DEACTIVATION AND PREPARATION OF FUSED SILICA OPEN TUBULAR COLUMNS FOR GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY

by

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I. INTRODUCTION

Chromatography is one of several techniques for separating mixtures of substances into individual components. What sets chromatography apart from other analytical methods is that the separation can be accomplished in shorter analysis times which accounts for the fact that chromatography is the most widely used analytical technique.

The basis for chromatographic separation is the distribution of analytes between two phases: one mobile and the other stationary. The mobile phase can be either a liquid or a gas. When a gas is used we speak of gas chromatography (GC). Subdivisions of gas chromatography include gas-solid chromatography (GSC) and gas-liquid chromatography (GLC) where the stationary phase is either a solid or liquid, respectively.

Chromatography was first used for the separation of gases and vapors by Ramsey in 1905 [1] in experiments using selective adsorption on, and desorption from solid adsorbents such as activated charcoal.

Modern gas chromatography was first suggested in 1941 by Martin and Synge [2] and later developed (1952) by James

and Martin [3,4]. Because of its unsurpassed resolving power, sensitivity, speed, accuracy, and sample size requirements, gas chromatography has become the most widely applied method in analytical chemistry.

Conventional GC columns are tubes made from copper, stainless steel, aluminum or glass that are tightly packed with either a solid adsorbent (charcoal, molecular sieve, porous polymer, etc.) for GSC or particles of a solid support which have been coated with a film of the stationary liquid (GLC). These columns, typically 1-5 meters in length, are capable of resolving fairly simple mixtures. They are of limited utility in applications dealing with complex mixtures such as waste water, physiological fluids and tissues, fossil fuels, flavors and fragrances, etc., which contain hundreds or even thousands of components. Samples such as these need the high resolution only available with open tubular or "capillary" columns.

Open tubular columns were first introduced in 1957 by M.J.E. Golay [5]. These columns were developed in the course of studying discrepancies noted between theoretical and actual packed column efficiencies that related to the particle size. In one of his experiments, Golay substituted a piece of Tygon tubing for the packed column [6] and discovered that the air peak was significantly narrower than in

previous experiments. His subsequent coating of this tubing resulted in the preparation of the first open tubular column. It should be noted that these columns with the liquid phase coated in the form of a thin, homogeneous film on the inside of the tube should properly be called wall-coated open tubular columns, or WCOT columns. However, most chromatographers refer to them simply as "capillary" columns because the tubing internal diameter is small (usually less than 1.0 mm). This terminology, although widely used, is strictly incorrect as it is the openness of the column rather than the small diameter that leads to the dramatically increased separation power over the packed column.

To visualize this, in the packed column the chromatographic process is inhibited by slow diffusion of the sample molecules in and around the porous support particles. The open tubular column provides an open, unrestricted path for the flow of carrier gas and sample molecules down the entire column length. The stationary phase being distributed in the form of a thin, even film on the inner wall provides for much easier diffusion of the sample molecules into and out of the phase than in a packed column where there exist deep pores plus liquid phase "puddles" of unequal depth. Figure 1 represents these phenomena. The major differences between packed and open tubular gas chromatographic columns are summarized in Table 1.

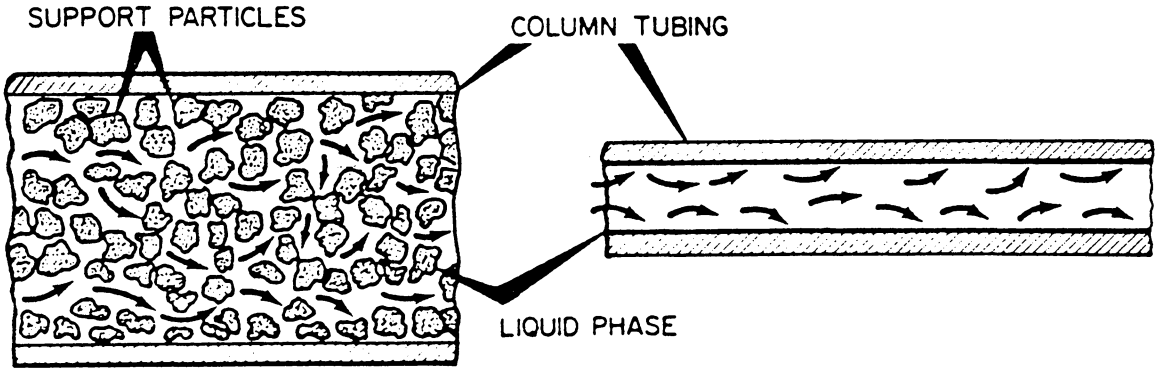


Figure 1: Comparison of solute migration through packed and open tubular gas chromatographic columns. (From ref. 12)

Table 1. Comparison of packed and capillary columns.

