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INVESTIGATIONS INTO THE PREPARATION OF GLASS OPEN-TUBE GAS CHROMATOGRAPHY COLUMNS

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SUMMARY

The approaches taken by other workers using chemical and physical modification of the glass surface are examined. The gas phase etching of soda glass is investigated by varying the etching temperature and studying the results by use of the scanning electron microscope and by contact angle measurements. The role of the solvent used in the dynamic and static coating procedures is examined and it is shown that the presence of this solvent increases the contact angle between the stationary phase and the glass surface. This effect can be sufficiently overcome by double hydrogen chloride etching to enable even the most polar phases to be coated successfully.

INTRODUCTION

The traditional use of open-tube columns is in the analysis of natural products where high resolution is necessary. The lengths of column used in this field of analysis are usually 30-100 m. If shorter columns (10-30 m) are used, however, an increase in speed of analysis can be achieved at the expense of resolution.

In process control, quality control and technical service work, data-processing systems are commonplace in the larger laboratories. Their use has led to savings in labour costs and calculation times. The next fruitful area of investigation might be in the reduction of analysis times so that information is more rapidly available and more analyses per unit time can be carried out on a gas chromatograph. When compared with an equivalent packed column, improved resolution is still apparent, even when the speed of analysis is increased by a factor of 4 or 5.

Whatever methods of automatic peak detection are used, digital voltmeter, or analogue or digital integrator, there must be an improvement in peak detection which results from the production of sharp peaks by the use of open-tube columns and short analysis times. The problem of distinguishing low late peaks from baseline drift is very much reduced by the use of these columns.

In the technical service laboratory, a range of columns is usually available to cover the many different types of samples handled. The use of open-tube columns in such laboratories should reduce the number of columns necessary by making use of

resolving power rather than selectivity. Thus, the use of open-tube compared to packed columns in our laboratory offers three possible advantages: (1) reduction in analysis time, (2) improvement in automatic peak detection, and (3) reduction in the number of different types of column necessary to carry out the work.

Open-tube columns made of stainless steel have been in regular and wide use in many laboratories for some years. The internal bore of such columns is easily coated with a wide range of stationary phases, probably because of the surface roughness produced in the drawing process. Stainless steel as a material of construction for open-tube columns is satisfactory in the analysis of most hydrocarbons. Its high surface activity, however, makes it unsuitable for the analysis of certain heat-sensitive, labile and very polar compounds. Glass, on the other hand, has a surface which, though not perfect, is less active than that of stainless steel.

The problems of coating non-polar phases onto glass have largely been solved but in order to achieve a wide use it is clearly desirable to be able to produce a glass open-tube column coated with any stationary phase and this is the main aim of the work described in this paper.

REVIEW OF THE PROBLEM

The non-chromatographic work of Zisman¹ and Fox *et al.*² explains many of the phenomena observed in the production of open-tube columns. Zisman has advanced two concepts which are relevant to gas chromatography. Firstly, the idea of critical surface tension, defined as that value of the liquid surface tension above which liquids show finite contact angles on the given surface, *i.e.*, the critical surface tension of the surface, must be numerically higher than the surface tension of the liquid for complete wetting. Secondly, the fact that the wetting properties of solid surfaces can be seriously modified by adsorbed organic layers.

Universal coatability

Three different approaches have already been taken to achieve the aims of universal coatability, *viz.* work on surface compatibility, work on carbonisation, and etching.

Work on surface compatibility. Grob³ was the first worker to pioneer this approach. He admits, however, that the materials he has used only allow non-polar and medium polar phases to be coated onto glass. The elegant work of Novotný and Grohmann⁴ and Bartle and Novotný⁵ with monochlorodimethyl-[3-(4-chloromethylphenyl)butyl]silane has advanced the concept. With this complex molecule, however, when a compatible group is inserted, the group only amounts to about 10% of the molecule anchored to the surface and it is unlikely that a powerful effect could be exerted.

Work on carbonisation. Grob's work³ on the gas phase carbonisation of methylene chloride, leading to a fine layer of carbon attached to the glass, allows only non-polar and moderately polar phases to be coated.

Etching. The earlier etching work of Mohrke and Saffert⁶, Bruner and Cartoni⁷ and Kiselev⁸ produced very active surfaces which were only useful for gas-solid chromatography. The gas phase etching using hydrogen chloride, first suggested by Tesařík and Novotný⁹ and later used by Alexander and Rutten^{10,11} and Alexander *et al.*¹², so

far seems to offer the most fruitful and practical approach to the production of a universally coatable surface. This goal, however, has not yet been achieved. Although in ref. 11 the authors show that polyethylene glycol (PEG)-400 and 1,2,3-tris-(cyanoethoxy)propane have zero contact angles on hydrogen chloride-etched glass and that, in any case, it is only necessary to have greater than 12% etching coverage, no workers have been able to obtain columns with efficiencies of over 2,000 plates/m with such phases coated onto glass columns, as far as we are aware.

That the compatibility approach has been unsuccessful is not surprising. A study of Table III in ref. 5 and of Table III in ref. 11 reveals that chemical modifications have only increased the critical surface tension of soft glass by a maximum of $1.1 \times 10^{-2} \text{ N m}^{-1}$ and $0.45 \times 10^{-2} \text{ N m}^{-1}$, respectively. In contrast, however, hydrogen chloride etching increased the critical surface tension by at least $2.2 \times 10^{-2} \text{ N m}^{-1}$ up to a value of at least $5.2 \times 10^{-2} \text{ N m}^{-1}$, *i.e.*, sufficiently high to enable any phase to wet this surface.

Thus physical modification of the surface results in a far greater increase in critical surface tension and it is a general treatment applicable to all stationary phases. Chemical surface modification, on the other hand, has only a small effect on critical surface tension and it is a specific treatment which has to be tailored to the particular system under consideration.

