SURFACE CHARACTERISTICS OF TREATED GLASSES FOR THE PREPARATION OF GLASS CAPILLARY COLUMNS IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The wettability of borosilicate and soda-lime soft glasses was studied by measuring critical surface tensions (CST) of the glasses and taking scanning electron micrographs (SEM) before and after various treatments: etching with hydrogen chloride gas, silanization, impregnation with surface-active agents, and combinations of these. Considerable increase in CST values was found after the etching of the soda-lime glass, and this effect could be explained by a geometrical model of the surface.

The CST values, together with the surface tensions of a series of gas chromatographic stationary phases, can help in the preparation of glass capillary columns, as was illustrated by SEM micrographs of coated internal surfaces of capillary columns.

INTRODUCTION

In gas–liquid chromatography, the performance of open tubular columns largely surpasses that of packed columns in separation power, speed of analysis and sensitivity. Especially in the analysis of biochemical compounds, which are often present in complex mixtures, high resolution is required. Because of their catalytic activity at higher temperatures, metal capillary columns can hardly be used in the gas chromatography of these thermo-labile substances of limited volatility. Consequently, one is forced to work with a less active material, that is, glass.

Open-hole glass columns can easily be drawn from thick-walled tubes in a wide range of dimensions. Besides their low cost, this is a definite point in favour of glass columns.

The wettability of glass capillary columns compared with metal columns, however, is poor. This may be attributed to two properties: firstly, most liquids do not

spread freely on a glass surface, but show a finite contact angle; secondly, the inner wall of a freshly drawn glass capillary column is fire-polished and thus, in contrast to steel, is extremely smooth. Therefore, glass capillary columns can only be prepared satisfactorily with a very limited choice of stationary phases (polydimethylsiloxanes), unless the glass receives a special pre-treatment prior to coating to make the phase spread or adhere to the wall.

In this paper, the effects of such treatments, firstly etching with gaseous hydrogen chloride, are discussed.

ANALYSIS OF THE PROBLEM

The wettability of a surface can be expressed in terms of "critical surface tensions" (CST, γ_c). Zisman[1] defined the critical surface tension as that value of the liquid surface tension (γ_L) above which liquids show a finite contact angle (θ) on a given surface. The value of γ_c is obtained from a plot of $\cos\theta$ vs. γ_L, which is usually a straight line; the intercept with the $\cos\theta = 1$ line gives γ_c.

In spite of their basic importance, the availability of contact angle and CST values is limited in the case of glasses, and data are found mainly in the non-chromatographic literature.

Recently, Dann[2] reconsidered the critical surface tension concept in terms of polar and non-polar contributions to the interfacial tension. It became clear that the concept should be used, with certain care, for high-energy surfaces (glasses, metals, minerals).

In an extensive comparative study by Fox et al.[3] and Hare and Zisman[4], the wetting properties of some high-energy surfaces were examined. It was found that in the case of many liquids factors other than surface tension can also control spreading, namely the formation of oriented monolayers or the presence of impurities.

Farré-Rius et al.[5] measured some CST data and these have been quoted many times. Recently, Gassiot-Matas et al.[6] and Bartle[7] reported contact angle and CST values, respectively, for a limited number of glass surface types and test liquids.

Lieng-Huang Lee[8] and Bascom[9] measured CST values on glass surfaces treated with a series of reactive organosilanes similar in structure to the compound which recently was found effective in glass capillary column preparation by Novotný and Grohmann[10].

To promote spreading of the stationary phase, the glass surface may be chemically or physically modified.

Chemical modifications of glass surfaces

The treatments mentioned in the literature are: silylation with polar silyl reagents[7,10–12], chlorination followed by a reaction with an alcohol[13,14], organo-lithium compound[14–17] or Grignard reagent[17,18], *in situ* formation of a polymer layer[14], carbonization of the wall[14,19] and application of surface-active agents[20–22].

The main difficulty with most types of intermediate layers is their low thermal stability. At higher temperatures, organic interlayers may decompose, detergents may desorb and polymers may swell.

Another difficulty arises from the fact that the film of the stationary phase inside a capillary column has a concave cylindrical surface; the surface tension of the

liquid tends to contract this surface, and induce the accumulation of the stationary phase into tiny droplets.

Physical modification of the surface (roughening)

On a rough surface, the situation is different, as the stationary phase will penetrate or retract itself into the scratches, holes and corners. The influence of surface roughness becomes apparent by a decrease in the (macroscopic) contact angle. Wenzel[23] gave the following equation:

$$\frac{\cos \theta'}{\cos \theta} = \frac{A'}{A} = r \tag{1}$$

where

θ = contact angle on the smooth surface;
θ' = contact angle on the roughened surface;
A = macroscopic surface area;
A' = microscopic surface area;
r = roughening factor.

This equation clearly illustrates the importance of surface roughening. The wall of a steel capillary is highly irregular[24]. Besides the better wetting properties of steel compared with glass, this seems to be an essential reason for the easier coating of steel capillary columns.

The importance of surface roughening has been stressed by Liberti[25]. He explained the success of the carbonization pre-treatment according to Grob[19] also in terms of roughening.

Glass can be etched with an alkali (sodium hydroxide, ammonia)[26-28] or with acids (hydrofluoric, hydrochloric), either in aqueous solution[29] or in the gaseous phase. Grob[14] was unable to obtain satisfactory results with etching columns by aqueous solutions. In general, a porous layer of silica is formed and adsorption is very strong, resulting in asymmetrical peaks. Tesařík and Novotný[30] consider that any etching procedure involving water yields undesirable effects. They developed etching procedures in the gaseous phase using hydrogen chloride, hydrogen fluoride or methyl trifluorochloroethyl ether (CH_3OCF_2CHFCl), which splits off HF on heating.

In a previous paper[31], we reported the etching of soft soda-lime glass columns with gaseous hydrogen chloride. Preliminary microscopic investigation indicated a very regular etching pattern. The coating of such columns with polar OV-225 silicone phase produced good columns for steroid analyses.

In a recent paper[32], the same method was used to produce columns with various polar coatings.

In our present study, the evaluation of the surface treatments is mainly "non-chromatographic". Instead of producing experimental glass capillary columns, sheet glasses were etched and CST values measured. These data and further scanning electron microscopic (SEM) pictures of the surface were primarily used as evaluating parameters. This involves the assumption that if the CST value measured after a certain treatment permits complete wetting for a certain stationary phase, a capillary column of a glass having the same composition, treated in the same way, and coated

by the same liquid, will be of high efficiency. This assumption seems to be justified by the chromatographic results already published[32].

