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METHOD FOR PREPARING GLASS CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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SUMMARY

A method is given to prepare glass capillary columns with almost any stationary phase. The method is based on etching the soda-lime glass capillary tubing by dry gaseous hydrochloric acid. Coating the columns by the static method results in high-performance apolar and polar phase columns. The polar columns can be used even for the analysis of highly polar solutes. Studying the etched surface of soda-lime glass, the presence of a uniform layer of microcrystalline NaCl was found.

INTRODUCTION

The use of glass capillary columns in gas chromatography (GC) has been of increasing interest in recent years. Reviews^{1,2} covering the field point out that copper, stainless steel, etc., could well be replaced by glass as a structural material. Moreover, glass tubing has several advantages over metals: its catalytic activity and adsorptivity are lower and it is cheaper than metal equivalents.

However, results reported with glass capillaries have not been uniformly good. Some reasons have been well summarized by K. Grob and G. Grob³; difficulties are mainly connected with the GC apparatus used and the injection techniques employed. It is not necessary to repeat these here in detail, but it should be emphasized that a certain skill and proper instrument adaptation are required to utilize the possibilities of the high-performance capillary columns.

In column preparation there are two main problems, *viz.* (i) the catalytic activity of the glass wall, which is smaller than that of metals but high enough to cause serious difficulties when sensitive solutes, mainly of biological origin, are to be analyzed; and (ii) the poor wettability of glass by stationary phases.

The problem of catalytic activity now seems to be solved by deactivating the surface by silylation⁴⁻⁸ or by a simple procedure using thermostable ionic surface-active agents⁹. Very effective columns could be prepared by these methods with apolar phases, usually dimethylsiloxanes.

On the other hand, coating problems are more complex and are still unsolved. It has been proved⁹ that phases such as SE-30 and OV-101 spread spontaneously over the glass surface, and no treatment is necessary to obtain high-efficiency columns. More polar phases, however, *i.e.* liquids with surface tensions higher than that of apolar silicones, did not wet the glass.

Several approaches have been tried to make the glass more wettable¹: chemical modifications (including silylation) and roughening by either acids or bases in solution or by gaseous methods, *i.e.* carbonization or by gaseous acids.

Results can be summarized as follows. Wet methods have deeply modified the structure of glass¹⁰; columns have been suitable only in some special applications in gas-solid chromatography.

Other treatments reported in the literature have been more or less successful, but only in cases with apolar or moderately polar phases. It seems that the more polar the phase, the less the efficiency of the capillary column.

While for apolar silicones N/L (number of theoretical plates per column length, in meters) values reported were well over 2000, or even 3000 (ref. 9), similar data for polar phases, as far as is known, were much lower. For example, Necasová and Tesarik¹¹ prepared capillary columns with a polar coating (1:1 mixture of PEG-400 and diglycerol) and reported an N/L value of 800. For moderately polar phases Novotny and Bartle¹², using selective silylating agents to treat the glass wall, mentioned an N/L value of 1800 as the best for dinonylphthalate, while Liberti and Zoccolillo¹³, applying carbonization as pretreatment, reported an N/L value of 1700 for the moderately polar phase "Trimer Acid".

In the present paper a method is described to prepare glass capillary columns for almost all stationary phases. It is based on a procedure of etching the glass wall by gaseous hydrochloric acid¹⁴. This method results in a wettable, uniformly etched surface only if a suitable, alkali-containing glass is selected as capillary tubing and if during the whole etching and coating procedure water-free conditions are kept.

EXPERIMENTAL

Preparation of capillary tubing

Capillary tubes were drawn by a machine which was a slightly modified version of the type proposed by Desty *et al.*^{15,*}. Capillaries were drawn usually from soda-lime soft glass. Only capillaries of this type were suitable for the etching procedure described below to prepare the capillary wall for coating by polar phases.

The glass tubing was thoroughly cleaned before drawing by carefully rinsing with chromic acid. The acid was washed out by water, followed by acetone, and then the tubes were allowed to dry. Instead of chromic acid, hydrofluoric acid can be used with the same results.

The capillaries had an I.D. of 0.2–0.25 mm and an O.D. of 0.5–0.6 mm.