	Packed	Capillary
Length, meters	1-5	5-100
I.D., millimeters	2-4	0.1-0.7
Flow, ml/min	10-60	0.5-40
Pressure Drop, psi	10-40	2-40
Total Plates (2 meter, 50 meter)	5,000	150,000
Plates per Meter (ID)	2,500 (2mm)	3,000 (0.25mm)
Liquid Phase Film Thickness (d_f)	1-10 um	0.05-8 um
Capacity	10 ug/peak	50 ng/peak (d_f = 0.25 um)

Although the introduction of open tubular column chromatography caused much excitement in the late 1950's, its development into a routine analytical tool has been fairly slow until recently (certainly in the United States). Many analysts have been reluctant to take advantage of this technique, probably due to limitations in instrument design and column preparation. While most design problems with instrumentation have been overcome, the act of preparing a good capillary column is most often considered more of an art than a science. There have been a number of significant advances in column preparation over the years, but there still does not exist a "perfect" column. The major limitation to the production of highly efficient, inert, and thermally stable open tubular columns lies in the nature of the material used for column fabrication. In the beginning, materials such as plastics, stainless steel, copper, nickel, and even gold were used. Some years later glass was introduced as a column material and even though the glass columns were somewhat fragile, they all but replaced the other materials due to their more inert surface. In 1979, columns made from flexible thin-walled fused silica were introduced and now have replaced glass as the column material of choice in all but a few cases. This type of material is preferable over other materials due to its low catalytic surface activ-

ity. There are numerous reviews available which describe in detail the development of open tubular column gas chromatography [7-19].

With the use of fused silica as column material, there can be difficulty in obtaining an inactive surface that is wettable by the stationary phase; especially the more polar ones. Therefore, the scope and objective of this work was to investigate methods for producing a highly deactivated surface that remains wettable by the stationary phase. In addition to this, several novel stationary phases were synthesized and compared to commercially available phases in terms of polarity, thermostability, cross-linking efficiencies with various free radical initiators, and suitability for use in supercritical fluid chromatography (SFC).

II. CAPILLARY COLUMN TECHNOLOGY

Glass and Fused Silica Chemistry

Glass Structure and Composition

Glass is a noncrystalline solid which may be comprised of both organic and inorganic materials as long as there remains an absence of long range order in the atomic structure. The American Society for Testing and Materials (ASTM) has defined glass as "an inorganic product of fusion which has cooled to a rigid condition without crystallizing" [20].

There are well over 700 different glass compositions in commercial use today [21]. The only glasses that have been used for the fabrication of columns for capillary gas chromatography are those that contain silica, SiO_2, as their primary constituent. It has been shown by Warren [22] that silicon atoms possess a coordination number of four in amorphous silicon dioxide with four oxygen atoms bonded to each silicon. According to Taylor [23], in the glasslike state the basic unit of the crystalline structure is retained (the SiO_4 tetrahedron) but they are linked together at slightly distorted angles forming a three-dimensional polymer network. Accordingly, these silicon and oxygen

atoms form somewhat irregular six-membered rings which have relatively good stability due to the ease of deformation of the Si-O-Si bond angles. Such a six-membered ring, characteristic of pure silica, is diagrammed in Figure 2A.

Various metal oxides are often added to pure silica to reduce its viscosity and to lower the temperatures necessary to process the glass industrially. The two most common glass types used for glass capillary column material are the soda-lime and the borosilicate types.

For soda-lime (or "soft") glass, the major additive is soda, Na_2O. The addition of soda softens the glass structure by disrupting the Si-O bonds. This is schematically represented in Figure 2B. The soda-lime glass is characteristically alkaline in nature due to the high content of the Na_2O.

