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PREPARATION OF GLASS CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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1. INTRODUCTION

Glass capillary column gas chromatography is presently in an era of rapid growth. Once a novel separation theory, capillary column gas chromatography has become a vital tool for analytical chemists worldwide. The resolving power of the capillary column has led to its use in studies of many analytical problems involving complex organic mixtures. The literature today is filled with new applications of this technique in solutions of complex real-world problems. A number of excellent reviews are available that describe the development of the glass capillary column[1–10].

Although efficient sample introduction devices, sensitive detectors, sophisticated electronically controlled ovens, high-speed recorders and other devices are essential components in modern high-resolution gas chromatographic systems, the column remains the heart of the analytical instrument. The growth in the use of capillary column chromatography parallels the development of column technology. As improvements in surface deactivation and coating efficiency have been made, demands for more sensitive detectors, more carefully controlled oven temperatures, faster recorders and more efficient sample introduction devices have been made.

In 1958, Golay[11] introduced the theory of capillary gas chromatography. Since then, many technological developments have been made in the columns themselves. Although early studies used various materials (plastics, copper, nickel, stainless steel) for the fabrication of capillary columns, glass has essentially replaced these materials today. The reasons for this are low catalytic activity of glass compared with these other materials and the ability to modify the glass surface easily, both physically and chemically, to accomodate better selected stationary phases and to make it more inactive towards trace organic compounds.

There are two goals that must be met in preparing ideal glass capillary columns. Firstly, the surface must be completely deactivated, such that the column wall does not participate in retention or adsorption of any components to be separated. In addition, the capillary wall must be modified such that the stationary phase can coat evenly on the surface. These goals have led chromatographers to study glass surface chemistry in more detail.

The objective of this review is to combine the wealth of information contained in the literature on the preparation of glass capillary columns with what is presently known about the glass surface chemistry. It is hoped that this approach will help to emphasize the important concepts in glass capillary preparation and at the same time to expose many incorrect and inconsistent statements contained in the literature.

In the last year, fused silica capillary columns have become increasingly important and the continuing growth of their application can be predicted. As mentioned below, fused silica may be considered as the "ideal glass". Although its characteristics are somewhat different than those of glass (*e.g.*, flexibility), most of the techniques developed for glass capillary columns are also fully applicable to fused silica columns. Whenever special requirements exist, these will be mentioned in this review.

The correct technical name of the columns discussed herein is *open-tubular columns*, expressing that not the smallness but the openness of these columns is the important characteristic[6]. However, as the term "capillary column" is now used almost universally, we are also using this term as a convenient abbreviation.

2. GLASS SURFACE CHEMISTRY

2.1. Composition and structure of the bulk glass phase

The commercially available glasses which are used for fabrication of capillary columns contain silica (SiO_2) as the major component. However, there is still considerable controversy over the exact structure of even the simplest glass, fused silica. Warren[12] has shown that the silica in glass has the usual tetrahedral arrangement of four oxygen atoms bonded to each silicon atom. The silica tetrahedra are linked together at slightly distorted angles to give a three-dimensional polymer. Thus, the silicon and oxygen atoms form irregular six-membered rings (Fig. 1A) which are relatively stable because the Si–O–Si angle is easily deformed. In different allotropic forms, bond angles between 150° (quartz) and 180° (β-cristobalite) are formed[13].

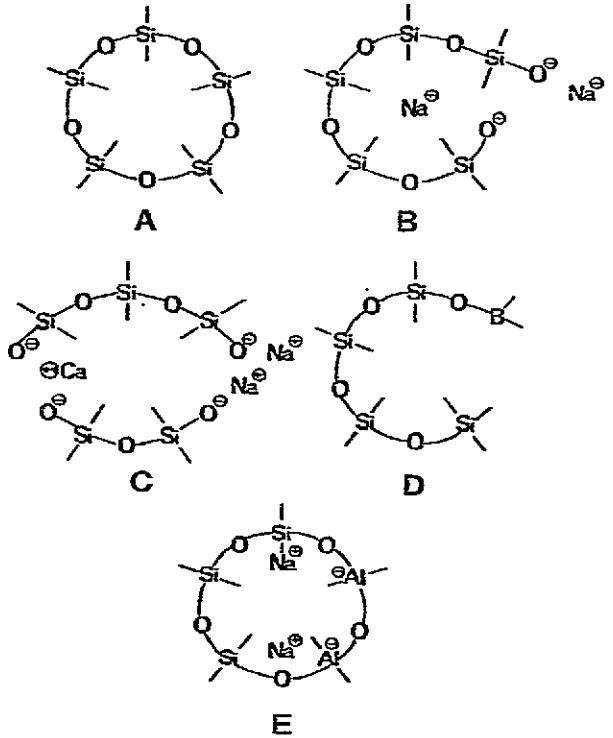


Fig. 1. Schematic representations of glass structures. Si–O–Si indicates bonding through bridging oxygens common to two SiO_4 tetrahedra.

Fused silica, the "ideal" glass, possesses a highly cross-linked, three-dimensional structure, and thus has a high melting point, a low coefficient of thermal expansion and high resistance to chemical attack[14].

Various metal oxides are added to silica during the glass manufacturing process in order to modify some of its chemical and physical properties. An excellent review of the composition, manufacture and properties of glasses has been published[14]. Soda

(Na_2O) "softens" the glass by disrupting Si–O–Si bonds, as shown in Fig. 1B. This decreases its viscosity, increases its thermal expansion, increases its solubility in aqueous media and lowers its chemical durability. Calcium oxide (CaO) and magnesium oxide (MgO) are added to sodium silicate glasses (Fig. 1C) to decrease their solubilities and to make them more chemically durable. Boric oxide (B_2O_3) enters the silica network as shown in Fig. 1D. The boron atom is surrounded by only three oxygen atoms in trigonal coordination. This planar structure, when inserted into the silica tetrahedral environment, exhibits weak forces in one direction and softens the glass. The addition of B_2O_3 does not increase the expansion of glass as much as the alkali or alkaline earth metal oxides. The addition of alumina (Al_2O_3) to alkali silicate glasses increases their viscosity, increases their resistance to devitrification and enhances their chemical durability by assuming a tetrahedral coordination and re-forming Si–O bonds which were severed by alkali additions (see Fig. 1E).

Although at one time glass was considered to have a simple homogeneous structure, it is now apparent that many, if not all, glasses consist of two or more phases that are in equilibrium with each other. This is exemplified by the borosilicate systems. During heat treatment the glass separates into two distinct, but continuous glassy phases (B_2O_3 and SiO_2) that can be seen as a turbidity that can vary from clear to complete milkiness, depending on the thermal conditions[15]. Fig. 2 shows this phase separation phenomenon as evidenced by an electron micrograph of a fractured sample of borosilicate glass heated in air at 800°C[16].

The most commonly used glasses for the construction of glass capillary columns are soda-lime (soft) or borosilicate (Pyrex) types. The borosilicate glasses are

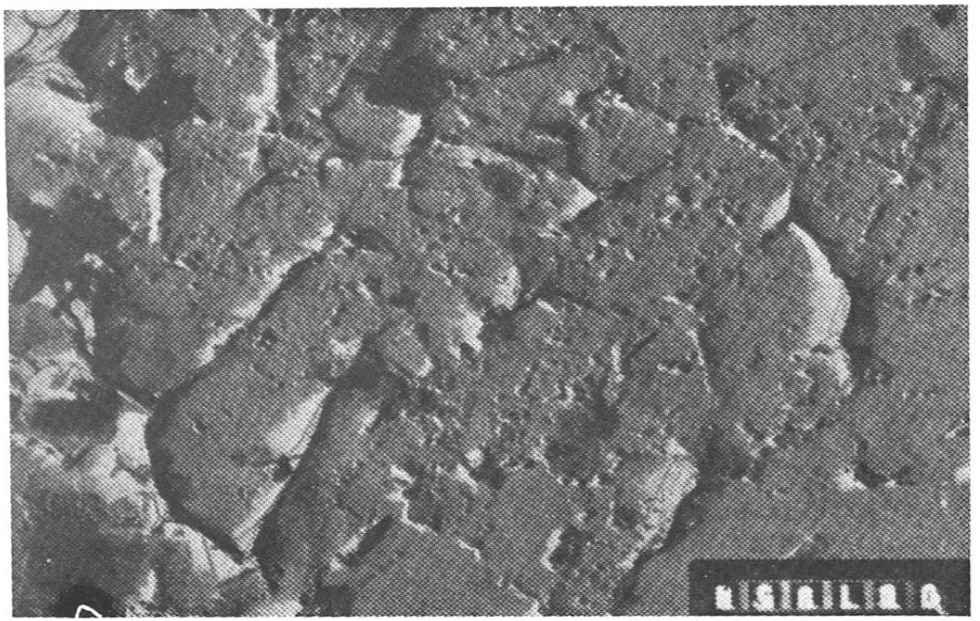


Fig. 2. SEM of Pyrex glass heated in air at 800°C. Reproduced from the *Journal of Chromatographic Science*[16] by permission of Preston Publications, Inc.

more thermally durable, having a softening temperature about 125°C higher than the soft glasses. Capillary columns drawn from the borosilicate glasses also tend to be less fragile than geometrically similiar soft glass columns. Soft glasses tend to be alkaline in nature due to the high content of Na_2O while the borosilicate glasses are somewhat acidic as a result of the B_2O_3 phase.

The bulk compositions of a number of glasses used in the manufacture of glass capillary columns for gas chromatography are given in Table 1. As can be seen, differences in composition exist even among those belonging to the same general classification, *e.g.*, soft glass. In addition, capillaries fabricated from uranium and potash soda lead glasses were recently studied[17].

TABLE 1

BULK GLASS COMPOSITIONS

Component	*Type of glass**							
	AR	*RÖ*	*B44*	*Unihost*	*PN*	*R6*	*PWM*	*7740*
SiO_2	67	70	70.2	68.6	67.0	67.7	71.4	81.0
Na_2O	15	17.8	12.6	17.8	13.5	15.6	15.0	4.0
CaO	7	8.8	6.0	5.5	6.5	5.7	4.6	0.5
ZnO	7	0.5	—	—	8.0	—	—	—
Al_2O_3	2.5	2.3	4.2**	3.9	3.0	2.8	2.2	2.0
B_2O_3	—	—	1.0	—	2.0	—	—	13.0
MgO	—	—	1.9	2.9	—	3.9	4.0	—
BaO	—	—	—	—	2.0	0.8	0.8	—
MnO	—	0.6	—	—	—	—	—	—
K_2O	—	—	—	1.3	—	0.6	1.7	—
Other elements	—	Traces	—	—	—	—	0.2	—

* Symbols: AR = A.R. glass, Schott-Ruhrglass, Wertheim, G.F.R. RÖ = Röntgen glass 05, Philips, Eindhoven, The Netherlands. B44 = Verre sodocalcique B44, Choisy-le-Roi, France. Unihost = Soda-lime soft glass, Jablonec Glass Works, Czechoslovakia. PN = Soda-lime soft glass, Jablonec Glass Works, Czechoslovakia. R6 = R6 Flint, soda-lime soft glass, Kimble Glass Works, Toledo, OH, U.S.A. PWM = Soda-glass, Chance, Smethwick, Great Britain. 7740 = Pyrex 7740 glass, Corning Glass Works, Corning, NY, U.S.A.

** Also includes Fe_2O_3.

2.2. *Glass surface chemistry*

Of more importance than bulk glass composition in capillary gas chromatography is the actual glass surface composition and structure. Considerable progress in the characterization of glass surfaces has been possible through the development of a number of new surface analytical techniques, *e.g.*, Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), ion scattering spectroscopy (ISS) and X-ray photoelectron spectroscopy (XPS or ESCA). Through the use of these tools, it is now known that the composition of a glass surface is usually significantly different from the bulk composition[18–21]. In addition to the bulk composition, factors such as environment, fabrication variables and thermal history all affect the formation and stability of surface layers developed on glasses[22,23]. It is from these surface

layers that important molecular interactions arise affecting the preparation and chromatographic performance of glass capillary columns. AES determinations of surface compositions of freshly drawn, untreated, glass capillary columns as compared to their bulk compositions are given in Tables 2 and 3[24].

TABLE 2

COMPOSITION OF KIMBLE R6 FLINT GLASS CAPILLARIES

Element	*Bulk (atomic-%)*	*Surface (atomic-%)*
Si	23.4	11.4
O	59.4	57.8
Na	10.4	16.0
Ca	2.1	12.0
B	1.0	1.6
K	0.3	1.2
Mg	2.0	—
Ba	0.2	—
Al	1.2	—

TABLE 3

COMPOSITION OF PYREX 7740 GLASS CAPILLARIES

Element	*Bulk (atomic-%)*	*Surface (atomic-%)*
Si	25.5	24
O	64.0	69
Na	2.5	—
Ca	0.2	—
B	7.0	7
Al	0.8	—

Glass is generally considered to be an inert substance in regard to adsorptive effects and catalytic activity. In glass capillary column applications, however, it can manifest undesirable activity. Such activity, particularly evident when polar compounds are chromatographed, is characterized by tailing peaks, and in severe circumstances by complete peak adsorption[25–30]. Interactions between the solute and the column wall are particularly noticeable on thin-film columns where the degree of shielding provided by the stationary phase is minimal. Slight surface activity is also undesirable when smaller concentrations (picogram range) of solutes are being separated. In a recent paper[31], Verzele and Sandra remarked that "column wall activity is one of the most troublesome difficulties of (GC)²".

Column wall activity can be attributed to the silica surface structure and to impurities found in the surface monolayers of the glass matrix. The various metallic oxides, added during the manufacture of glass, that are present on or near the surface of the glass can act as Lewis acid sites[11,24,32–34]. These sites are considered to be cationic, in which the positive charge is concentrated on a cation of small radius while the negative charge is distributed over the internal bonds of the incomplete

silica tetrahedra[35]. Lewis acids function as adsorption sites for lone-pair donor molecules such as ketones and amines. The strength of the adsorption depends not only on the donor properties of an adsorbed molecule, but also on the strength of the electron-accepting Lewis acid. Sodium and potassium are weaker Lewis acids than magnesium and calcium, which are in turn weaker than boron and aluminum. Molecules containing π-bonds, such as aromatic compounds and olefins, also interact with Lewis acid sites. Filbert and Hair[36,37] demonstrated that the presence of calcium ions in glass supports used for packed column gas chromatography increases surface activity, thus causing peak tailing of lone-pair donor molecules. It has also been firmly established that boron impurities in silica provide surface Lewis acid sites that are capable of chemisorbing electron-donating molecules[38–41]. The absence of these adsorption sites on fused silica is thought to give it a higher intrinsic degree of inertness than untreated glass.

The surface of silica and adsorption on that surface have been the subject of many investigations. Infrared spectroscopy of high surface area silicas has led to an acceptable understanding of that surface. Unfortunately, the silica surface of glass has not been probed as thoroughly, its low surface area rendering infrared techniques unsuitable. However, it is usually assumed that the silica surface of glass behaves similiarly to other silicas.

Undoubtedly, the single most important structural detail of the silica surface is the hydroxyl groups that are attached to the surface silicon atoms. These silicon atoms are presumably tetrahedrally coordinated to three other oxygen atoms and, hence, to the bulk silica. This infers that at low temperatures the surface silicon atoms prefer to complete their coordination requirements by attachment to monovalent hydroxyl groups rather than by formation of strained siloxane bridges or charged species[42]. Several types of hydroxyl groups are found. Those which are attached to adjacent silicon atoms are termed vicinal. When two hydroxyl groups are attached to the same silicon atom, the term geminal group has been applied. In addition to surface hydroxyl groups there are also hydroxyl groups within the silica structure which are usually termed intraglobular hydroxyls[43–46].

Many of the surface hydroxyls are hydrogen bonded to one another and are described as being "bound". Those which are not perturbed or involved in any interactions are described as "free". Whether two adjacent hydroxyl groups are bound or free is determined by the distance of one hydroxyl group from the oxygen atom of the adjacent hydroxyl group. Hydroxyls which are separated from adjacent oxygen atoms by more than 3.1 Å appear to be incapable of hydrogen bonding[47–49]. For optimal hydrogen bonding, the hydroxyl–oxygen distance should be between 2.4 and 2.8 Å (ref. 50). If a continuum of values is assumed for the distances between neighboring hydroxyl groups in an amorphous silica surface, then a continuum of hydroxyl "types" exists, ranging from free to strongly bound[51]. As vicinal hydroxyl groups are separated by at least 3.1 Å, it is unlikely that they are hydrogen bonded to one another. Geminal hydroxyl groups also are probably not bonded to their partners because a five- or six-membered ring is normally needed for intramolecular hydrogen bonding. Triplet OH groups [–Si(OH)$_3$] should be equally free from internal bonding[52]. Although some controversy exists over the number and nature of the surface hydroxyl groups, some studies indicate that approximately 50% of the surface hydroxyl groups are hydrogen bonded to one another[53,54].

If it is assumed that a silicon atom on the surface of silica must complete its tetrahedral coordination with a hydroxyl group, the number of surface hydroxyl groups can be calculated from geometrical considerations[55,56]. By assuming one hydroxyl group per surface silicon atom, there are approximately eight groups per 100 Å^2. Experimental determinations, however, indicate that at ambient temperatures the surface hydroxyl concentration corresponds to about 5 groups per 100 Å^2 (refs. 57–59).

Under normal atmospheric conditions, it is thought that water is adsorbed to the hydrogen-bonded surface hydroxyls[60]. Heat treatment can remove the physically adsorbed water, leaving only the surface and intraglobular hydroxyls. Prolonged and more intense heating actually dehydrates the silica surface by the condensation of neighboring hydroxyl groups. A number of mean surface concentrations of hydroxyl groups on silica, after vacuum treatment, at different temperatures are given in Table 4[59]. From room temperature to approximately 165°C, only physically adsorbed water is removed from the surface of the silica. Between 165°C and about 400°C, hydroxyl groups are thermally removed from the surface. Upon cooling and re-exposure to water these sites hydrate, re-forming the original hydroxyl groups. Above 400°C, hydroxyl groups continue to be removed from the surface as the temperature is increased. However, as the treatment temperature increases, a decreasing number of hydroxyl groups can be re-formed on the surface. At about 800°C, the re-addition of water is futile and the dehydration process is irreversible. Between 165°C and 400°C, the hydroxyl groups removed from the surface are those that are hydrogen bonded to one another; the most strongly hydrogen bonded groups disappearing first and the number of free groups remaining almost unchanged[44,54,61–65]. The molecular view of the processes occurring during dehydration and rehydration of silica is shown in Fig. 3. The intraglobular hydroxyls are removed and water is evolved throughout the entire temperature range of heating, starting at room temperature and continuing up to 1200°C[43].

The hydrogens of the surface hydroxyl groups (also named silanol groups) are partially acidic owing to d-electron cloud vacancies in the silicon atoms[66]. Consequently, the silanol groups are available as proton donors for hydrogen bonding sites. Hence molecules containing high peripheral electron densities are adsorbed on a hydroxylated surface. A peripheral concentration of negative charge density arises from the π-electron bonds in unsaturated or aromatic hydrocarbons, and also from the

TABLE 4

MEAN SURFACE CONCENTRATIONS OF HYDROXYL GROUPS ON SILICA AFTER VACUUM TREATMENT AT DIFFERENT TEMPERATURES

Temp. of vacuum treatment (°C)	*OH groups per 100 Å^2*
200	4.8
300	3.6
400	2.7
500	2.1
600	1.6
700	1.2
800	0.9
900	0.7

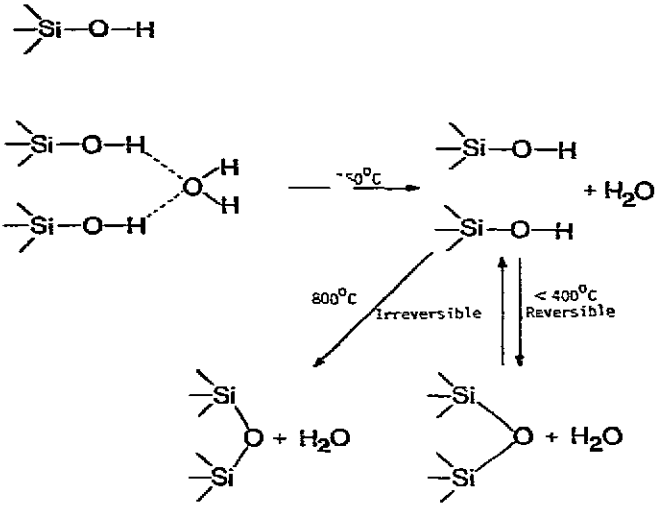


Fig. 3. Molecular processes occurring during dehydration–rehydration of silica surfaces.

free electron pairs of the oxygen and nitrogen atoms in hydroxyl, ether, carbonyl and amino groups. Although the mechanism of adsorption is more complicated than an electrostatic hydrogen bond interaction, the type of adsorption involved closely resembles hydrogen bonding[67]. In addition to the specific interactions of the silica surface with polar molecules, a weak non-specific dispersion type of interaction is observed that is independent of the degree of surface hydroxylation and independent of the electron density distribution of the adsorbate[68,69]. In contrast, the heat of adsorption of polar molecules is highly dependent on the silica surface and increases with greater surface hydroxylation[70]. For the most part, the free hydroxyl groups are the strongest surface adsorption sites. Mutually hydrogen bonded surface hydroxyl groups, however, interact only slightly with lone-pair and hydrocarbon adsorbates. This interaction takes place only with the most weakly hydrogen bonded groups. Water interacts strongly with those groups and can form several molecular layers. The adsorbed water can then act as specific adsorption sites for molecules containing high electron densities in much the same manner as free surface hydroxyls. Fig. 4 shows a model depicting the behavior of the surface hydroxyl groups as discussed above[71].

During heat treatment, hydroxyls can condense to form water in two ways. Firstly, adjacent hydroxyls on adjacent silicon atoms condense to form siloxane bridges. Secondly, two hydroxyl groups on the same silicon atom (geminal pair) react to form a >Si=O group. As silicon does not form such a group very readily[72], dehydration probably involves condensation to form siloxane bridges[73]. Such a bridge would have longer than optimal bond lengths between the oxygen and silicon atoms, thus decreasing its stability and increasing its reactivity[65]. Such a strained structure could possess a high degree of ionic character[52]. Kunawicz *et al.*[74] have reported that the siloxane bridges resulting from the high-temperature (700°C) evacuation of silica are more reactive than the remaining free hydroxyls. The siloxane

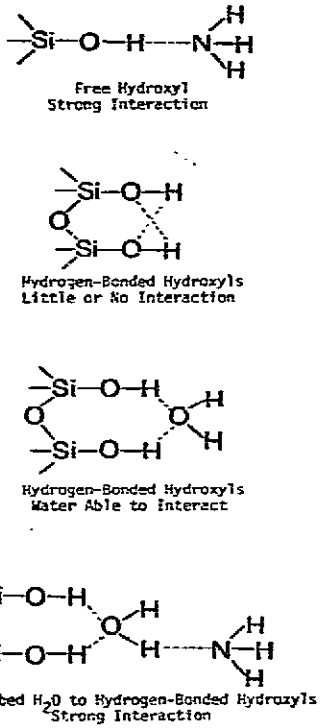


Fig. 4. Model for surface silanol interactions.

bridge can function as a proton acceptor in hydrogen bonding interactions. It has also been shown that alcohol molecules can interact significantly with the siloxane surface by Van der Waals interactions[75]. These interactions become more marked as the chain length of the adsorbate alcohol increases. In a chromatographic study relating retention to adsorption, it was also concluded that the siloxane bridge is an active site[76].

In addition to the surface silanols and the siloxane bridges, the silica surface obviously has an underlying backbone structure of silicon–oxygen bonds. The exact nature of the tetrahedral silicon–oxygen bond in bulk silica is not known. Pauling[77] assigned 50% ionic character to the silicon–oxygen bond using empirical calculations from electronegativities. Values of up to 80% covalent, however, may be obtained by selecting different heat of formation data. From electron density contours of quartz, it is evident that the silicon–oxygen bond is intermediate between homopolar and heteropolar[78]. It is reasonable that such a bond, which may be largely covalent in the bulk structure, could give rise to a nearly homopolar surface bond through deformation of the electron distribution owing to the imbalance of bonding forces at the surface. Evidence indicates that a silica surface void of the active sites previously mentioned has silicon–oxygen surface bonds that are nearly homopolar[65]. Of course, such a surface would experience only weak dispersion interactions.