* The machine was constructed and operated in the laboratory of the Research Group for Petrochemistry, Hungarian Academy of Sciences, Veszprém, Hungary.

Surface treatment (etching)

Etching was found to be indispensable before coating with any phase other than dimethylsiloxanes.

HCl gas was generated from dry crystalline NaCl and concentrated sulphuric acid in a glass flask. The pressure developed in the flask was high enough (about 0.1–0.3 atm, gauge) to force gaseous HCl through the attached capillary column. Appearance of the acid gas at the end of the tubing was indicated by reagent paper. The HCl was passed for a further 10–15 min through the capillary and then the absence of air was determined by a simple test: using a small flame, a short (about 10 cm long) section of the tubing was cut from the outlet end. The open tip of this piece of capillary (the other end having been closed in the flame) was immediately dipped into water. This, dissolving HCl, rose into the short capillary until only air remained in the gaseous phase. The percentage of the length filled by the fluid gave directly the percentage of HCl gas in the capillary. The HCl stream was passed until the HCl concentration was found to be more than 90%. Then both ends of the column were closed by a small flame.

The columns filled with pure, dry HCl gas were then put into an oven at 350–380° for about 2 h. Both the temperature and the reaction time can be varied between certain limits without influence on the result. After cooling down to room temperature, both ends of the capillary were opened and excess HCl was forced out by dry nitrogen.

After this treatment the glass wall should turn white and opaque. In fact, this happens only if the glass is of the soda-lime type. Columns in which the opaque layer was not completely uniform were discarded.

Glass tubing of the Pyrex type never showed any change in transparency.

Coating procedure

For the coating of glass capillary columns usually two methods are used, *i.e.* the dynamic method¹⁶, and a version of the static method (as introduced by Bouche and Verzele¹⁷).

The two methods have been recently compared⁹, and the static method has been found considerably more effective. This was also confirmed by our results, and therefore in all the cases reported here the static coating procedure was applied.

A solution of the stationary phase was prepared in a volatile solvent, usually hexane or dichloromethane; the phase ratio in the column was directly predetermined by the concentration of the phase in this solution. In order to remove dissolved gases, a few millilitres of the solution were diluted by pure solvent to about twice the volume, then gently boiled to the original volume on an oil-bath. Afterwards the solution was cooled down to room temperature as quickly as possible, while taking care not to shake it, to avoid re-dissolution of air. De-gassed solution should be used to fill the column immediately.

Capillary tubes were always filled with the above solution by suction and not by pressure. Closing off at one end was done by using latex, *i.e.* rubber emulsion. The advantage over the originally proposed waterglass¹⁷ is that it turns hard within 20 min, instead of the 24 h for waterglass. A small piece of rubber made a completely air-tight seal at the column tip and evaporation could be started immediately.

Evaporation of the solvent was performed at room temperature under pressure

of a few mm Hg; the time required to complete the coating of a 20-m column was two to three days.

Gas chromatography

Columns were tested in a Perkin-Elmer Model 900 gas chromatograph (Perkin-Elmer, Norwalk, Conn., U.S.A.) equipped with a flame ionization detector (FID). It was adapted to glass capillary work by replacing its original splitting device by a modified splitter through which the straightened end of the capillary could be driven into the glass insert of the evaporator. For the connection of the columns, PTFE shrinkable tubing and/or silicone rubber washers were used. According to our experience both of these materials could be used up to 230° and even, for short periods, up to 250°. High-purity-grade nitrogen was used as the carrier gas. At the outlet end of the column an excess stream of nitrogen was mixed with the effluent to decrease the effect of dead volumes between the column and the FID.

For conditioning, it proved to be adequate to keep the column near the recommended maximum temperature for a couple of hours.

In order to test the columns, the number of theoretical plates and separation numbers (according to Kaiser¹⁸) were measured by injecting *n*-alkanes.

A capillary column can be very well characterized by the coating efficiency (Ettre¹⁹). This number relates HETP value to the theoretically possible minimal HETP, the latter being expressed as

$$\text{HETP}_{\min.} = r \sqrt{\frac{1 + 6k + 11k^2}{3(1 + k)^2}}$$

where *r* is the internal radius of the column and *k* is the capacity ratio of the peak involved. Both *k* values and coating efficiencies were calculated.