For the borosilicate type of glass, the major additive is boric oxide, B_2O_3, which is believed to enter the silica framework as depicted in Figure 2C. The boric oxide does not raise the thermal expansion coefficient of silica glass as much as the alkali oxides do. As a result, this type of glass has found wide use in laboratory glassware under the familiar trademarks Pyrex and Kimax. Also, this borosilicate glass has been preferred for glass capillary column fabrication as they are less fragile than columns drawn from

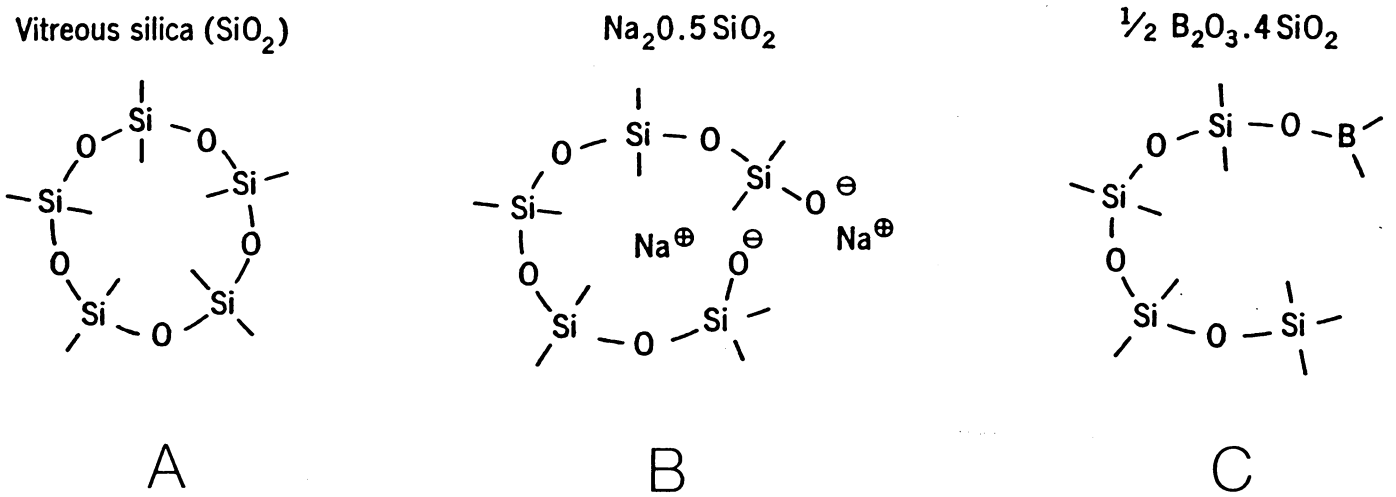


Figure 2: Schematic representations of glass structures: (A) fused silica, (B) soda-lime (soft) glass, and (C) borosilicate glass. (From ref. 21)

soda-lime (soft) glass. In contrast to the soda-lime glass, the borosilicate glass tends to be somewhat acidic due to the incorporation of the B_2O_3.

Typical compositions of each type of glass are listed in Table 2 [19].

Fused silica can be described as the simplest glass and in many respects as an ideal glass. Fused silica is simply pure silica (SiO_2) without any additives used to modify its chemical or physical properties. Because it contains no modifiers to lower its viscosity, the pure silica glass has an extremely high melting point (1800°-2200°C) and is difficult to prepare by standard techniques. However, for the same reason, this material has a high tensile strength which allows a thin walled capillary to be drawn that exhibits a great deal of flexibility.

Two types of silica are available. The first type, called fused quartz, is manufactured by the melting of natural quartz in vacuum at high temperature (1900°C). The major disadvantage in the use of this type of material for capillary columns is that the purity of the manufactured material depends on the purity of the original quartz. Most fused quartz has less than 100 ppm total metal. On the other hand, the second type of pure silica (the so-called fused silica) is prepared synthetically so that the result-

Table 2. Typical bulk glass compositions of soda-lime and borosilicate glasses (%).

	SiO_2	Na_2O	CaO	Al_2O_3	B_2O_3	MgO	BaO	K_2O
Soda-lime soft glass	68	16	6	3	--	4	1	1
Borosilicate glass	81	4	0.5	2	13	--	--	--

ing metal content is negligible (usually less than 1 ppm) with high purity material available containing less than 0.1 ppm metals. Table 3 [25] lists typical metal impurities in various types of fused silica.

The synthesis of the fused silica is based on the flame hydrolysis of purified $SiCl_4$ [24] according to the reaction:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

The silicon dioxide formed is condensed on a substrate and allowed to accumulate to the desired thickness.

A schematic representation comparing a multicomponent glass (such as soda-lime or borosilicate glass) and fused silica is given in Figure 3 (adapted from [21]).