EXPERIMENTAL AND APPARATUS

Production of the tubing

Prior to drawing, the glass tubes were treated by drawing up chromic acid into the vertically held tube which was then allowed to drain for at least 24 h. Because of the high viscosity, the walls of the tube were effectively in contact with the acid for this time. The tubes were then washed with distilled water and finally dried by sucking acetone through them.

Capillary tubes (coiled for columns and straight for contact angle measurements) were drawn from 7-mm-O.D. \times 1.8-mm-I.D. soda glass (Gallenkamp, Stockton-on-Tees, Great Britain) and 7-mm-O.D. \times 1.2-mm-I.D. P.W.M. soda glass (Chance, Smethwick, Great Britain).

A "home-made" glass drawing machine¹³ was used. Communication with other workers in the field of glass open-tube columns has indicated that problems are sometimes encountered with the coiling process. We have shown that to achieve trouble-free coiling, it is essential that the straight part of the coiling tube is at least 20 cm in length and that the non-earthed electrical connection is situated on the first quadrant of the coiling tube to ensure that breakages do not occur within the tube. This coiling tube is polished internally by rodding it with fine carborundum paste and by lubricating it with "Aquadag" (Acheson, Plymouth, Great Britain). In use "Aquadag" is also coated onto the glass capillary as it enters the coiling tube. In this way the machine will produce about 50 m of capillary with almost no attention.

The coiling tube was designed to produce coils of 13 cm in diameter. The internal diameter of columns was 0.2 mm. This was achieved by using a drawing ratio of about 40:1.

Tubes made for experimental work rather than columns were about 2 m in length and were formed into rectangles about 10 cm \times 20 cm in size.

Etching of soda glass

Etching of soda glass tubes was carried out according to the procedure first suggested by Tesařík and Novotný⁹ and later used by other workers¹⁰⁻¹².

Hydrogen chloride gas was generated by the action of concentrated sulphuric acid on sodium chloride and it was found that the rate of evolution of hydrogen chloride gas was more even if old, crushed IR sodium chloride cell windows were used rather than Analytical Reagent quality sodium chloride, which has a smaller particle size. In the experimental work, etching was carried out at 250°, 360° and 450° for various times. After etching, the tubes were purged with nitrogen at 110° and then were immediately sealed at both ends. To produce "double etched" columns, the above procedure was carried out twice.

Methods of coating

*Dynamic method*¹⁴. 0.2 cm³, or 15% of the column volume for columns longer than 50 m, of a 5-15% v/v methylene chloride solution of the stationary phase was introduced into the column by means of a modified 1-ml Hamilton "gas-tight" syringe. The solution was dried by anhydrous sodium sulphate before use. The syringe modification involves a "Swagelok" 1/16-in. stud coupling bored out so that it can be attached by means of epoxy resin glue to the Luer taper of the syringe. A perforated silicone rubber septum was used in the 1/16-in. coupling for attaching the modified syringe to the glass column. The solution was forced through the column by applying helium under pressure to move the "slug" at 0.02 m sec⁻¹. The pressure was applied by means of a Brooks (Hatfield, Pa., U.S.A.) Model 8601 pressure controller. Because of the low gas flow through the column, a vent (a Perkin-Elmer (Beaconsfield, Great Britain) Model F 11 air restrictor Part No. 454-0032), was attached downstream of the pressure controller to ensure a good flow through the controller. A 0-60 p.s.i.g. pressure indicator was also mounted downstream of the pressure controller. A 10-m "tail" of similar glass tube was attached to the outlet of the column to keep the velocity of the "slug" constant as it left the column.

After the "slug" had left the column, the gas pressure was raised to smooth out the "lenses" which invariably form and to evaporate the solvent. Purging in this way was carried out for 3 h. Certain columns were coated twice by repeating the above procedure but by passing the "slug" in the opposite direction on the second pass.

During the coating procedure the coil of tubing was mounted in the horizontal position and was protected from sunlight and draughts in order to maintain a reasonably constant temperature.

*Static method*¹⁵. The column was filled with a 0.3-1% v/v solution of the stationary phase in methylene chloride or other suitable low-boiling solvent. The solution was dried by sodium sulphate before use. The solution and the column were degassed for 5 min by evacuating the empty column, sealed at one end, and by applying a vacuum of 0.2 mm Hg to the solution while cooling in a solid carbon dioxide-acetone mixture. The column was filled by breaking the sealed end and immediately plunging it under the surface of the cooled, degassed solution held in a reservoir at a height of 30 cm above the end of the column at which the vacuum was applied. When the tube was full and the vacuum was disconnected from the column, a very slow syphon was formed. The lower open end of the column was sealed by forcing Fortifix QS/B4

cement (Fortifix, Peterborough, Great Britain) into the bore with a 1-ml disposable medical syringe. The cement was also coated around the end of the column and was allowed to dry for 18 h, after which it was coated with nail varnish.

With the column protected from draughts, the same vacuum was applied at the opposite end to the seal and the solvent was evaporated at ambient temperature. Providing the seal holds within the first minute, evaporation should proceed smoothly. A success rate of 60–70% has been achieved with the above method of sealing. Using acetone as solvent, a 15-m column was completed in about 24 h. The rate of evaporation decreases with time so that it takes an impractically long time to make columns 50–100 m in length by this method.

Simulated static and dynamic coating procedures. In the experimental work, the effect of the solvent alone on the glass surface was studied by simulated static and dynamic coating.

In the simulated static coating procedure, tubes 0.5–2 m in length formed into rectangles measuring 10 cm × 20 cm were submitted to the static coating described above but omitting the stationary phase.

In the simulated dynamic procedure, similar tubes were used. A small "slug" of pure solvent was propelled at a velocity as close as possible to 0.02 m sec^{-1} . The solvent was evaporated by maintaining the helium flow for about 1 h after the "slug" had left the end of the tube.