The various etching procedures were studied microscopically with the aid of SEM. The micrographs revealed much about the etching procedures and the distribution of stationary phase on the roughened wall of the capillary. The microstructure of the glass surface has been studied by Tichane[33] for borosilicate glass and by Tichane and Carrier[34] for soda-lime glass using transmission electron microscopy and replica techniques. Although the resolving power of transmission electron microscopy considerably exceeds that of electron scanning microscopy, it may not be expected that this would be needed in the study of etching procedures of capillary columns, as the surface irregularities to be produced should be of the same or somewhat larger dimensions than the film of stationary phase, i.e., 0.5 μm. Therefore, SEM is the preferred method because of its easier technique for the preparation of the samples. Moreover, its great depth of field gives the image a three-dimensional appearance, which is very useful in the study of etching.

EXPERIMENTAL

Contact angle determinations

Sample preparations and treatments. Two kinds of glasses were used throughout the experiments: a borosilicate glass (Pyrex, Sovirel, Paris, France) and a soft glass (Schilling, Glasskeramik, Berlin, G.D.R.) with a higher alkali content. From both glasses, 5 × 5 × 0.5 mm sheets were prepared. Before measurements (as untreated glass) or treatments, the sheets were cleaned by rinsing with acetone and chloroform, then dried on a hot-plate at about 100–110°.

Treatments with two surface-active agents (benzyltriphenylphosphonium chloride, BTPPC, and trioctadecylammonium bromide, Gas Quat L) were performed according to Rutten and Luyten[22]; the glass sheets were rinsed in a 1% solution of the agent, dried over the hot-plate, rinsed in pure solvent and dried again. The period of the first rinsing was varied, as will be discussed.

For gas phase treatments (etching and/or silanization), the glass sheets were closed into glass bulbs. For etching with hydrogen chloride, the pure gas was drawn through the bulb; after forcing the air out, the bulb was sealed in a flame.

Silanization was performed in the gas phase by the vapourization of a mixture of hexamethyldisilazane and trimethylchlorosilane (5:1, v/v). The procedure was carried out again in a glass bulb, in nitrogen containing 20% vapour. Care was taken during the procedure to avoid any condensation of the silanizing agents on to the sample sheets.

Etching with methyl trifluorochloroethyl ether ("etching ether") was done also by the glass bulb technique.

Contact angle measurements were performed immediately after the treatments, except when otherwise stated.

Contact angle measurements. Measurements were carried out at room temperature by the sessile drop method using a goniometer microscope. As test liquids, four common stationary phases of reasonably low viscosity were chosen, according to Table I. Stationary liquids are very practical for this purpose because of their inherently low vapour pressure; however, no suitable liquid phase could be found with a surface

TABLE I

TEST LIQUIDS AND THEIR SURFACE TENSIONS

Room temperature data, measured in this study.

Test liquid	Surface tension (dyne/cm)
Squalane	29.7
Methylphenylsilicone, DC 704	36.5
Polyethylene glycol, Carbowax 400	46.7
1,2,3-Tris(2-cyanoethoxy)propane, Fraktonitril III	52.4
Formic acid	39.2
Nitrobenzene	45.5
Glycerol	64.5
Water	71.5

* The surface tension values have not been corrected (see Note added in proof on p. 100).

tension higher than that of Fraktonitril III, (52.4 dyne/cm). In all cases when a complete wetting by this liquid occurred, the CST value was referred to as >52.4 dyne/ cm. One series of determinations was made using more than four test liquids; these are also contained in Table I.

Surface tensions of the test liquids were determined with a du Noüy-type tensiometer (A. Krüss, Hamburg, G.F.R.), at room temperature. The surface tension values have not been corrected (see the Note added in proof on p. 100).

For contact angle measurements, a 1-μl droplet of the test liquid was applied on to the sample sheet. Several angle readings on both sides of the droplet were performed until equilibrium was reached. Before applying the next test liquid, the previous one was washed off by chloroform, then the sheet was allowed to dry on the hot-plate to avoid condensation of air moisture.

For each type of treatment, at least six parallel test glass sheets were produced. The average of all the parallel readings was accepted as the contact angle value.

CST values were determined graphically, constructing the diagram of cosθ values of the test liquids vs. their surface tensions.

Precision of CST determinations. The precision of the angle measurement itself was about 0.5°. However, the deviation between the results on parallel samples was considerably larger; besides, there was a difference between standard deviation of data for silanized samples and that of other samples. The standard deviation of the contact angle values for silanized samples was 3.1°, while that for all other contact angle data was 1.8°. They correspond to a standard deviatoin of about 3 and 2 dyne/cm, respectively, in CST values.

Scanning electron microscopy

The technique of the contact angle measurements obviously required flat surfaces that are large compared with capillary column dimensions. For taking SEM micrographs, however, curved surfaces are as satisfactory, and therefore small pieces of capillaries and capillary columns were chosen as samples.

The glass capillary columns were etched according to the methods already described[30–32]. Some turnings of the column were broken off, sealed under nitrogen

and kept aside for microscopic investigation. If etching was the only subject of the microscopic study, samples could be taken from various parts of the column, otherwise only from the ends to keep the column intact.

Immediately before the SEM investigation, the samples were split open lengthwise by means of a bench-vice and the resulting pieces were kept in a desiccator over silica gel. A layer of carbon and next a layer of gold were evaporated under vacuum on to the pieces, after which they were ready to be placed into the electron scanning microscope (Stereoscan, Cambridge Instruments, Cambridge, Great Britain).

RESULTS AND DISCUSSION

Glass, being a so-called "high-energy surface", is assumed to have a surface energy of the order of hundreds to a few thousand erg/cm². At high temperatures and under a strictly controlled atmosphere, a CST value of 270 dyne/cm has been reported[35]. Under less extreme conditions, the surface is always covered with adsorbed impurities, mainly water[3,4], and therefore its surface characteristics are determined by this surface layer and can change in an unpredictable manner.

First of all, the concept of critical surface tensions was verified by measuring contact angles on untreated Pyrex glass, using a series of test liquids of different structures. The results are given in Table II and Fig. 1. It can be seen that, in spite of the diversity of the test liquids, the $\cos\theta$ *vs.* surface tension plot is a straight line which defines a CST value well. All the following measurements were performed with the four stationary liquid phases according to Table I.
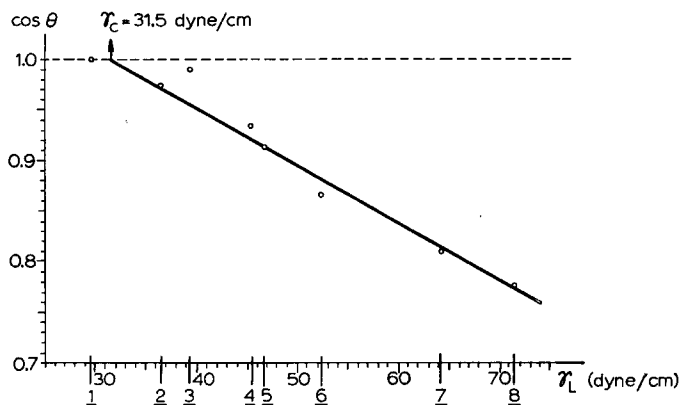

Fig. 1. Cosine of contact angles of various liquids on untreated Pyrex glass as a function of the surface tensions of the liquids. 1, Squalane; 2, silicone DC 704; 3, formic acid; 4, nitrobenzene; 5, polyethylene glycol Carbowax 400; 6, 1,2,3-tris(2-cyanoethoxy)propane Fraktonitril III; 7, glycerol; 8, water.