Surface Chemistry of Silica Glasses

For chromatographic considerations, the structure and composition of the glass surface is of more importance than that of the bulk glass itself. Through the use of sophisticated surface analytical techniques such as Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS), and x-ray photoelectron spectroscopy (XPS or ESCA) it has been established that the surface composition of glass usually differs significantly from the bulk composition [26-29]. Factors other than the

Table 3. Metal impurities in various types of fused silica (ppm).

Fused Silica Type	Al	Ca	Cu	Fe	Mg	Mn	Ti	Na	K	B	P
Natural quartz	30-50	1.0	0.8	2.0-3.3	1.0	0.03	3	2.0	2.0	0.3	0.5
Purified natural quartz	1-10	0.1	---	0.5	0.3	0.01	---	<0.5	1.0	---	---
Synthetic fused silica	0.1	0.1	0.004	0.2	0.1	0.01	---	0.4	0.001	0.01	0.1
High-purity synthetic fused silica	0.03	---	0.01	0.03	---	---	---	0.004	0.005	---	---

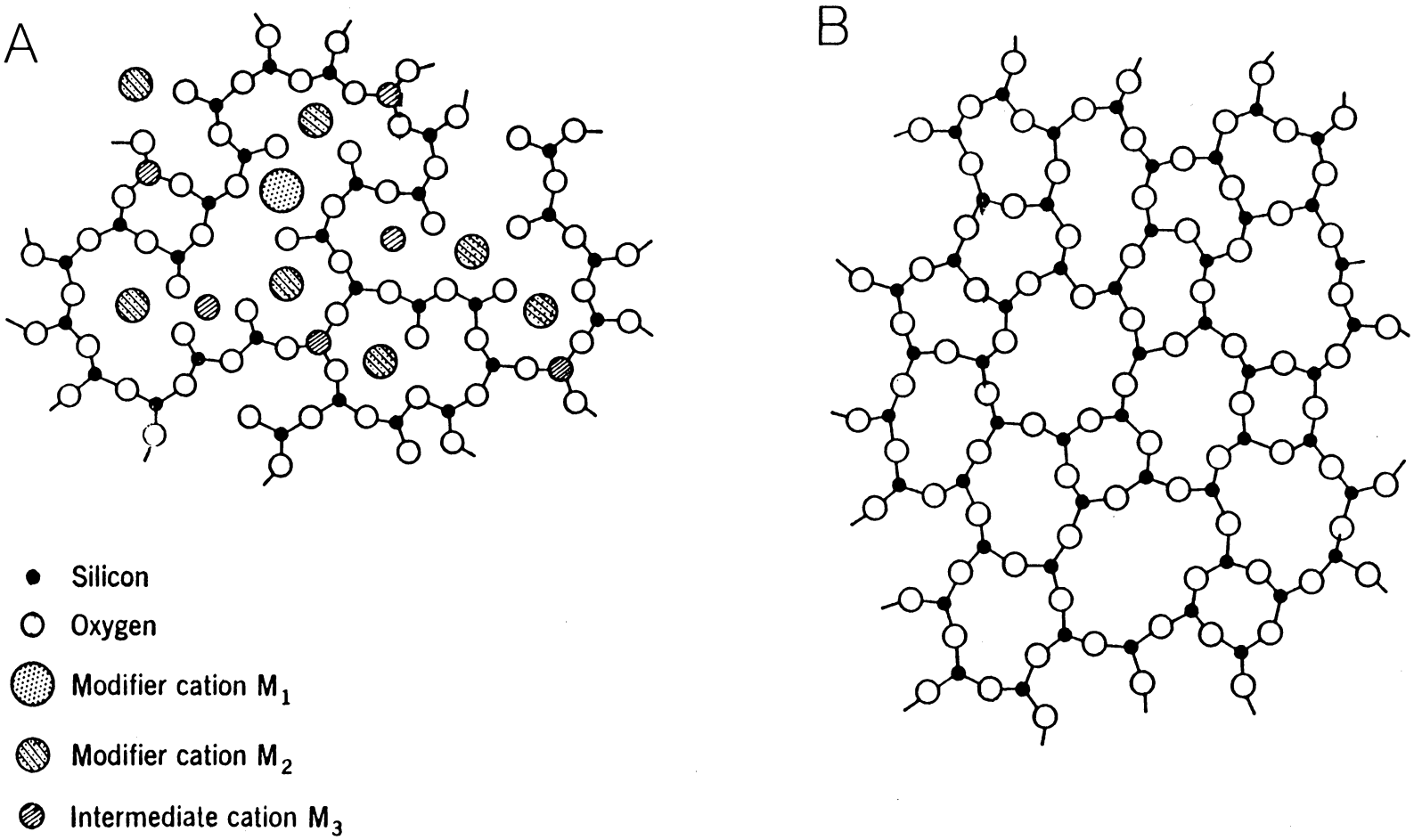


Figure 3: Two dimensional schematic representation of (A) multicomponent glass and (B) fused silica. (From ref. 21)

bulk chemical composition also affect the surface structure. These factors include the environment of both the manufacturing stage and the storage and handling stage of the glass in addition to the thermal history of the material. It is the nature of the surface layers present that critically influences the preparation, performance, and stability of capillary columns.