Deactivation procedure

For columns to be coated with non-polar phases, the etched glass surface was deactivated using a procedure based on the method of Hastings *et al.*¹⁶. The column was first coated with 5% PEG-20M in methylene chloride at a coating velocity of 0.01 m sec^{-1} . After the solvent had evaporated, both ends of the column were sealed, taking care to exclude air as far as possible. The sealed column was maintained at 250° for 16 h, after which it was washed out twice with 1 cm³ of methylene chloride and dried prior to coating with the non-polar phase.

Contact angle measurements

Contact angle measurements using the capillary rise method were carried out on straight pieces of tube about 12 cm in length taken from the above-mentioned rectangular "columns". It was necessary to allow 2–3 h for the meniscus to reach its maximum height before a measurement was made.

The tube radius was measured by introducing a plug of mercury into the tube and determining its length and weight.

Gas chromatograph

Columns were evaluated in a Perkin-Elmer F33 gas chromatograph. 1/8-in. "Graphlok" ferrules Type GFF/812 with a 1-mm hole (Scientific Glass Engineering, London, Great Britain) were used to attach the columns.

Scanning electron microscopy

The scanning electron microscopy work was carried out on a Cambridge Stereoscan Model 2A. The tubes were crushed and suitable pieces selected for

examination. Prior to examination the specimens were coated with approximately 20 nm of gold/palladium.

For each experiment, micrographs were made from 4-6 samples of each 2-m length of glass tube.

RESULTS AND DISCUSSION

Discussion of experimental procedures

Production of tubing and coating procedures. During our early investigations into poor efficiencies obtained from both soda glass and Pyrex columns, it was decided to study the coating process. A small amount of methyl violet dye was incorporated into the coating solution during the dynamic coating of methyl silicone oil SF 96. After the solvent had been evaporated, two different types of dye intensity were noted. Firstly, a rapid variation in intensity along the length of the column caused by the apparent break up of the "lenses" formed during the dynamic coating procedure. Thus even though the "lenses" appear to be smoothed out as solvent evaporation proceeds, the higher dye intensity suggests that the stationary phase is thicker in these areas. We consider these areas are the main cause why use of the dynamic procedure generally results in less efficient columns than in the case of the static procedure. As mentioned above, some of our columns were coated twice in opposite directions. Generally, these columns were very successful and we noted that on the second pass fewer "lenses" were formed. The second type of dye intensity differences was of a very gradual nature. If the column was mounted in such a manner that each coil touched its neighbour, the graduations in dye intensity along the column could easily be seen. This variation led us to suspect that the internal diameter of the column was sufficiently variable to cause variations in film thickness.

Desty *et al.*¹³ found bore variations of about $\pm 2\%$ at a drawing ratio of about 50:1. We investigated the uniformity of the bore at three different drawing ratios by means of the mercury plug method already described. Fig. 1 is a plot of per cent standard deviation of the bore of 0.2-mm-I.D. columns *versus* the drawing ratio. It shows that the bore becomes less uniform as the drawing ratio increases. Thus, it is better to employ a low drawing ratio and to draw the column from tubing of small diameter.

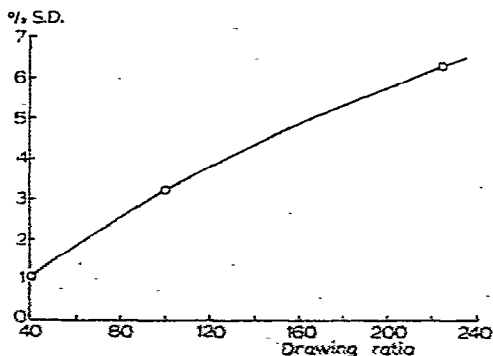


Fig. 1. Per cent standard deviation of the diameter of 0.2-mm-I.D. columns *versus* drawing ratio.

TABLE I

PREDICTED AND DETERMINED FILM THICKNESS FOR THREE PHASES OF DIFFERENT POLARITY COATED ONTO ETCHED SODA GLASS BY THE SINGLE DYNAMIC COATING PROCEDURE

Stationary phase	Polarity	Coating solution	Coating velocity ($m\ sec^{-1}$)	Film thickness $\times 10^6$ (m)		Solute
				Predicted by Fairbrother- Stubbs	Determined by V_g	
Methyl silicone oil MS-200	non- polar	10% v/v in $CHCl_3$	0.02	0.15	0.17	benzene
Bis(2-ethyl- hexyl) sebacate	medium polar	20% v/v in $CHCl_3$	0.02	0.30	0.32	decane
PEG-400	polar	15% v/v in CH_2Cl_2	0.03	0.40	0.34	<i>n</i> -butanol

We studied the applicability of the Fairbrother-Stubbs equation¹⁷ to phases of varying polarity coated onto etched soda glass by the dynamic procedure. This equation relates the final film thickness to the various parameters used in the coating procedure. Other workers^{5,18-20} have shown that the equation will predict the film thickness in their systems. Table I compares the film thickness d_f predicted by the Fairbrother-Stubbs equation and determined using the specific retention volume V_g . As might be expected, prediction is less precise for the polar phase. This is presumably because V_g data for polar phases are affected by the support used.

Etching of soda glass. Most of our columns were drawn from Chance PWM soda-lime glass. It has the following composition: SiO_2 , 71.4%; CaO , 4.6%; Na_2O , 15.0%; K_2O , 1.7%; MgO , 4.0%; Al_2O_3 , 2.2%; BaO , 0.8%; and SO_3 , 0.2%.

A 50-m \times 0.35 mm-I.D. etched uncoated column made from the above glass was filled with distilled water, sealed and heated for 3 h at 100°. It was then washed out and Ca, Mg, K, Na, and Cl ions were determined in the washings. The washings were made up to 100 cm³ and found to contain 13.9 ppm of NaCl and 1.3 ppm of KCl; Ca and Mg ions could not be detected. This agrees with the findings of other workers¹² that the etch consists mainly of sodium chloride.