All the results are given in Table III. In the cases when the contact angle of only one liquid was different from zero, the CST value was obtained by drawing a straight line through this single point with the slope of the straight lines on the other diagrams. The slope being somewhat different in the various diagrams, CST values in these cases should be considered as approximations.

TABLE II

CONTACT ANGLES ON UNTREATED PYREX GLASS

Test liquid	Contact angle (°)
Squalane	0
DC 704	13
Formic acid	8
Nitrobenzene	21
Carbowax 400	24
Fraktonitril III	30
Glycerol	36
Water	39

TABLE III

CONTACT ANGLES AND CRITICAL SURFACE TENSIONS FOR VARIOUSLY TREATED GLASSES

No.	Type of glass and description of treatment*	Contact angle (°)				CST** (dyne/cm)
		Squalane	DC 704	PEG 400	Fraktonitril III	
1	Pyrex, no tm.	See Table II and Fig. 1				31.5
2	tm. BTPPC, st. overn.	0	15	23	28	30
3	tm. Gas Quat L, st. overn.	0	17	25	31	30
4	silanized	0	20	33	43	30.5
5	"etched" (HCl)	0	14	25	33	31
6	Soft, no tm.	0	15	23	30	30
7	tm. BTPPC, st. overn.	0	15	24	32	32
8	tm. Gas Quat L, st. overn.	0	16	28	37	34
9	silanized	0	14	29	38	34.5
10	HCl etched	0	0	0	0	>52.4
11	+ tm. BTPPC, r.	0	0	10	18	45
12	+ tm. BTPPC, st. overn.	0	11	22	29	34.5
13	+ tm. Gas Quat L, r.	0	0	17	26	42
14	+ tm. Gas Quat L, st. overn.	0	10	25	32	35
15	+ silanized	0	15	36	41	34.5
16	+ st. 45 min in $CHCl_3$	0	0	0	13	~50
17	HCl etched, 15 min	0	0	0	0	>52.4
18	+ r. in $CHCl_3$	0	0	5	16	46.5
19	HCl etched, 1 h	0	0	0	0	>52.4
20	HCl etched, r. H_2O, EtOH	0	0	15	26	45
21	same, + heated	0	0	10	16	44
22	Soft, heated	0	0	12	18	44
23	Soft, HCl etched, + air (24 h)	0	0	0	16.5	~50
24	HCl etched, washed H_2O then etched (3 times)	0	0	0	0	>52.4
25	Soft, etched ("ether")	0	0	0	0	>52.4
26	+ r. $CHCl_3$	0	0	0	10	~51
27	+ st. 45 min, $CHCl_3$	0	0	0	20	~46.5

* tm. = treatment (with); st. = steeping; overn. = overnight; r. = rinsing; air = left to stand in laboratory air.
** See Note added in proof.

Glasses without etching

The CST value of untreated (that is, chloroform-rinsed) Pyrex glass is found to be 31.5 dyne/cm (No. 1 in Table III), which is to be compared with the value of 28 dyne/cm found by Farré-Rius *et al.*[5] for acetone-washed Pyrex glass. The CST value found for untreated soft glass was 30 dyne/cm. These data agree also with the values reported by Shafrin and Zisman[36] and Bernett and Zisman[37] for glasses or practically any high-energy surface kept in a moist atmosphere and covered with an adsorbed polymolecular water layer.

It can be expected that any treatment which changes the composition of this more or less unstable surface layer will also change the CST value. Experiments Nos. 2, 3 and 4 with Pyrex glass and Nos. 7, 8 and 9 with soft glass were performed in order to study the effect of deactivating treatments. In the case of BTPPC and Gas Quat L treatment, the glass samples were left in a solution of the agent overnight, instead of a short rinsing as originally proposed[22]. Surprisingly, the change in CST values was rather small: within, or slightly greater than the experimental error. Chromatographic experience, however, is not in contradiction with this result: all the stationary phases that have been applicable to the untreated glass capillary could be used after BTPPC or Gas Quat L treatment, as well as after silanization.

Glasses etched by gaseous hydrogen chloride

In experiment No. 5, Pyrex glass was treated with hydrogen chloride gas for 2 h at 360–380°. No change in transparency could be observed. Fig. 2 shows the micrograph of a Pyrex glass tube etched under identical conditions. Only very few crystals can be observed and it is even questionable whether these originated from the etching,
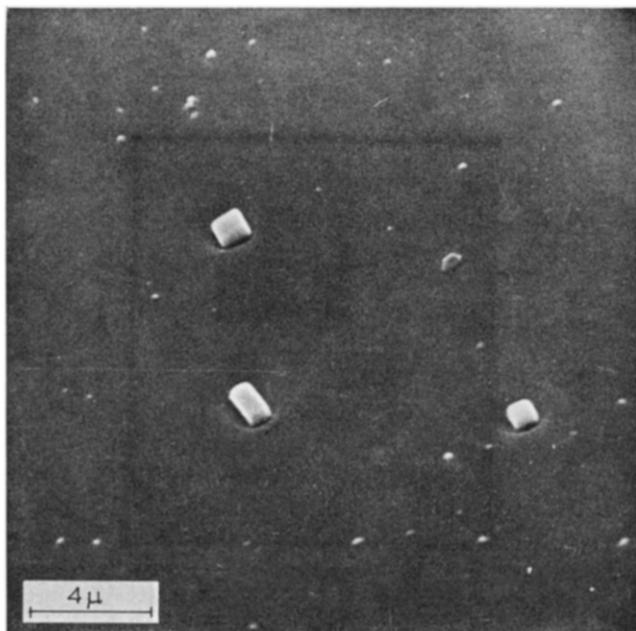

Fig. 2. Scanning electron micrograph of an "etched" Pyrex glass surface. Etching was made with HCl gas for 2 h at 360–380°.