Although glass is generally considered to be moderately inert in regard to adsorptive and catalytic activity, untreated glass and fused silica are known to exhibit undesirable surface activity in capillary column applications. Such activity, particularly noticeable when chromatographing polar types of compounds, can be visually evident from tailing peaks. However, symmetrical peaks do not guarantee the lack of surface activity affects. In many cases peaks of symmetrical shape but reduced height and area are observed while in extreme cases the entire peak may disappear from the chromatogram [30-35]. Such interactions between the analyte and the surface are particularly evident when chromatographing extremely low (nanogram) levels of material.

The activity associated with the column wall is attributable to the surface structure of the silica itself and also to impurities that are found on the surface either from adsorption onto the surface after fabrication or intentional

inclusion in the raw material. For composite glasses, the metal oxides added during manufacture can act as Lewis acid sites [36-38] in which the acid site is considered to be cationic with the associated positive charge concentrated on the cation and the negative charge distributed over the internal bonds of the incomplete silica tetrahedra [39]. These Lewis acid sites can function as sites of adsorption for several classes of molecules including molecules which can donate a lone-pair of electrons such as amines and ketones and molecules containing π-bonds such as aromatic compounds and olefins [40,41]. It is the absence of these adsorptive metallic impurities which gives the synthetic fused silica its greater degree of inherent inertness.

In regards to chromatographic performance, the most important structural feature of the silica surface is the presence of hydroxyl groups attached to the surface silicon atoms. Presumably, these surface silicon atoms are bound to three other oxygen atoms in the silica framework. This would deem it likely that the completion of the tetrahedral coordination of the surface silicons would occur by the attachment of monovalent hydroxyl groups rather than by forming strained siloxane bridges or charged species [42].

There have been several types of hydroxyl groups found on silica surfaces. Two hydroxyl groups attached to adja-

cent silicon atoms are called vicinal and two hydroxyl groups attached to the same silicon atom have been termed geminal. In addition to the surface hydroxyls (or silanols) there can also be hydroxyl groups within the silica structure which are usually termed intraglobular hydroxyl groups [43].

Many of the surface silanols are described as "bound" since they are hydrogen bonded to one another. The silanols that are not involved in hydrogen bonding are described as "free" [19]. The distance separating one surface hydroxyl group from the oxygen atom of an adjacent hydroxyl group determines whether they are free or bound. Silanols with greater than 3.1 angstrom separation are considered to be incapable of hydrogen bonding [44]. Since the hydroxyl groups described as vicinal are separated by more than 3.1 angstroms, it is doubtful that they are hydrogen bonded to one another. The geminal hydroxyl groups are also probably not bound since a five or six-membered ring is usually required for intramolecular hydrogen bonding. The optimum hydroxyl-oxygen distance for hydrogen bonding is considered to be 2.4 to 2.8 angstroms [45]. Since the spacing between neighboring surface hydroxyls is a continuum, there exists a continuum in the degree of interaction of these hydroxyls from free through strongly bound [46].

Water is adsorbed onto the hydrogen bonded surface hydroxyl groups under normal atmospheric conditions [47]. Thermal treatment of the silica can remove the water that is physically adsorbed on the surface leaving only surface and intraglobular hydroxyls. Intense heating can actually dehydrate the silica surface by the condensation of two neighboring hydroxyl groups to form a siloxane bridge and a molecule of water. At temperatures up to about 165°C, only physically adsorbed water is removed from the silica surface. Between 165°C and 400°C, hydroxyl groups that are hydrogen bonded to one another are removed thermally from the surface. If the silica is allowed to cool at this stage in the presence of water these sites can rehydrate forming the original silanol groups. However, above 400°C, the process of dehydroxylation becomes more irreversible with rehydroxylation unable to occur spontaneously after heating to 800°C and above. A molecular model for these processes of silica dehydration and rehydration is given in Figure 4 [48].