Spectroscopic evidence indicates that at least some of the boron impurities that are found on the surface of glass also have attached hydroxyl groups[79–82]. These

boronol groups are not only more reactive than the silanol groups, but they also enhance the reactivity of the neighboring silanol groups. It is also known that these groups are present in both single and geminal configurations. The bonds formed by reaction of coupling reagents with the B–OH groups also appear to be more easily hydrolyzed than are the bonds formed with silanol groups. These data show that impurities on the silica surface greatly complicate the surface chemistry.

In summary, the adsorptive interactions that can arise with the glass surface are as listed below:

(1) The metallic oxides used in the manufacture of glass give rise to cationic positive charge locations that function as Lewis acid sites which are adsorptive sites for molecules having a region of localized high electron density such as alcohols, ketones, amines and π-bond-containing molecules.

(2) The surface hydroxyl groups act as proton donors in hydrogen bond interactions and can function as very strong adsorptive sites for molecules having localized high electron density.

(3) The surface siloxane bridges act as proton acceptors in hydrogen bond interactions and function as adsorptive sites for molecules like alcohols. In addition, these sites give rise to significant Van der Waals interactions.

(4) Weak dispersion interactions can arise from the silicon–oxygen network and the other functionalities present on the glass surface.

Recently, a review describing the structure and properties of glassy support surfaces used in gas–liquid chromatography was published[83].

2.3. Glass surface wettability

To achieve a high separation efficiency with a glass capillary column, a uniform and homogeneous film of stationary phase must be applied to the inner wall of the tube. Furthermore, this thin film must maintain its integrity and not rearrange to form droplets as the temperature is varied.

When a liquid droplet is placed on a solid surface, it may spread to cover the surface or it may remain as a stable drop. The angle between the tangent to the liquid drop and the solid surface is defined as the contact angle (θ) (see Fig. 5). When $\theta = 0$, the liquid spreads freely over the surface. As θ increases, the tendency for a liquid to spread decreases. Therefore, the contact angle is a useful inverse measure and cos θ is a direct measure of wettability.

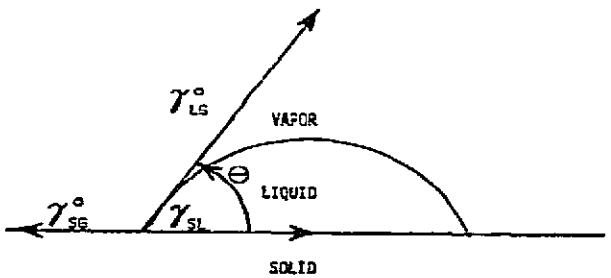


Fig. 5. Contact angle diagram.

The correlation of the forces that act between the liquid and solid surface is described by the Young equation[84]:

$$\gamma^{0}_{SV} - \gamma_{SL} = \gamma^{0}_{LL} \cos\theta \qquad (1)$$

Three surface tensions γ^{0}_{SV}, γ_{SL} and γ^{0}_{LL} exist at the phase boundary of a drop of liquid at rest on a solid surface. The wettability is a thermodynamic function of the equilibrium between the cohesion forces inside the liquid and the energy of the solid surface. The cohesion forces inside the liquid are characterized by the surface tension, and the energetics of the solid surface by the surface free energy. The contact angle depends upon the specific surface free energy of the solid and of the liquid. Spreading generally occurs when the specific surface free energy of the liquid is less than that of the solid. Compositions of both the solid surface and the spreading liquid are of primary importance since the surface atoms of both phases are attracted to each other by London dispersion forces. Atoms more than a few Ångstroms from the surface should have little or no influence on wetting phenomena, but ions or uncompensated charges in the glass may play some role.

Zisman[85] defined the critical surface tension (CST, γ_c) as that value of the liquid surface tension above which liquids show a finite contact angle on a given surface. The value of the CST is obtained from a plot of $\cos\theta$ *versus* the surface tensions of a homologous series of liquids. This plot usually forms a straight line and the point at which the line crosses the intercept, $\cos\theta = 1$, is the critical surface tension. For all liquids that have a surface tension less than the critical surface tension of the solid, the contact angle is zero and there is complete wetting of the solid by the liquid.

Glass is usually described as a high energy surface[86,87], and is assumed to have a surface energy on the order of a hundred to a few thousand erg/cm (ref. 88). Such surfaces readily undergo adsorption and hydration, which change their properties to those of low energy surfaces. Consequently, most organic liquids exhibit large contact angles on glass and do not form uniform films, but break up into droplets[89]. Using the critical surface tension as a measure of wettability, it has been shown that the CST for smooth, clean glasses is $\leqslant 30$ dyne/cm and the surface tensions of typical stationary phases are in the range of 30–50 dyne/cm[90–95]. By definition, these values lead to non-wettability of glass surfaces. Tables 5 and 6 list the surface tensions of a number of solvents and stationary phases, respectively[90,94,95]. The critical surface tensions for Pyrex glasses which have been subjected to various treatments are listed in Table 7[95].

Fortunately, various modifications can be employed to raise the critical surface tension of the glass. In some instances, the surface tension of the stationary phase is lowered by the addition of a surfactant. Such modifications will be discussed in later sections.

Wettability is also affected by liquids that are unable to spread on a monolayer of their own molecules. Such a phenomenon is known as autophobicity[96]. Liquids that are not autophobic should have surface tensions that are lower than the critical surface tensions of their own adsorbed monolayers. For example, polymethylsiloxane liquids will spread on high-energy surfaces because their surface tensions of 19–20 dyne/cm are always less than the critical surface tensions of their own adsorbed films. Many ester-type liquids, however, hydrolyze slightly on glass surfaces and the resulting

TABLE 5

SURFACE TENSIONS (γ) OF SOLVENTS AT 20°C

Solvent	γ *(dyne/cm)*	*Solvent*	γ *(dyne/cm)*
n-Pentane	16.0	Ethanol	22.3
n-Hexane	18.4	*n*-Propanol	22.9*
n-Heptane	20.4	Di-*n*-propyl ether	20.0**
n-Octane	21.8	Di-*n*-butyl ether	22.0*
Benzene	28.9	*n*-Propyl chloride	20.0*
o-Xylene	29.1*	*n*-Amyl fluoride	20.0
Dichloromethane	28.1	Chlorobenzene	33.1
Tetrachloromethane	25.6*	Dichlorobenzene	41.4
Acetone	23.3	Chloronaphthalene	41.8
Methanol	22.6	Bromonaphthalene	44.6

* Measurement at 30°C.
** Measurement at 25°C.

TABLE 6

SURFACE TENSION (γ) OF STATIONARY PHASES AT ROOM TEMPERATURE

Stationary phase	γ *(dyne/cm)*	*Stationary phase*	γ *(dyne/cm)*
Squalane	29.95	Citroflex 4	30.4
Polypropylene glycol	31.30	OV-17	31.4
Triton	34.00	UCON 50 LB 550X	31.4
Diglycerol	50.3	Apiezon L —	33.2
Ucon oil (DLB-100-B)	28.3	UCON 50 HB 2000	35.7
Tricresyl phosphate	40.9	Dimethylsulpholane	38.1
Dioctyl sebacate	32.2	Polypropylene sebacate	40.2
Bis(2-ethylhexyl) phthalate	31.3	OS-124	46.1
Methylsilicone oil	19.20	β,β'-Oxydipropionitrile	48.6
OV-101	20.4	Diethylene glycol succinate	50.9
QF-1	24.6	1,2,3-Tris(2-cyanoethoxy)propane	49.2
OV-210	23.6	Carbowax 400	44.2
1-Octadecene	27.6	Dinonyl phthalate	28.8
Didecyl phthalate	28.5	Di(ethylhexyl) sebacate	31.1

TABLE 7

CRITICAL SURFACE TENSION (γ_c) OF PYREX GLASS SUBJECTED TO DIFFERENT TREATMENTS

Treatment	γ_c *(dyne/cm)*
Acetone washed	28
Chromic–sulfuric acid cleaned	44
NaOH etched	32–34
Carbonized surface	41

monolayer has a critical surface tension that is less than the surface tension of the liquid. Such behavior is consistent with observations of capillary columns losing their efficiencies after a few days of operation due to film breakup.

It has also been suggested that factors other than surface tension can influence the wettability and spreading of some liquids[89,97]. Factors such as the formation of oriented monolayers and the presence of impurities were cited.

3. CAPILLARY DRAWING PROCEDURES

3.1. Pre-drawing treatments

During the cooling process in the manufacture of glass tubing, the product is exposed to oils and greases. In addition, organic vapors may adsorb on the glass surface during storage. A number of different solutions and solvents have been used to clean the inner walls of glass tubing prior to drawing capillaries. These include dilute acids and bases, and organic solvents such as acetone, diethyl ether, methanol and methylene chloride. It was found in a recent Auger electron spectroscopy study by Wright *et al.*[24] that although solvent cleaning of the glass removed much of the adsorbed material a considerable amount of adsorbed carbon still remained on the glass surface, even after drawing.

Onuska *et al.*[98] studied the effects of leaching the glass tubing with acid solutions prior to drawing. In one case, Pyrex glass tubes were filled with a chromic acid–sulfuric acid mixture and allowed to stand at room temperature for 48 h. The resultant surface after drawing was partially roughened with tiny holes. Subsequent chromatographic performance tests showed that this treatment provided a better deactivation of the surface than solvent cleaning alone.

In another case, Pyrex glass tubes were filled with 10% hydrofluoric acid (HF) and allowed to stand at room temperature for 48 h. They were then filled with concentrated nitric acid and allowed to stand at room temperature for 1 h, after which they were rinsed with 10% HF and deionized water. The resultant surface after drawing gave a sintered appearance with numerous pit-holes (Fig. 6). This surface appeared to be deactivated better than the untreated or chromic acid–sulfuric acid treated columns.

Cronin[99] prepared a porous-layer open-tubular (PLOT) capillary column by first coating the interior wall of a glass tube with a mixture of powdered glass and Celite prior to drawing. The powdered glass served as a binder to fix the Celite permanently to the capillary wall. More recently, Torline and co-workers[100,101] coated Pyrex tubes with 5-μm quartz powder prior to drawing. The resultant capillary inner surface was shown to consist of an even distribution of quartz particles fused to the walls.

3.2. Capillary drawing

The first glass capillary column drawing machine was designed and built by Desty *et al.*[102] and is shown schematically in Fig. 7. Two pairs of rollers, one before and one after an electrically heated furnace, control the draw ratio, and hence the length and diameter of the column. As the capillary is drawn from the molten glass in the furnace, it is forced through a heated coiling tube to form a helix. A more detailed description of the drawing process is given in a previous review[3].

It has been reported by several authors[102–105] that non-uniformity of the column inner diameter can affect the performance of high-efficiency capillary columns. Such

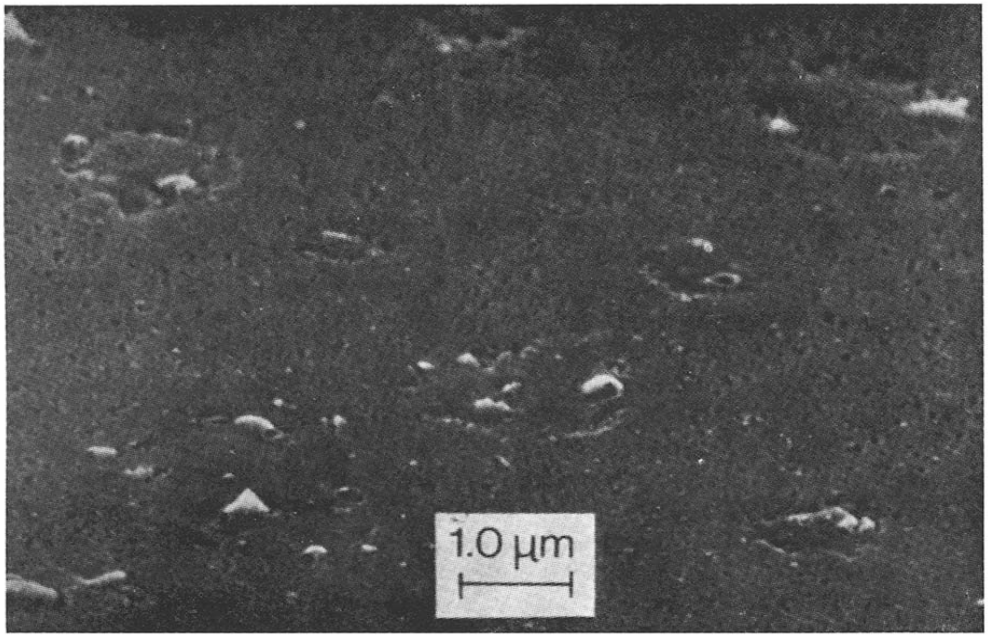


Fig. 6. Sintered surface of HNO_3–HF capillary. Reprinted with permission[98].

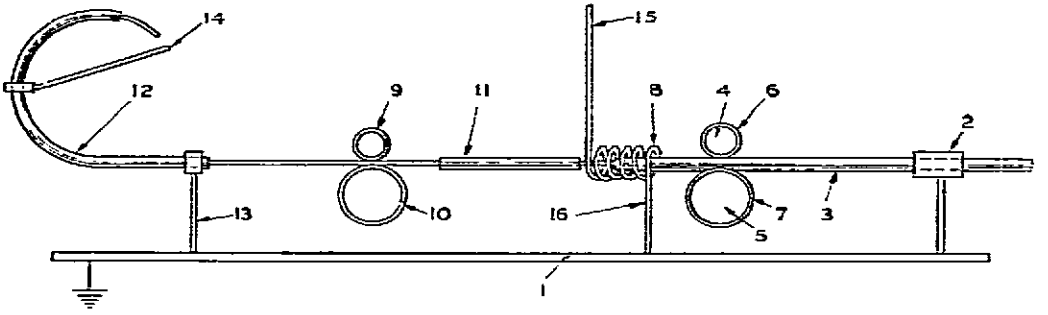


Fig. 7. Capillary drawing apparatus. 1 = Brass base plate; 2 = support; 3 = thick-walled glass tube; 4, 5 = feed rollers; 6, 7 = rubber tires; 8 = furnace; 9, 10 = draw rollers; 11 = porcelain tube; 12 = bending tube; 13 = bending tube support and ground connection; 14 = connection to low-voltage transformer; 15 = connection to low-voltage transformer; 16 = furnace support and ground connection. Reprinted with permission from *Analytical Chemistry*[102]. Copyright by the American Chemical Society.

variations have been reported to be less than $\pm 5\%$[102,103], $\pm 7.4\%$[104] or even $\pm 3\%$[105] when the drawing machine was carefully operated and selected pieces of glass tubing were used. Schenning *et al.*[105] obtained a precision of $\pm 1.5\%$ by making several modifications to a commercial glass drawing machine. Although variations in furnace temperature, non-uniform shifting of the glass tube by rollers and other mechanical problems have led to non-uniform column diameters in the past, modern glass drawing machines are now commercially available that eliminate most of these problems. In a study by Marshall and Parker[107] it was found that the capillary bore

becomes less uniform as the draw ratio increases. Thus, it is better to employ a low draw ratio and to draw the column from tubing of small diameter.

More recently, the desire to draw fused silica or quartz capillaries led to the development of new technology for glass drawing and handling. In 1975, Desty[108] modified his original glass drawing machine to attain the necessary drawing temperature for quartz by using a special propane–oxygen burner. The inability to build suitable coiling tubes was the limiting factor in the use of this prototype machine. The discovery by Dandeneau and Zerenner[17] that thin-walled capillary columns of high flexibility could be drawn straight and then coild to normal dimensions by merely bending them into the desired shape has greatly increased the interest in and use of fused silica capillaries. The glass drawing machine used by Dandeneau and Zerenner is based on advanced fiber optics technology, although less expensive machines have been built and used by others.

The small outside diameters and thin walls of fused silica capillaries permit a high degree of flexibility owing to the high tensile strength of the pristine silica surface. This strength is greatly reduced, however, by surface imperfections, micro-

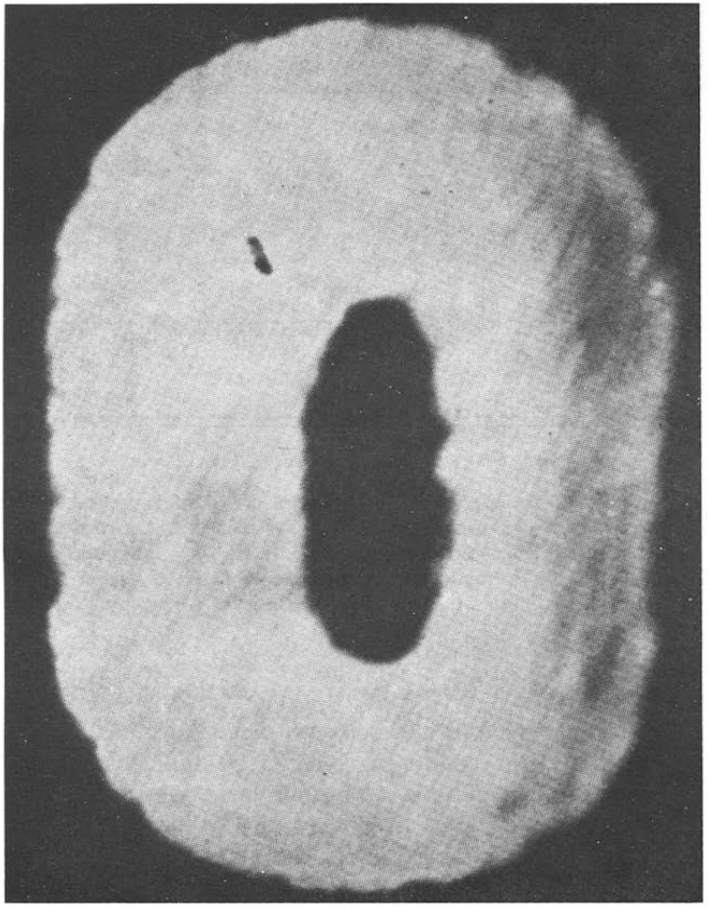


Fig. 8. Transverse section of a flat capillary column. Reprinted with permission[110].

cracks or minute scratches caused by dust particles or fingerprints. For this reason, a mechanically durable, thermally stable polyimide coating is applied to the outer capillary surface immediately after drawing[109]. This coating provides good mechanical protection and shows negligible bleed under conditions of maximum sensitivity for columns up to a temperature of approximately 300°C.

In Golay's original theoretical treatment of capillary column gas chromatography[11], it was shown that flat tubes have the advantage of reducing the effect of the crosswise gas diffusion term which is responsible for a large proportion of the HETP. Desty[108] and Desty and Douglas[110] used a simple roller arrangement just after the drawing machine furnace, which pinched the hot capillary as it was drawn to produce non-round capillaries, as shown in Fig. 8. DuPlessis *et al.*[111] produced more uniform flat capillaries by drawing the column from a flat glass tube in a conventional glass drawing machine. Subsequent studies[110,112] have shown that slightly higher column efficiencies can be obtained using flat capillary columns. Recently, flat fused silica columns have also been prepared[113].

A similar roller arrangement using toothed cogs[108,110] was used to produce non-uniform columns with flat necks between circular sections (crinckled), as shown in Fig. 9. It was proposed that such columns would disturb the laminar flow profile and produce crosswise mixing by a convective rather than a diffusive mechanism. Other approaches with this same objective included drawing a regularly deformed wire or

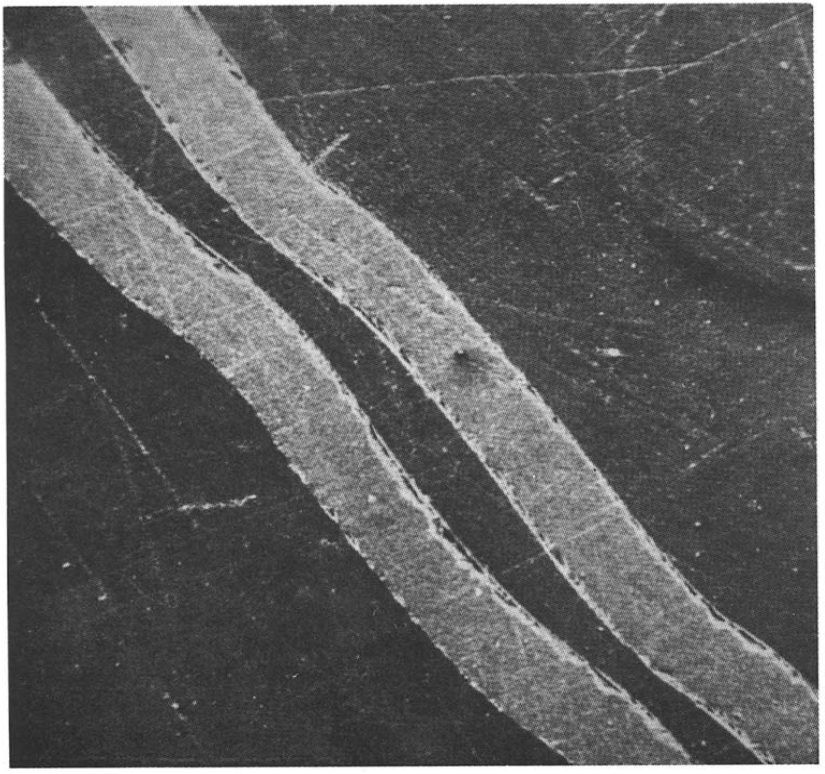


Fig. 9. Longitudinal section of a crinkled capillary column. Reprinted with permission[110].

twisted Nichrome tape into the capillary[108,114] and the construction of a spinning band capillary column[114]. These latter approaches appear to offer no advantages over conventional capillary columns.

Although the most widely used process for preparing PLOT columns consists in coating the drawn capillary with very fine porous particles[7], several studies[115,116] have resulted in the successful preparation of such columns by packing Pyrex tubes with Celite and lithium chloride[115] or powdered glass[116] around a small metal wire which has been previously inserted into the glass tube. During the drawing process, the end of the wire is positioned just outside the drawing furnace, and the tube and its packing are drawn down over the wire to leave a final orifice of the same diameter as the wire. The lithium chloride or powdered glass serve to bind the diatomaceous earth support to the capillary wall.

3.3. Chemical treatment during drawing

The incomplete removal of carbon contamination on the inner capillary wall by solvent washing (as described earlier) has led to the use of gas purging methods during capillary drawing. Simon and Szepesy[117] used a stream of very dry argon during drawing to flush and dehydrate the inner glass surface. Although it was claimed that the purge gas left a clean and smooth surface, there is no evidence that the adsorbed carbon was completely removed.

Wright *et al.*[24] used a purified oxygen purge during drawing. At the high drawing temperatures, any remaining adsorbed carbon was oxidized and the resultant gases removed by the oxygen stream. Surface analysis by Auger electron spectroscopy showed little or no carbon present.

A similar gas purging procedure during drawing was reported by Diez *et al.*[16], except a 1:3 mixture of nitrogen and ammonia was used. Results from electron microscopy showed that no separation of phases was observed, probably owing to the formation of nitride groups in the glass structure, forming Si–N–B bonds. Although improved surface deactivation was obtained by this procedure considerable tailing was still observed for polar compounds such as nitromethane, pyridine and alcohols.

4. CAPILLARY SURFACE ROUGHENING

4.1. General considerations

One of the most widely used methods for modification of the inner surfaces of glass capillary columns is physical roughening. Such roughening greatly enhances the wettability of the glass surface by the liquid stationary phase. Generally, a liquid will spread better on a rough than a smooth surface because the surface covered by the liquid drop releases more energy due to interfacial forces. For a rough surface, there is more area under the liquid drop and, therefore, more energy is released. The influence of surface roughness becomes apparent by a decrease in the contact angle. Wenzel[118] defined a roughness factor as follows:

$$r = \frac{\cos \theta'}{\cos \theta} = \frac{A'}{A} \tag{2}$$

where A' and A refer to the microscopic and the macroscopic surface areas, respectively, and θ' and θ refer to the apparent contact angles measured on the roughened

and the smooth surfaces, respectively. The value of r is close to unity for freshly drawn (fire-polished) glass, but becomes greater than unity as the surface is roughened and, correspondingly, the apparent contact angle becomes smaller. The validity of this expresssion has been fully proven[119].

Suprynowicz *et al.*[120] developed a method for the direct determination of the specific surface areas of glass capillary columns by the thermal desorption of nitrogen. Using this technique it was determined that roughening with etching ether at 380°C gave a roughness factor, r, of 5.3 for one type of soft glass, 7.8 for another and 4.1 for borosilicate glass. Such measurements could feasibly be used to evaluate and optimize various roughening procedures.