or were already present before etching. Pyrex glass sheets showed practically no change in CST, revealing the absence of any beneficial effect. After etching soft glass (No. 10) the samples turned opaque white because of the formation of a microcrystalline layer of sodium chloride[32]. A CST value of >52.4 dyne/cm (the highest γ_L value involved) resulted. The SEM picture of the same surface (Fig. 3) shows these sodium chloride crystals, regularly distributed across the apparently smooth surface. This type of roughening can easily be correlated to a model, and the effect of the etching could be predicted by means of eqn. 1. Tamai and Aratani[38] successfully applied a more complicated model to a much less regularly roughened glass surface.
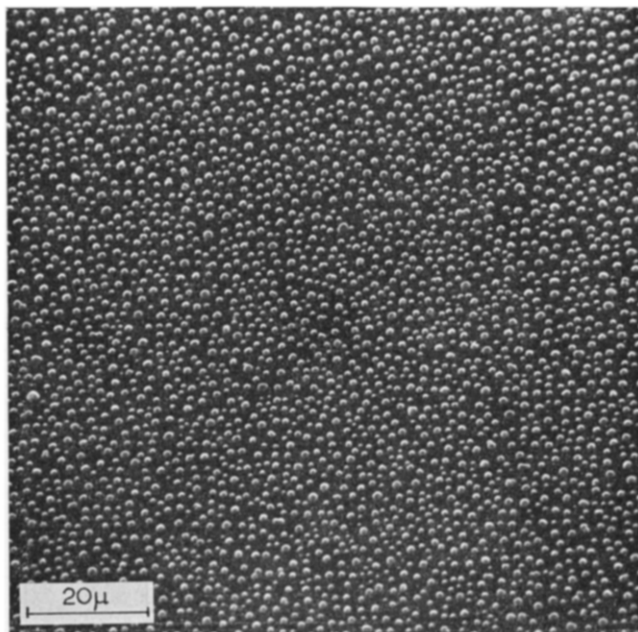
Fig. 3. Scanning electron micrograph of an etched soft glass surface. Etching conditions as in Fig. 2.

Model of the surface increase after etching

The particles on the etched surface can be considered as cubes or, more generally, as truncated pyramids, thus taking some distortion as the consequence of the deteriorating effect of moisture into consideration also. Let the fraction x of the originally smooth surface area A be covered by truncated pyramids (Fig. 4). Introducing
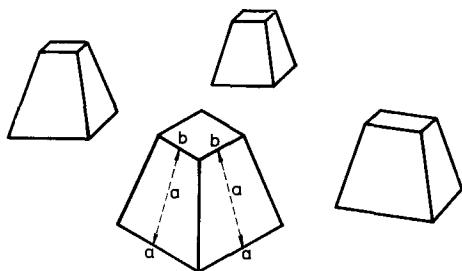

Fig. 4. A truncated pyramid as a distorted cube (see explanation in text).

a distortion factor, $q = b/a$ $(0 \leqslant q \leqslant 1)$, the surface area of the truncated pyramid is $a^2[(q + 1)^2 + 1]$. As the surface area covered by the truncated pyramid is a^2, then it follows for the increase ratio, F, that

$$F = (q + 1)^2 + 1$$

F applies to the covered fraction x of the surface; the overall increase factor r will be

$$r = \frac{A'}{A} = x F + (1 - x) = x (F - 1) + 1 \tag{2}$$

Putting the value of F into eqn. 2:

$$r = x(q + 1)^2 + 1 \tag{3}$$

Let us define in connection with etched surfaces a "critical contact angle", θ_c, which is the contact angle of a hypothetical liquid on the smooth surface which will just spread over the roughened surface. With θ_c we obtain from eqn. 1:

$$\frac{1}{\cos \theta_c} = r \tag{4}$$

and with eqn. 3 we obtain

$$\theta_c = \text{arc cos } [x(q + 1)^2 + 1]^{-1} \tag{5}$$

Note that r and θ_c are independent of a, that is, of the size of the particles. However, practical requirements of column preparation demand that the size of the particles be of the same dimensions as the thickness of the liquid film.

In Fig. 5, θ_c is plotted *vs.* x for the two limiting values of q, $q = 1$ (undistorted
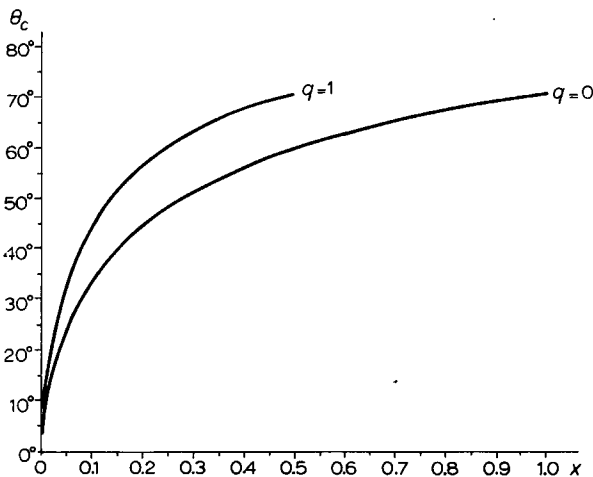

Fig. 5. The "critical contact angle" as a function of the fraction of the surface covered with cubes (upper curve, $q = 1$) or pyramids (lower curve, $q = 0$).

cubes) and $q = 0$ (pyramids). It can be seen that the curves are non-linear: the first few percentages of coverage have the largest effect; *e.g.*, 10% coverage increases θ_c from 0 to 34–44° (depending on q), which corresponds (see Fig. 1) to at least 50 dyne/cm in CST.

This has several consequences. (i) On etched soft glass samples, the coverage of the surface is considerably greater than 10% (see SEM picture, Fig. 3) and therefore the CST value should be considerably higher than 50 dyne/cm. Quantitative estimation of the CST value for the roughened surface is difficult, because linearity of the $\cos \theta$ *vs.* γ_L line cannot be checked for γ_L values higher than that of Fraktonitril III, that is, 52.4 dyne/cm. (ii) A surface etched with hydrogen chloride should be stable towards disturbing effects; a decrease in the coverage from, *e.g.*, 30 to 10% (or a serious distortion of the cubes, which has the same effect), that is, to one third of the original value, results in about a 30% decrease in θ_c. This means that θ_c decreases to a value of not less than 34–44°, which still permits full spreading for practically all stationary phases. Therefore, no coverage of the surface of more than 10–12% seems to be necessary to reach an ultimate gas chromatographic aim: to make the column wall coatable by any stationary phase. However, column walls with more than 12% coverage have a unique advantage: such surfaces inherently contain a reserve against attack; the higher the coverage, the larger is the reserve.

Stability of the etched surface*

The results of two deteriorating effects were tried: washing with a solvent, and standing in laboratory air.

Rinsing for a few seconds in chloroform was made regularly, several times in the course of the contact angle measurements, without any visible and measurable effect. However, immersion in chloroform for 45 min (Expt. No. 16) decreased the CST to 50 dyne/cm from the value of 52.4 dyne/cm and the same effect was produced on standing for 24 h in the laboratory air (Expt. No. 23). These results can obviously be explained by the effect of moisture on the fine structure of the microcrystalline layer of sodium chloride.