The hydrogens of the surface silanol groups are known to be partially acidic due to d-electron cloud vacancies in the silicon atoms [49] and the formation of $\pi(d,p)$ bonds between the oxygen and silicon atoms [50]. As a result, the surface hydroxyl groups can function as proton donors for

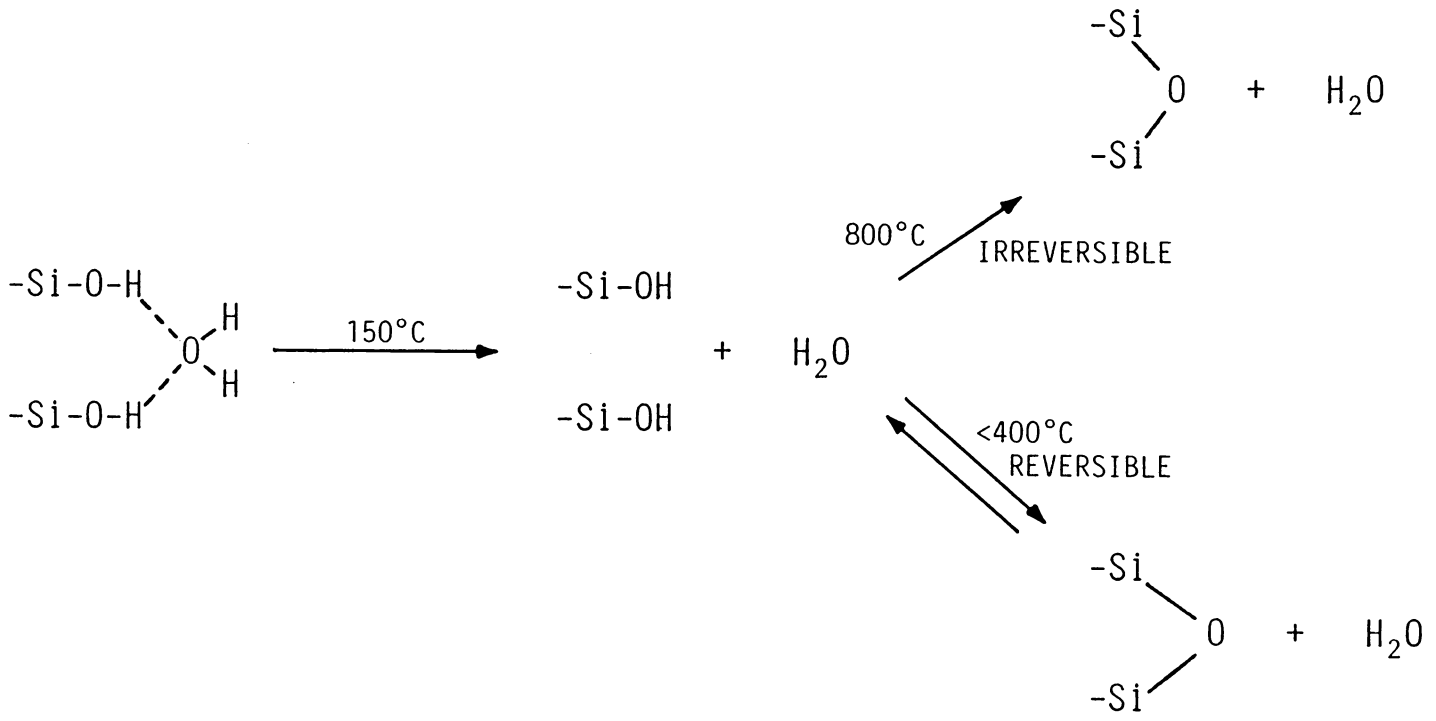


Figure 4: Model for silica dehydration and rehydration.

hydrogen bonding sites causing adsorption of molecules with high peripheral electron densities such as unsaturated or aromatic hydrocarbons, alcohols, ethers, amines, and compounds containing the carbonyl functionality. Water can also interact strongly with the surface hydroxyl groups. The adsorbed water can then act as adsorption sites for compounds with high electron densities in much the same way as the free surface silanols [47].