Some surface roughening treatments may also form selective surface layers that have higher surface energies than the original glass surface. For instance, the sodium chloride layer formed by HCl gas roughening provides a high surface energy having contributions from both dispersion and non-dispersion forces[121] which arise from the ionic character of the NaCl crystals. Several workers have determined critical surface tensions of glass surfaces roughened by various methods[88,121–124]. Some of these values are given in Table 8.

TABLE 8

CRITICAL SURFACE TENSIONS (CST) FOR ROUGHENED GLASSES

Glass	*Treatment*	*CST (dyne/cm)*
Pyrex	None	31.5*
Pyrex	HCl gas	31*
Soft	None	30*
Soft	HCl gas	>52.4*
Soft	HCl gas, rinsed with $CHCL_3$	46.5*
Soft	HCl gas, rinsed with H_2O and with EtOH	45*
Soft	None	44
Soft	HCl gas	50
Soft	Double HCl gas	>63
Pyrex	None	27
Pyrex	Carbon coating	41

* Values were uncorrected and are up to 10% too high.

Scanning electron microscopy (SEM) provides a very useful method for studying the structural details of a roughened glass capillary column. With the application of this technique to glass capillary columns by Alexander and Rutten[125] in 1973, a means was provided for systematically observing the effects of various treatment methods and conditions. Furthermore, chromatographic performance can be correlated with the type of physical surface achieved and treatment conditions modified to give optimal performance. However, chemical differences in the roughened surfaces may grossly alter the chromatographic performance and make some comparisons very difficult. With this in mind, some workers have attempted to analyze surface compositions by energy-dispersive X-ray analysis (EDAX) or with an electron-beam microprobe (EMP) (attachments usually found on modern SEM instruments). However, these methods of analysis provide compositional data for a depth of about the

first 10 μm of the glass, rather than the true surface composition[126,127], and therefore little useful information is obtained.

Samples are prepared for SEM analysis by either cracking the columns lengthwise and looking directly at the exposed surface (after coating with thin layers of carbon and gold to minimize charging), or by looking directly into the bore of the capillary at an angle of approximately 30° from the vertical. Schieke *et al.*[128] prefer the latter method as the inner surface has less chance of being damaged or contaminated during the cracking process. Charging effects, however, are much more pronounced when viewing the capillary in this manner, and image quality is poor. Consequently, it is necessary to minimize charging effects by first exposing the glass capillary sample to the vapors of a 0.1% solution of osmium tetroxide in water for 16–30 h at room temperature[129] prior to carbon–gold coating. Samples treated in this manner give high-quality images.

Various techniques of surface roughening have been studied, and include aqueous surface corrosion, induced crystal growth with HCl or HF gas, and deposition of barium carbonate, carbon black, sodium chloride or silica. These modification techniques will be discussed in the following sections.

4.2. Aqueous surface corrosion

The roughening of capillary inner surfaces has been reported using solutions of ammonia[130,131], sodium hydroxide[132,133], hydrofluoric acid[134,135], hydrochloric acid[136] and successive treatments with several of these solutions[137]. Leaching of a sodium borosilicate (7% Na_2O, 23% B_2O_3 and 70% SiO_2) glass capillary with 0.1 *N* hydrochloric acid at 25°C for 5 min gave a porous film which was found to be 0.1 mm thick[136].

Heckman *et al.*[135] recently reported the use of aqueous solutions of potassium hydrogen difluoride (KHF_2) for etching of both borosilicate and soda-lime glass capillaries. Fig. 10 shows an electron micrograph of a KHF_2-etched capillary surface. It has been proposed but not confirmed that the crystalline material is K_2SiF_6.

Most of these aqueous methods deeply attack the glass surface[27,122,138] and produce strongly adsorbing columns that are useful only in some special applications in gas–solid chromatography. Aqueous leaches for surface roughening have been found useful in gas–liquid capillary chromatography mainly when used as a treatment for glass tubing prior to drawing the capillary[98]. This has been described in Section 3.1. The use of aqueous leaches for deactivation will be discussed in detail in Section 5.5.

4.3. Gaseous HCl-induced crystal growth

Surface roughening with gaseous HCl was first described by Tešarik and Novotny[139], and studied in detail later by a number of workers[90,107,125,140–144]. The most widely used general procedure consists in filling the capillary column with gaseous HCl, sealing both ends with a microflame and heating the column to a high temperature for a specified period of time. The result is the formation of regularly spaced chloride crystals on the surface. Pyrex columns of low alkali content show very little reaction with HCl gas and remain transparent, while soda-lime glass is very

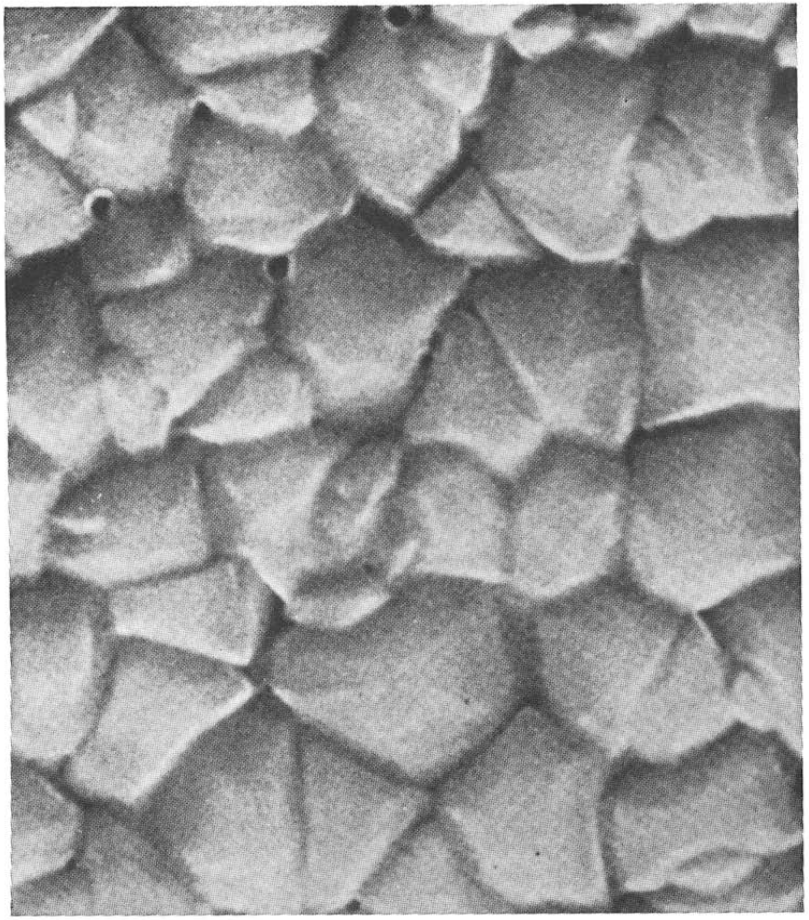


Fig. 10. SEM of a KHF_2-etched capillary column. Reprinted with permission from *Analytical Chemistry*[135]. Copyright by the American Chemical Society.

reactive and turns an opaque white after treatment. Elemental analysis of the crystals yields principally Na and Cl with much lower amounts of K and Ca[107,142].

Franken *et al.*[142] discussed in detail the formation of NaCl crystals on the glass surface. This process can be summarized as follows:

(1) During the drawing of capillary columns, vapor-phase Na_2O condenses on the column surface during cooling, forming an alkali-rich surface layer which serves as sites for nucleation.

(2) The sodium ions become more mobile at the high temperatures needed for reaction. Because of their small diameters, these ions move rather freely through the lattice toward the surface. At the same time H^+ ions from the HCl gas diffuse into the glass surface.

(3) At the surface, sodium ions exchange with hydrogen ions according to the following equation:

$$\text{–Si–ONa} + H^+ \rightarrow \text{–Si–OH} + Na^+ \qquad (3)$$

(4) The Na^+ ions move across the glass surface, associate with Cl^-, and randomly locate on a nucleation site. Consequently, the initial NaCl particles formed tend to have circular flattened convex shapes, as shown in Fig. 11.

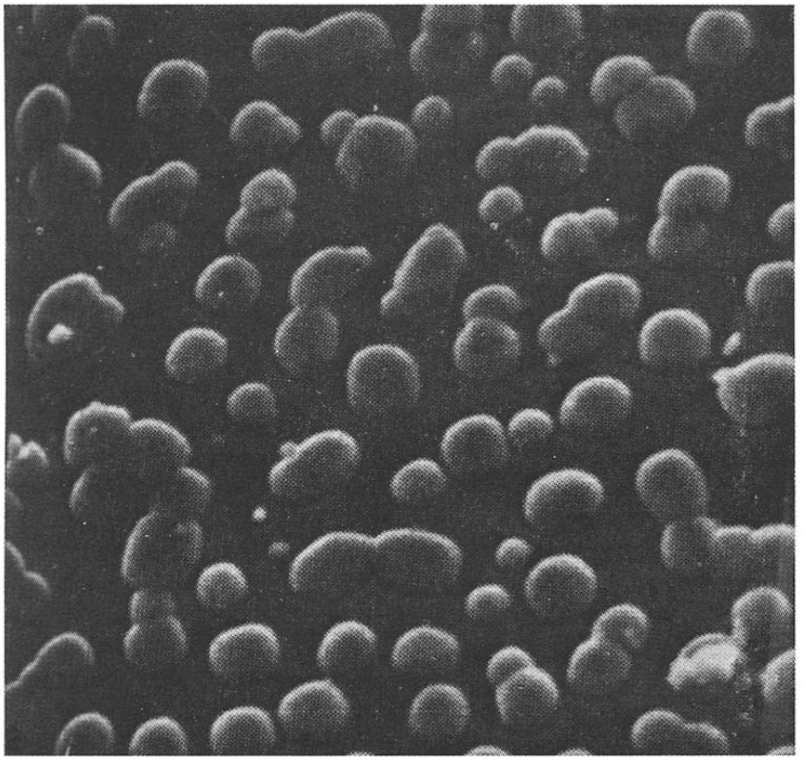


Fig. 11. SEM of a soft-glass column statically treated with HCl gas at 350°C for 30 min. Reprinted with permission[142].

(5) As the HCl gas is consumed, particle growth slows down and recrystallization becomes competitive. Ultimately, the development of low index planes becomes predominant and rectangular crystals are formed as shown in Fig. 12.

(6) If the heat treatment is continued for long periods, large NaCl crystals grow at the expense of smaller ones (Fig. 13).

In the previously described static procedure, the amount of HCl gas remaining in the column can be easily determined by melting off approximately 25 cm of the capillary and breaking one end under water. The water rises into the capillary by dissolution of HCl. The filled length is a direct measure of the HCl content in the column[142].

The formation of NaCl crystals on the capillary surface by continuously passing the HCl gas through the column while heating has been studied[142]. Crystal formation was found to be much slower by this dynamic method. It has been proposed[142] that at high temperatures adjacent hydroxyl groups split out water to form siloxane bridges which shield the glass from attack by HCl. During the static

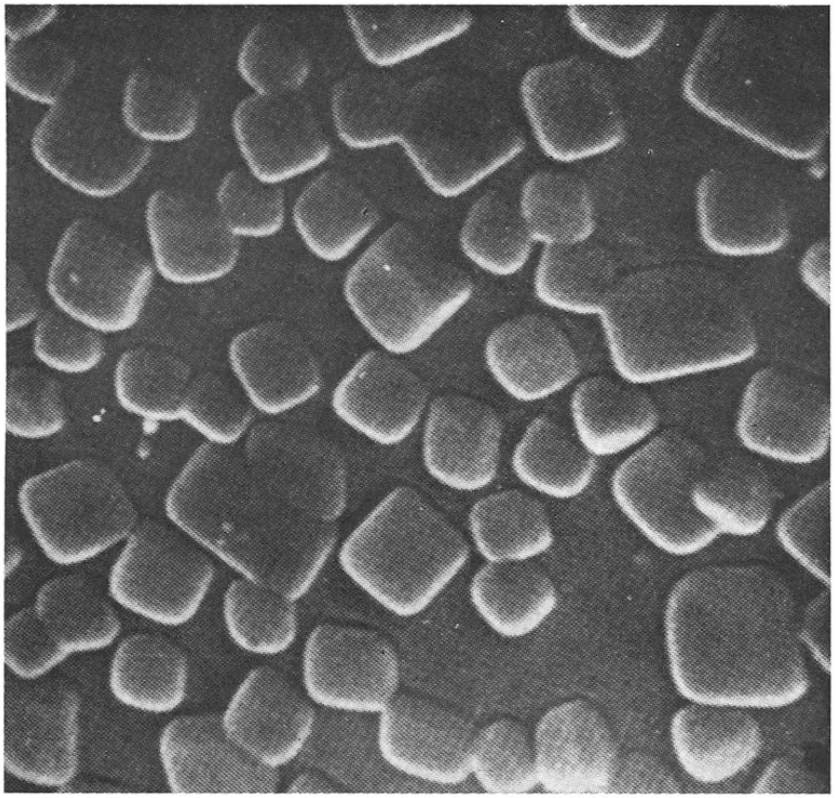


Fig. 12. SEM of soft-glass column statically treated with HCl gas at 350°C for 240 min. Reprinted with permission[142].

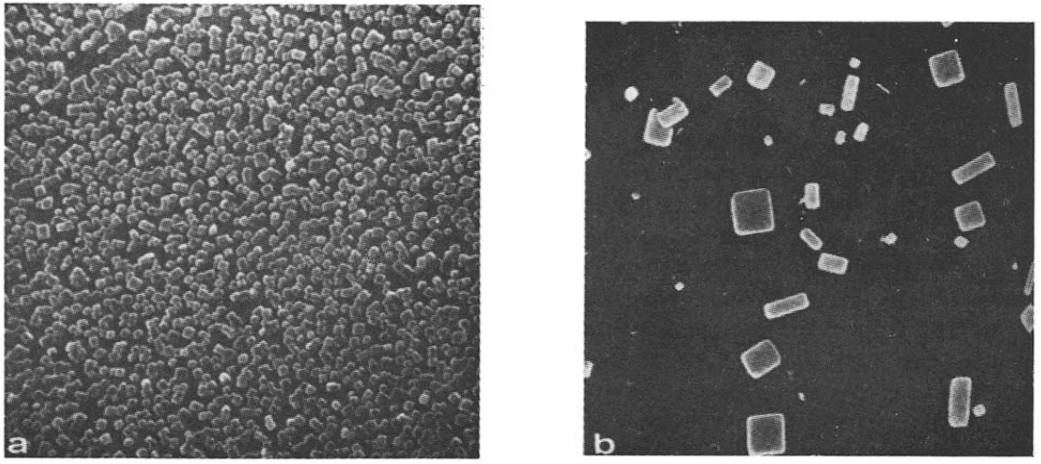


Fig. 13. SEM of soft-glass column statically treated with HCl gas at 350°C for (a) 2 and (b) 22 h. Reprinted with permission[142].

procedure, the rate of elimination of water from the glass is reduced by the vapor-phase water which cannot leave the sealed column. Hence, the development of the shielding layer is retarded, and larger amounts of NaCl crystals can be formed.

It has also been observed[142] that the dynamic procedure yields a large number of relatively small particles of dissimilar size and shape. This is because the HCl is present in excess and, therefore, particle growth is comparatively much more rapid than recrystallization.

In studying the effect of temperature on crystal growth, it was found[142] that at 300°C the process was slower and at 400°C the distribution of NaCl was not uniform. Therefore, 350°C was selected as the optimal temperature. Marshall and Parker[107] preferred a temperature of 360°C for 3 h, while Badings *et al.*[144] preferred 300°C for 1–2 h.

Badings *et al.*[144] studied the effects of storage on the distribution of NaCl crystals on the capillary inner wall. It was found that capillaries which were sealed after HCl treatment and stored for 1 week showed irregularities when compared with freshly treated ones. The particles were larger and irregular in shape. It was concluded that residual water in the capillaries (formed during the reaction of HCl with the soda-glass) caused migration and recrystallization of the NaCl particles. When columns were stored under vacuum, the integrity of the surface was retained.

In conclusion, the limitations of this method of surface roughening are as follows:

(1) Crystal growth depends to a large extent on the surface composition of the glass and, therefore, the reproducibility of an ideal micro-roughness is difficult.

(2) The procedure is essentially limited to soft glass columns.

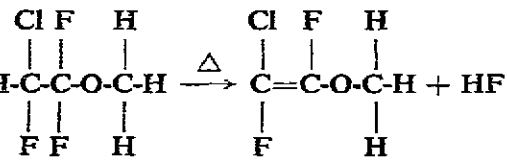
(3) The solubility of NaCl in various liquids can present a problem during coating of columns with the stationary phase[107].

(4) Columns coated with thin films show some adsorption properties resulting from the weak Lewis acid behavior of the sodium ions[145].

(5) High alkali concentrations on capillary surfaces increase the catalytic decomposition of various stationary phases with resultant bleeding at higher temperatures.

4.4. Silica whisker formation

It was demonstrated by Tešarik and Novotny[139,145] in the late 1960s that surface roughening in glass capillaries could be accomplished by reaction of the glass surface with HF gas at elevated temperatures. The general procedure involved filling the capillary with the etching vapor, sealing both ends in a flame and subjecting the column to high temperature for a selected period of time. The etching vapor was either dry HF or 2-chloro-1,1,2-trifluoroethyl methyl ether, which cleaves off HF on heating according to the following reaction[139]:



(4)

Although the columns prepared this way were observed to contain an opaque white deposit, it was not until 1975 that the true nature of the deposit was discovered

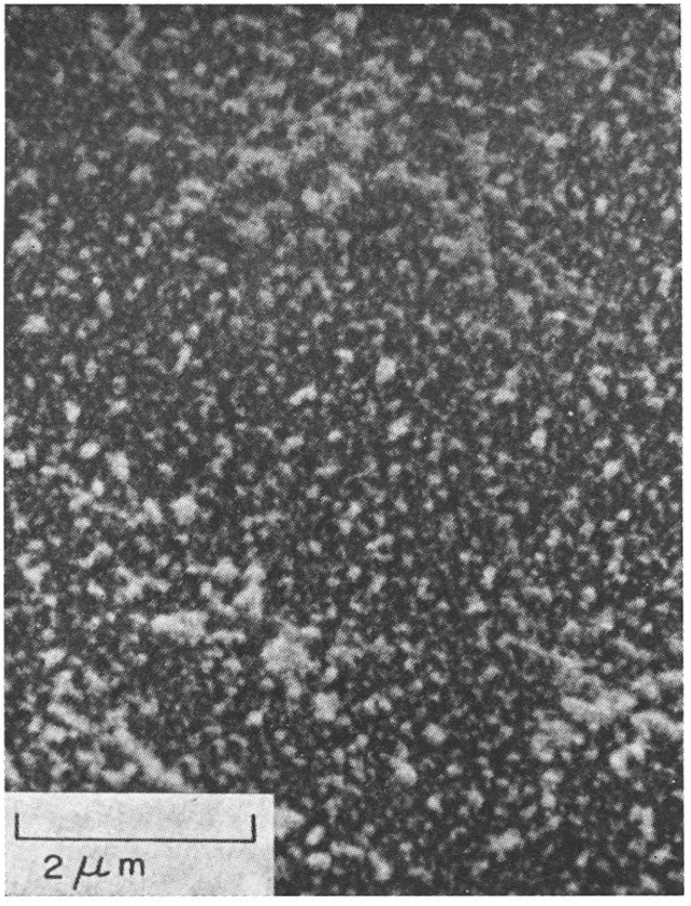


Fig. 14. SEM of a capillary column etched with 2-chloro-1,1,2-trifluoroethyl methyl ether after the method of Tešarik and Novotny[139]. Reprinted with permission[147].

using scanning electron microscopy[128,146,148]. Fig. 14 shows an electron micrograph of the inner surface of a Pyrex capillary which has been treated with the fluoroether according to the method of Tešarik and Novotny[139]. Under these conditions of low fluoroether concentrations, whisker formation does not take place, although the glass surface has definitely been etched.

Schieke *et al.*[128,146–148] have shown that on using higher concentrations of the fluoroether silica whiskers are formed. The length and shape of these whiskers are controlled mainly by reagent concentration, temperature and reaction time. Schieke *et al.*[147] reported on experiments carried out with fluoroether concentrations of 2.5%, 5.0% and 10.0% (concentration is defined as the volume of liquid ether to the total column volume, expressed as a percentage), temperatures of 250, 300, 350, 400 and 450°C and heating times of 4, 10 and 24 h. Their results can be summarized as follows:

(1) At temperatures of 250°C and lower, whisker formation does not occur, regardless of the concentration of the ether.

(2) As the reaction temperature and/or concentration of the fluoroether is

increased, the whiskers change from short and sparse to forms that are longer, thicker and denser.

(3) At relatively high fluoroether concentrations, the whiskers tend to be less uniform. If the concentration is too high, some of the ether is not vaporized and the liquid that remains on the surface prevents access of HF and little or no etching takes place.

(4) Whisker length and surface density increase with the length of the growth period. Under the conditions studied by Schieke *et al.*[147], whisker growth appeared to be complete after 24 h.

(5) A temperature of approximately 400°C yields the best results. Whisker length and density can be controlled at this temperature by varying the concentration of the ether in the range 2.5%–10%. This has also been confirmed by Sandra and Verzele[149].

Fig. 15 shows an electron micrograph of a cross-section of a column which was treated with 10% fluoroether at 400°C for 24 h. Fig. 16 shows the same surface at a higher magnification. Treatment at a higher temperature (450°C) but much lower ether concentration (2.5%) yielded whiskers that were much thinner and more sparse (Fig. 17). Non-uniform whisker growth such as shown in Fig. 18 was attributed by Clarke[150] to too high a concentration of HF available in the gas phase.

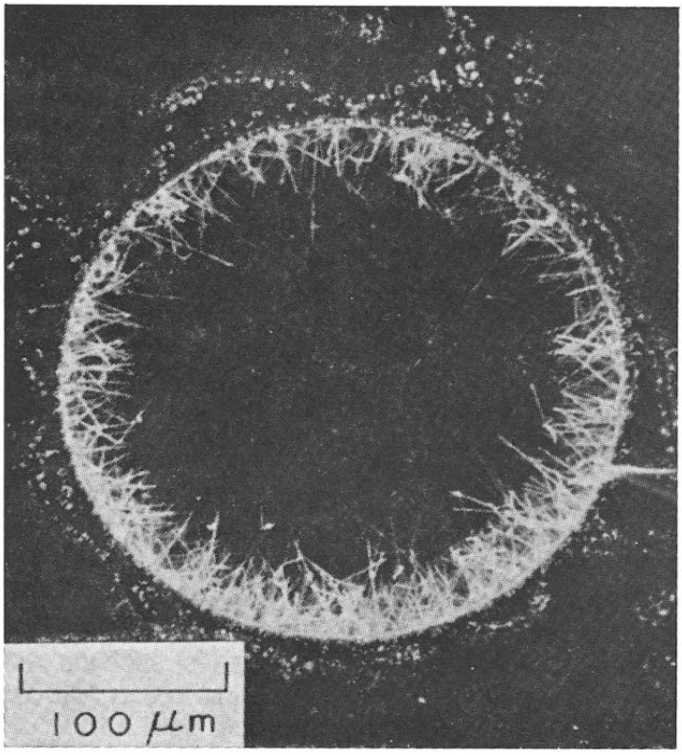


Fig. 15. SEM of a column cross-section that was prepared by etching with 10% fluoroether at 400°C for 24 h. Reprinted with permission[147].