X-Ray diffractometry of glass powders

For the detection of NaCl on the surface of the glass powder particles (see Results and discussion) a Phillips X-ray diffractometer (with Müller-Micro 111 Type generator, Cu cathode, Ni filter, 20 kV/20 mA source, and GM-tube recorder) was used.

RESULTS AND DISCUSSION

Column efficiency

Columns coated with apolar phase. The principal aim of our work was to develop a method to prepare columns coated with a polar phase. However, several columns were coated with an apolar phase, mainly to study the coating procedure and to create a basis for comparison with the ones coated with a polar phase. In Table I the results for capillary columns with OV-101, Apiezon L (APL) and Dexsil-300 GC coatings are given. The figures for coating efficiency are somewhat uncertain, as the accuracy of the I.D. determination was only about ±10%. It should be noted that APL and Dexsil-300 GC columns could be prepared only by using etched capillary tubings, while for OV-101 etching was not necessary.

It can be seen from Table I that the efficiency of the columns was rather good.

Columns coated with a polar phase. In Table II the results on columns coated with a polar phase are given.

It can be seen that N/L values and coating efficiencies of polar columns are only slightly lower than those of apolar ones. In addition, the results reported here are considerably better than those reached by other means of surface treatment^{12,13}.

To prove the effect of etching, column No. 10 was prepared. Because of some impurities within the capillary (the purification before drawing was omitted here), the etching procedure by gaseous HCl was not completely successful; the opaque layer was defective as could well be seen by eye. After coating and conditioning the column in the usual way, no droplets could be observed on the wall, but efficiency was still low. In the case of some other columns with polar phases and without any etching, at the end of the static coating process the layer of stationary phase seemed to be uniform, but after conditioning the liquid phase formed droplets and efficiency was extremely low (N/L values were in the order of 100, or lower; data are not reported here).

Analysis of polar solutes; examples for column application

The quality of a column is very well indicated by chromatograms and performance data for polar compounds. One of the reasons for preparing columns with polar coating is that the polar phase itself has some deactivating effect on the catalytic and absorptive activities of the glass surface²⁰.

In Fig. 1 chromatograms of a so-called "polarity mixture" are given on two of the apolar (Nos. 4 and 5) and two of the polar (Nos. 8 and 9) columns. Compounds in the "polarity mixture" are: ethanol, methyl ethyl ketone, benzene and cyclohexane, *i.e.* substances of very different polarities.

It can be seen that the peak shapes of the polar compounds are considerably different in the four chromatograms. Ethanol, having a symmetrically shaped peak on