The determination of surface hydroxyl concentration of silica glasses is a difficult task, even for porous (i.e.: high surface area) silica. The currently accepted value for an annealed, fully hydroxylated silica surface is one hydroxyl group per silicon atom at a concentration of about 4.6 OH/nm^2 [51]. The analytical techniques commonly used for surface silanol concentration determination of porous silica such as IR and NMR spectroscopy, thermogravimetry, reaction titrations, and deuterium exchange are not applicable to low surface area materials such as glass and fused silica. Recent experiments involving tritium exchange of the surface hydroxyl protons have yielded surface hydroxyl concentrations for actual glass and fused silica capillary column surfaces [52]. These results are summarized in Table 4. The concentration found for a hydroxylated glass surface was less than the value of similar porous silica (2.8 vs.

Table 4. Surface hydroxyl concentration of fused silica and glass.

Column type	Pretreatments	Surface hydroxyl concentration (OH/nm^2)
Hydroxylated glass	Acid leached, water rinsed, heat treated at 150°C for 12 hours	2.84 ± 0.09
Dehydroxylated glass	Heat treated at 600°C for 8 hours	0.36 ± 0.02
Fused silica	Heat treated at 150°C for 4 hours	0.21 ± 0.04

4.6 OH/nm^2). Conclusions from this work were that hydroxyl groups on the glass are fewer in number and more easily removed than on porous silica. The very low concentration of silanols on the fused silica is consistent with its extremely high drawing temperature and also with its lower chromatographic adsorptivity.

It has been claimed that siloxane bridges are relatively inert [53]. However, it is known that during heat treatment of silica, surface hydroxyls condense to form water and siloxane bridges [54]. Such a strained siloxane bridge could possess longer than normal bond lengths, decreasing its stability and increasing its reactivity, and even containing some degree of ionic character [55]. It has been reported that siloxane bridges formed from a 700°C treatment of silica are more reactive than remaining free hydroxyls [56]. The possibility exists for releasing this bond strain (and thus decreasing the reactivity) by treating the silica at temperatures greater than 900°C [54]. As a result of this bond strain and reactivity, the siloxane bridge can act as a proton acceptor in hydrogen bonding interactions with alcohols [57]. In an independent chromatographic study relating adsorption to retention, the conclusion was drawn that the siloxane bridge was an active site [58]. Another study has shown that strained siloxane

bridges result in the chemisorption of alcohols and amines [59].

Pretorius has published a review in which the structure and properties of siliceous supports used in gas chromatography are described [60].

Capillary Drawing Procedures

Glass Predrawing Treatments

In the manufacture of glass tubing, the material is exposed to oils and greases during the cooling process. In view of this and the fact that organic vapors adsorb onto clean glass during storage, a number of solutions have been used to clean the glass surface prior to drawing. These include acids, bases, and the usual organic solvents such as acetone, ether, methanol, and methylene chloride.

Glass Capillary Column Drawing

The invention of the glass drawing machine is attributed to Desty in 1960 [61]. It simply consisted of two pairs of rollers; a set of feed rollers before an electrically heated furnace and a set of draw rollers after the furnace. The ratio of roller speeds controls the draw ratio while the ratio of the inside and outside diameter remains the same in the drawn capillary as it was in the stock.

After the draw rollers the drawn capillary is fed through a coiling tube to shape the capillary into a helix. Temperatures needed to draw composite glass depend on the type of glass used. Typical temperatures are between 600° and 700°C. Novotny and Zlatkis have published a more detailed description of the drawing process [19].

Several authors have reported a deleterious affect of non-uniformity of column inner diameter on the column performance [61-64]. Such variations usually range around ±5% and are caused by fluctuations in furnace temperature, slipping of the tube in the rollers, etc.

Fused Silica Predrawing Treatments

As mentioned previously, the preforms for drawing fused silica are built up to the desired thickness (and ratio of inner to outer diameter) on a substrate. These preforms contain small imperfections on both the inner and outer surface and these must be removed prior to drawing. This is usually accomplished in a two step procedure. The first step entails treating the preform in a dilute hydrofluoric acid solution and rinsing with ultrapure water [25]. The second step involves high temperature annealing of the preforms by fire polishing them in a precision glass turning lathe.

Fused Silica Capillary Column Drawing

In 1975, Desty modified his original glass drawing machine to attain the drawing temperature necessary for quartz by replacing the electrically heated furnace with a special propane/oxygen burner [65]. However, he was unable to successfully build suitable coiling tubes for the machine and this proved to be the limiting factor of the prototype machine. In 1979, Dandeneau and coworkers [66,67] discovered that thin wall capillary columns of high flexibility could be drawn straight and then coiled simply by bending them. This discovery has proved to be the most significant advance in capillary column technology since the first use of glass as a column material.