"Etching" is in fact a misnomer. Scanning electron microscopy shows that the glass surface is not corroded but remains as smooth as an untreated glass. The sodium ions become mobile at the etching temperature. Because of their small diameter, they can move freely through the lattice. As they reach the surface they react with the hydrogen chloride to produce an efflorescence of sodium chloride crystals. The migrating sodium ions leave behind a layer at the surface consisting essentially of silica. Thus the etched surface consists of sodium chloride crystals on a smooth silica platform. The results obtained on our columns indicate that the system appears to behave remarkably like a conventional white support. In certain applications, however, the surface is less active, as will be seen from our work on the analysis of the lower fatty acids, where it was unnecessary to deactivate the surface.

Discussion of surface treatments

Tables II, III and IV show contact angles obtained for variously treated glass

TABLE II

CONTACT ANGLES OF THREE PHASES OF DIFFERENT POLARITY FOR ETCHED AND UNETCHED SODA GLASS SURFACES

Tube No.	Description of treatment	Contact angle		
		MS-200	Bis(2-ethylhexyl) sebacate	PEG-400
1	No treatment; unetched	0°	24°	43°
2	Etched for 3 h at 360°	0°	0°	0°

surfaces. The figures quoted represent the average of a number of determinations and are, therefore, significant. It is estimated that the values of the contact angles obtained are accurate to $\pm 10^\circ$.

Effect of etching on the critical surface tension. The results in Table II demonstrate the effect of etching on the critical surface tension of soda glass. On the untreated glass surface (tube No. 1) only MS-200 (surface tension $\gamma = 0.0203 \text{ N m}^{-1}$) exhibits a zero contact angle. Bis(2-ethylhexyl)sebacate ($\gamma = 0.0311 \text{ N m}^{-1}$) and PEG-400 ($\gamma = 0.0425 \text{ N m}^{-1}$) do not completely wet the glass. The critical surface tension for untreated soda glass is, therefore, somewhat less than 0.0311 N m^{-1} , which is consistent with the findings of Alexander and Rutten¹¹.

On a hydrogen chloride-etched surface (tube No. 2), all three stationary phases exhibit zero contact angles, which suggests that the critical surface tension of singly etched soda glass is in excess of 0.0425 N m^{-1} . It is significant, however, that the etched tube (tube No. 3, Table III) is not completely wetted by the more polar 1,2,3-tris(cyanoethoxy)propane ($\gamma = 0.0519 \text{ N m}^{-1}$).

Role of the solvent used in coating. During the preparation of a column either by the dynamic or by the static procedure, the situation is further complicated by the presence of a solvent which may well affect the surface characteristics which determine the wetting properties of the system.

Other workers^{5,11} have quoted critical surface tension and contact angle data but have not investigated the role of the solvent. Alexander and Rutten¹¹ have treated variously etched glasses with chloroform but have not related their findings to the real situation of column preparation. Their general conclusion from contact angle determinations appears to be that almost any stationary phase can be coated onto etched glass, but examples of high-efficiency glass capillary columns coated with polar phases are limited.

Table III (tubes Nos. 4–6) demonstrates the effect of simulated static and dynamic coating procedures on the wetting properties of PEG-400 on etched soda glass. In each case, non-zero contact angles are obtained after solvent treatment.

Nature of etched surface. The above results led to more detailed investigations into the nature of the etched surface. Fig. 2a shows the scanning electron micrograph of a singly etched soda glass tube and Fig. 2b shows the electron micrograph of a singly etched tube after it has been subjected to a simulated dynamic coating procedure with acetone. No significant difference in the etching pattern is evident. It should be noted, however, that areas of uneven etching were present in a singly etched tube. Two effects were noticed: "macro" variations were present which were visible

TABLE III

CONTACT ANGLES OF TWO POLAR PHASES ON VARIOUSLY TREATED ETCHED SODA GLASS SURFACES

Tube No.	Description of treatment	Contact angle	
		PEG-400	1,2,3-Tris(cyanoethoxy)propane
3	Etched for 3 h at 360°	0°	20°
4	Etched for 3 h at 360° + simulated static procedure with acetone	38°	
5	Etched for 3 h at 360° + simulated dynamic procedure with acetone	43°	67°
6	Etched for 3 h at 360° + simulated static procedure with methylene chloride	22°	
7	Doubly etched for 2 × 3 h at 360°	0°	
8	Doubly etched for 2 × 3 h at 360° + simulated static procedure with acetone	0°	
9	Doubly etched for 2 × 3 h at 360° + simulated dynamic procedure with acetone	43°	

to the naked eye and "micro" variations in crystal size and distribution were apparent on the scanning electron micrographs.

In an effort to obtain greater uniformity of etching, soda glass capillaries were subjected to a double etching procedure. In general, double etching improved the uniformity of crystal size and distribution but areas of uneven etching were still present. The electron micrographs obtained for doubly etched glass (Figs. 3a and b) illustrate the variation in etching pattern.

Doubly etched tubes were subjected to simulated static and dynamic coating procedures with acetone (Table III, tubes 8 and 9). A zero contact angle was obtained for PEG-400 after the simulated static procedure although dynamic coating still resulted in a non-wettable surface.

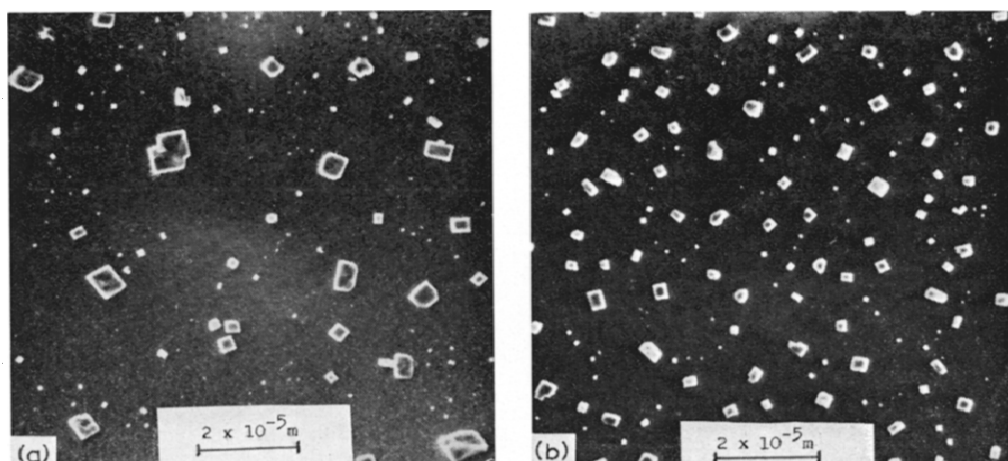


Fig. 2. Electron micrograph of a tube singly etched at 360° for 3 h (a) before and (b) after simulated dynamic coating with acetone.