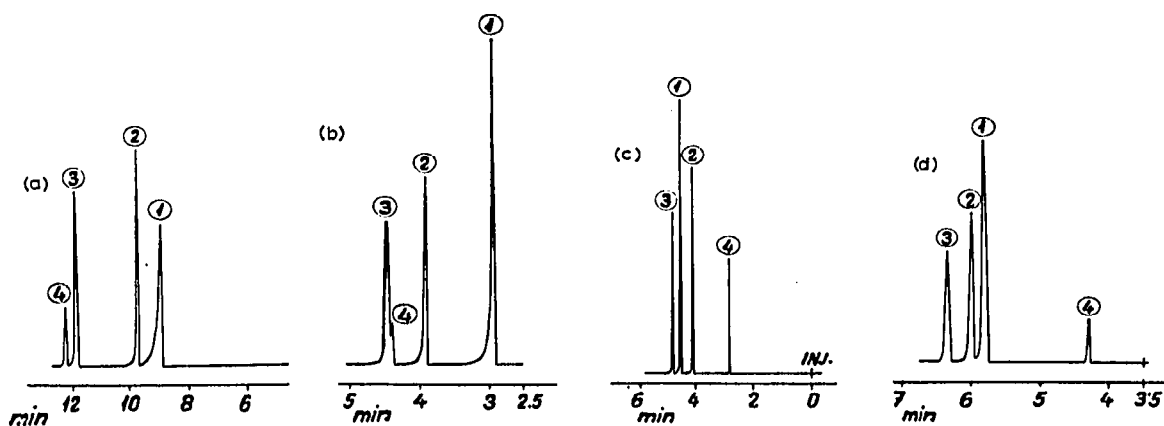


Fig. 1. Chromatograms of a polarity mixture on four columns. 1 = Ethanol; 2 = methyl ethyl ketone; 3 = benzene; 4 = cyclohexane. (a) Column No. 4 (Apiezon L); for column data see Table I. Temperature, 70°; carrier velocity, 11.0 cm/sec; detector, 5×10^{-9} A f.s.d. (b) Column No. 5 (Dexsil-300 GC); for column data see Table I. Temperature, 50°; carrier velocity, 13.3 cm/sec; detector, 5×10^{-9} A f.s.d. (c) Column No. 8 (Carbowax 20M); for column data see Table II. Temperature, 50°; carrier velocity, 12.0 cm/sec; detector, 5×10^{-9} A f.s.d. (d) Column No. 9 (DEGA); for column data see Table II. Temperature, 40°; carrier velocity, 95 cm/sec; detector, 5×10^{-9} A f.s.d.

TABLE I
PERFORMANCE DATA FOR COLUMNS COATED WITH APOLAR PHASES

Column No.	Stationary phase	Column length and I.D.	Phase ratio (nominal)	Temp. (°C)	Linear carrier velocity (cm/sec)	n-Alkanes	Capacity ratio	Theoretical plates, N	Theoretical plates/m, N/L	Separation No.	Coating efficiency (%)
1	OV-101	20 m × 0.20 mm	400	100	13.9	C ₁₁	2.24	108 000	5400	38.5	76
						C ₁₂	4.25	107 000	5350	39.5	91
						C ₁₃	7.9	88 000	4400	79	
2	OV-101	20 m × 0.22 mm	600	100	9.8	C ₁₀	0.82	76 000	3800	24.0	55
						C ₁₁	1.56	100 000	5000	31.9	81
						C ₁₂	2.91	98 000	4900	91	
3	OV-101	80 m × 0.20 mm	400	100	19.9	C ₁₀	1.06	305 000	3810	45.0	55
						C ₁₁	1.86	350 000	4370	69.9	71
						C ₁₂	3.61	383 000	4788	92	
4	Apiezon L	50 m × 0.24 mm	400	60	11.0	C ₈	0.41	241 000	4820	39.0	58
						C ₉	0.97	224 000	4480	63.5	67
						C ₁₀	2.31	260 000	5200	94	
5	Dexsil-300 GC	20 m × 0.24 mm	200	118	9.5	C ₈	0.80	73 000	3650	22.0	44
						C ₉	1.47	89 000	4450	31.0	55
						C ₁₀	2.80	96 500	4825	37.0	75
						C ₁₁	5.18	95 500	4775	81	

TABLE II
PERFORMANCE DATA FOR COLUMNS COATED WITH POLAR PHASES

Column No.	Stationary phase	Column length and I.D.	Phase ratio (nominal)	Temp. (°C)	Linear carrier velocity (cm/sec)	n-Alkanes	Capacity ratio	Theoretical plates, N	Theoretical plates/m, N/L	Separation No.	Coating efficiency (%)
6	OV-225	20 m × 0.24 mm	600	130	19.6	C ₁₈	3.59	80 500	4025	23.8	77
						C ₂₀	9.29	58 500	2925	61	
7	Cyclohexanedimethanol succinate	20 m × 0.24 mm	300	100	8.4	C ₁₂	0.92	36 600	1780	13.6	26
						C ₁₃	1.67	29 800	1490	25	
						C ₁₄	3.05	46 800	2340	19.0	45
						C ₁₂	1.73	108 000	5400	28.0	83
8	Carbowax 20M	20 m × 0.24 mm	200	85	13.9	C ₁₃	3.17	63 500	3175	29.0	61
						C ₁₄	5.90	58 200	2910	59	
						C ₁₂	1.27	55 700	2785	20.5	43
9	Diethylene glycol adipate (DEGA)	20 m × 0.24 mm	200	82	10.1	C ₁₃	2.30	52 500	2625	11	46
						C ₁₀	1.07	14 900	745	12.3	16
10	DEGA*	20 m × 0.24 mm	200	60	9.8	C ₁₁	2.14	18 300	915	15.2	16
						C ₁₂	4.28	15 200	760	15	

* Defective etching.

