separation power, it is necessary to determine their optimal operating conditions. The optimal operating conditions can be achieved with a suitable temperature programme, as shown for a squalane column in Table VI.

The data in Table VII show that isothermally it is not possible to exploit the separating power of the column. It can be concluded that the comparison of different types of columns gives a true picture of the real potentialities of the columns only if each of them is working at the optimal operating conditions.

A further advantage of this type of column is that because of the very thin

uniform film, the analysis of a sample can be accomplished well below (about 100°) the boiling points of the sample components without tailing or a decrease in efficiency.

There are several disadvantages of the use of thin-film small-diameter columns, such as the low sample capacity. The volume of sample injected cannot be greater than 0.1 μl with a splitting ratio of 100:1 to 300:1, otherwise there is a serious risk of overloading the column with the whole sample or locally in the neighbourhood of components in high concentration. Consequently, it is necessary to work at a very high detector sensitivity and under very stable operating conditions of the gas chromatograph. Another disadvantage is that extra-column factors affect the efficiency of the separation more significantly. The most important factors are the construction of the sample injection system and the manner of the injection.

CONCLUSIONS

The advantages of thin-layer, small-diameter glass open-tubular columns prepared by dehydratation of the glass surface are their high efficiency, high resolution, chemically inert inner walls, simplicity of manufacture, good reproducibility and ease of coupling in a combined gas chromatography–mass spectrometry system because of the low gas loading of such chromatographic columns.

Problems arising from the geometry of the columns (small diameter, thin liquid film) can be overcome by suitable selection of the operating parameters.

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