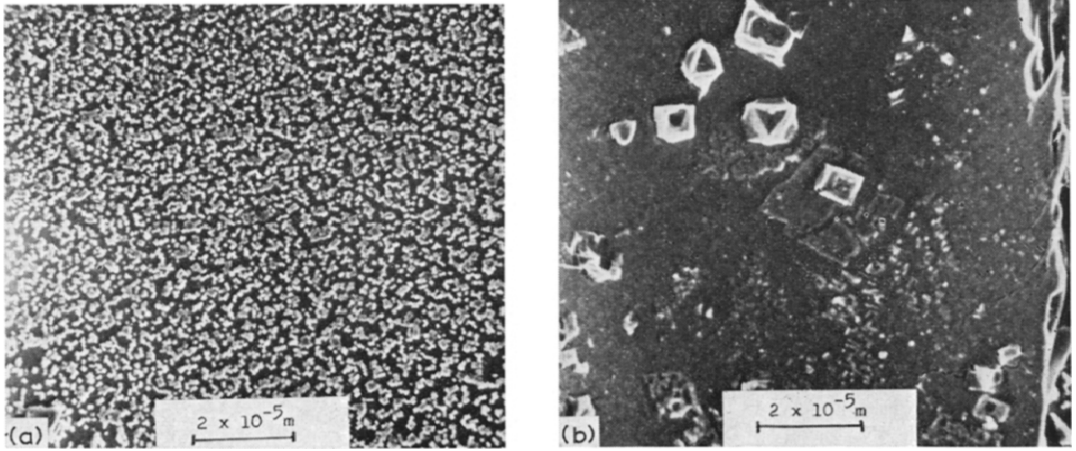


Fig. 3. Electron micrographs of two areas from a tube doubly etched for 3 h at 360°.

Effect of chromic acid treatment and etching temperature on etching pattern. A number of workers^{12,18} have stressed the importance of cleaning the glass with chromic acid prior to drawing the capillaries and Nečasová and Tesařík²¹ have shown that the critical surface tension of Pyrex glass can be substantially increased by treatment with chromic acid.

Soda glass capillaries which had been drawn from glass tubes cleaned with chromic acid were subjected to various etching procedures, *viz.*

Singly etched for 65 h at 250°

Doubly etched for 3 h at 360°

Singly etched for 3 h at 450°

Doubly etched for 3 h at 450°.

The most even etching pattern was obtained by double etching at 360°. Fig. 4 is a scanning electron micrograph of such a surface. Further electron micrographs taken at several different areas along the tube showed the same uniformity of etching.

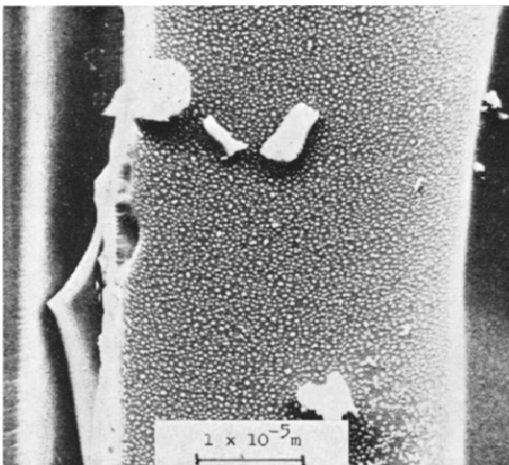


Fig. 4. Electron micrograph of a tube doubly etched for 3 h at 360°.

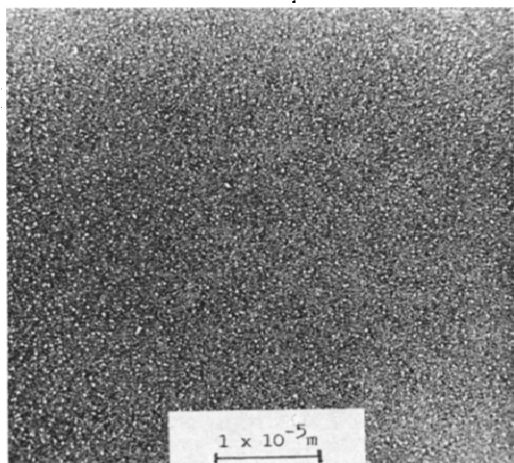


Fig. 5. Electron micrograph of a tube singly etched for 65 h at 250°.

Fig. 5 is an electron micrograph of a tube which had been etched for 65 h at 250°. The crystal size and distribution were extremely uniform but the tube had a paler appearance than the tube etched at 360° and this effect could readily be seen with the naked eye.

Fig. 6 is the electron micrograph of a tube which had been doubly etched at 450°. An uneven etching pattern was obtained and variations in the intensity of etching were clearly visible to the naked eye.

Table IV shows the results of a number of contact angle measurements on the variously etched tubes.