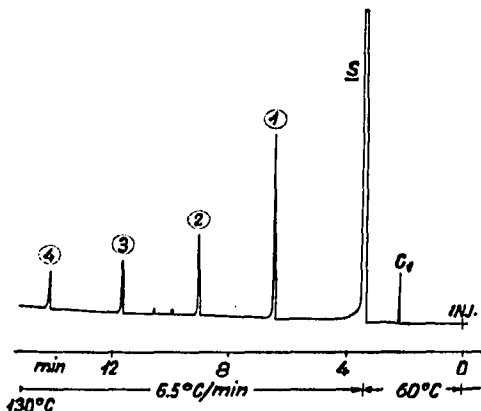


Fig. 2. Analysis of *n*-alkanol homologues on column No. 8 (Carbowax 20M); for column data see Table II. Carrier velocity, 15.6 cm/sec; detector, 7×10^{-10} A f.s.d. C_1 = Methane; S = solvent; 1 = *n*-butanol; 2 = *n*-pentanol; 3 = *n*-hexanol; 4 = *n*-heptanol.

Carbowax 20M and DEGA, eluted in the form of considerably tailing peaks from Dexsil-300 GC, and especially from APL; the differences between the methyl ethyl ketone peaks are much less pronounced. This means that if very polar compounds are to be eluted from a column coated by an apolar phase, the glass wall requires some kind of deactivating treatment. Experiments not reported here show, however, that deactivation methods used in, *e.g.*, steroid analysis⁹ are inadequate for this purpose; to find an efficient way to avoid tailing of polar compounds on apolar coated columns requires more research.

On the other hand, it seems that polar phases, like Carbowax 20M and DEGA, give a rather effective deactivation. Fig. 2 shows a programmed temperature analysis of *n*-alkanols; it can be seen that the peaks are free of tailing. Separation numbers calculated for *n*-alkanol pairs (Table III) are about the same as those for *n*-alkanes.

TABLE III

SEPARATION NUMBER VALUES OF *n*-ALKANOL HOMOLOGUES ON A COLUMN COATED WITH CARBOWAX 20M

For column data, see Table II; for analysis conditions, see Fig. 2.

Column No.	Stationary phase	Substance eluted	Separation No.
8	Carbowax 20M	<i>n</i> -Butanol	31.0
		<i>n</i> -Pentanol	32.0
		<i>n</i> -Hexanol	31.5
		<i>n</i> -Heptanol	

The quality of the polar columns is further illustrated in Table IV, where data calculated from the chromatograms of polar solutes on column No. 9 (coated with DEGA) are given.

In Figs. 3, 4 and 5 three more examples are presented of difficult separations and of analyses of polar solutes and complex mixtures.

TABLE IV

PERFORMANCE DATA FOR A COLUMN COATED WITH DEGA, MEASURED WITH POLAR SOLUTES

For column data, see Table II.

Column No.	Stationary phase	Temp. (°C)	Linear carrier velocity (cm/sec)	Substance eluted	Capacity ratio	Theoretical plates, N	Theoretical plates/m, N/L	Coating efficiency (%)
9	DEGA	150	9.0	Phenol	3.03	77 000	3850	72
		120	14.3	Isononanol	1.71	92 500	4625	86

In Fig. 3 separation of some aromatic compounds is shown on a 20-m-long DEGA column. (Note the complete resolution between *p*- and *m*-xylene; this separation has been a traditionally difficult task in GC.)

Fig. 4 shows a chromatogram of some phenolic polar solutes, made on the same DEGA column, while in Fig. 5 analysis of a complex mixture of polycyclic methylsiloxanes is given. These latter are pyrolysis products of a branched-chain methylsilicone resin and have been prepared and studied mainly by GC²¹. On the chromatogram separation is almost complete in the important range of the spectrum, but identification of the single peaks has not yet been solved. It is an example of the increasing importance of coupling high-efficiency capillary columns to mass spectrometers.

Study of the etched glass surfaces

It became clear after the very first experiments that Pyrex columns of glass of low alkali content were not etchable by HCl gas and remained transparent; subsequent polar phase coatings proved to be unstable. Therefore, it may be assumed that the opaque layer is produced by a reaction between the alkali ions in the surface layer of glass and gaseous HCl.