Effect of etching time

Experiments Nos. 17, 18 and 19 show that even etching for 15 min will increase the CST above 52.4 dyne/cm, but a single rinse for a few seconds with chloroform causes a considerable decrease (to 46.5 dyne/cm). Etching for 1 h resulted in a coverage dense enough to keep full wettability even after solvent rinsing. For column preparation, a 2-h etching period was acceptable.

Further treatments of the etched surfaces

Analysis of biological substances is possible only after deactivation of the glass surface[22]. Either a special treatment is applied for this purpose (such as those involved in this study) or, if the etched surface has been coated with a strongly polar phase, the phase itself can have a deactivating effect[31,39].

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* It should be noted that in contrast to other wettability data, results for stability measured on sheets should be correlated with small-bore capillaries with certain care, because the internal walls of the capillaries are better protected against attacking effects. However, comparison with other results obtained also with sheet glasses is possible without any restriction.

There are, however, stationary phases of medium polarity (*e.g.*, OV-17, OV-210) that spread freely after an etching procedure, but for which the surface still needs deactivating treatment. Therefore we examined whether these treatments have any deteriorating effect on the CST value and to what extent.

Experiments Nos. 11, 12, 13 and 14 show that if the etched samples were left in the solution of either of the two surface-active agents overnight, CST values decreased to 34.5 and 35 dyne/cm. If, however, only a short rinsing was performed, as had originally been proposed[22], the decrease was less, to 45 and 42 dyne/cm. Silanization had also a deteriorating effect (Expt. No. 15).

Effect of thorough cleaning

Assuming that increased wettability of the soft glass after etching results entirely from the increased surface area, it would be expected that removal of the microcrystalline sodium chloride would restore the original CST value. However, washing the etched soft glass samples with water, then ethanol, and drying over the hot-plate (No. 20), the CST value of the resulting transparent surface was found to be 45 dyne/cm. It remained the same after heating for several hours at 360° (No. 21).

Fig. 6 shows the surface of a hydrogen chloride-etched soft glass tube after washing with water. Very small particles (0.3 and 0.1 μm) can be observed.

The treatment of the surface with gaseous hydrogen chloride at high temperatures and the subsequent washing and drying can be interpreted as a thorough cleaning, which changes the original surface layer and leaves an adsorbed water film of only a few molecules thick. The 45 dyne/cm CST value is in good agreement with the values
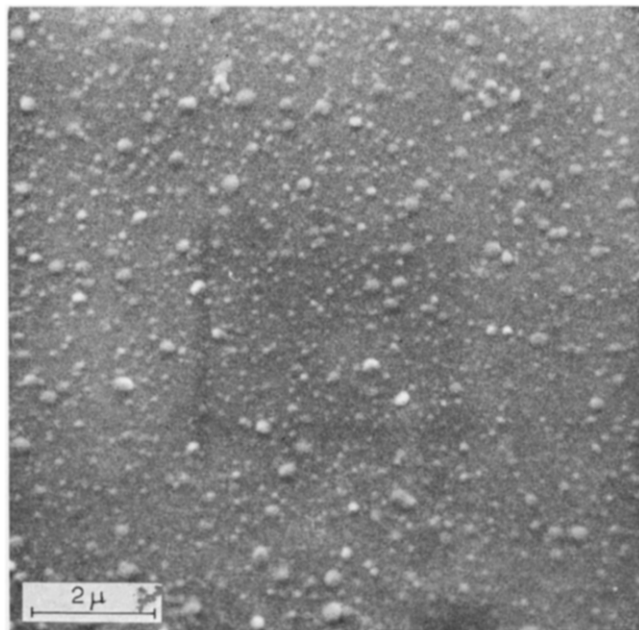

Fig. 6. Scanning electron micrograph of an etched soft glass surface after washing with water. Etching conditions as in Fig. 2.

reported by Shafrin and Zisman[36] for a thoroughly cleaned and dried soda-lime glass surface, and further with the results of Farré-Rius *et al.*[5] for a chromic acid-treated Pyrex glass surface. The supposition is further supported by experiment No. 22; a CST value of 44 dyne/cm resulted on simply heating an untreated sample at 360–380° for 3–4 h. However, the clean state of these surfaces proved not to be stable: after standing overnight in laboratory air, CST values decreased irreproducibly to 28–36 dyne/cm.

Etching with the "etching ether"

Etching soft glass samples according to the method of Tesařík and Novotný[30] (Nos. 25, 26, 27) resulted in a CST value higher than 52.4 dyne/cm, but a single rinsing with chloroform decreased it to 51 dyne/cm, and steeping for 45 min in chloroform decreased it to 46.5 dyne/cm. As the change in transparency was hardly visible in this case, it indicates that probably attack of the whole glass structure occurred, instead of the development of a microcrystalline layer (SEM picture). This difference results in a less stable effect because of the lack of reserve. Fig. 7 shows the surfaces of a capillary column etched with "etching ether". Besides the formation of crystals, it can be seen that the glass surface is not smooth, as opposed to the etching with hydrogen chloride. Apparently the hydrogen fluoride attacks the vitreous framework.

Repeated etching

Removal of the sodium chloride layer and etching again, repeated three times,
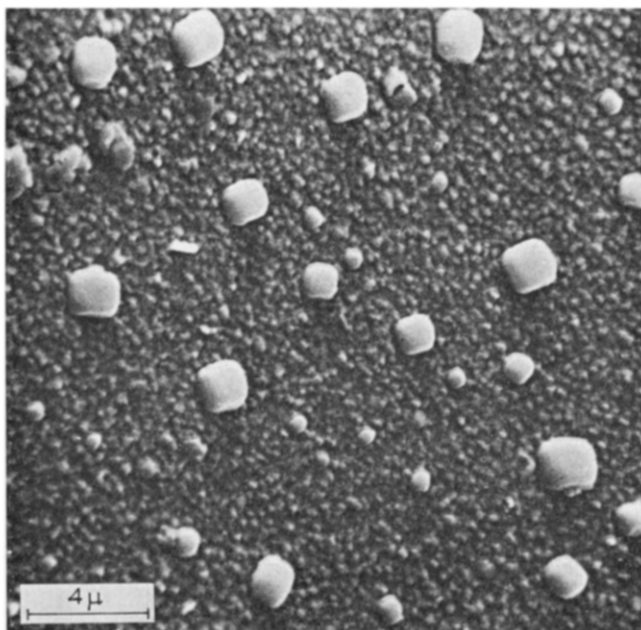

Fig. 7. Scanning electron micrograph of a soft glass surface etched with methyl trifluorochloroethyl ether for 2 h at 350°.

showed that after the third etching the CST value still remained above 52.4 dyne/cm, and it had the same stability as after the first etching.