Tubes which had been doubly etched at 360° exhibited zero contact angles with PEG-400 after simulated dynamic coating procedures with acetone and methylene chloride (tubes Nos. 10–12). Complete wetting was also obtained with the very polar stationary phase 1,2,3-tris(cyanoethoxy)propane after a simulated dy-

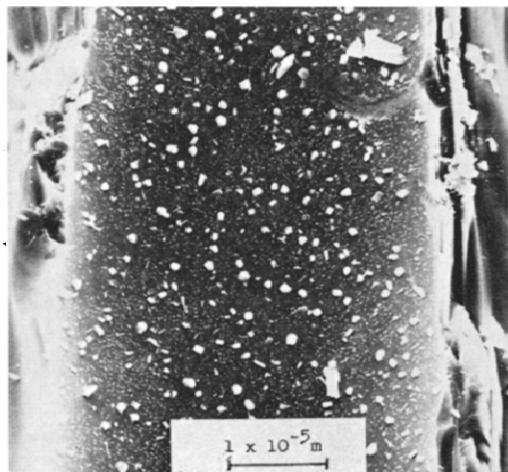


Fig. 6. Electron micrograph of a tube doubly etched for 3 h at 450°.

TABLE IV

CONTACT ANGLES OF TWO POLAR PHASES FOR VARIOUSLY TREATED SODA GLASS SURFACES AFTER TREATMENT WITH CHROMIC ACID

Tube No.	Description of treatment	Contact angle	
		PEG-400	1,2,3-Tris(cyanoethoxy)propane
10	Doubly etched for 2 × 3 h at 360°	0°	0°
11	Doubly etched for 2 × 3 h at 360° + simulated dynamic procedure with acetone	0°	23°
12	Doubly etched for 2 × 3 h at 360° + simulated dynamic procedure with methylene chloride	0°	0°
13	Etched for 3 h at 450°	0°	
14	Etched for 3 h at 450° + simulated dynamic procedure with acetone	41°	
15	Doubly etched for 2 × 3 h at 450°	0°	
16	Doubly etched for 2 × 3 h at 450° + simulated dynamic procedure with acetone	18°	
17	Etched for 65 h at 250°	0°	
18	Etched for 65 h at 250° + simulated dynamic procedure with acetone	27°	

amic coating procedure with methylene chloride (tube No. 12). Etching the tubes at 250° and 450° resulted in incomplete wetting with PEG-400 after subsequent solvent treatment (tubes Nos. 13-18).

Our work on the etching of soda glass with gaseous hydrogen chloride has shown that the best results are obtained at an etching temperature of 360°. Furthermore, if the procedure is repeated (double etching), a more intense etching pattern is obtained. It is also essential that the original tube be thoroughly cleaned with chromic acid before the capillary is drawn. Chromic acid treatment appears to have two important effects. The critical surface tension of the glass surface is increased and the treated surface produces a more even etch after reaction with hydrogen chloride at 360°.

We consider that the role of the chromic acid is more subtle than just the removal of surface contaminants and organic films (which would in any case be oxidised by passing the tube through the furnace in the drawing process). It is probable that chromic acid treatment results in the removal of inorganic materials from the glass and may fundamentally alter the surface characteristics of the glass matrix.

We further suggest that capillary rise experiments in isolation do not represent the real situation which occurs when preparing a column. Stationary phases which originally wet an etched glass surface may not do so when subjected to a static or dynamic coating procedure in which the solvent is an integral part of the system.

Scanning electron micrograph analysis of the solvent-treated glass showed no significant differences in the etching pattern compared with the untreated glass surface. The difference in wetting properties of the etched soda glass after solvent treatment may be due to the deposition of a film of higher boiling trace impurities present in the solvent onto the glass surface. Fox *et al.*² have explained the changes in wetting

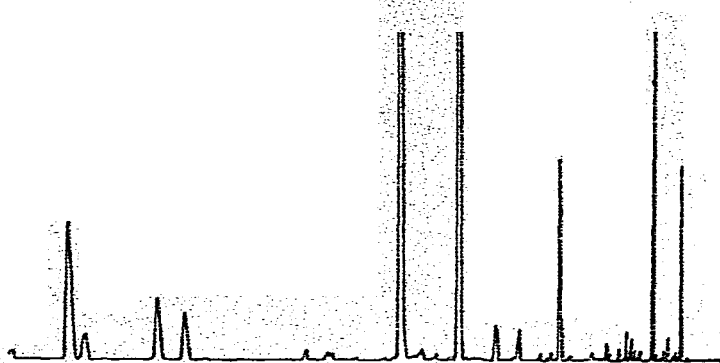


Fig. 7. Chromatogram of paint solvent on a 20-m \times 0.2-mm-I.D. soda glass column coated with bis-(2-ethylhexyl) sebacate, at 50°.

behaviour which occur from the standpoint of adsorbed surface films and Farré-Rius *et al.*²² have also recognised that poor efficiency may result from non-spreading of the coating solution even in cases where the liquid phase is capable of wetting the surface.

By careful control of etching conditions and by the use of a suitable solvent, the results above suggest that it should be possible to prepare glass capillary columns coated with even very polar stationary phases ($\gamma \approx 0.05 \text{ N m}^{-1}$).

Application of results to production of columns

Column performance. To assess column performance, the experimental plate number (n) and the "coating efficiency"^{15,23} were calculated. The latter quantity is defined as the ratio of the highest attainable experimental plate number to the

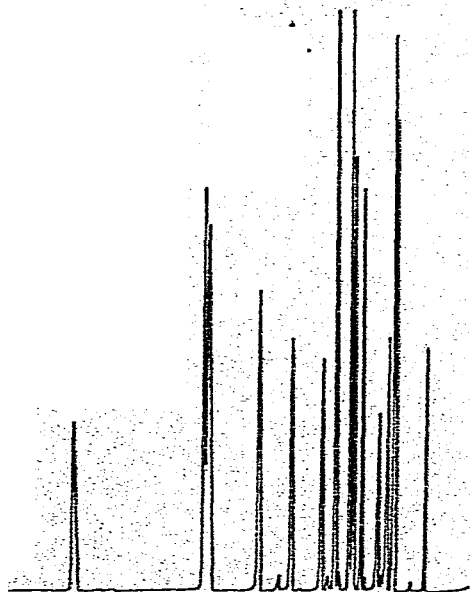


Fig. 8. Chromatogram of alcohols, esters and ketones (up to C_6) on a 20-m \times 0.2-mm-I.D. soda glass column coated with 1,2,3-tris(cyanoethoxy)propane, at 50°.