A scanning electron microscopic (SEM) study of the inner wall of etched soft glass capillaries (see Fig. 1 in ref. 20) showed uniformly distributed particles of more

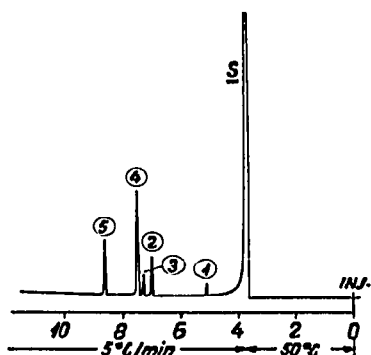


Fig. 3. Analysis of aromatic compounds on column No. 9 (DEGA); for column data see Table II. Carrier velocity, 15.0 cm/sec; detector, 6×10^{-10} A f.s.d. S = Solvent; 1 = toluene; 2 = ethylbenzene; 3 = *p*-xylene; 4 = *m*-xylene; 5 = *o*-xylene.

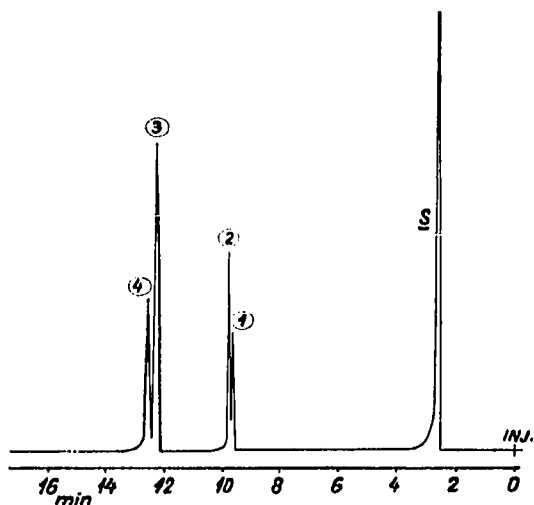


Fig. 4. Analysis of phenols on column No. 9 (DEGA); for column data see Table II. Temperature, 150°; carrier velocity, 15.0 cm/sec; detector, 2×10^{-10} A f.s.d. S = Solvent; 1 = *o*-cresol; 2 = phenol; 3 = *m*-cresol; 4 = *p*-cresol.

or less cubic shape on a smooth glass surface. This observation, as well as chemical evidence, suggested that the opaque layer was formed by microcrystalline sodium chloride.

This supposition was also proved by another independent method. Glass powder was prepared from the same soft glass as the capillaries were drawn from. This powder (having a 1.0–1.5 m²/g specific surface) was treated under conditions identical to those used for capillaries. The treated powder was then examined by X-ray diffractometry and the characteristic diffraction pattern of NaCl could be observed over a diffuse hump caused by the amorphous glass. A detailed description of these experiments will be reported later²².

On comparing the peak shape of ethanol on an etched and apolar coated column (*e.g.* column No. 4, APL-coated, Fig. 1a) with that on an untreated but apolar-coated one (*e.g.*, OV-101; the chromatogram is not given here) there is no significant difference. This means that etched soft glass columns do not seem to be

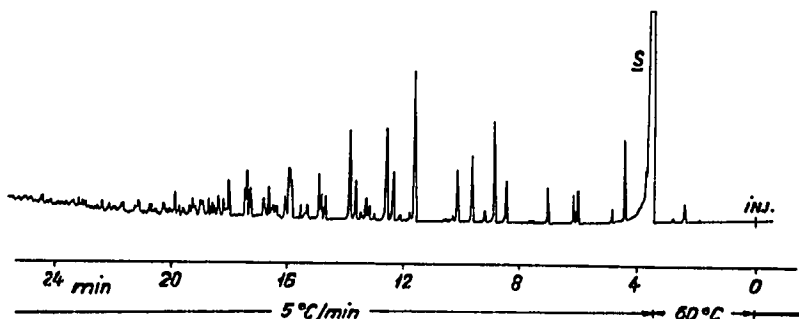


Fig. 5. Pyrogram of a branched-chain methylsilicone resin on column No. 8 (Carbowax 20M); for column data see Table II. Carrier velocity, 16.0 cm/sec; detector, 2×10^{-10} A f.s.d.

more adsorptive than untreated ones. This can be explained by two facts: it has been found that an acidic treatment did not increase the number of adsorptive silanol groups on the glass surface²³ and, on the other hand, NaCl has been used as one of the most inert, less adsorptive GC supports²⁴. Therefore, the inner wall of an etched column can be considered as a relatively inert surface, namely glass, which is uniformly coated by microcrystals of a substance which is completely non-adsorptive.