Temperature dependence of the contact angle and CST values

All the data listed in Table III were measured at room temperature. However, as columns are to be used at higher temperatures, the validity of the conclusions at higher temperatures should be established. Contact angles of some stationary phases were measured on glass samples as a function of temperature up to 250° in an apparatus not described here. The results were of low reproducibility; the only conclusion that applies to all of the data is that contact angles never increased with temperature. This means that, if a stationary phase wets the surface at room temperature, it should wet it at higher temperatures also. This is in agreement with the data of Gassiot-Matas et al.[6] and with those of Shafrin and Zisman[40], who stated that at higher temperatures CST values would decrease, but the same applies to the surface tensions of the liquids as well. The resulting effect will be a decrease in the contact angle or, in limiting cases, θ will be unchanged.

Micrographs of coated columns

The wettability of the column wall by the stationary phase can be correlated with the critical surface tension data using the surface tension of the stationary liquid. The surface tensions of a number of stationary phases, the viscosity of which permitted simple room temperature measurements, are given in Table IV[41]. Micrographs were taken from a selection of etched and subsequently coated columns in order to study the effect of surface roughening on the actual distribution of the stationary phase. The

TABLE IV

SURFACE TENSIONS OF GAS CHROMATOGRAPHIC STATIONARY LIQUID PHASES[41]
Room temperature data.

| Stationary phase	Surface* tension (dyne/cm)
OV-101 (dimethylsilicone)	22.0
QF-1 (trifluoropropylsilicone)	26.8
OV-210 (trifluoropropylsilicone)	25.7
1-Octadecene	28.9
Didecyl phthalate	30.1
Citroflex 4 (tributyl citrate)	32.1
UCON 50 LB 550X	33.1
OV-17 (methylphenylsilicone)	33.5
Apiezon J	34.7
OV-225 (cyanopropylphenylsilicone)	36.4
UCON 50 HB 2000	37.4
Dimethylsulpholane	40.0
Tricresyl phosphate	· 41.5
Polyppylene sebacate	41.9
OS-124 (polyphenyl ether)	47.9
β,β'-Oxydipropionitrile	49.9
Diethylene glycol succinate	52.7

* See Note added in proof.
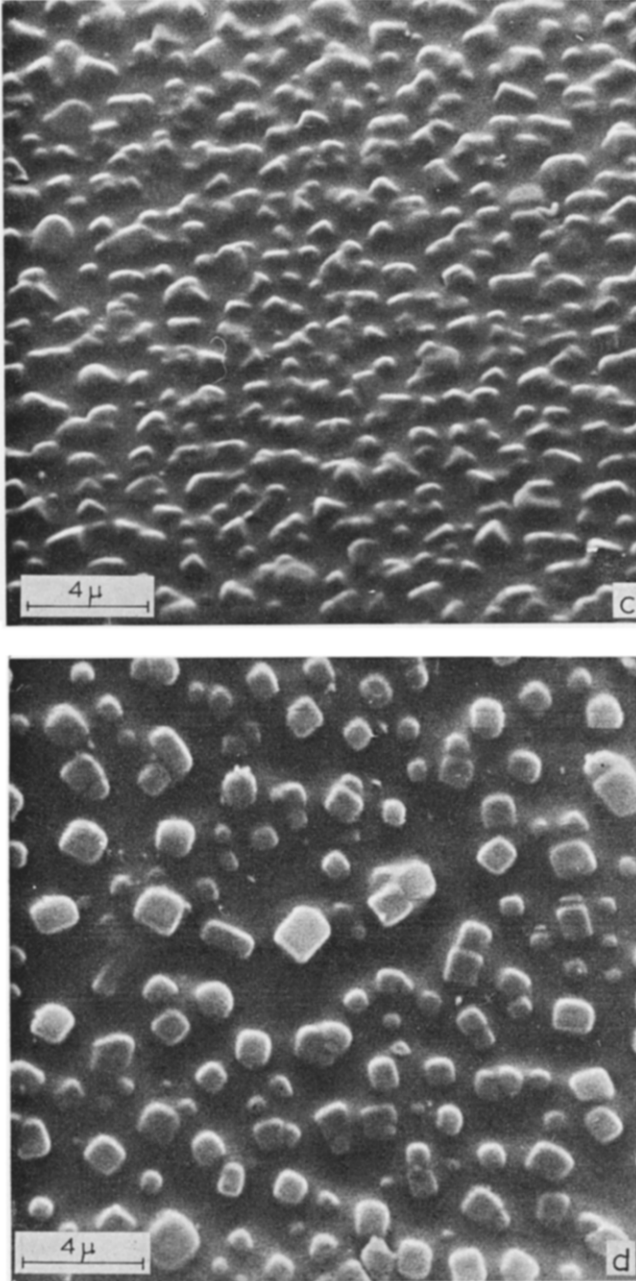
Fig. 8.

4 μ

c

4 μ

d
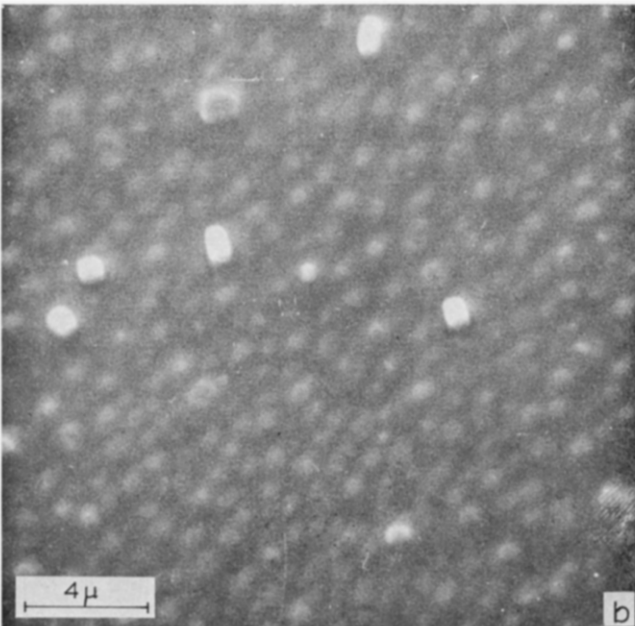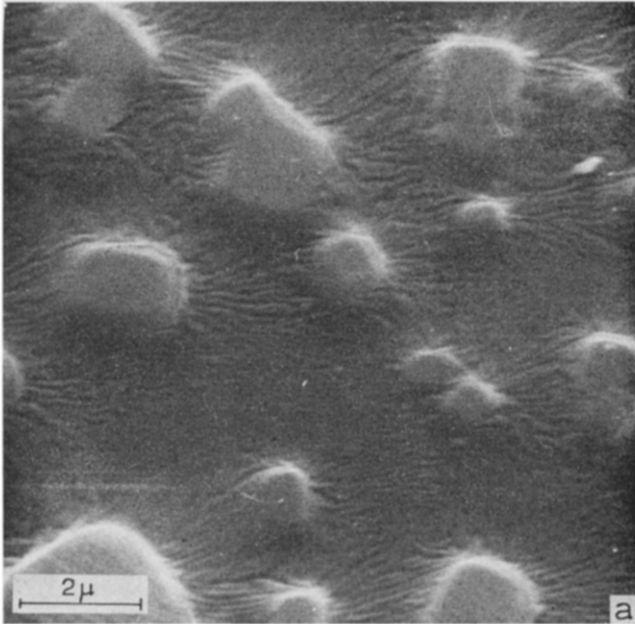
Fig. 8. Scanning electron micrographs of the internal wall of etched soft glass capillary columns. Coating: (a) SE-30; (b) OV-210; (c) SP-2401; (d) OV-225.