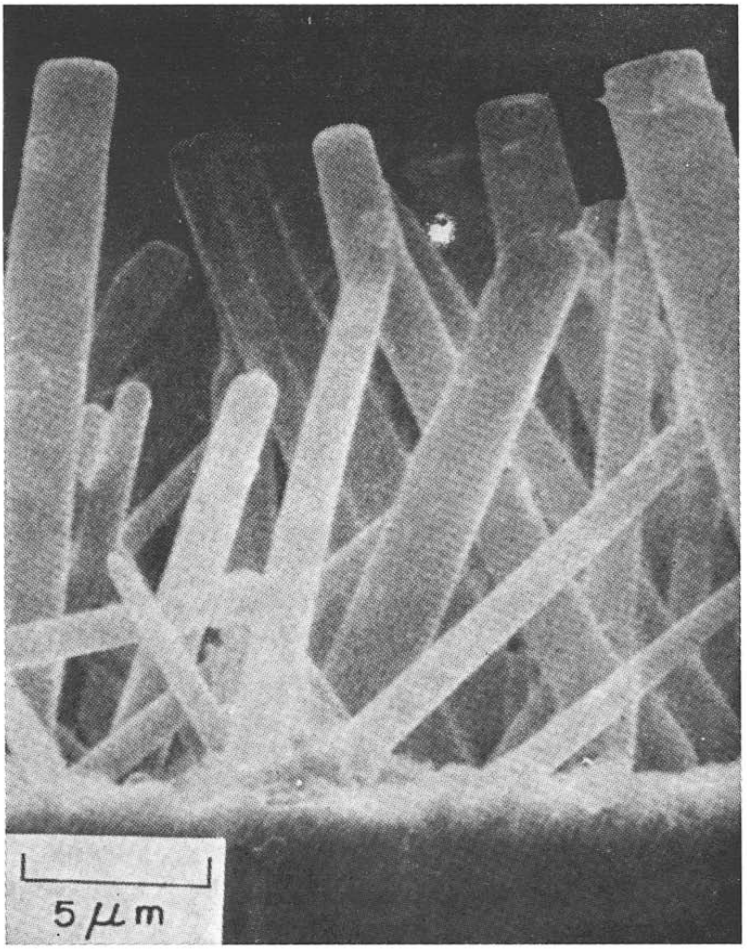


Fig. 16. SEM of a column that was prepared by etching with 10% fluoroether at 400°C for 24 h. Reprinted with permission[147].

One of the greatest experimental difficulties in making whisker columns lies in the introduction of the etching gas or liquid. The method used can greatly affect the uniformity of whisker growth throughout the column. While Schieke *et al.*[147] introduced the fluoroether by injecting a desired liquid volume through a septum into the column which was under vacuum, Clarke[150] reported better uniformity by dynamically coating the column with the fluoroether followed by sealing the ends before heat treatment.

Another problem in using the fluoroether is that a carbon deposit is formed on the inner glass surface during the high temperature decomposition of the ether[147]. This carbon deposit can be very difficult and time consuming to remove. For this reason, Onuska and Comba[151] studied whisker formation using hydrogen fluoride gas. The gas from a lecture bottle was introduced into the column which was under vacuum, the ends were sealed in a flame and the temperature maintained at 400°C

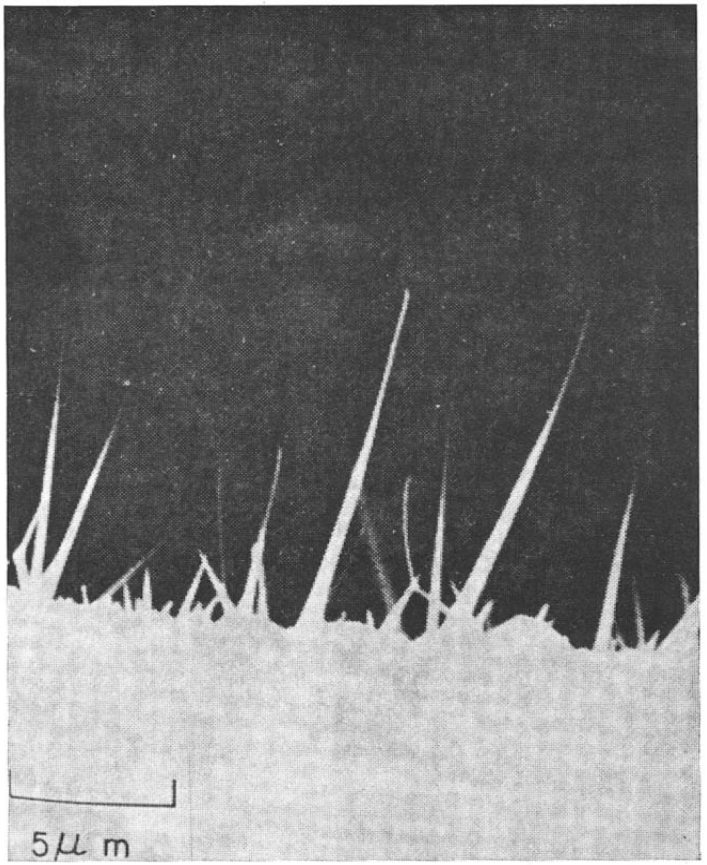


Fig. 17. SEM of a column that was prepared by etching with 2.5% fluoroether at 450°C. Reprinted with permission[154].

for 12 h. Fig. 19 shows an electron micrograph of the whisker formations on a soft (soda-lime) glass prepared in this manner. The whiskers were 2–3 μm in length, coral-like in nature and relatively uniform. Fig. 20 shows the results obtained using Pyrex glass. The whiskers are finer, 3–5 μm in length and resemble glass-wool. These filamentary crystals exhibit high mechanical strength and increase the glass surface area up to 1000-fold[152].

The direct use of HF gas is somewhat undesirable because of safety considerations and often observed non-uniformity in whisker growth. These problems were solved (in addition to solving the problems mentioned when using the fluoroether) by using ammonium hydrogen difluoride which dissociates to produce gaseous hydrogen fluoride and ammonia when heated[152]. Columns were filled with a 5% (w/v) saturated solution of ammonium hydrogen difluoride in methanol and allowed to stand for 1 h before removing the solution with a flow of nitrogen gas. The columns were sealed and heated at 450°C for 3 h. Fig. 21 shows an electron micrograph of a capillary surface treated in this manner. Whisker lengths of 4 μm were commonly observed. An additional advantage of this method is that maximum whisker growth and symmetry occurred after only 3 h.

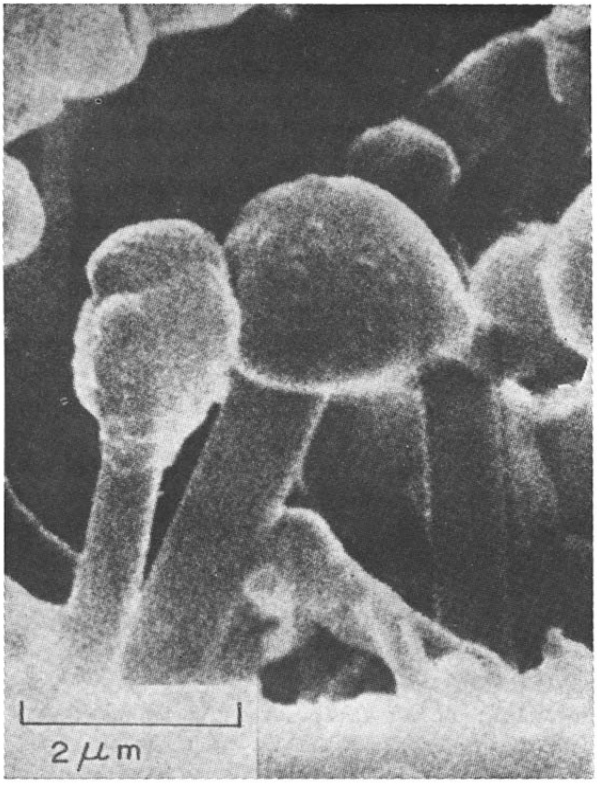


Fig. 18. SEM of a column exhibiting knob-like tops produced from too high a concentration of HF. Reprinted with permission[147].

It is generally believed that the mechanism of formation of the silica whiskers involves reaction of hydrogen fluoride with the glass to form silicon tetrafluoride, which is then converted into silicon dioxide and deposited in the form of whiskers. A more in-depth discussion of this process can be found elsewhere[153]. Energy-dispersive X-ray analysis of a single whisker and the X-ray powder diffraction pattern indicate that the whiskers consist of microcrystalline silica[147,148]. Surface analysis using Auger electron spectroscopy verifies these results[24].

Sandra *et al.*[154] have summarized the advantages and disadvantages of whisker surfaces. An obvious advantage is that with the increase in surface area, a larger sample capacity is obtained. Furthermore, silica whiskers stabilize all stationary phases, and droplet formation is seldom observed. The main disadvantage is that whisker surfaces are extremely active and most deactivating methods are inadequate[155–157]. In addition, the high degree of roughening decreases the separation efficiency.

4.5. Barium carbonate deposition

In 1976, Grob and Grob[158] reported a new procedure for surface roughening based on the production of a layer of barium carbonate crystals, grown from nuclei

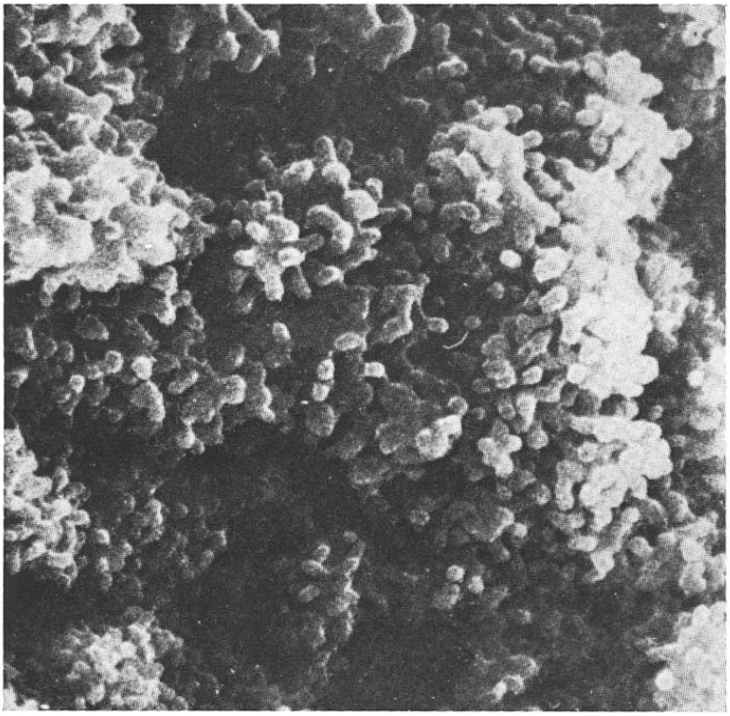


Fig. 19. SEM of whisker formation on the inner surface of soft glass produced by etching with HF. Reprinted with permission[151].

on the glass surface. The general procedure consists in dynamically coating the glass surface with barium hydroxide solution using carbon dioxide gas to push the plug of hydroxide solution through the column. During this process, barium carbonate crystals are produced on the glass surface. A number of subsequent papers[159–163] give descriptions and modifications of this original procedure.

It was found that the structure of barium carbonate layers produced on the inner surface of glass capillaries is influenced by a large number of experimental variables, including glass surface structure, crystallization temperature and addition of stationary phase modifiers (surfactants)[159,163]. Fig. 22 shows an electron micrograph of a Pyrex capillary which had been pre-treated with hydrochloric acid solution before barium carbonate deposition at 80°C. The crystals on the inner capillary walls are mostly in the shape of needles with poorly defined edges, probably owing to dendritic growth. Their average length is 3–4 μm and their diameter is 2000–3000 Å[163]. As can be seen in Fig. 22C, many crystals are aligned vertically from the surface. This can be compared with Fig. 23 which represents the same procedure except for a crystallization temperature of 25°C. A decrease in the crystallization temperature results in smaller and more closely packed particles[163]. In this case, no upright needles are observed. Barium carbonate crystals grow on any kind of glass surface, but the glass structure influences the size, shape and distribution of the crystals. On untreated soft glass, smaller and less distant particles are formed than on untreated Pyrex glass[159]. These differences become smaller, however, with prior acid leaching.

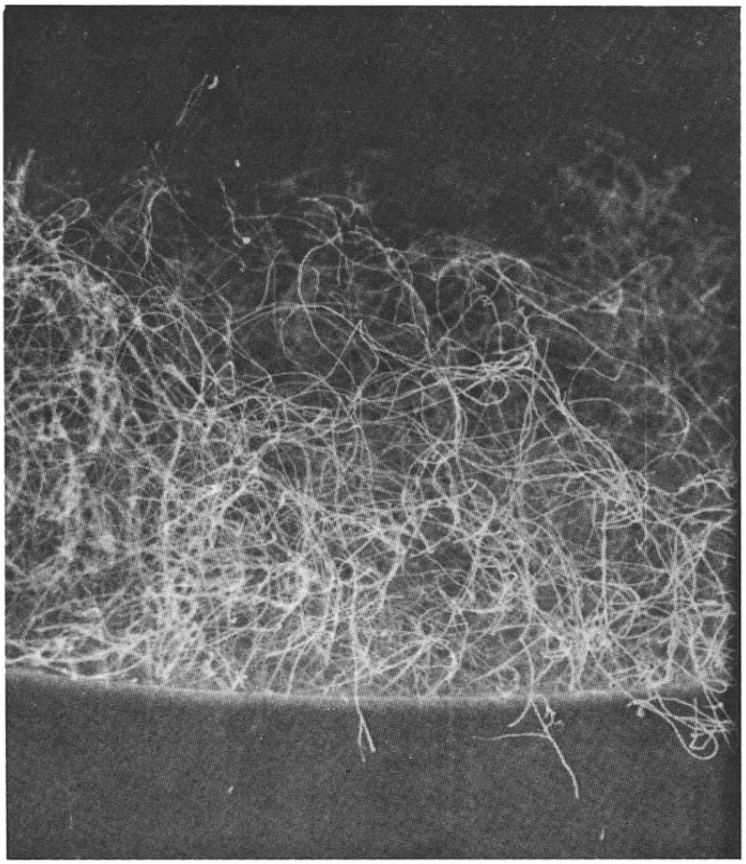


Fig. 20. SEM end-view of whiskers formed in a Pyrex glass column etched with HF. Reprinted with permission[151].

Three specific procedures are outlined for the formation of barium carbonate layers. By varying the concentration of the barium hydroxide solution, different degrees of surface coverage are possible. Saturated barium hydroxide produces thick layers of barium carbonate that are suitable for coating with polar stationary phases. For less polar phases, a 1:10 dilution of the barium hydroxide is used. Finally, for the preparation of apolar columns, a 1:100 dilution of the barium hydroxide is used. This dilute solution does not form distinct crystals of barium carbonate[162].

Although the deposition of barium carbonate roughens the glass surface and, therefore, improves the wettability of the surface, especially for polar stationary phases, there exist several problems concerning surface activity which are discussed in Section 5.2.

4.6. Carbon black deposition

In the mid-1960s, Grob[27,164] reported studies of several procedures designed to deposit carbon black on the inner walls of glass capillaries by pyrolyzing hydrocarbon gases or liquids inside the column. Extreme care and high temperatures at the

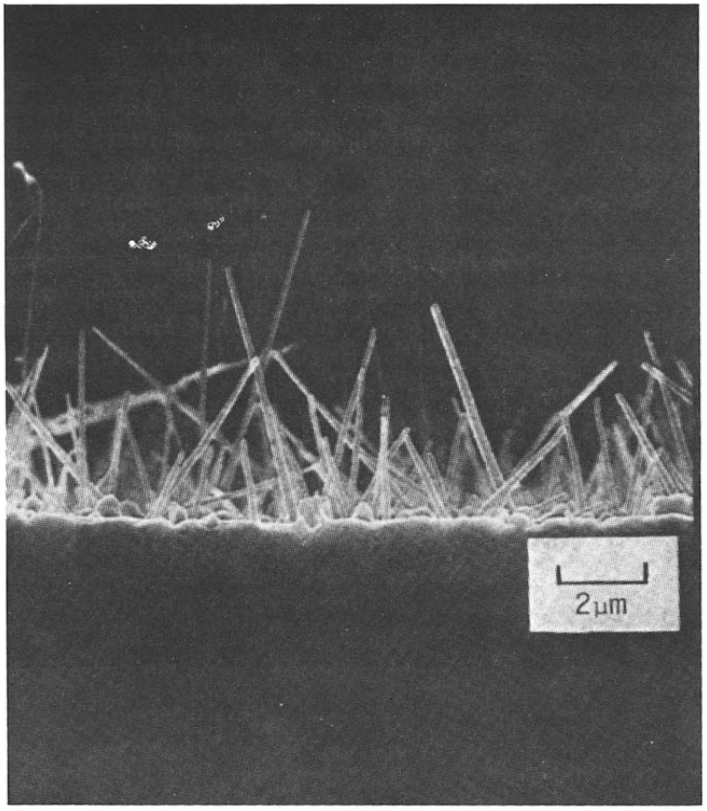


Fig. 21. SEM showing whisker formation in a capillary column etched at 450°C for 3 h after treatment with 5% (w/v) NH_4HF_2. Reprinted with permission[152].

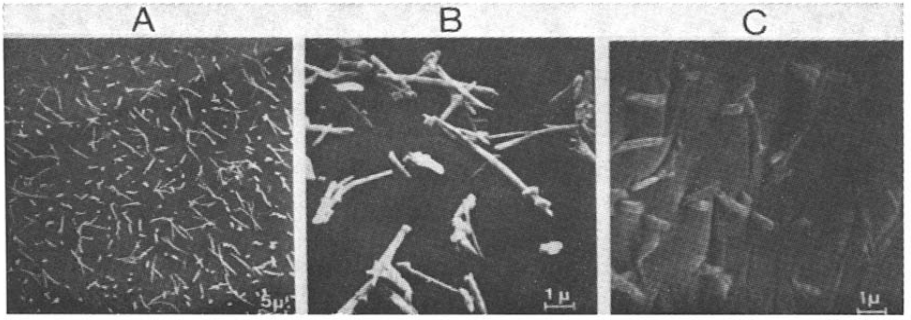


Fig. 22. SEM of a Pyrex glass capillary column pretreated with hydrochloric acid solution before barium carbonate deposition at 80°C. Reprinted with permission[165].

glass softening point were needed to produce uniform layers of carbon black approximately 0.001 μm thick. The deposition of a carbon layer by means of the pyrolysis of methylene chloride was one of the more effective methods[164]. The uniformity of the carbon layer was particularly affected by the speed of pyrolysis of

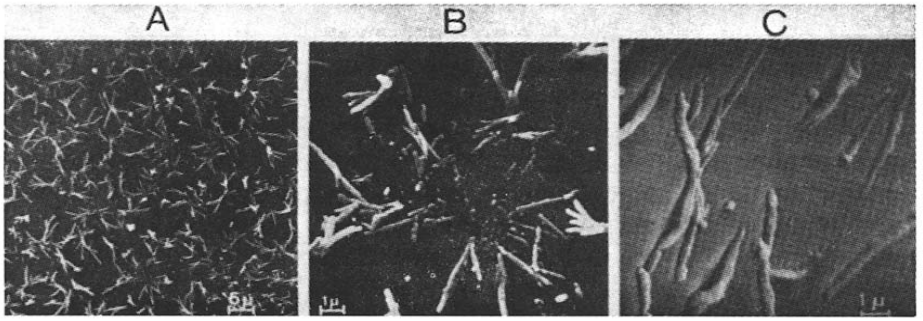


Fig. 23. SEM of a Pyrex glass capillary column pre-treated with hydrochloric acid solution before barium carbonate deposition at 25°C. Reprinted with permission[163].

methylene chloride and the uniformity of heat transfer[27]. Furthermore, the carbon layer must be protected from moisture[165]. These factors have led to relatively poor reproducibility.

More recently, stable carbon layers have been deposited on glass capillary walls by dynamic[166–169] or static[170] coating with a colloidal solution of graphitized carbon black. The resultant layer strongly adheres to the glass surface and is not removed by washing with different polarity solvents.

Studies of different stationary phase film thicknesses on graphitized carbon black[168–170] demonstrate that by operating with a small concentration of stationary phase the adsorption properties of graphitized carbon black may also play an important role, whereas by using a large amount of stationary phase this effect is negligible and only partition occurs. It has been claimed that for this reason, "tailor-made" columns for specific purposes can be prepared[169].

It has been found that graphite-coated capillary columns permit the use of a wide range of stationary phases, while those prepared by the method of Grob[27,164] are suitable only for a restricted range of moderately polar phases.

4.7. Sodium chloride deposition

Since HCl gas etching of soda-lime glass results in a crystalline layer of sodium chloride, it is logical to form a similiar layer by direct deposition of sodium chloride. Such an approach is also useful for roughening Pyrex glass.

Watanabe and Tomita[171] first prepared columns in this way by dynamically coating with a 10% (w/v) aqueous solution of sodium chloride and then drying the column at 200°C for 10 h while purging with nitrogen. Results indicated that columns coated with these crystals prior to deactivation and coating were less active than untreated columns. However, the deactivation effect probably resulted from the screening effect of the thicker filmed stationary phase on the roughened column. Further work[172] indicated that the degree of crystal coverage of the glass surface is dependent on the concentration of the NaCl coating solution. The ratio of the number of crystals formed is about 1:10:50 for columns prepared from 1%, 5% and 10% solutions, respectively, with the 10% solution giving approximately a 20% surface coverage. Fig. 24 shows an SEM of a column coated with a 10% solution.

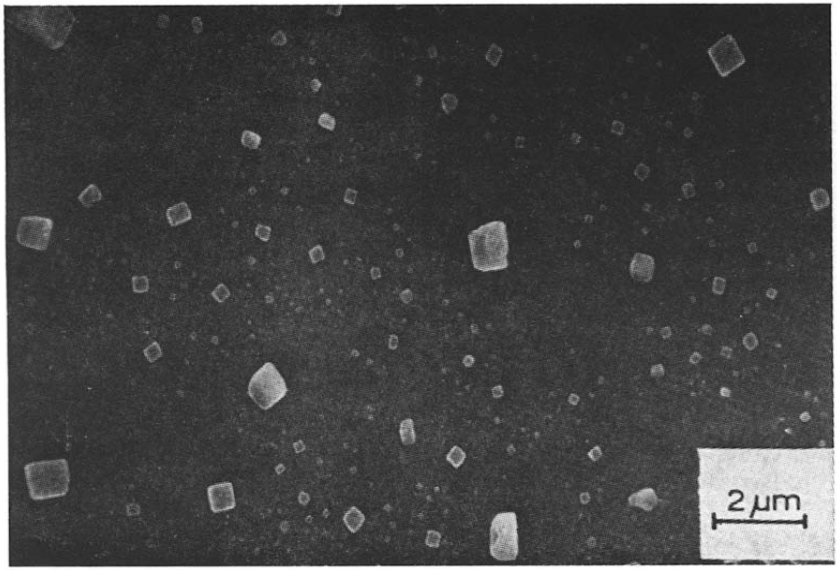


Fig. 24. SEM of a glass capillary column after coating with a 10% aqueous solution of NaCl. Reprinted with permission[172].

Similar work was done by Sandra *et al.*[173] except that dynamic coating was carried out at 60°C. These columns were termed "dendrite" columns. Although the columns provided adequate roughening for apolar phases, the degree of roughness was insufficient to stabilize and maintain thermostable columns of the more difficult to coat polar phases.

A more elaborate method of NaCl deposition for use in polar phase column preparation was reported by Franken *et al.*[142]. In this procedure a suspension of NaCl, obtained from the addition of a saturated solution of NaCl (in methanol) to 1,1,1-trichloroethane, was passed through the column. After the solvent was evaporated, the procedure was repeated four more times to increase the amount of NaCl deposited on the wall. Finally, the NaCl conglomerates were recrystallized at 350°C for 1 h. The same group of workers[174] have recently developed a theoretical model based on electrostatic interactions for the mechanism of the deposition of NaCl, and an improved procedure that gives highly reproducible surface coverage. Rather than forming a film of particles behind the coating plug, as originally thought, the particles deposit spontaneously from the bulk solution and become attached to the column wall without evaporation of the solvent. The amount of NaCl deposited on the column wall is a function of the volume of the suspension passed through the column and the contact time of the suspension with the column wall. Ultimately, the amount of NaCl per unit surface area approaches a maximum as the attraction forces of the surface diminish. To achieve maximum surface coverage a minimum amount of suspension corresponding to 25 μl/cm^2 of column surface should be passed through the column with a total contact time of at least 40 min at a velocity of 1–5 cm/sec. Fig. 25 shows an SEM of a borosilicate glass capillary column coated with NaCl by this method. The surface coverage is nearly complete.