TABLE V
PERFORMANCE DATA FOR COLUMNS COATED WITH STATIONARY PHASES OF VARIOUS POLARITY

Column No.	Stationary phase	Method of preparation	Column length (m)	Column internal diameter $\times 10^3$ (m)	Temperature ($^{\circ}\text{C}$)	Capacity ratio of peak used for efficiency measurement	Theoretical plates (n)	Theoretical plates/m	Coating efficiency (%)
1	Bis(2-ethylhexyl)sebacate	Dynamic (doubly coated)	20	0.20	50	8.6	80,000	4,000	71
2	1,2,3-tris(cyanosthoxy)propane	Dynamic (doubly coated)	20	0.20	50	10.0	83,000	4,200	75
3	1,15-Pentadecanedicarboxylic acid	Static	13	0.20	115	6.0	39,600	3,000	52
4	PEG-400	Dynamic	20	0.20	40	8.0	69,500	3,500	61
5	OV-101	Dynamic	35	0.25	180	5.5	56,000	1,600	34
6	OV-101	Dynamic (doubly coated)	18	0.20	190	8.5	69,000	3,800	67
7	OV-17	Dynamic (doubly coated)	35	0.20	190	4.1	67,000	1,900	31
8	Hexadecane	Dynamic	48	0.20	40	4.6	68,700	1,400	24

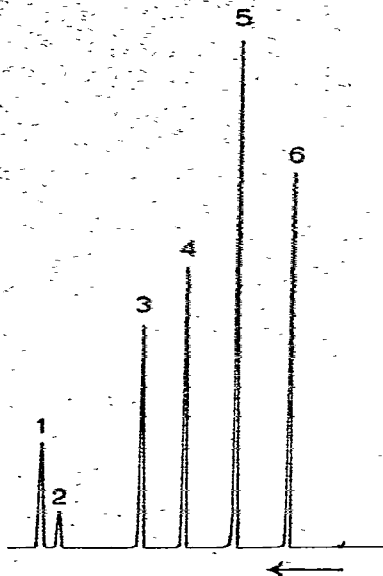


Fig. 9. Chromatogram of C_2 - C_5 fatty acids on a 13-m \times 0.3-mm-I.D. soda glass column coated with 1,15-pentadecanedicarboxylic acid, at 120°. 1 = 3-Methylbutyric acid; 2 = 2-methylbutyric acid; 3 = *n*-butyric acid; 4 = isobutyric acid; 5 = propionic acid; 6 = acetic acid.

theoretically maximum possible plate number. The expression used to calculate the experimental plate number was

$$n_{\text{exp}} = 5.54 (t_R/W_{h_x})^2.$$

Columns prepared. Table V shows performance data for columns coated with stationary phases of various polarity. In general, high plate numbers and coating efficiencies were obtained particularly for the more polar columns.

Column No. 1, coated with bis(2-ethylhexyl)sebacate, has been used in the analysis of over 50 samples, many containing more than 70% water, and has shown no decrease in performance. Fig. 7 is a chromatogram of a sample of paint solvents containing ketones, esters and aliphatic and aromatic hydrocarbons which was analysed on this column and demonstrates the high efficiency and peak symmetry obtained.

Fig. 8 shows a chromatogram of a test mixture containing essentially polar materials on a 1,2,3-tris(cyanoethoxy)propane column (column No. 2). This column exhibited an efficiency of over 4000 plates m^{-1} and, as far as we are aware, no other workers have produced columns of comparable efficiency coated with stationary phases of this polarity.

Column No. 3 was prepared by the static procedure and is coated with the novel stationary phase 1,15-pentadecanedicarboxylic acid, which was predicted on theoretical grounds to be particularly suitable for a special separation problem²⁴. Fig. 9 shows a tail-free chromatogram of the lower fatty acids obtained with this stationary phase on a column which had not been deactivated prior to coating.

We experienced some difficulty in coating PEG-400 onto an untreated doubly etched surface. Fig. 10a shows a chromatogram of a test mixture on a dynamically

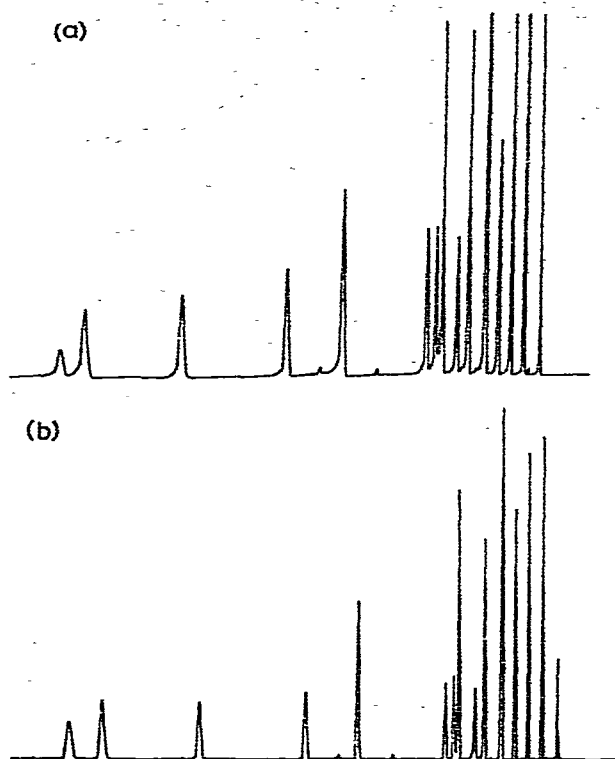


Fig. 10. Chromatograms of alcohols, esters and ketones (up to C_6) on a 20-m \times 0.2-mm-I.D. soda glass column coated with PEG-400, at 50° (a) before heat treatment and (b) after heat treatment and recoating.