stationary phases were SE-30, OV-210, SP-2401, OV-225 and Dexsil 300 GC (Figs. 8–10); the thicknesses of the layers were about $0.2–0.3\,\mu$m. SE-30 (Fig. 8a) spontaneously wets the smooth glass surface. The microphotograph presented here is only
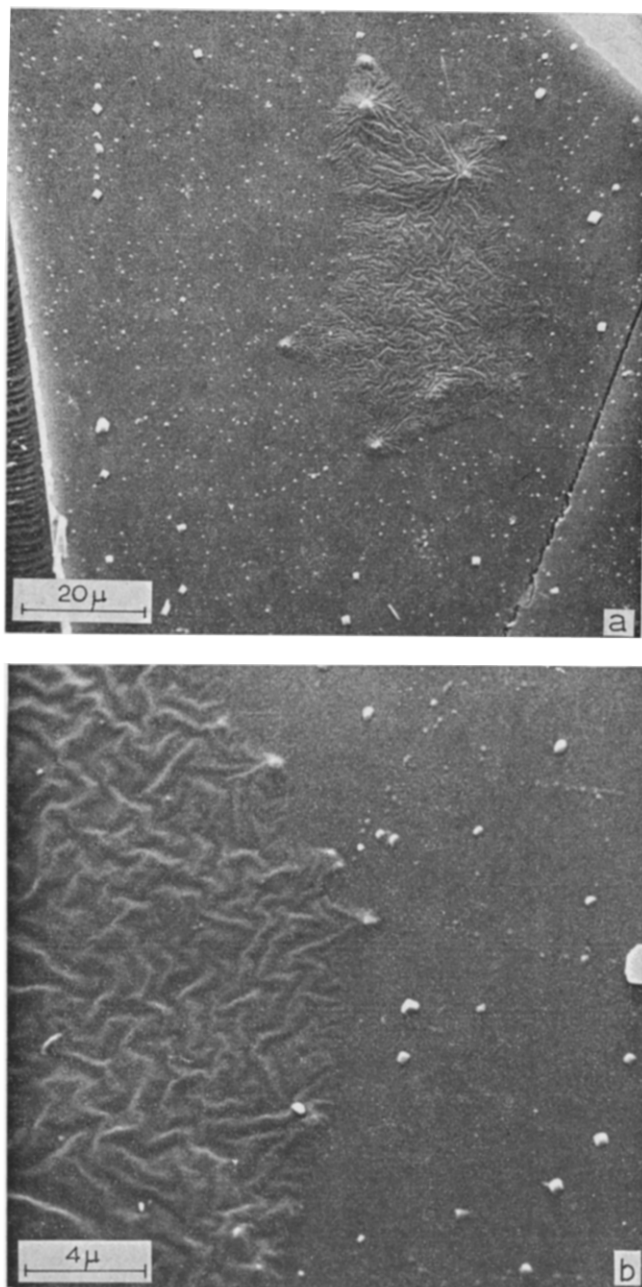
Fig. 9. Scanning electron micrographs of the internal wall of a low-efficiency glass capillary column coated with Dexsil 300 GC. (b) is an enlargement of part of (a).

intended to illustrate the distribution of a low-surface-tension phase on the etched glass surface. The other three stationary phases (OV-210, SP-2401 and OV-225) (Fig. 8b–d) do not wet the smooth glass surface unless etched. It can be observed from the
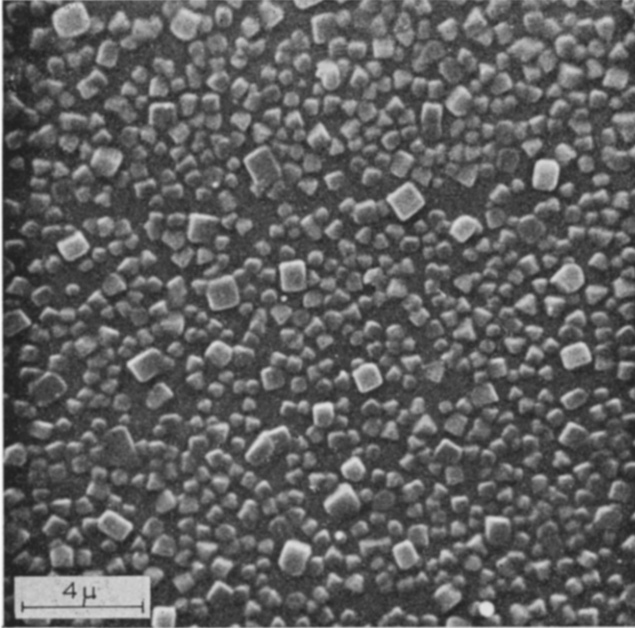
Fig. 10. Scanning electron micrograph of the internal wall of an etched and silanized soft glass capillary column, coated with Dexsil 300 GC as stationary phase.
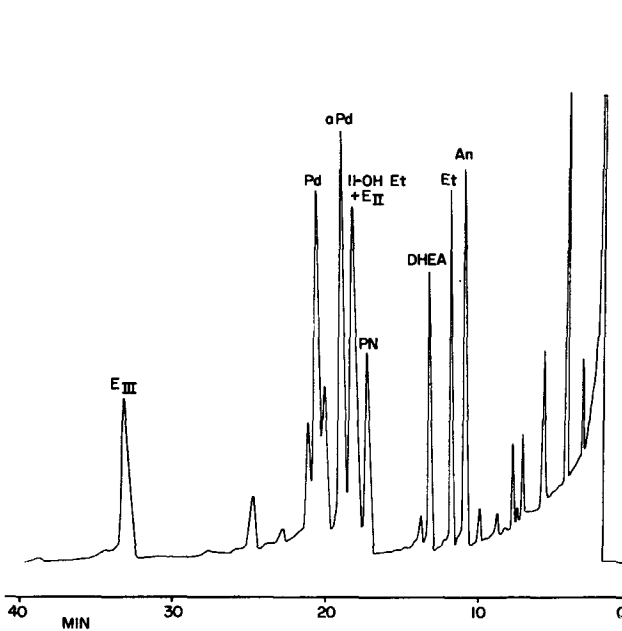