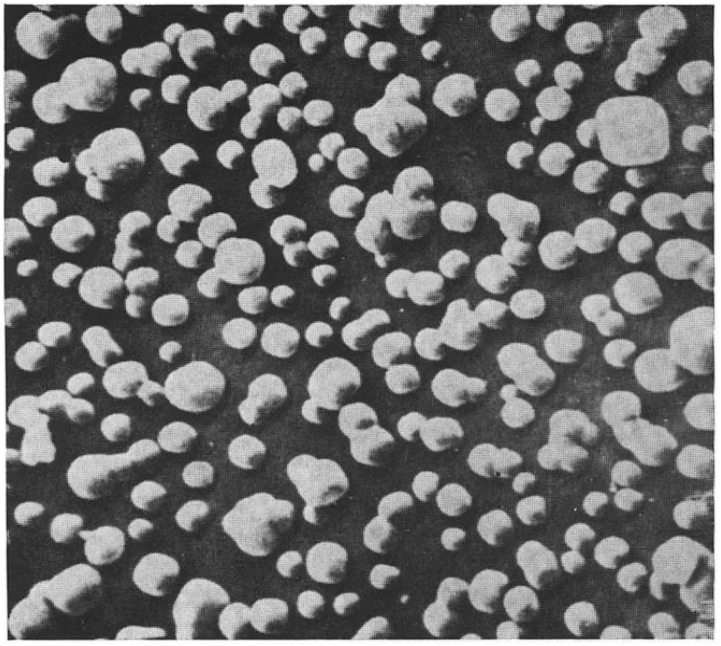


Fig. 25. SEM of a borosilicate glass capillary column after coating with a suspension of NaCl. Reprinted with permission[174].

4.8. Silica deposition

Horning and co-workers[175,176] developed a method of surface roughening by suspending fine particles of silanized silicic acid in the stationary phase as it is coated on the inner wall of the column. These particles in the liquid phase change the spreading characteristics of the film and greatly enhance its stability. The silicic acid used in these preparations is Silanox 101, a trimethylsilylated fumed silica with a primary particle size of 7 nm. As these particles do not adhere to the glass surface or self-aggregate they must be coated with a binder. The stationary phase itself and, in some instances, a surfactant such as benzyltriphenylphosphonium chloride (BTPPC) are used as the binder. Experience has shown that when an adequate amount of stationary phase, solvent and Silanox are suspended together, the solution is too viscous to coat properly. Therefore, a two-step coating procedure is employed. As two steps are involved, it closely resembles SCOT column preparation procedures. In fact, columns prepared in this manner are often described as being SCOT columns.

In the first step, a dilute solution of stationary phase is supended together with the Silanox to act as a binder and passed slowly through the column leaving behind a film of silica particles bound to the glass wall by the stationary phase. In the second step, a more concentrated stationary phase is passed through the column, thus increasing the total amount of stationary phase on the column wall. A typical coating solution used in the first step of this process is made by sonicating approximately 0.5 g of stationary phase, 2 g of Silanox and 100 ml of a high-density solvent (necessary to keep the Silanox in suspension), such as CCl_4 or $CHCl_3$. In the initial coating step,

the wall is first wetted with the solvent used in the suspension, and then a plug (25% of the column length) of the suspension is passed through the column at approximately 5 cm/sec. After the liquid plug is expelled from the column, a nitrogen flow is continued for 3 h to dry the coating. A 2% solution of stationary phase in a less viscous solvent, such as isooctane, is then passed through the column at 2 cm/sec to complete the second coating step for increasing the amount of stationary phase on the column wall. Fig. 26 shows an SEM of a Silanox -SE-30 coated column which illustrates that the small Silanox particles do not form a porous layer, but are more or less regularly distributed over the column wall[177].

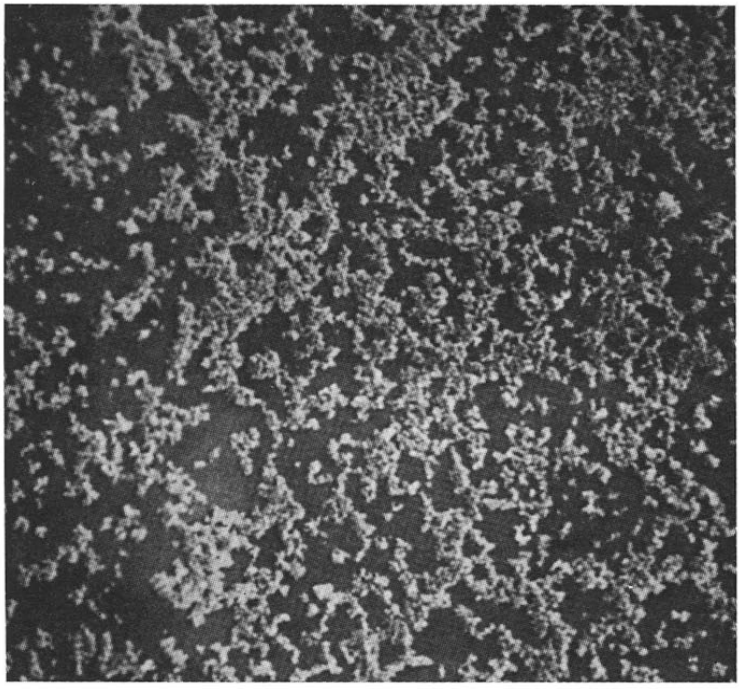


Fig. 26. SEM of a SCOT column coated with Silanox and SE-30. Reprinted with permission[177].

Unfortunately, the two-step dynamic process described above is not useful in the preparation of polar columns. It has not been possible to choose solvent combinations that result in even coatings and high column efficiencies. By using a static coating procedure for the second step, however, the undesirable stripping effects of the solvent during dynamic coating can be eliminated[178], but owing to the slowness of the evaporative technique, the practical limit of column length is about 20 m. This problem is overcome by utilizing the forced evaporative coating technique (discussed in Section 6.3) in place of the regular static procedures. In this method, the entire column is filled with a solution of the liquid phase, together with a small amount of pentane which is added as a low-boiling constituent. The column is then slowly introduced into a heated oven which vaporizes the solvent.

Blakesley and Torline[179] have successfully produced a variety of polar columns by a modification of the two-step dynamic method. Igepal CO-880, a surface-active agent, is added to the suspension of Silanox and the coating procedures are carried out as previously described. However, surfactants may alter the retention characteristics of a phase, so McKeag and Hougen[180] modified the solvent system of Horning *et al.*[175,176] to chloroform–acetone (10:1) in both steps of the coating process. One-step dynamic procedures[181,182] have also been used to coat polar columns, but the coating is not as even or desirable as two-step coating methods[183].

The hydrophobic surface of Silanox is not compatible with polar stationary phases and will show poor wettability. It would seem logical to use an unsilylated fumed silica (Cab-O-Sil) in much the same way that Silanox has been used. Pellizzari[184] developed a method of coating columns with a Cab-O-Sil suspension, followed by *in situ* silylation where the particles are cross-linked to themselves and to the column wall by dimethyldichlorosilane. This surface proves suitable for coating with the moderately polar stationary phase OV-17. Cramers *et al.*[185] have developed a method in which Cab-O-Sil is used as a stabilizer for the polar stationary phase OV-225. Cab-O-Sil stabilized columns are prepared following the two-step dynamic procedure[175,186] discussed above. The Cab-O-Sil is prepared by treatment with a 1% solution of BTPPC in methylene chloride. After centrifugation, the Cab-O-Sil is washed with methylene chloride and carbon tetrachloride. The treated Cab-O-Sil and a solution of OV-225 in CCl_4 are suspended together by sonication, and then pushed through the column at 4–5 cm/sec. After drying with nitrogen, additional OV-225 is deposited by coating with a 10% solution in toluene.

Schulte[187] described a method of directly coating a thin film of colloidal silicic acid on the inner wall of borosilicate glass. A 15% aqueous solution of colloidal silicic acid (Merck 12475) is diluted with acetone to form a 0.3% solution and centrifuged to remove the larger particles from the suspension. The column is then dynamically coated with the suspension in the usual way. After the plug of the silicic acid suspension leaves the column, the temperature is raised to 90°C to evaporate the solvent. Finally, the column is heated under a nitrogen flow at 150°C.

Another method involves depositing only a minute amount of silica on the inner wall of the capillary column[188]. A liquid plug of dilute water glass is passed through the column followed by a flow of gaseous HCl. In this way, a thin film of water glass is left on the glass surface which reacts with the HCl gas to produce amorphous silica. The coating conditions have to be chosen carefully to prevent the formation of an unsuitable surface. Generally, a 5–10% water-glass solution is forced through the column at 60°C at a velocity of 5 cm/sec. The column is stabilized by sealing the ends and heating for 1 h at 150°C.

Quartz has also been used to roughen the inner surface of glass capillary columns. The quartz is deposited on the glass tube prior to drawing so that when the column is drawn, an even distribution of quartz is fused to the capillary walls (see Section 3.1 and refs. 100 and 101).

4.9. Other roughening methods

Recently, a novel method of roughening glass capillary columns by a low temperature plasma etch was described[189]. In this etching process, performed at low

pressure, fluoro compounds under the influence of an RF discharge form a plasma that reacts with the glass wall. The plasma consists of atoms, free radicals and excited molecules. It is thought that the principal etching mechanism is the reaction of fluorine radicals with the silica of the glass surface. This procedure can be controlled by merely timing the length of the etch. Fig. 27 shows an SEM of a glass capillary column that has been plasma etched for 8 h with carbon tetrafluoride.

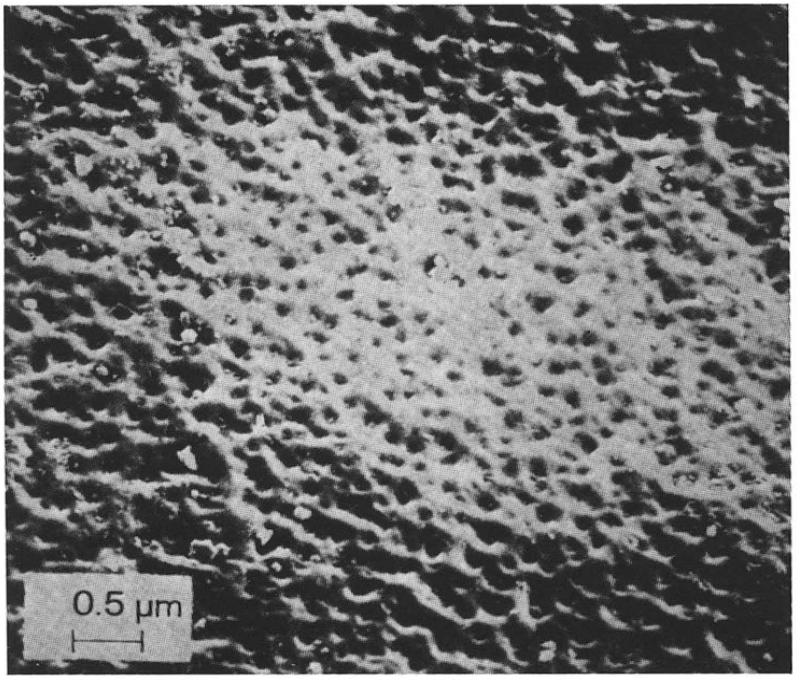


Fig. 27. SEM of a plasma-etched glass capillary column after treatment with CF_4 for 8 h. Reprinted with permission[189].

5. SURFACE DEACTIVATION AND CHEMICAL MODIFICATION

5.1. General considerations

As discussed in Section 2.2, the glass surface has several different types of active sites originating from various glass ingredients or from the silica structure itself. The earlier surface modifications were aimed mainly at providing better wettability of the glass surface with respect to the stationary phase. More recently, attention was directed towards deactivation of the surface. This is a result of the increased interest in trace analysis and the development of more sensitive detectors.

Fortunately, however, it has been shown that the best deactivation methods also modify the glass surface and provide better wettability. In this section, the various approaches to deactivation are outlined and discussed in some detail.

5.2. Roughening methods

Surface roughening methods provide some, although often limited, deactivation in two different ways. The first way involves physically covering many of the more active sites. For instance, the crystallization of sodium chloride on the glass surface results in the covering of active glass ingredients by crystals of a somewhat weaker Lewis acid, sodium. The net effect is a less active surface. In addition, the surface roughening often provides better wettability of the surface, which results in better coverage by the stationary phase and less net surface activity. The stationary phase itself provides a certain degree of deactivation, especially when coated in rather thick films.

Although the barium carbonate procedure was originally developed as a treatment for roughening the glass surface (see Section 4.5), it has also been claimed by Grob *et al.*[159,162] that in addition to forming crystals, barium carbonate covers the entire glass surface in a very thin, smooth layer, and thus produces an inert background for durable deactivation. In fact, it is claimed that when using a very dilute solution of barium hydroxide, as in the preparation of apolar capillary columns, only a smooth surface cover with no observed crystals is obtained[159]. There are several contradictions to this claim, even within Grob *et al.*'s own work. For instance, it was found that the glass surface after barium carbonate treatment was slightly basic, and that acids with pK_a values lower than 6 (*i.e.*, most fatty acids) have difficulty passing over the carbonate surface[158]. Furthermore, it was found essentially impossible to deactivate satisfactorily barium carbonate crystals which were not covered by liquid stationary phase films[163]. In fact, Grob *et al.* recommend a Carbowax deactivation after barium carbonate treatment[158–162]. Onuska and Comba[156] have found that deactivation of a barium carbonate treated surface with Carbowax is insufficient to prevent the adsorption of propionic acid.

The thermal stabilities of stationary phases coated on capillary columns after various pre-treatments have been studied by Schomburg and co-workers[190,191]. They observed a rapid bleeding of the phase on alkali glasses even after $BaCO_3$ deposition (see Fig. 31).

Recent analyses of surfaces after barium carbonate treatment by X-ray photoelectron spectroscopy (ESCA) and Auger electron spectroscopy (AES)[24] have shown that the surfaces are not completly covered with barium carbonate.

It has become apparent that the barium carbonate procedure is principally a surface roughening technique and it is somewhat improper to refer to the technique as one which also produces surface deactivation.

5.3. Surface-active agents

Molecules of surface-active agents adhere to the inner wall of a capillary column, forming an oriented monomolecular layer. This layer can shield the surface and provide a simple and versatile method of deactivation. The surface-active agents can be added to the stationary phase or used separately to pre-treat the wall before coating with the stationary phase.

A number of workers[91,192–199] reported the use of surface-active agents as additives to liquid phases to improve the properties of stainless-steel capillary columns.

These materials usually have a polar end that is adsorbed on the capillary wall which deactivates its active sites. The other end of the molecule presents a surface which decreases the surface tension of the liquid stationary phase. Metcalfe and Martin[196] proposed the use of a quaternary ammonium compound, trioctadecylmethylammonium bromide (Gas-Quat L), as a surface modifier for use in coating glass capillaries with various phases.

Grob[27] later described the detailed experimental procedures applicable to glass for this approach. It was originally believed that the cationic portion of the quaternary ammonium ion combined with the negatively charged $-Si-O^-$ function of the glass surface. This in reality was not achieved[3] and the usefulness of the procedure is questionable.

More recently, several workers used benzyltriphenylphosphonium chloride (BTPPC)[29,141,149,200,201] or sodium tetraphenylborate (Kalignost)[29,200] for deactivation of glass capillary columns. Both BTPPC and Kalignost are believed to adhere to the glass surface rather than to react with it, and should provide deactivation for both silanol groups and Lewis acid sites[29]. Kalignost is an anionic agent, while Gas-Quat L and BTPPC are cationic. Typically, columns are deactivated by repeated rinsings with dilute solutions of the agent and pure solvent.

There have been recent reports of the use of diisobutylphenoxyethoxyethyldimethylbenzylammonium chloride[149,202], triethanolamine[149] and triisopropanolamine[154] as surface modifiers.

Thin coatings of basic salts such as K_2CO_3, Na_3PO_4[203,204] and KF[205] have also been used successfully to interact with active surface sites and produce less active columns. These procedures are especially useful for the preparation of polar columns for the analysis of organic bases such as amines.

The main drawbacks of these approaches are the often ready displacement of the monolayers by other substances, their limited thermal stabilities and their inherent activities toward many sensitive compounds. It is also possible that these additives may affect the retention characteristics of the stationary phase.

5.4. Organic polymer coatings

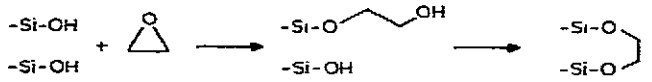
Aue *et al.*[30] found that when Carbowax 20M was coated on a diatomaceous earth support, heat-treated at 280°C, and the resultant packing exhaustively extracted with boiling methanol to remove the phase, a highly efficient, well deactivated packing with very low bleed characteristics was produced. It was proposed that the long polyethylene glycol chains were permanently bonded in a near monomolecular layer to the silica surface by means of hydrogen bonding and various types of Van der Waals bonds. More details on this method of deactivation for chromatographic packings have come from subsequent studies by this group[206–211].

Cronin[212] applied a non-extractable Carbowax 20M film to capillary columns by dynamically coating the columns with a 2% (w/v) solution in methylene chloride, sealing the capillary ends and placing them in an oven at 280°C for 16 h. After this treatment, the coating was removed by washing the column successively with methylene chloride and methanol. The resultant surface was found to be suitable for further coating with Carbowax 20M. Other variations of this method have been published[26,33,158]. The later version of Grob and Grob[158] involved repetitive coating with more dilute solutions followed by heat treatments.

Although Grob and Grob[158] claimed that the strongly polar polyethylene glycol deactivated surface is "poorly wettable by apolar phases", Blomberg and Wannman[213] found the surface to be very compatible with apolar phases such as SP-2100 and OV-101. It was suggested that a similar effect occurs to that found with a thin layer of octadecanol coated on diatomite, in which the hydroxyl groups are oriented toward the support surface and the film surface thus exhibits a non-polar character[214].

Deactivation of glass capillaries with Carbowax 20M via the gas phase was more recently reported[215,216]. A glass tube, packed with 5% Carbowax 20M on Chromosorb W AW, was inserted into the hot zone of the injection port of a gas chromatograph, which was maintained at approximately 250°C. The volatiles from the pre-column were allowed to bleed into the capillary column overnight at a temperature 5–10°C lower than the injector port and at a nitrogen flow-rate of 1–3 ml/min. It was found that the process of deactivation took place uniformly over the entire column length at a rate determined by slow reaction kinetics rather than by a limited availability of the bleeding products. This was consistent with the observation that the deactivation process was not influenced by column length, column diameter or carrier gas flow-rate.

The exact mechanism of bonding of Carbowax to the glass surface is not known. Whereas earlier reports[26,30,33,158,212] suggest that hydrogen bonds and Van der Waals bonds are involved, it is believed by some[217] that pyrolysis of Carbowax produces organic species, such as oxirane, which are chemically bound to the glass by reaction with the surface silanol groups:



(5)

While some form of chemical bond cannot be entirely ruled out, most bonds are not expected to withstand the vigorous extraction procedure with methanol during preparation[30,212]. It is known that the presence of surface silanol groups is necessary. It was shown by Daniewski and Aue[209] that a drastic decrease in the number and type of silanol groups from the silica surface by heat treatment at 850°C under a dry nitrogen flow can be detrimental to the successful bonding of Carbowax.

In addition to Carbowax 20M, a number of other organic polymers have been used for deactivation. These include Carbowax 1000[162], Carbowax 400[107], Emulphor O[26], squalane[218], ethoxycarbonylpolyphenylene[219], alkylpolysiloxanes[157], poly-N-β-hydroxyethylaziridine[149], N-isopropyl-3-azetidinol[142] and N-cyclohexyl-3-azetidinol[149], the last two which, although not polymeric, can be heat polymerized at relatively low temperatures.

The thermal stabilities of Carbowax deactivated columns are a matter of controversy. Although claims have been made of stability even at temperatures above 300°C, studies have shown[157,216] that these columns are not stable for extended use above 250°C. On the other hand, Schomburg *et al.*[191] found that by coating capillaries with alkylpolysiloxanes (OV-1, OV-101, OV-17, Dexsil 400, SE-52 and SE-54), heating the sealed columns to 450°C and re-coating with the same stationary phase,

columns were produced which were stable up to nearly 300°C. They suggested that the decomposition products of the polymer undergo chemical bonding to the glass surface by reaction with the surface silanol groups, very similar to the process of silanization.

In addition to thermal instability, polar polymer deactivation layers can also influence the polarity of the stationary phase. This is especially noticeable for columns coated with thin film of apolar phases[33].

5.5. Acidic leaching

Leaching refers to the removal of soluble components from a heterogeneous matrix, usually with the use of an aqueous solution. As discussed earlier (see Section 2.2), glass contains metallic cations which function as Lewis acid sites and give the glass undesirable chemical activity. Controlled acidic leaching can remove these active sites from the glass capillary column wall and form a silica-rich surface that greatly enhances chromatographic performance[24]. The formation of a silica-rich surface layer greatly minimizes the effects of glass variety on subsequent treatments and lends a higher degree of reproducibility to column preparation. The general reaction can be understood in terms of electrophilic or nucleophilic attack on the siloxane bridges (Fig. 28). Electrophilic attack on the acidic siloxane bridge is unlikely and dissolution of silica in acidic solutions will be a slow process. Nucleophilic attack, however, can occur readily and accounts for the increased solubility of silica in alkaline solutions. In order to better understand the leaching process, some of the fundamental mechanisms are described below.

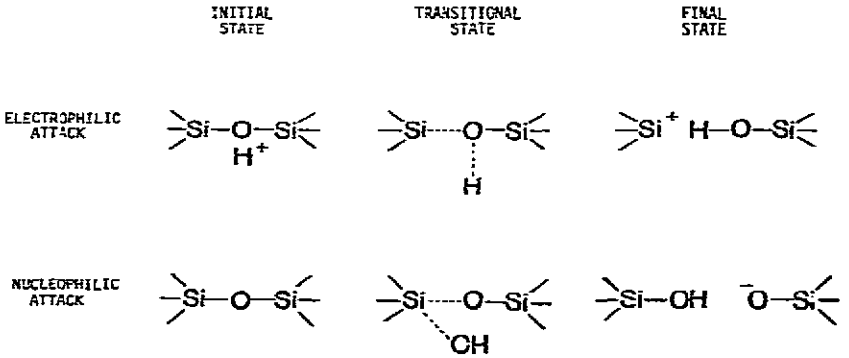


Fig. 28. Diagram of electrophilic and nucleophilic attack on Si–O–Si bonds.

Below a pH of about 7, glass is hydrolytically decomposed. The Si–O–R bonds rather than the Si–O–Si bonds are cleaved. R, an alkali or alkaline earth metal ion, can form a water-soluble salt that passes into solution and is replaced by an H^+ ion. The original Si–O–R bond is converted to an Si–OH bond and a surface gel is formed. This type of process is generally thought to be diffusion controlled with the amount of alkali extracted proportional to the square root of time[220–223].

Obviously, acidic leaching of a glass surface increases the density of the surface

hydroxyl groups. Consequently, acidic leaching must be followed by some treatment that effectively blocks the surface silanol groups, or the net effect is an increase in surface activity. Fortunately, silanol groups can be adequately deactivated by silylation (see Section 5.6), whereas the original Lewis acid sites cannot be blocked or otherwise deactivated. The only alternative for ridding the column wall of their effects is to remove them.

During acidic leaching the alkali and basic oxide components are dissolved to yield a silica-rich surface layer. For example, secondary ion mass spectrometry of a piece of soda-lime glass that had been washed in water for 60 min at 37°C revealed a sodium and calcium depletion layer several hundred ångstroms thick[224]. Other recent studies indicate that both sodium and calcium are removed from the surface in about the same proportion to one another as they exist in the bulk glass[225,226]. These results do not support some earlier theories which postulated that acidic leaching preferentially removes sodium ions and leaves a surface layer enriched not only in SiO_2, but also calcium ions.

Below pH 7, the original glass backbone of Si–O–Si is unaffected. Alkaline solutions (NaOH), however, break the Si–O–Si bonds and form Si–OH and Si–O–Na, thus bringing about the actual dissolution of the silica surface. Rather than an enriched surface layer of silica, a porous surface structure is formed. Instead of diffusion kinetics, an interface reaction predominates with the amount of material leached being linearly dependent on time.

Acidic leaching of solid supports for packed column chromatography has been carried out since the inception of gas chromatography. This treatment was done empirically without any clear idea of its purpose, although it was generally thought that mineral impurities were removed[227]. Horning *et al.*[228] were the first to show that the tailing of steroids is reduced by washing the support with acid prior to silylation. Early results of acid leaching in the preparation of capillary columns, however, were not favorable. Some glass capillary columns were leached so intensely that they were made porous, and were consequently so adsorptive that they were suitable for use only in gas–solid chromatography (see Section 4.2). Other workers evidently experienced disappointing results when trying to apply acidic leaches. Novotny and co-workers[3,139] suggested that any treatment involving aqueous solutions actually worsened column performance. A few years later, however, Novotny and Bartle[229] recognized that an acid leach would be useful for the removal of reactive metallic cations from the glass. Later in the same year (1974), Díez *et al.*[16] also concluded that acid leaching would remove the reactive cations and give improved chromatographic performance.