coated PEG-400 column. Although peak widths at half height are consistent with an efficient column, all peaks show unacceptable tailing. The column was, therefore, subjected to the previously described deactivation procedure based on the method of Hastings *et al.*¹⁶ except that instead of using PEG-20M the original coating of PEG-400 was subjected to the prescribed heat treatment. After washing the column with methylene chloride, it was recoated dynamically with PEG-400. Fig. 10b shows a chromatogram of the same test mixture on the heat-treated column. Symmetrical tail-free peaks are now obtained for all components, including alcohols. It is assumed that the original peak tailing was caused by an uneven deposition of stationary phase onto the etched glass surface. The improvement obtained on heat treatment can presumably be explained using the concept first advanced by Hastings *et al.*¹⁶ that the high temperature increases the mobility of the polymer chains contacting the surface and allows them to rearrange physically to a minimum potential energy configuration. The resulting monolayer is non-extractable and is capable of being completely wetted by a secondary film of PEG-400. We have prepared other PEG-400 columns and on each occasion have noticed the significant improvements in peak shapes after heat treatment.

Fig. 11 is a chromatogram of simulated recovered C_7 - C_9 aliphatic alcohols, used in the preparation of phthalate esters, obtained on an OV-101 column which

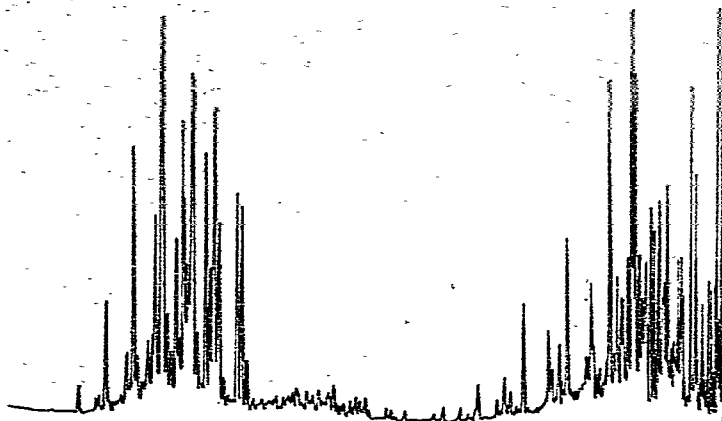


Fig. 11. Chromatogram of simulated recycled phthalate alcohols on a 40-m \times 0.25-mm-I.D. soda glass column coated with OV-101, programmed from 100–300° at 3° min⁻¹.

had been deactivated by heat treatment with PEG-20M prior to coating. The peak shape of polar materials is particularly good on this column, which is clearly demonstrated by the alcohol components which appear as the first group of peaks in the chromatogram. The second group of peaks are the phthalate esters.

Column No. 6 is a further OV-101 column which was prepared by a double dynamic coating procedure and shows over twice the efficiency of the singly coated column No. 5. As stated previously, double coating generally produces very good columns and we have noticed a tendency for reduced lens formation during the second pass of the plug of coating solution. This phenomenon warrants further investigation.

CONCLUSIONS

It is concluded that the double etching procedure described in this paper enables glass open-tube columns to be coated with the most polar phases.

It is also concluded that it is not possible to predict the success or failure of a column by carrying out contact angle measurements of the phase on hydrogen chloride-etched soda glass. The deleterious effect of the solvent used in the static and dynamic coating procedures must be taken into account. For the polar phases used in this work double etching overcame the effect of the solvent.

For open-tube columns coated with PEG-400 an improved performance was obtained if the coated column was heated, washed out, and subsequently recoated.

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REFERENCES

- 1 W. A. Zisman, *Advan. Chem. Ser.*, 43 (1964) 1.
- 2 H. W. Fox, E. F. Hare and W. A. Zisman, *J. Phys. Chem.*, 59 (1955) 1097.

- 3 K. Grob, *Helv. Chim. Acta*, 51 (1968) 718.
- 4 M. Novotný and K. Grohmann, *J. Chromatogr.*, 84 (1973) 167.
- 5 K. D. Bartle and M. Novotný, *J. Chromatogr.*, 94 (1974) 35.
- 6 M. Mohnke and W. Saffert, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 216.
- 7 F. A. Bruner and G. P. Cartoni, *Anal. Chem.*, 36 (1964) 1522.
- 8 A. V. Kiselev, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. XXXIV.
- 9 K. Tesařík and M. Novotný, in H. G. Struppe (Editor), *Gas Chromatographie 1968*, Akademie-Verlag, Berlin, p. 575.
- 10 G. Alexander and G. A. F. M. Rutten, *Chromatographia*, 6 (1973) 231.
- 11 G. Alexander and G. A. F. M. Rutten, *J. Chromatogr.*, 99 (1974) 81.
- 12 G. Alexander, G. Garzó and G. Pályi, *J. Chromatogr.*, 91 (1974) 25.
- 13 D. H. Desty, J. N. Haresnape and B. H. F. Whyman, *Anal. Chem.*, 32 (1960) 302.
- 14 G. Dijkstra and J. de Goey, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 56.
- 15 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
- 16 C. R. Hastings, J. M. Augl, S. Kapila and W. A. Aue, *J. Chromatogr.*, 87 (1973) 49.
- 17 F. Fairbrother and A. E. Stubbs, *J. Chem. Soc.*, (1935) 527.
- 18 K. Tesařík and K. Nečasová, *J. Chromatogr.*, 65 (1973) 39.
- 19 M. Novotný and K. D. Bartle, *J. Chromatogr.*, 93 (1974) 405.
- 20 M. Novotný, L. Blomberg and K. D. Bartle, *J. Chromatogr. Sci.*, 8 (1970) 390.
- 21 K. Tesařík and M. Nečasová, *J. Chromatogr.*, 79 (1973) 15.
- 22 F. Farré-Rius, J. Henniker and G. Guiochon, *Nature (London)*, 196 (1962) 63.
- 23 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965, p. 15.
- 24 J. L. Marshall, in preparation.