Fig. 11. Chromatogram of steroid methoxime-trimethylsilyl (MO-TMS) derivatives on an HCl-etched glass capillary column coated with SP-2401 stationary phase. Sample: synthetic mixture; An = androsterone; Et = etiocholanolone; DHEA = dehydroepiandrosterone; PN = pregnanolone; E_{II} = oestradiol; 11-OHEt = 11-hydroxyetiocholanolone; Pd = pregnanediol; aPd = allopregnanediol; E_{III} = oestriol. Column, 31 m × 0.25 mm; carrier gas, nitrogen, 0.7 atm; temperature, 200° (isothermal); film, 0.2 μm.

micrographs that the stationary phase is regularly distributed between the particles. In one case (OV-210), there is even complete coverage of the crystals. Even OV-225, which has a high surface tension (38.2 dyne/cm), is regularly distributed. The performance of these columns was good. Fig. 11 shows a chromatogram of a steroid mixture on the SP-2401 column. The performance of the OV-225 column was also very good[31,32].

Dexsil 300 GC does not wet the surface of smooth glass. Fig. 9 shows a non-etched soft glass capillary column "coated" with Dexsil 300 GC. In this particular column, droplets were soon formed during the conditioning at 230°. Consequently, its performance was very bad. The micrographs show only some patches of the phase adhering to some crystals that are always present on a glass surface. Fig. 10 shows an etched and subsequently silanized column coated with Dexsil 300 GC. No "pooling" of the phase is observed. The performance of this column was very good, as illustrated in Fig. 12 by a chromatogram of steroids.
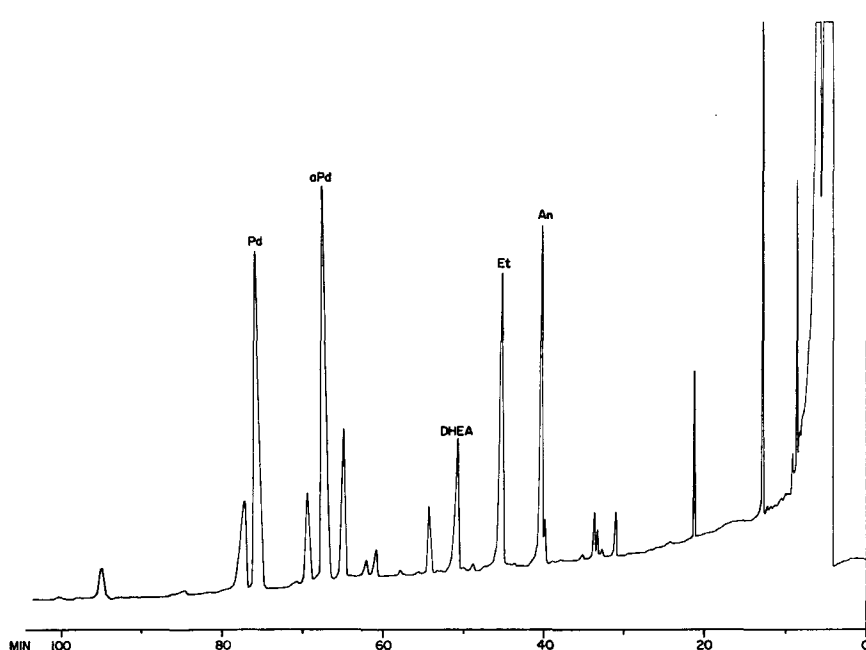

Fig. 12. Chromatogram of steroid TMS derivatives on an HCl-etched glass capillary column coated with Dexsil 300 GC stationary phase. Sample components as in Fig. 11. Column, 46 m × 0.25 mm; carrier gas, nitrogen, 1.6 atm; temperature, 230° (isothermal); film, 0.3 μm.

CONCLUSIONS

It has been proved that the concept of critical surface tension can be successfully applied to untreated and treated glass surfaces. It was possible to develop a simple model for the etched glass surface. By means of this model it could be shown that the etching method described produces a surface that possesses considerable reserves to compensate for deterioration effects. The usual deactivation treatments for glass columns cause a decrease in the CST value, but for the medium-polarity, medium-

surface-tension stationary phases, which generally require such treatments, the glass surface remains wettable afterwards.

Thorough cleaning of the glass also results in an increase in wettability, but the sensibility towards deterioration effects is high.

All of the above results can be applied to coating capillary columns. From Tables III and IV, the success or failure of a column preparation can be predicted, as far as the surface treatments discussed here are involved. According to our practical experience, the column will be of high efficiency when the critical surface tension value exceeds the γ_L of the stationary phase and, on the other hand, the column will be of low efficiency if $\gamma_c - \gamma_L$ has a negative value. Hence the quantity $\gamma_c - \gamma_L$ can be taken as a measure of the coatability of the column wall by the stationary phase.

From this point of view, the etching procedure with gaseous hydrogen chloride is very satisfactory, because the increase in CST is high. Even after deterioration treatments it exceeds the surface tension of most stationary phases. From the microscopic point of view, the etching with hydrogen chloride gas produces a very regular surface roughening of the right dimensions. Finally, it can be stated that the etching procedure has no serious deterioration effect on the adsorptive properties of the column wall. In our experience, the deactivating treatments which are sometimes necessary can be performed more easily than for a non-etched column.

NOTE ADDED IN PROOF

The surface tension values given in this paper were not corrected using the tables of Harkins and Jordan[42] and Fox and Chrisman[43]. Therefore these values are up to 10% too high. The same applies to the CST values. Consequently the estimation about the wettability remains valid provided that consistently uncorrected values are compared. The corrected values which were kindly supplied to the authors by Franken[41] are (in dyne/cm): OV-101, 20.4; QF-1, 24.6; OV-210, 23.6; 1-octadecene, 27.6; didecyl phthalate, 28.5; Citroflex 4, 30.4; UNCON 50 LB 550X, 31.4; OV-17, 31.4; Apiezon J, 33.2; OV-225, 34.6; UNCON 50 HB 2000, 35.7; dimethylsulpholane, 38.1; tricresylphosphate, 39.5; polypropylenesebacate, 40.2; OS-124, 46.1; β,β'-oxydipropionitrile, 48.6; diethylene glycol succinate, 50.9; squalane, 27.8; 1,2,3-tris(2-cyanoethoxy)propane, 49.2; Carbowax-400, 44.2.

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