It was not until 1975, however, that leaching was successfully used in the routine preparation of glass capillary columns. Lee[230] reported that columns washed with formic acid were superior to those which had not been acid treated. In this procedure, soft-glass columns were first treated with HCl gas, and then thoroughly washed with concentrated formic acid by slowly forcing approximately 40 ml of the acid through the column. Although NaCl is only moderately soluble in this organic acid, the excess acid solution completely removes the NaCl crystals. After deactivation by silylation, columns prepared in this manner have proved suitable for the analysis of polycyclic aromatic hydrocarbons. Numerous chromatograms obtained with columns prepared in this manner have been published[231–233].

Borwitzky and Schomburg[234] recently reported a procedure that is similar to that just discussed. In their procedure, the sodium chloride crystals formed on the inner surface of alkali-glass capillaries by HCl gas are removed by forcing water through the capillaries followed by subsequent rinsings with acetone and diethyl ether. Such a treatment forms a thin layer of dealkalinized glass on the surface. This leads to increased temperature stability of the coated stationary phase (see Section 8.4). The surfaces obtained after removing the NaCl layer are smooth, but are easily wettable by most methylsilicone stationary phases[191,234].

In 1977, Grob *et al.*[159] reported on modifications and improvements of their original $BaCO_3$ column preparation procedure (see Section 4.5), among which was an acid leach. The treatment was designed to produce a silica layer that was compatible with $BaCO_3$ crystallization. The type of leach described, and that which is still advocated by Grob *et al.*, is a static leach in which the capillary column is almost completely filled with 20% hydrochloric acid. After the ends have been sealed, the column is heated to 150–180°C and left overnight. The exact temperature of the treatment depends upon the type of glass, Pyrex requiring the higher temperatures. After cooling, the column is rinsed with a one-quarter column length plug of distilled water, and then with the same amount of methanol. To remove completely any water and to dehydrate the silica surface, the Grob recipe advocates heat treatment at 300°C under a moderate carrier gas flow for several hours.

Lee and co-workers[24,235,236] prefer dynamic over static leaching. In this method, 20% HCl is slowly forced through the glass capillary column at approximately 110°C, the boiling point of the acid solution. By preventing the formation of steam, the surface is not roughened excessively and longer leaching times may be applied to allow reactive cations to diffuse more effectively from the glass matrix and into the leaching solution. Since the rate of extraction of ions is proportional to the square root of time, a longer, milder leach is preferable. Generally, a 90-m length of capillary column is leached for about 50 h with 50 ml of acid solution. SEM analysis of capillaries leached in this way show no distinguishable surface roughening. However, it is possible that the extraction of ions leaves the surface somewhat irregular on a molecular scale. After leaching with acid, columns are rinsed with copious amounts of deionized water to remove all traces of HCl residues. These residues can lead to poor thermostability of the stationary phase and to active surfaces. A heat treatment is also necessary to remove physically held water from within the leached silica surface, and from the surface itself. To prevent surface dehydroxylation the temperature should not be above 150°C (see Section 2.2). Once again, a longer, milder treatment gives optimal results. Generally, overnight treatment with carrier gas flow at about 100°C and then a few hours at 150°C is sufficient to remove undesirable water. Excessive moisture not only decreases the wettability of the glass surface, but also interferes with chemical modifications such as silylation.

After phase separation of Pyrex glass (see Section 2.1) induced by heat treatment, the borate phase is soluble in acids, and therefore readily extractable by acid leaching[237]. Although complete phase separation takes a long time, it is possible that the high temperatures involved in drawing glass capillary columns can also induce some phase separation. Nevertheless, the boric oxide phase itself, being amphoteric in nature, is also extractable by acidic leaching[238]. However, infared studies[239] of leached glasses (porous glass–96% silica) have indicated that a surface highly en-

riched in boron exists. In fact, the B:Si ratio may be as high as 1:3. The surface excess of boron is assumed to be caused by a re-precipitation process during the leaching of the glass wherein a borosilicate gel is formed[240].

This re-precipitation process (if it actually occurs) can be avoided by preventing a build up in concentration of boron and silica in the leaching solution by continually providing fresh leaching solution. Essentially, the dynamic leaching method of Lee and co-workers[235,236] fulfills this requirement. Auger electron spectroscopy and ESCA surface data[24] indicate that dynamically leached Pyrex glass capillary columns have a surface completely free of boron and other metallic impurities. In fact, depth profile analyses indicate that a relatively thick layer of pure silica is formed[24]. Thus, a leached glass surface of this nature has many of the same properties that give fused silica its intrinsic inertness.

Under static conditions it is possible that boron ion re-precipitation could take place. The other ions extracted from the surface could also be re-precipitated. In fact, surface analysis data of glass capillary columns prepared after the manner of Grob *et al.*[159,241,242], which utilizes a static leach, indicate that a pure silica surface is not always formed[24]. Furthermore, as the pH of the static leaching solution increases from the alkali extracted into it, the reaction kinetics could change from diffusion-controlled to interface-controlled. When this happens the silica-rich surface region starts to depolymerize and is eroded away[224].

Grob *et al.*[243] recently recognized some of the inherent problems associated with a static leaching procedure and suggested modifications to compensate for them. For instance, since dissolved ions have a tendency to be readsorbed on to the silica, they suggest that after statically leaching a column, it should be flushed with dilute HCl (a dynamic leach). They also suggest that this treatment should be done at room temperature instead of 150–180°C. They further recommend that dehydration of the surface be done for both shorter lengths of time and at lower temperatures; 30–90 min instead of 12 h and 220–250°C instead of over 300°C. Clearly, this milder dehydration treatment does not lead to as excessive surface dehydroxylation as the earlier described treatments.

5.6. Modification by chemical bonding

One of the most practical methods of eliminating the undesirable activity of the surface hydroxyl groups is to replace them chemically with inert groups. Furthermore, the glass surface wettability can be enhanced by choosing modifying groups that are compatible with the desired stationary phase. Chemical similarities between the column wall and the stationary phase are conductive to its efficient spreading. Non-chromatographic work indicates that for low-energy surfaces, such as chemically modified glass, the temperature dependence of the critical surface tension of the surface and of the liquid surface tension are comparable only if the surface and liquid are chemically similar[244]. This is of particular concern, since elevated temperatures and temperature programming are commonly used in the operation of glass capillary columns. The hydroxyl groups on the glass surface offer a number of possibilities for modification, some being more effective than others.

Early modification methods included the formation of Si–O–C, Si–C–C and Si–O–Si–C bonds. In the formation of Si–O–C bonds[27,245], the hydroxyl groups are

first chlorinated and then reacted with an alcohol. However, since the ester bond has low thermostability and is easily hydrolyzed, this method has found little practical value in glass wall modification[27]. Chlorinated silica surfaces can be further modified by using Grignard[246,247] or organolithium compounds[27,247–249] for the formation of Si–C–C bonds. The carbon atom bound directly to the silicon atom is more stable than in the case of esters, but the limited selection of organolithium compounds decreases the value of this approach. The use of phenyl- and butyllithium for the modification of glass capillaries has been described[27].

One of the most widely applied methods of chemical surface modification in glass capillary column preparation is silylation or silanization, the terms being synonymous. In this reaction, the surface hydroxyl groups of the glass are replaced with silyl ether groups. Modifications produced in this manner are extremely stable, owing to the strength of the Si–O–Si linkage. The polarity and chemical characteristics of the modified layer that is formed by silylation can be controlled by the choice of constituents of the silylation reagent. Silylation of glass capillaries was first reported by Kiselev[250] and Kiselev and Shcherbakova[251], who used trimethylchlorosilane (TMCS).

TMCS reacts with the surface hydroxyl groups according to the following reaction:

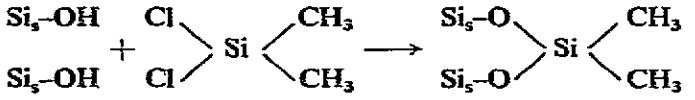
$$Si_s\text{–}OH + Cl\text{–}Si(CH_3)_3 \rightarrow Si_s\text{–}O\text{–}Si(CH_3)_3 + HCl \quad (6)$$

Gravimetric and spectroscopic studies of silica surfaces indicate that only the free surface hydroxyl groups are involved in this reaction[53,252–254]. The hydrogen-bonded hydroxyls react little, if at all, and lead to defects in the chemically bonded surface layer. The reaction of alkylchlorosilanes with the surface groups may be considered to involve a bimolecular transition state, and in the case of hydrogen-bonded hydroxyls, steric hindrance prevents the approach of the silane to the oxygen atom of the hydroxyl group and the subsequent formation of the transition state[254]. It is known that at lower temperatures, methylchlorosilanes are physically adsorbed on the silica surface and are not chemically reacted[255,256]. Although the literature contains contradictions, it would appear that reaction temperatures of 300–400°C are necessary to ensure complete (available) reaction[61,254–258]. Physically adsorbed surface water and structural intraglobular water, however, react readily with methylchlorosilanes at room temperature, the water being a better nucleophile than the surface hydroxyl groups[256]. In fact, dimethyldichlorosilane forms polymethylsiloxane macromolecules in the presence of water[252].

As discussed previously (see Section 2.2), dehydration at 150°C removes most of the physically adsorbed water from the silica surface and provides a maximum number of bonded silanol groups, *i.e.*, about 5 per 100 Å^2. Dehydration at 400°C essentially removes only hydrogen-bonded hydroxyl groups and leaves the number of free silanol groups unchanged. This has been confirmed in glass capillary column studies[259]. It would therefore be expected that the density of bonded silyl groups would be as great for the 400°C dehydrated surface as for the surface dehydrated at 150°C, since only free hydroxyl groups react. In fact, since the area of the trimethylsilyl group is approximately 40 Å^2 (refs. 56 and 258–260), only about 2.5 surface silanol groups per 100 Å^2 are capable of being blocked by silylation. Steric hindrance would limit reaction of any greater number. The residual hydroxyl groups might

be considered as being covered with an umbrella formed by the $-Si(CH_3)_3$ ligands.

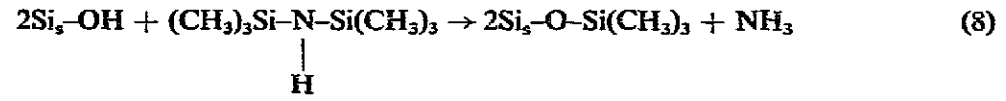
The kinetics of reaction for TMCS (eqn. 6) with the surface silanol groups are expected and confirmed to be first order. With dichlorodimethylsilane in this reaction, a first-order reaction is no longer obtained. It has been proposed that bifunctional silanes can react according to the equation



(7)

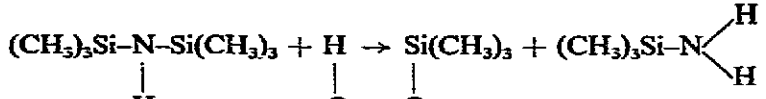
Second-order reaction kinetics might be expected, but 1.6 reaction order kinetics are observed[257]. This can be accounted for by assuming that 60% of the hydroxyls react bifunctionally as suggested above, and that 40% react monofunctionally as does TMCS. This indicates that 60% of the silanol groups are sufficiently close together that they can react bifunctionally, yet sufficiently far apart that they do not hydrogen bond to one another[257].

With hexamethyldisilazane (HMDS) the overall reaction taking place with the surface is



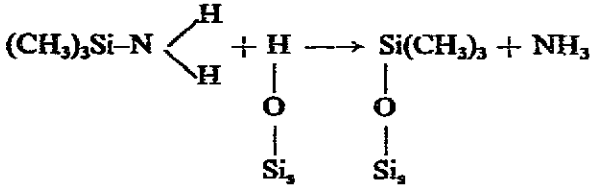
(8)

The freely vibrating hydroxyl groups are essentially monoenergetic, that is, the reactivity of all the groups is the same. This means that these groups react randomly. It has been determined that the reaction of HMDS with a silica surface follows second-order kinetics[261]. In other words, when one HMDS molecule reacts with the surface, two OH groups are removed. The second-order kinetics can be accounted for by two reaction schemes. The first scheme as shown in eqn. 8 is a simple, one-step, three centered reaction, and implies that all the hydroxyl groups are sufficiently close that they react in pairs. Alternatively, the reaction can be thought of as proceeding by a series of reactions where a reactive intermediate product is formed which immediately reacts further with the surface. Such a scheme is shown below[81]:



(9)

followed by



(10)

The data indicates that about 70% of the HMDS molecules are adsorbed on two sites, and 30% adsorbed on a single site[261]. HMDS is considerably more reactive towards surface silanols than chlorosilanes, with chemisorption taking place at a

lower temperature[258,260,261]. The >N–H of the HMDS is a much stronger proton acceptor than is the chlorine of the TMCS molecule[258].

In reactions of chlorosilanes, HCl is a reaction product. Likewise, NH_3 is a reaction product when HMDS is used. It has been suggested that the HCl reacts with the silica surface, perhaps at the siloxane linkage, to form additional silanol groups. However, experimental evidence does not support this theory[81,262] and theoretical considerations would deem it unlikely. With a glass surface containing metal oxides, however, HCl reaction could certainly form additional silanol groups. NH_3, on the other hand, has been shown to adsorb physically on the silica surface at temperatures less than 170°C[260]. At higher temperatures it is also possible for the NH_3 to react with the surface by nucleophilic attack on the silica structure.

The bonded silyl groups are extremely stable and may be heated to 500°C in vacuum or 400°C in air[256] without decomposition. Other studies show that silylated surfaces are stable up to 350°C[263]. HMDS silylated surfaces are stable to at least 400°C, even with water vapor present[81]. Boron, present as boronol groups (B–OH), behaves very similarly to silanol groups. The boronol groups are, however, much more reactive, and tend to form less stable ether groups. In fact, the ether formations are easily hydrolyzed by water at 400°C.

Since fused silica capillary columns are drawn at an extremely high temperature (around 2150°C), the surface is probably completely dehydroxylated[17,55]. Furthermore, at temperatures greater than 800°C, the silicon tetrahedra are able to rearrange and partially relieve the strained siloxane linkages formed from the condensation of surface hydroxyl groups[73]. This rearrangement decreases the reactivity of the siloxane bridge and makes rehydration difficult. Likewise, the adsorptive effects of this bridge are probably reduced. Consequently, the surface of fused silica has fewer active sites than does regular silica or glass, but the possibilities of chemical surface modification are also restricted. This could limit the number of stationary phases that can be effectively coated on fused silica.

In glass capillary column silylation, Novotny and co-workers[145,264] demonstrated that silylation with a gaseous mixture of HMDS and TMCS of previously etched columns improved their coating with apolar stationary phases. This procedure was carried out by passing the vapor of a 5:1 mixture of HMDS and TMCS through the column for 30 min. The ends of the capillary were sealed and the column was heated at 150°C for 48 h[264]. This treatment, however, reduced the column efficiency in the case of polar stationary phases. Such behavior would be expected since the hydrophobic silylated surface would be less wettable by the polar stationary phase than the original hydroxylated glass surface. In an attempt to improve wettability of the glass surface by polar stationary phases, Novotny and co-workers[265–267] used a variety of differently substituted silanes to form surfaces of "tailor-made" polarity. In this work, an attempt was made to match the chemical character of the stationary phase with similiar groups on the glass surface. For example, polar stationary phases such as polyethylene or polypropylene glycols are spread uniformly on hydroxyl monolayers, while the incorporation of cyano groups into the surface structure induces a regular coating of 2,2′-oxydipropionitrile. Surface measurements of contact angles and critical surface tensions were carried out and correlated with chromatographic performance[267]. This work demonstrates that the wettability of glass surfaces can be significantly improved by chemical modification.

Rutten and Luyten[209] used a modified version of the silylation procedure described by Novotny *et al.*[264] for the preparation of apolar glass capillary columns for steroid analysis. Rather than passing the vapor of a 5:1 mixture of HMDS and TMCS through the column, 25% of the column length was filled with the solution. After forcing this plug through the column the ends were sealed and the column heated to temperatures above 150°C for a few days. It was found that columns treated at 150°C deteriorated rapidly, while those treated at 200°C were stable for several months. These observations were explained by the assumption that at 150°C certain reaction products are deposited that lead to a layer favorable for the spreading of the stationary phase, but when heated to 250°C, the reaction products degrade. It was theorized that at 200°C these reaction products do not form. However, a more probable explanation is that at lower temperatures the silylating agents are physically adsorbed on the surface and desorb on heating, thus promoting column deterioration. At the higher temperature, some chemical bonding occurs, and a more stable deactivation is produced.

Welsch *et al.*[268] were the first to attempt high-temperature silylation of glass capillary columns. After experimenting with various silylating agents, solvents and reaction temperatures, it was concluded from chromatographic performance tests that pure HMDS at 300°C for 20 h gave the most favorable surface silylation. In this treatment, a plug of HMDS is quickly pushed through the column at 4–5 cm/sec. After all the reagent has been expelled, the column ends are sealed and the entire column is slowly heated to 300°C and maintained there for 20 h.

A few years later, Grob *et al.*[269] began using a modified procedure similiar to that of Welsch *et al.* In this pocedure the columns are heat treated at 400°C, which undoubtedly gives better surface silylation. Grob *et al.* also suggested that diphenyltetramethyldisilazane may give a more stable surface layer than HMDS. Its larger size, however, probably inhibits complete surface reaction. In studies with silica, it has been found that bulky phenylsilanes provide less substitution due to steric hindrance[270]. These bulky silanes, though, may provide a better shielding layer or umbrella effect to cover reactive silanols.

Lee and co-workers[24,235] have also shown that silylation at 400°C is superior to that obtained at lower temperatures. In this procedure, dynamic gas phase conditions are used to ensure excess reagent and to minimize reaction product interferences. Both the vapors of HMDS alone and of a 5:1 mixture of HMDS and TMCS have been used successfully. Surface analysis data[24] indicate that no ammonium chloride is deposited during reaction with a mixture of HMDS and TMCS as has been postulated[268].

Clearly, the degree of surface coverage by silylation is related to the number of hydroxyl groups on the surface (at least to a certain limiting concentration). Aue and Hastings[271] found that larger amounts of silane could be bonded to a solid support that had been previously hydroxylated by acid treatment. This same general relationship was found to apply to capillary column preparation[272]. More recently, Grob *et al.*[243] found that a maximum density of silanol groups increases the degree of deactivation and thermostability obtainable by silylation. Such findings are in agreement with studies by Wright *et al.*[24].

With static silylation (ends sealed) it is difficult to obtain complete reaction by simply providing excess reagent. Grob *et al.*[269] suggest that the NH_3 liberated during

the reaction of HMDS with the silanol groups reacts corrosively with the silica, thus continuously providing additional reactive silanol groups. Prolonged reaction of this type can result in the formation of an undesirable sponge-like surface layer. In addition to possible adverse adsorptive effects for small apolar molecules (induced by the surface porosity), such surfaces resemble the resinous polymeric nature of di- and trichlorosilane polymers. As discussed by Novotny *et al.*[273], these formations complicate wetting phenomena and produce adverse mass transfer problems during chromatography. Dynamic silylation, however, minimizes the effects of NH_3 formation, in that fresh silylating vapors are continuously being flushed through the column, and the associated reaction products being continuously purged. Thus, the NH_3 concentration is unable to build to a sufficient level to be significant.

Schomburg *et al.*[191] have described a deactivation procedure in which a non-extractable layer of polymethylsiloxane phase is produced on the glass surface. With this technique, glass capillary columns are dynamically coated with a polymethylsiloxane phase, such as OV-101, filled with N_2 and sealed by melting the ends, and then heated to 450°C for 2–20 h. During heat treatment, the polymethylsiloxane partially decomposes with probable bonding taking place between the decomposition products and the surface silanol groups. It is believed that this *in situ* silylation procedure is similiar to the oligomerization of chemically bonded stationary phases (see Section 7.3). After heat treatment the column is rinsed with solvent to remove non-bonded stationary phase. The column is then recoated with the same stationary phase to produce a film of defined thickness and polarity.

A similiar procedure has also been described by Lee *et al.*[274]. In this deactivation treatment, dichlorooctamethyltetrasiloxane (available commercially as Surfasil) is dynamically coated in the capillary and, after evacuation of air, the ends are sealed and the column is heat treated at 400°C for 1–2 h. Afterwards, the column is heated to 400°C and flushed with N_2 to remove any non-bonded or weakly bonded fragments. The chloro groups on the siloxane (Surfasil) react easily with the silanol groups forming a surface layer easily wettable by apolar phases.

6. COLUMN COATING

6.1. General considerations

The main objective in coating the capillary column with the stationary phase is to provide a uniform film, usually 0.1–1.5 μm thick, throughout the length of the column. This is necessary in order to obtain the highest possible separation efficiency and resolution.

Coating can be accomplished by either the dynamic or static method. Both methods are discussed in the next sections.

6.2. Dynamic methods

The dynamic method was first described by Dijkstra and De Goey[275] and generally consists in filling two to fifteen coils of the column with a solution of the stationary phase, followed by forcing this volume through the column at a velocity of approximately 1–2 cm/sec with helium pressure. A thin film of this solution is left behind on the capillary wall. Continual flushing with helium after coating evaporates the remaining solvent, and leaves a thin coating of stationary phase.

Non-uniform films are often obtained by this method. The reasons for this non-uniformity are as follows:

(1) As the coating solution is discharged from the end of the column, the coating velocity increases sharply, which results in a thicker film at that end of the column. A buffer column is often attached to the end of the capillary to avoid this problem.

(2) The consumption of some of the coating solution during the coating process results in a faster linear velocity of the solution plug as coating proceeds and, therefore, an increasing film thickness.

(3) When a fairly large amount of solution is deposited on the column wall, the liquid may drain from the walls and collect in the lowest parts of the coils. Proper orientation of the column in a horizontal direction around a cylinder can help to reduce this effect[3,276].

(4) The solvent evaporation step involves transport of some of the stationary phase towards the end of the column, resulting in increasing film thickness along the column[277,278].

(5) Small temperature differences or fluctuations along the column cause the solvent to distil from the warmer parts of the column and condense at the cooler parts. This results in droplet formation and film non-uniformity[279].

(6) The formation and growth of wave disturbances have been treated theoretically[280–282] and have been observed in capillaries coated by the dynamic method[264,277]. The instability of an annular coating of liquid due to axial disturbances on the inside of a capillary tube results in a wavelength of the disturbance which is independent of surface tension and viscosity, and equals $2\pi r/0.7$, where r is the radius of the tube. This means that for columns of diameter 0.2 mm the wavelength and, therefore, the resultant lens spacing would be 0.9 mm[121].

(7) Poor wettability of the glass surface by either the stationary phase solution or the stationary phase itself can result in droplet formation and subsequent non-uniform stationary phase films.

A number of solutions to these problems have been proposed. The wettability problem is very dependent on the critical surface tension of the glass surface, and the surface tensions of the stationary phase coating solution and the stationary phase itself. Critical surface tensions of glass surfaces after various treatments have been discussed in Section 2.3 and listed in Tables 7 and 8. Similarly, the surface tensions of various stationary phases are listed in Table 6. Solutions of stationary phases generally have lower surface tensions than the pure stationary phases, but higher surface tensions than the pure solvents. The actual surface tensions of a stationary phase solution can be expressed by the additive equation

$$\gamma = \gamma_1 x + \gamma_2 (1 - x) = \gamma_2 + (\gamma_1 - \gamma_2)\, x \tag{11}$$

where γ, γ_1 and γ_2 are the surface tensions of the mixture and of components 1 and 2, respectively, and x is the proportion (w/w) of component 1 (ref. 95). In most cases, empirical equations are used, *e.g.*

$$\gamma = \gamma_2 + kx + (\gamma_1 - \gamma_2 - k)x^2 \tag{12}$$

or

$$\gamma = \frac{\gamma_2 + (k\gamma_1 - \gamma_2)\, x}{1 + (k - 1)\, x} \tag{13}$$

where the values of k are obtained by experimental measurements. Table 9 lists the surface tensions of a number of stationary phase solutions[94,95,105,277]. For uniform spreading of the stationary phase, the critical surface tension of the surface must be greater than the surface tension of the liquid[95]. Marshall and Parker[107,121] have discussed in great detail the effect of coating solvents on the wettability of the glass surface. During the coating of a column, the stationary phase and the solvent compete for adsorption sites. According to Fox *et al.*[283], the relative proportions of surface covered by each are dependent not only on the relative proportion of solute and solvent, but also on their relative adsorptivities.