The well-known Wenzel equation (see, *e.g.*, in ref. 10)

$$\frac{A'}{A} = \frac{\cos \Theta'}{\cos \Theta}$$

(where A is the area of the smooth surface, A' is the increased, microscopic area of the roughened surface, and Θ and Θ' are the contact angles of a liquid on smooth and roughened surfaces, respectively), gives a simple, quantitative formula to estimate the effect of etching on wettability.

Based on the model suggested by the SEM study, *i.e.* cubic microparticles on a smooth surface, it can easily be calculated²⁵ that if only 10% of the surface is covered by regularly cubic microparticles (this can easily be achieved by etching, as the SEM studies suggest), every liquid having a contact angle smaller than 44° on the smooth surface should wet the roughened surface. Assuming less regular particles, this angle should decrease, but not more than about 10°.

To verify this theory, contact angles were measured²⁵ on small, soda-lime glass sheets, both untreated and etched. As test liquids a series of GC liquid phases of different polarity were used, all of them having reasonably low viscosity. In Table V the contact angles measured on untreated glass are given, together with surface tension values of the liquids.

It can be seen that while even squalane does not wet the glass, an HCl-etched glass surface covered for not more than 10% by NaCl crystals should be coatable by even the highest-surface-tension highest-polarity liquid phases. This was verified by contact angles measured on the etched sheets: All of the liquids in Table V wetted the etched surface completely, *i.e.* with zero contact angles.

Further results with experimental columns prepared with the liquid phases mentioned are as follows. The only phase which could be coated on untreated glass was the apolar dimethylsiloxane; squalane and all the other phases formed droplets and the columns were of low efficiency. On HCl-etched capillaries, however, squalane

TABLE V

CONTACT ANGLE VALUES* ON UNTREATED GLASS SURFACE, AND SURFACE TENSIONS* OF THE TEST LIQUIDS

<i>Test liquid</i>	<i>Surface tension (dyne/cm)</i>	<i>Contact angle, Θ</i>
OV-101	19.5	0°
Squalane	29.7	5.3°
Phenyl silicone oil DC-704	36.5	10.6°
Carbowax 400	46.7	20.0°
Tris(cyanoethoxy)propane	52.4	32.0°

* Room temperature data.

and even phases of higher polarity spread well, and columns proved to be nearly as good as dimethylsiloxane-coated ones.

This means that, as coatability in our case is the result of surface geometry and not of surface chemistry (as with selective silylation¹²), the method of surface treatment can be the same for all stationary phases, irrespective of their chemical nature. The only limiting factor is the surface tension of the stationary phase; the limiting value seems to be well over 50 dyne/cm. Therefore, presumably the method will be capable of producing good columns with many other phases besides those mentioned in this paper.

The coatability due to the finely divided NaCl will exist only as long as the microcrystalline structure over the surface remains intact. This means that during the whole etching and coating procedures and later on, during the use of such columns, care should be taken to avoid any moisture getting into the column. According to our experience, however, no special measures are necessary; using moisture-free carrier gas and avoiding water-containing samples seems sufficient. Up till now, after several months of use, no deterioration of any of our columns has occurred.

CONCLUSIONS

It has been shown that the etching procedure with gaseous HCl will be effective only if the appropriate glass, *i.e.* soda-lime glass of considerable alkali content, is chosen for drawing the capillary columns. Tubing etched by the process described can be uniformly coated with both apolar and polar phases. The columns prepared have rather good performance characteristics (plate numbers, separation numbers and coating efficiencies). Polar phases deactivate the glass surface so that polar solutes can be analysed without the usual tailing. For apolar phases a proper deactivation process is yet to be found to achieve this aim.

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