TABLE 9

SURFACE TENSIONS (γ) OF STATIONARY PHASE SOLUTIONS

Stationary phase	*Solvent*	*% (v/v)*	*% (w/v)*	*% (w/w)*	*Temperature (°C)*	*γ (dyne/cm)*
SF-96	Toluene	10			25	25.0
SF-96	Toluene	2			25	24.5
SF-96	Toluene	10			22	24.9
Apiezon L	Cyclohexane	12.8	10		22	25.1
SE-30	Chloroform	5.9	5.4		22	25.6
SE-30	Chloroform	3.6	3.3		22	25.7
OV-17	Toluene	10			22	28.7
Carbowax 20M	Chloroform	5	5		22	26.9
Dinonyl phthalate	Toluene	10			22	28.2
Di-*n*-decyl phthalate	*o*-Xylene	15			22	33.8
DC-560	Acetone			20	25	23.3
DC-560	Acetone			12	25	22.9
PEG-400	Acetone			20	25	25.5
PEG-400	Acetone			10	25	23.4

It has been shown that treatment with pentane, methylene chloride, or acetone reduces the critical surface tension of glass up to 50%[121]. Furthermore, it is suspected that the coating solvent is not completely desorbed during conditioning, and that the effects of these solvents are still present.

The addition of surface active agents to the stationary phase solution can increase the wettability of the surface and improve the film uniformity. This has been discussed in Section 5.3.

The formation of droplets or plugs (assuming the glass surface is wettable) can be largely avoided, or at least greatly reduced, by controlling the coating speed[279], temperature[279], concentration of the coating solution[105], solvent volatility[111] and rate of solvent evaporation[278]. Methylene chloride has been a popular solvent for the dynamic coating procedure because of its low boiling point (41°C), good solvent properties and non-flammability. However, the high vapor pressure of methylene chloride increases the probability of droplet and lens formation during coating. Temperature programming the capillary column in a water-bath from 22°C to 32°C during coating, and up to 42°C during the solvent evaporation step has been found to be effective in eliminating this problem by ensuring that the temperature never falls below the dew-point of the solvent vapor[121]. Maintaining a gas flow through the column for several hours after coating helps to evaporate the solvent

and reduce the formation of droplets. When a plug or droplet is formed, a resultant constriction in the column momentarily occurs, which leads to pressure differences and condensation of the solvent from the saturated gas stream. These plugs will break up when a higher gas pressure is applied, but the coating will no longer be uniform. Blomberg[278] found that at low solvent evaporation rates (*ca.* 0.25 cm³/min), some of the stationary phase is transported from the column as hundreds of moving droplets of solution, leaving a very thin film of stationary phase uniformly distributed throughout the column. With rapid evaporation (*ca.* 4.00 cm³/min), only lenses of short duration are formed, and as a consequence there is no phase transport except at the very beginning of the column. This results in thicker, uniform films. Intermediate flow-rates have resulted in non-uniform films.

Several different approaches to improving the dynamic coating method have been proposed. Levy *et al.*[284] have described the use of a flow restriction device placed downstream from the column to be coated, which stabilizes the flow-rate in the column during the entire coating process. Van Dalen[285] and, later, McConnell and Novotny[286] connected the capillary to a syringe pump, filled the entire length of tubing with the solution of stationary phase, applied a gas pressure at the other end of the column and withdrew the solution by operating the syringe in the withdrawal mode. The syringe pump serves as a brake, preventing a change in coating speed as the plug length diminishes. The variation in film thickness obtained by this method was within 2%.

Probably the most significant development in the dynamic coating method was the introduction of the "mercury plug" method of Schomburg and co-workers[26,287]. This method involved adding a mercury plug between the solvent plug and the driving gas which, because of its high surface tension, wipes most of the coating solution off the surface as the plug moves through the column. More concentrated solutions are used in this procedure, resulting in the formation of films which resist drainage during the drying step.

Predictions of the film thickness (d_f) in dynamically coated capillary columns have been made using several mathematical relationships. Kaiser[288] related d_f to the concentration of the stationary phase coating solution, c, the capillary radius, r, and the velocity of the coating plug, u, according to the following equation:

$$d_f = \frac{c}{200\,r}(0.265\,u + 0.25) \tag{14}$$

Novotny and co-workers[264,289], however, found that d_f depends directly on r and $u^{\frac{1}{2}}$, in agreement with the Fairbrother–Stubbs equation[96]:

$$d_f = \frac{rc}{200}\left(\frac{u\eta}{\gamma}\right)^{1/2} \tag{15}$$

η and γ are the viscosity and surface tension of the solution, respectively. Tešarik and Necasova[94] confirmed the dependence of d_f on r and η. Guiochon[290] suggested that the equation

$$d_f = \frac{1.34\,rc}{100}\left(\frac{u\eta}{\gamma}\right)^{2/3} \tag{16}$$

should be applicable to the coating of capillary columns. Bartle[277] has evaluated and compared these equations with experimental results. Eqn. 15 was found to be the most useful, except for in the case of $u\eta/\gamma < 1 \cdot 10^{-3}$ (thin films or low solution viscosities), in which case the use of eqn. 16 is necessary[105,277]. It was demonstrated by Alexander and Lipsky[291] that the same type of equation as those best describing the film thickness in the dynamic method is applicable also to the "mercury plug" dynamic method.

A number of methods have been proposed for the determination of the average film thickness in dynamically coated capillaries. The specific retention volume, V_g, as measured on packed columns[94,95,105,267,277,278,292] or obtained from the literature[294], can be used in the following equation to give the approximate film thickness:

$$d_f = \frac{273\, rk}{2\, V_g T_c \varrho_T} \tag{17}$$

where ϱ_T is the density of the phase at the column temperature, T_c, and k is the capacity ratio. Film thickness can be obtained from measurements of capacity ratios and β-values of statically coated columns[104,105,264] by using the following equation:

$$d_f = \frac{rk_2}{2\beta_1 k_1} \tag{18}$$

where k_1 and k_2 are the capacity ratios for the statically and dynamically coated columns, respectively, and β_1 is the phase volume ratio for the statically coated columns.

The value of d_f has also been calculated from the difference in volume of the coating solution before and after coating[6,279,295], and from the weight of stationary phase that can be rinsed out of the column[105,164,296].

Roeraade[279] described a simple method for calculating the film thickness. In his procedure, a few coils of the column are coated with a plug of solution of a given length, and the shortening of the plug over a given column length is measured. This procedure is repeated several times with increasing coating speed each time. The film thickness at these different coating speeds can be easily calculated from the concentration of the solution, the amount of solution used over a given length and the internal diameter of the column. A graph can be constructed of the coating speed *versus* film thickness, from which the coating speed can be selected to give a desired film thickness.

6.3. Static methods

The static coating method was first developed by Golay[11] and later described for glass capillaries by Bouche and Verzele[297]. The general procedure involves filling the capillary with a dilute solution of the stationary phase, sealing the capillary at one end and evaporating the solvent from the other end under vacuum. This leaves a thin film of stationary phase, the thickness of which can be easily calculated from the equation

$$d_f = \frac{r}{2\beta} \tag{19}$$

where r is the radius of the capillary and β is the phase ratio. An important advantage of the static method is that the phase ratio is known accurately and, therefore, the film thickness can be accurately determined. To calculate the phase ratio from a weighed amount of stationary phase, the density of the stationary phase must be known. Rutten and Rijks[298] have recently tabulated a number of stationary phase densities, which are listed in Table 10.

TABLE 10

SPECIFIC WEIGHTS OF SOME STATIONARY PHASES

Stationary phase	*Specific weight*	*Stationary phase*	*Specific weight*
AN-600	1.08	OV-101	0.96
DC-200	0.97	OV-105	0.99
DC-510	1.00	OV-210	1.32
DC-550	1.07	OV-225	1.09
DC-710	1.10	OV-275	1.16
DEGS	1.26	PEG 400	1.13
OS-124	1.21	QF-1	1.32
OV-1	0.98	SE-30	0.96
OV-3	1.00	SE-54	0.98
OV-7	1.02	SF-96	0.97
OV-11	1.06	Silar 5 CP	1.13
OV-17	1.09	Silar 10 C	1.12
OV-22	1.13	SP-2401	1.30
OV-25	1.15	Squalane	0.83
OV-61	1.09	XE-60	1.08

A number of papers[297–301] report the details of various static coating procedures. In practice, it is important that the coating solution be dust free and degassed to eliminate bumping during the solvent evaporation step, and that no air or vapor bubbles exist in the column, especially at the sealed end[297]. The column must be kept at a constant temperature to prevent non-uniform film deposition. A thermostated water-bath is not adequate because its temperature fluctuations, however small, produce sufficient contraction and expansion to cause the deposition of the stationary phase in the form of bands[298]. A room or water-bath of constant temperature is usually sufficient. If an increased temperature is needed, a simple and inexpensive solution to the problem is to place the column into a water-bath which is within another water-bath[279,300]. Although the outer container is controlled by a thermostat, the heat transfer from the outer to the inner container is very gradual.

The most popular solvent for static coating has been methylene chloride because of its excellent solvating properties and its low volatility. Grob[299] recently suggested the use of pentane for the coating of apolar gum phases because evaporation can be accomplished in approximately half the time necessary for methylene chloride solutions. Average coating times at room temperature range from approximately 15 h for methylene chloride solutions to about 8 h for pentane in a 20 m × 0.3 mm I.D. column[299]. Goodwin[301] claimed that many solvents including methylene chloride deposit the phase as droplets of about 0.01–0.05 mm diameter. Diethyl ether, however, was found to deposit the phase in a uniform film.

Although sodium silicate solution (water-glass) was originally used to seal

the ends of capillaries[297–299], several other methods of making seals have been suggested. These include cements[107], silica gums[105], adhesives[300,302,303], Apiezon N[304] and Vaseline hardened by addition of a small amount of histological wax[301]. Recently, mechanical attachment of a plug with shrinkable Teflon tubing was advocated[303].

The static coating method has been generally considered to be superior to the dynamic method[140,200], producing columns that are more efficient. Some stationary phases, however, cannot be successfully coated by the static method[276]. Less viscous liquid phases may flow down and accumulate in the lowest portions of the capillary. Occasionally, a concentration effect occurs at the front of the evaporating solution, which can eventually form a plug and block the column.

In Golay's original work[11], capillary columns were coated by filling them with a dilute solution of liquid phase, sealing one end, and drawing the column, open end first, through an oven. Mistryukov and co-workers[203,305,306] and later Jennings and co-workers[307,308] revised this method for glass capillaries by introducing the open end of the coil into a high-temperature oven, rotating the column around its coiling axis into the oven. As the column is screwed into the oven, the solvent evaporates and escapes through the open end leaving the stationary phase on the capillary wall.

Harrison[309] has reported a freeze-dry method of coating which involves filling the column with a solution of the stationary phase, freezing the solution and evaporating the solvent *in vacuo*. Uniform coatings were reported.

7. COLUMN PREPARATION AND STATIONARY PHASES

7.1. General considerations

Various gas chromatographic stationary phases can be coated on glass capillaries with different degrees of success. Columns with high numbers of theoretical plates per unit length can be prepared, in general, with any liquid phase, provided that the optimum treatments, coating solutions and other necessary parameters are chosen. The importance of stationary phase selectivity is, to a considerable degree, balanced by the large number of theoretical plates obtained in high-resolution work. The high efficiencies of glass capillary columns usually more than compensate for the selectivities of specific phases and most separations can be carried out on relatively few stationary phases. Thus, in choosing a stationary phase, factors such as performance and stability should be more important than selectivity.

For the preparation of highly efficient and inert apolar columns, two primary conditions must be met. These include the formation of a smooth and homogeneous film of stationary phase on an inert and non-adsorbing surface. Glass is usually wettable by most apolar liquids without previous surface modifications, but modifications can result in better wettability and more thermostable surfaces. The primary concern is the deactivation of the glass surface towards polar and mildly polar solutes. Thin films of apolar stationary phases do not deactivate the glass surface. Consequently, various methods have been devised to block active surface sites and have been discussed in detail in Section 5. Excessively roughened surfaces decrease film homogeneity and should be avoided for apolar columns. Various forms of mild surface roughening, however, have been used successfully for the preparation of apolar columns.

The main problem in the preparation of polar columns is the poor wettability of the glass surface by polar liquid phases. To enable the polar phase to spread and produce an acceptable coating, surface roughening is necessary. Roughening techniques such as barium carbonate deposition, whisker formation, double HCl gas roughening, and other methods which were discussed in detail in Section 4 fulfill the requirement. These phases usually deactivate the active sites on the glass surface, however, so that no other deactivation is necessary. In general, polar columns are less thermally stable and are less efficient than apolar columns. The roughened surface may partially account for their lower efficiency. The newly introduced Superox polar phases, however, wet the glass surface more readily and are more thermally stable than previously used polar phases. Consequently, it is now possible to prepare polar columns with both higher efficiencies and stabilities.

Moderately polar stationary phases require both a roughened and deactivated glass surface for satisfactory performance. The polarity of the stationary phase is not usually sufficient to deactivate the active sites on the glass. Thus, various combinations of roughening and deactivation must be combined to produce good medium-polarity columns.

7.2. Gum phases

Practical experiences in the coating of glass capillary columns have demonstrated that gum phases give columns of consistently higher quality. This is a result of their ready wettability of glass surfaces. Thermostability and resistance to droplet formation are enhanced by the cross-linkages between polymer chains, making the phase viscosity high, even at elevated temperatures. Several years ago, Grob[310] pointed out the benefits of gum phases and concluded that whenever possible a gum phase should be selected. With the recent development of the Superox gum phases[311,312], which have polarities very similar to that of Carbowax 20M. Verzele[313] has also commented on the superiority of gum phases. For example, Superox-4 has a higher upper temperature limit (300°C) and gives a plate number 20–25% higher than Carbowax 20M columns. Table 11 lists some of the stationary phases commonly used in coating glass capillary columns. The gum phases are marked with asterisks.

7.3. Bonded phases

Interest in the use of chemically bonded stationary phases in chromatography has grown in recent years[314,315]. Reports of the preparation of capillary columns containing chemically bonded silicones as the stationary phase were reported as early as 1968[316–318], but detailed descriptions of the preparation and application of such columns appeared in the literature only recently[319–326]. Chemical bonding has been shown to increase the stability of the stationary phase film as compared with the conventionally coated film[314].

Madani and co-workers[319–321,323,326] prepared methyl and methylphenyl polysiloxane polymers by hydrolysis of dimethyl- and diphenylchlorosilanes. After dynamically coating the polymeric mixture on the capillary wall, the column was filled with ammonia gas, sealed and heated at a high temperature for 24 h. Chemical

TABLE 11

COMMON STATIONARY PHASES

*Name**	*Chemical nature*	*Temperature range (°C)*	*Polarity***
Squalane	C_{30} alkane	−50–100	0
Kováts phase	Branched C_{27} alkane	40–200	71
Apiezon L, M, N	Alkane, cross-linked with soaps	20–200	143, 138, 216
SF-96, OV-101	Methylsilicone fluid	0–200, 260	205, 229
RSL-110*	Polyhydrocarbon	−320	—
SE-30*, Ov-1	Methylsilicone gum	20–350	216, 217
SE-52*	5% phenyl, methylsilicone gum	20–350	334
SE-54*	1% vinyl, 5% phenyl, methyl-silicone gum	20–350	337
SP-2125*	2% cyanopropyl, 5% phenyl-silicone gum	20–320	—
RSL-210*	Polyunsaturated hydrocarbon	−275	—
Dexsil 300	Carborane, methylsilicone oil	20–375	474
UCON LB 550	Polyethylenepropylene glycol, *ca.* 10/90	−20–160	496
Pluronic 61	Polyethylene–propylene glycol, *ca.* 10/90 block copolymer	0–200	—
Dexsil 400	Carborane, methylphenylsilicone oil	20–375	587
OV-7	20% phenyl, methylsilicone oil	20–300	592
OV-17	50% phenyl, methylsilicone oil	20–300	884
OV-25	75% phenyl, methylsilicone oil	20–300	1175
OS-124	Pentametaphenyl ether	20–180	1216
QF-1, OV-210	50% trifluoropropyl, methyl-silicone oil	20–200	1500, 1520
Emulphor O	Polyethylene glycol–octadecyl ether	20–220	1587
Triton	Polyethylene glycol–nonylphenyl ether	20–220	1634
UCON HB 5100	Polyethylene–propylene glycol, *ca.* 50/50	20–200	1706
Pluronic 64	Polyethylene–propylene glycol, *ca.* 50/50, block copolymer	20–240	—
XE-60	25% cyanoethyl, methylsilicone oil	50–200	1785
OV-225	25% cyanoethyl, 25% phenyl-methylsilicone oil	50–220	1813
Carbowax 20M	Polyethylene glycol	80–250	2308
Superox-0.1*	Polyethylene glycol gum, mol.wt. 100,000	50–280	—
Superox-4*	Polyethylene glycol gum, mol.wt. 4,000,000	50–300	—
Silar 5 CP, SP-2300	50% cyanopropyl, 50% phenyl-silicone oil	50–240	2428, 2424
SP-2340	75% cyanopropyl, methylsilicone oil	100–240	3678
POLY-S 179	Polyphenylether sulfone	200–400	—
Silar 10C, OV-275	100% cyanopropyl silicone oil	100–240	3682, 4938

* Asterisk indicates gum phase.

** McReynolds constant ($\Sigma\Delta I$).

bonding to the glass surface was thus accomplished under base-catalyzed conditions. The synthesis of siloxane polymers from a mixture of two differently substituted silanes provides a method for the manufacture of highly stable glass capillaries of accurately controlled polarity[323,326].

Blomberg and co-workers[324,325] reported the *in situ* synthesis of methyl and phenyl polysiloxanes by dynamically coating the capillary with silicon tetrachloride followed by a solution of the polysiloxane polymer (formed by hydrolysis of mixtures of dimethyldichlorosilane and methyltrichlorosilane). The column was then sealed and heated at 320°C for over 20 h. This produced a moderate amount of cross-linking, in addition to chemical bonding to the surface, which has been suggested as a means to increase the film stability[310].

8. COLUMN EVALUATION

8.1. General considerations

The ideal glass capillary column is generally considered to possess a high separation efficiency and excellent tailing behavior (good deactivation) and temperature stability[157,287]. The chemical treatments and procedures which have been designed to produce the ideal capillary column from the original glass stock have been the subject of this review. However, like every finished product, a means of testing the quality of the product must be devised. Although several trends are obvious, there is presently no universally accepted method for evaluating a capillary column. For instance, in testing columns, the symmetry of peaks of selected test compounds which are contained in so-called "polarity mixtures" can give information concerning both the separation efficiency and deactivation of the column. In addition, bleed-rate experiments followed by peak symmetry tests can give information concerning film thermal stability. The difficulty in properly evaluating capillary columns lies in the choice of test compounds, chromatographic conditions and meaningful measurements. Grob *et al.*[327] listed the following criteria for an adequate column test:

(1) the test should consist of a single chromatographic run;

(2) the test mixture should contain all of the components necessary to give all of the basic information required;

(3) the same test should be applicable to all liquid phases;

(4) some quantitative aspects should be included; and

(5) conditions should be standardized so as to make test results comparable.

Different polarity mixtures have been suggested by Grob *et al.*[296,327], Schomburg *et al.*[26,157], Alexander *et al.*[140], Hartigan and Ettre[104], Sandra and Verzele[149,311], Welsch *et al.*[268], Cram *et al.*[328], De Nijs *et al.*[174] and Dandeneau and co-workers[17,109]. These mixtures contain components with a variety of functional groups. Saturated hydrocarbons, alcohols, aromatic compounds, aldehydes, phenols and amines have been widely used. Fig. 29 shows a chromatogram of one of these polarity mixtures.

In the following sections, the use of test chromatograms for column evaluation is reviewed. The treatment is divided into the three categories separation efficiency, deactivation and temperature stability.

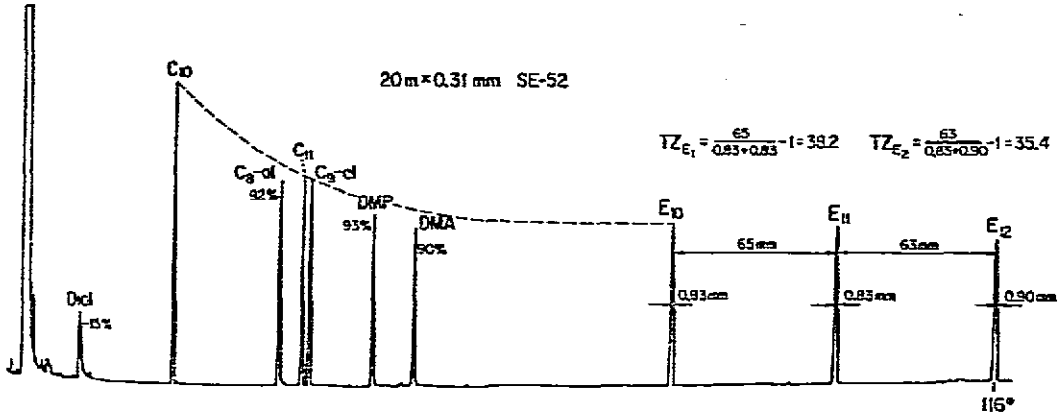


Fig. 29. Test chromatogram obtained with an SE-52 column illustrating the Grob polarity mixture. Reprinted with permission[327].

8.2. *Separation efficiency*

The performance of capillary columns has been reviewed in detail by Ettre[6] and Ettre and Purcell[329]. The efficiencies of capillary columns have been described by several terms as follows:

(1) The number of theoretical plates, n, where

$$n = 16\left(\frac{t_R}{w_b}\right)^2 \tag{20}$$

The value of t_R is determined by the retention time of the compound of interest and w_b is the width of the peak at its base. Often, the width at half height, w_h is used instead of w_b. This requires a constant equal to 8 ln 2 (or 5.545) instead of 16 to give

$$n = 5.545\left(\frac{t_R}{w_h}\right)^2 \tag{21}$$

(2) The number of effective theoretical plates, N_{eff}, proposed by Desty *et al.*[330], where

$$N_{eff} = 5.545\left(\frac{t_R'}{w_h}\right)^2 \tag{22}$$

The term t_R' is the adjusted retention time and is calculated from $t_R' = t_R - t_M$, where t_M is the gas hold-up time, the elution time of an unretained compound. The effective plate number can be calculated from n by the following equation[331]:

$$N_{eff} = \left(\frac{k}{k+1}\right)^2 n \tag{23}$$

where the capacity ratio, k, can be determined from

$$k = \frac{t_R'}{t_M} \tag{24}$$

Since capillary columns are usually operated at low capacity ratios, their efficiencies are lower than indicated by the theoretical plate number. It is important to emphasize that both n and N are strongly dependent on the k-value of the evaluated peak[237,332] and that the required pressure drop for the optimal carrier gas flow-rate has an influence on the separation efficiency per meter.

(3) The number of real theoretical plates, N_{real}, as proposed by Kaiser[333] and Said[334]:

$$N_{real} = 5.545 \left(\frac{t_R'}{w_h'}\right)^2 \tag{25}$$

where w_h' is calculated from

$$w_h' = w_h - w_{Mh} \tag{26}$$

and w_{Mh} is the width at half-height of the unretained peak.

(4) The geometric mean of n and N, proposed by Golay[335].

(5) The reduced plate number proposed by Giddings[336] and by Horne *et al.*[337].

(6) The mean specific plate number, N_{MS}, proposed by Brown[338],

$$N_{MS} = \frac{r_g \left[1 + \left(\frac{k}{1+k}\right)^2\right]}{L} n \tag{27}$$

where L is the column length and r_g is the radius of the gas passage and is given by

$$r_g = (r - d_f) \tag{28}$$

where r is the internal radius of the capillary column and d_f is the average liquid phase film thickness. The mean specific plate number has the advantage over most parameters in that it has only a small dependence on the partition ratio and allows for the column diameter.

The composition of the efficiency test mixture should be chosen according to the nature of the liquid phase, and the efficiency should be calculated for a peak having $k<2$ (ref. 104). Efficiencies of 3000–5000 plates/meter can be routinely obtained using the present column technology. Both the compound tested and the k for that compound should be reported when reporting efficiencies.

Another approach to describing capillary column quality is the comparison of experimentally obtained plate numbers with theoretically predicted values. The coating efficiency, CE, has been defined as the ratio of theoretical to experimental plate height under optimal conditions[6,297]:

$$CE = \left(\frac{h_{theor}}{h_{exp}}\right)_{min} \tag{29}$$

The theoretical plate height, h_{theor}, is usually represented by the simplified Golay–Giddings[11,339] equation:

$$h_{theor} = r \sqrt{\frac{11k^2 + 6k + 1}{3(1+k)^2}} \tag{30}$$

The term h_{exp} or the experimental HETP is defined as the column length, L, divided by the number of theoretical plates, n.

Cramers *et al.*[340] recently discussed a more general treatment of the coating efficiency which does not neglect the effects of resistance to mass transfer in the liquid phase and the pressure drop. Provided that the diffusion coefficients of the solute in the stationary phase and carrier gas are known, a more accurate determination of the coating efficiency can be made.

The separation value concept and its meaning and relationship to existing column efficiency terms and chromatographic parameters has been discussed in detail by Ettre[341]. The Trennzahl or separation number, TZ, as described by Kaiser[202,342], is calculated from

$$TZ = \frac{(t_R)_2 - (t_R)_1}{(w_h)_2 + (w_h)_1} - 1 \qquad (31)$$

where the subscripts 1 and 2 refer to two specified components in a chromatogram, usually in a homologous series such as the *n*-alkanes. The calculated separation number is defined, therefore, as the number of peaks separated by approximately twice the width at half-height that can be fitted between the two standards. More general and detailed approaches have recently been described[334,343].

One problem in using *n*-alkanes for TZ measurements is their very different retentions on different stationary phases. At 70°C, different pairs of *n*-alkanes (C_{11}/C_{12} up to C_{17}/C_{18}) had to be used for different stationary phases[327]. These large differences in retention are related to changes in capacity for alkanes on stationary phases of different polarity. Grob *et al.*[327] have reported the use of fatty acid methyl esters (C_{10},C_{11} and C_{12}) as standards because of their similar partition coefficients (and therefore more similar retentions and capacities) in different kinds of stationary phases.

Grob *et al.*[327] also found that there was no significant difference between isothermal and temperature-programmed TZ values and, therefore, several values can be obtained by adding more than two homologous compounds.

A parameter that is often overlooked in capillary column evaluation, and has an effect on efficiency, is the sample capacity. An "overloaded" peak causes tailing on the leading edge of the peak and reduces the efficiency. Keulemans[344] and Klinkenberg[345] defined the maximum permissible sample size as the maximum amount which can be injected into the column without more than a 10% loss in efficiency. Grob and Grob[346] have defined this to be when the recorder pen takes more than twice the time to rise from the baseline to the peak maximum than to return to the baseline.

8.3. Deactivation

The extent of deactivation of glass capillary columns has usually been determined by the amount of peak tailing or extra retention of polar compounds, or as a function of the ratio of peak heights of polar to non-polar compounds. If the column is not sufficiently deactivated, it will contribute to the retention of the sample molecules and therefore the relative retentions and retention indices of mixture components containing different functional groups will change. Although Grob *et*

al.[327] claim that a column with the lowest retention for an alcohol is not necessarily that with the least retention, and that the nature of the glass surface and film thickness contribute to retention, nevertheless, if most parameters are kept constant, retention reproducibility is a very useful tool for evaluating capillary deactivation[347].

Peak shape has also been used as a measure of capillary column activity. The asymmetry factor, A_s, of Goretti *et al.*[167] is practically identical with the expression of Dal Nogare and Chiu[348] which was formulated mathematically by Ettre[349] as

$$A_s = \frac{a + b}{(a + b) - (b - a)} \tag{32}$$

where a is the front half and b the back half of the peak width at base, measured from the perpendicular drawn through the peak maximum. The asymmetry factor measures the deviation from a Gaussian distribution and is an indication of the interactions occurring in the elution process. As shown by Ettre[349], the square of its value actually is identical with the ratio of the HETP calculated for the asymmetric peak and for a symmetric peak the base width of which is identical with twice the shorter half:

$$\frac{h_{asym}}{h_{sym}} = A_s^2 \tag{33}$$

Schieke and Pretorius[155] defined a tailing factor, TF, as a percentage according to

$$TF = \left(\frac{b}{a}\right) 100 \tag{34}$$

where a and b are defined as above, except that they are measured at 10% of the peak height above the baseline. Cram *et al.*[328] have described the use of numerical methods to characterize capillary peak shapes.

Grob *et al.*[327] claim that the shape of the peak is not sufficient for detecting adsorption, because adsorption can cause (a) a broadened peak of Gaussian shape, (b) a tailing peak of more or less correct area, (c) a reasonably shaped peak of reduced area, or even (d) a misshapen peak of correct area but drastically increased retention. The worst of the different types of adsorption, irreversible adsorption, is not detected by peak shape. They suggest that the measurement of peak height as a percentage of that expected for complete and undistorted elution covers all types of peak distortions which are relevant in practice. To distinguish between reversible and irreversible adsorption, peak integration is necessary.

One of the most common test mixtures used to evaluate capillary columns has been described by Grob *et al.*[327], and its composition is given in Table 12. Alcohols are usually more sensitive to adsorption than most other functional groups. A number of studies have been conducted using only two components in the test mixture, an alcohol and an alkane[155,157,350]. 1-Octanol is a sensitive indicator of adsorption because it is well retained. The adsorption of the alcohol can be caused by hydrogen bonding to the silanol groups or siloxane bridges on the glass surface and by interaction with Lewis acid components of the glass. A dihydroxy compound,

such as 2,3-butanediol, is included as a more rigorous test. The acid–base properties of the column can be tested by the addition of compounds such as 2,6-dimethylaniline and 2,6-dimethylphenol to the test mixture. The addition of 2-ethylhexanoic acid and dicyclohexylamine can be made for a more rigorous acid–base test.

TABLE 12

COMPOSITION OF THE GROB TEST MIXTURE

Component	*Concentration (mg/l)*
C_{12}-acid methyl ester	41.3
C_{14}-acid methyl ester	41.9
C_{16}-acid methyl ester	42.3
Decane	28.3
Undecane	28.7
1-Octanol	35.5
Nonanal	40
2,3-Butanediol	53
2,6-Dimethylaniline	32
2,6-Dimethylphenol	32
Dicyclohexylamine	31.3
2-Ethylhexanoic acid	38

It is obvious that all mixtures do not put the same requirements on column performance[31]. Particularly difficult to chromatograph are the McReynolds standards, pyridine and nitropropane, and bifunctional compounds such as vanillin, methyl salicylate, nitrophenols and nitroanilines.

Several problems may be encountered when using a polarity test mixture for capillary evaluation. Components of the mixture may react with each other or decompose with time. During chromatography, strongly polar compounds may deactivate the surface for the subsequently eluted species[351].

Testing the behavior of the glass surface before coating has been helpful for the evaluation of different treatments during capillary preparation[157,352]. Schomburg *et al.*[157] have described a method for testing both coated and uncoated columns. The chromatographic system consisted of a capillary column with a polar stationary phase such a Carbowax 20M on which peaks of a polarity test mixture are eluted with perfect symmetry. A piece of the capillary to be tested is connected to this column by means of shrinkable Teflon tubing. The change in peak shape after passing through the test capillary indicates the extent of surface activity. This procedure eliminates the problem of unknown adsorption in the injector port and indicates only column activity.

The chromatographic conditions must be carefully controlled during evaluation of columns. While most testing has been performed under isothermal conditions, Grob *et al.*[327] suggest the following advantages of temperature programmed conditions:

(1) The necessity of finding the optimal temperature for the elution of a test compound for each liquid phase and film thickness is eliminated.

(2) A relatively large number of test substances can be selected which are distributed over the whole chromatogram.

(3) Isothermal runs show the first peaks to be eluted under better conditions than the more retained peaks. Temperature-programmed runs provide similar retentions for all components in the mixture, yielding better comparison within the chromatogram and with other columns.

(4) One test mixture can be used for all phases.

(5) Temperature-programmed runs elute peaks with an approximately constant width, and if a test mixture contains all components in amounts which have been corrected by response factors to give the same peak areas, then peak heights can give a quick quantitative interpretation.

(6) Peak tailing due to injection techniques and adsorption in the injection port is reduced by re-concentration at the capillary inlet during the early stages of temperature programming.

(7) Temperature-programmed runs leave three variables to be chosen: carrier gas flow-rate, temperature programming rate and amount of test compound injected.

The optimization of the carrier gas flow-rate and the temperature programming rate has been discussed in detail by Grob *et al.*[327]. For every temperature programming rate, there is an optimal carrier gas flow-rate. This optimum is shifted to a higher value if the rate of temperature programming is increased. In testing capillary columns, it is important that the program rate be kept low (1–4°C/min), and that the initial temperature be set below the elution temperature of the earliest eluting component in the mixture[353].

The amount of test sample injected is also an important factor in capillary testing. The extent of component losses by adsorption is dependent on the number of active sites in the column, and may be relatively negligible as long as high sample loads are used. Schomburg[351] has studied the irreversible adsorption of components in a polarity test mixture by plotting the relative peak areas/unit weight *versus* the amount injected for each component (Fig. 30). As shown in Fig. 30A, only dicyclohexylamine exhibits increasing response factors (*i.e.*, increasing losses by irreversible adsorption) in the lower nanogram range. In a different column (Fig. 30B), dicyclohexylamine is now eluted without significant increase of response factor, but the more polar *n*-octylamine exhibits adsorption behavior.

8.4. Thermostability

Since most chromatographic separations on glass capillary columns are performed at elevated temperatures or employ temperature programming, the temperature stability of a coated glass capillary column is of utmost importance. For a column to perform satisfactorily at higher temperatures the coated stationary phase must remain stable. That is, its decomposition must be minimal and it must remain as a thin, uniform surface film, and not break up into droplets. In addition, the surface beneath the stationary phase, *i.e.*, the deactivation layer must remain stable. In fact, the temperature stability of the deactivation layer is as important as the stability of the stationary phase itself. Consequently, a discussion of temperature stability must include considerations of the deactivation surface as well as of the stationary phase itself.

The amount of volatile decomposition products formed in the column per

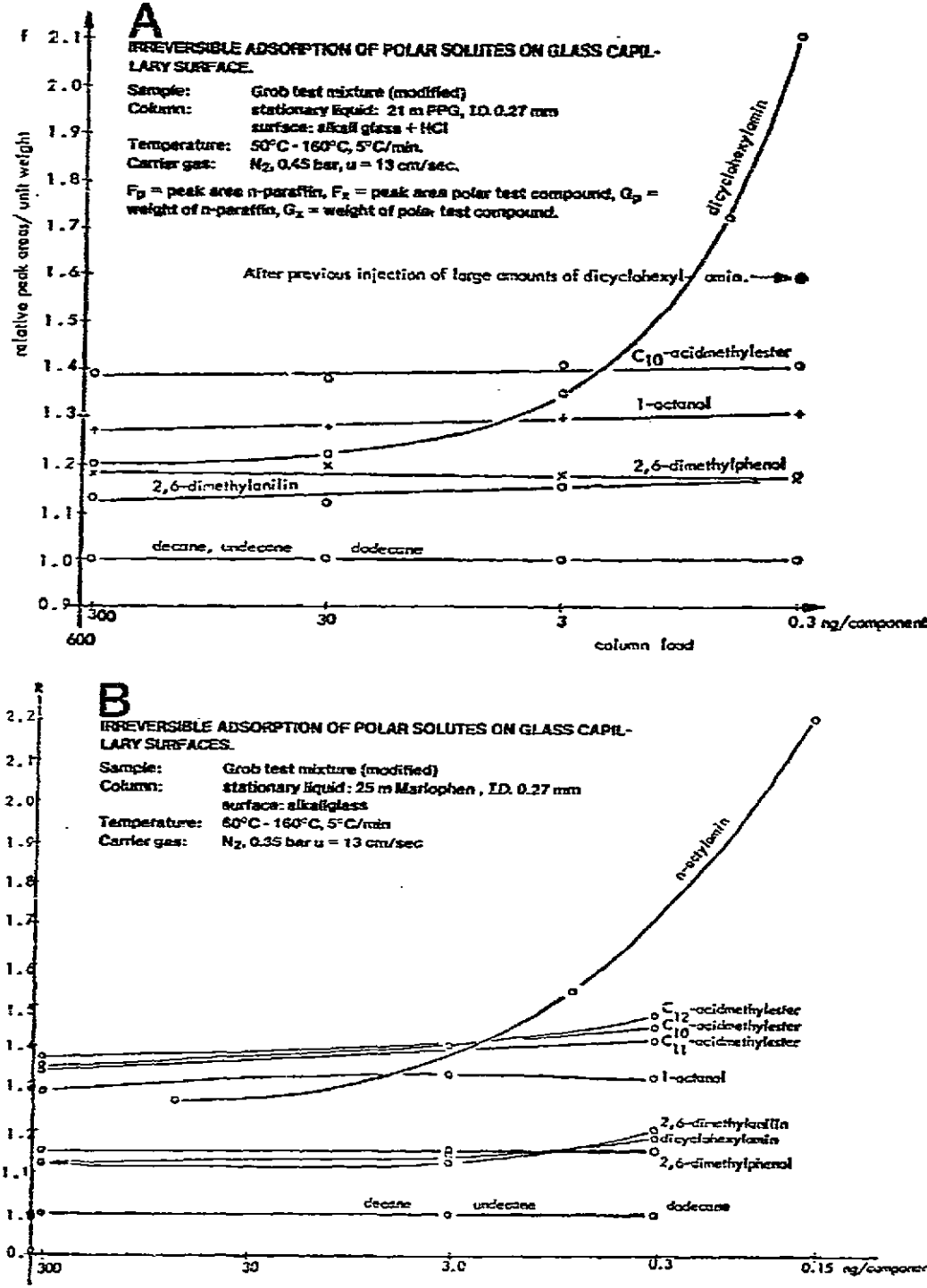


Fig. 30. Example of irreversible adsorption of polar solutes on glass capillary column surfaces. Reprinted with permission[351].

unit time depends on the stationary phase, temperature, surface properties of the support, surface area covered by the stationary phase and the film thickness. The mass flow of bleeding products at the column outlet depends on the column length, carrier gas flow-rate and the rate of formation of bleed products. Assessment of the temperature stability of columns is difficult, and depends on the type of analytical application involved and on the required standard of performance and reliability of the analyses. As suggested by Schomburg and co-workers[36,190,351] the following properties should not deteriorate or change substantially during extended high temperature operation:

(1) The capacity ratio (k) should not decrease significantly (indicating that the stationary phase is not decomposing to any great extent).

(2) The separation efficiency in terms of theoretical plates per meter should remain essentially constant (indicating that the quality and integrity of the stationary phase film is not being disrupted).

(3) The background signal arising from bleed products should remain constant and not exceed a defined limit (also indicating that the stationary phase and/or deactivating pre-coating layers are not decomposing significantly).

(4) The polarity in terms of retention indices of standard compounds should remain constant (indicating that the chemical nature of the stationary phase and/or the deactivation is not changing).

(5) The extent of surface deactivation for strongly polar solutes when using apolar stationary phases should remain stable. That is, the tailing behavior and adsorption of polar solutes at trace concentration levels should not become more pronounced after high temperature operation of the column.

Deterioration of the stationary phase results from two primary mechanisms. The first, and probably least serious, is temperature oriented and is related to the chemical composition of the stationary liquid phase. At elevated temperatures a point is reached where the stationary liquid exhibits a significant vapor pressure, and loss of the phase by evaporation becomes substantial. Further increases in temperature can result in chemical decomposition of the phase by pyrolysis. The maximum allowable operating temperature (MAOT) is usually specified by the manufacturer of the liquid phase. In practice, however, the specified MAOT is not usually obtainable in glass capillary column chromatography. This is partially due to surface catalytic effects (the second mechanism) which induces stationary phase decomposition. This mechanism of decomposition is of major importance since steps can be taken to alleviate or eliminate the undesirable consequences. Surface effects are particularly noticeable in capillary columns since the ratio of surface area to the amount of stationary phase is high.

Removal of alkali from glass surfaces increases the stability of methylsiloxanes considerably. It has been known for years that alkali tends to depolymerize polysiloxanes[354] and in chromatographic applications it has been shown that both alkaline and acidic surfaces cause decomposition of silicone oil phases[355]. This is consistent with observations made by Schomburg *et al.*[190] that columns prepared from borosilicate glasses (less alkali content) exhibit much better thermostability.

Recent work by Grob and Grob[356] shows that columns coated with stock solutions of SE-30 that have aged for several weeks produce more active and less thermostable columns. It was suggested that perhaps trace amounts of HCl present

in the coating solution, methylene chloride, was responsible for some sort of stationary phase degradation. Later work by Venema *et al.*[357] has verified that solutions of SE-30 and SE-54 stationary phases that have been slightly acidified degrade rapidly, as evidenced by a decrease in molecular weight. Thus, at elevated temperatures, the low-molecular-weight degradation products volatilize easily and produce unacceptable levels of bleed and a thinner and perhaps less perfect stationary phase coating. Other workers[358] have also observed that stationary phase solutions made from methylene chloride are responsible for increased column bleed, apparently due to HCl in the methylene chloride. Consequently, pentane has been suggested as a more inert solvent, and recommendations have suggested the use of freshly prepared stock solutions of stationary phases[356]. This illustrates the necessity of using pure solvents and stationary phases for the preparation of efficient and thermostable glass capillary columns.

In addition, Venema *et al.*[359] have studied the chemical resistance of OV-101 at 260°C to several compounds present in soft glass (soda-lime) or etched soft glass. Also, the effects of various chemicals used for other surface roughening techniques ($BaCO_3$ and NaF) or for deactivation purposes (BTPPC) were studied. Gel permeation chromatography was used to obtain diagnostic molecular weight data. Table 13 shows the qualitative results of this study. A preliminary investigation of the moderately polar phases OV-17 and OV-225 indicates that these phases behave similiarly to OV-101.

TABLE 13

EFFECT OF SEVERAL COMPOUNDS ON THE DEGRADATION OF OV-101 AT 260°C

Effect	*Formation of low-molecular-weight material*	*Molecular weight shift*	*Distribution broadening*
Strong effect	$BaCO_3$, $MgCl_2$, $CoCl_2$, $AlCl_3$, Al_2O_3, alkali glass	$CaCl_2$, $MgCl_2$, $CoCl_2$, $AlCl_3$, Al_2O_3	NaF, BTPPC, $MgCl_2$, $AlCl_3$, CoO, Al_2O_3
Moderate effect	NaF, BTPPC, $CaCl_2$, CaO, MgO, CoO	MgO, CoO	$BaCO_3$, $CoCl_2$, alkali glass
No effect	NaCl, borosilicate glass	NaCl, $BaCO_3$, NaF, BTPPC, CoO, alkali glass, borosilicate glass	NaCl, $CaCl_2$, CaO, MgO, borosilicate glass

Methods of column manufacture that remove alkali from the glass surface produce much better thermostability since the catalytic decomposition of methyl silicones is decreased. HCl gas treatment converts the metallic oxides into corresponding halides, which can then be removed by water[234] or acid[230] rinsing. Acid leaching removes these ions completely. Surface analysis data[24] indicate that back-diffusion of these ions from the bulk glass phase to the surface layer at elevated temperatures is minimal. Fig. 31 shows the results of standardized bleed measurements of OV-101 on different glass surfaces[191].

Although Carbowax-type deactivations were at one time considered to be adequate, they are unsuitable for high-temperature use. At temperatures in excess of

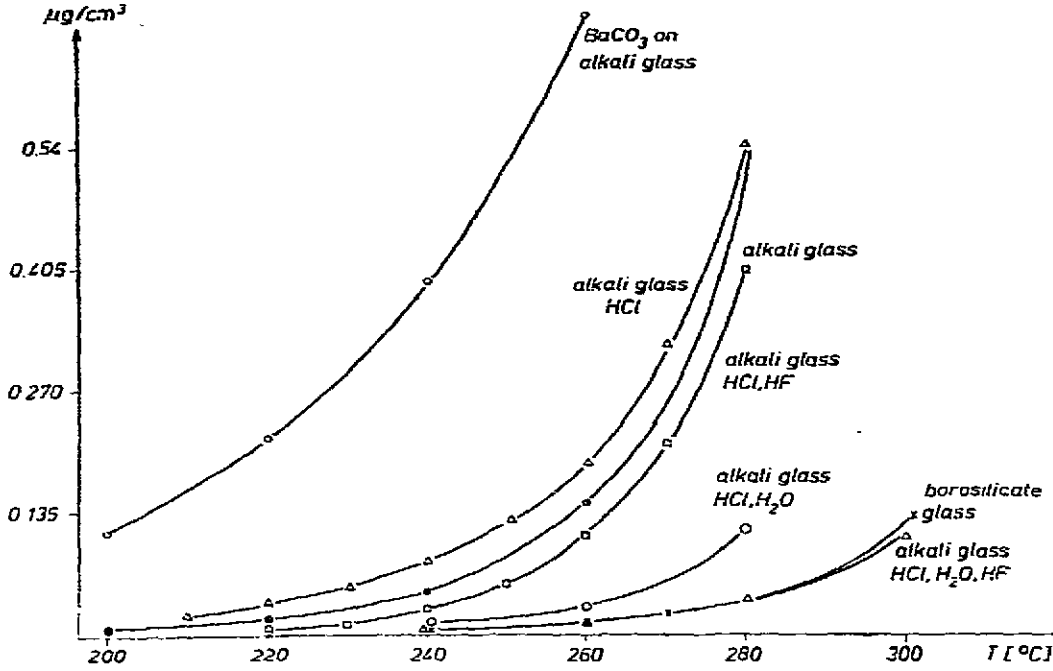


Fig. 31. Bleed rate of OV-101 on different glass surfaces with temperature. Reprinted with permission[191].

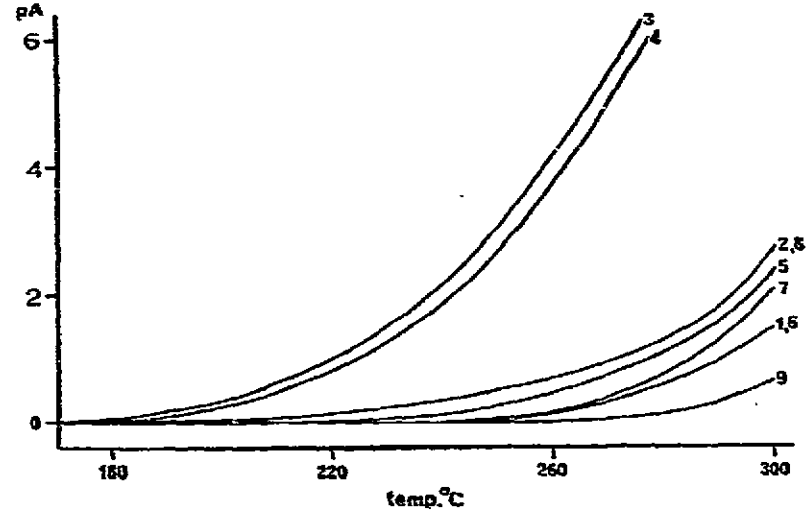


Fig. 32. Relative bleed rates of 20-m glass capillary columns under a temperature program of 5°C/min. Column types: 1, AR-glass + Carbowax; 2, etched AR-glass + Carbowax; 3, AR-glass + Carbowax + SP-2100; 4, etched AR-glass + Carbowax + SP-2100; 5, Pyrex glass + Carbowax; 6, etched Pyrex glass + Carbowax; 7, Pyrex glass + Carbowax + SP-2100; 8, etched Pyrex glass + Carbowax + SP-2100; 9, Pyrex glass + SP-2100. (Etched = HCl gas treatment). Reprinted with permission[213].

240°C these deactivating layers lose their effectiveness and column deterioration results[188,216]. Fig. 32 shows the relative bleed rates of a number of columns treated with Carbowax[213].

Silylation-type deactivations are much more stable. Since improved methods utilize treatment conditions of approximately 400°C, the deactivation is also stable at higher temperatures. When combined with previous acidic leaching, silylation provides an inert and highly thermostable deactivation. Catalytic surface effects from both alkali and acid (silanol groups) moieties should be minimal. The results of Grob *et al.*[241] indicate that columns treated in this manner and coated with silicone phases exhibit very low bleeding rates and good deactivation, even after programming to 350°C for several weeks. Results obtained in our laboratory also indicate that prolonged operation at temperatures up to 350°C is possible with columns deactivated in this manner and coated with SE-52.

The lifetime of glass capillary columns and the maximum operating temperatures are being increased at present, both by the production of more stable stationary liquids and by decreased surface catalytic activity.

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10. SUMMARY

This review critically summarizes the various procedures for the preparation of wall-coated open tubular columns for gas chromatography. The methods described are rationalized in terms of the chemistry of the glass surface and the factors which influence the nature and chromatographic performance of the stationary phase film.

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