Most fused silica capillaries are drawn under a "clean-room" atmosphere using advanced fibre optics technology. The capillary itself can be used as a fibre optic (light conduit) so that infrared laser radiation can be beamed continuously through the capillary and coupled to microprocessor controlled feedback circuitry to provide a method of obtaining remarkably uniform capillaries [68]. In order to draw fused silica the preform must be heated to ca. 2000°C. Heaters which have been used include electrical heaters (induction and resistive types) [69], lasers [70], and gas burners [71].

While the fibre optic technology used certainly produces excellent material, the enormous initial investment required has limited the number of worldwide facilities capable of drawing the fused silica to about 6. Recently, Desty and Pretorius have described a relatively simple method for drawing fused silica to a uniformity of better than 5% [72].

Fused Silica Postdrawing Treatments

Although the thin-walled fused silica has a high tensile strength and is very flexible, these properties are greatly reduced in a short period of time after drawing due to slight surface imperfections and atmospheric corrosion. The reason for the "clean-room" atmosphere is that the preform becomes charged by the heater at the point of drawing so that the freshly drawn tubing is charged and attracts dust. Dust accumulated in this way is thought to be the major cause of column fracture. To protect the freshly drawn tubing from dust accumulation, finger prints, and atmospheric corrosion, it is covered by a protective polymeric sheath as it emerges from the drawing furnace. Desirable attributes of this protective covering are that it be mechanically durable and thermally stable to high temperatures. Initially, silicone rubber materials were used but

they were soon abandoned due to lack of stability. The predominant coatings used today are polyamides and polyimides. None of these materials currently in use have a temperature limit above 360°C, although some may be heated to 400°C for short periods of time. Other protective coatings have been used (vitreous carbon [73]) and suggested (aluminum) to increase the upper temperature limit.

Surface Wettability

The production of high efficiency capillary columns requires that the stationary phase be deposited as a thin, homogeneous film on the surface of the capillary tubing. The initial attainment of an even film on the surface is dependent upon the ability of the stationary liquid to completely wet the surface of the tube wall.

In the wetting of a solid by a liquid, the liquid spreads so as to increase the solid-liquid and liquid-gas interfacial areas while decreasing the solid-gas interfacial area. The surface tension of a liquid, γ_ℓ, is the force per unit length on the surface of the liquid that opposes the expansion of the liquid surface area.

At a liquid-solid-gas interface there is a characteristic contact angle, θ. The contact angle is defined as the angle formed between the tangent to the liquid drop and the

solid surface, as drawn through the liquid. This is represented schematically in Figure 5. For a liquid that completely wets the surface the contact angle is zero. As the tendency for the liquid to not wet the surface increases, so does the contact angle. This situation arises when the cohesive forces of the liquid are greater than the adhesive forces between the liquid and solid. Therefore, the contact angle is an inverse measure of the wettability of the solid by the liquid.

At equilibrium, the three interfacial tensions shown in Figure 5 must balance along the line of contact (Figure 6) so that:

$$\gamma_{sg} = \gamma_{s\ell} + \gamma_{\ell g}\cos\theta$$

where γ_{sg} is the surface tension of the solid in equilibrium with gas (vapor of the wetting liquid); $\gamma_{\ell g}$ is the surface tension of the wetting liquid in equilibrium with its vapor; and $\gamma_{s\ell}$ is the surface tension (or surface energy) of the solid in equilibrium with the liquid.

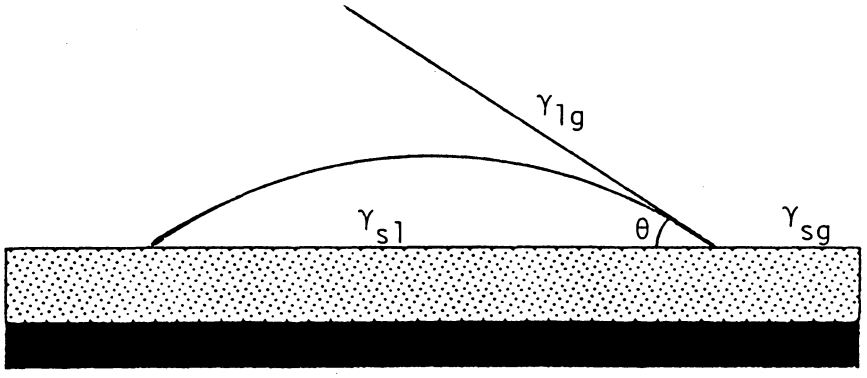


Figure 5: Drop of liquid in contact with a solid surface.

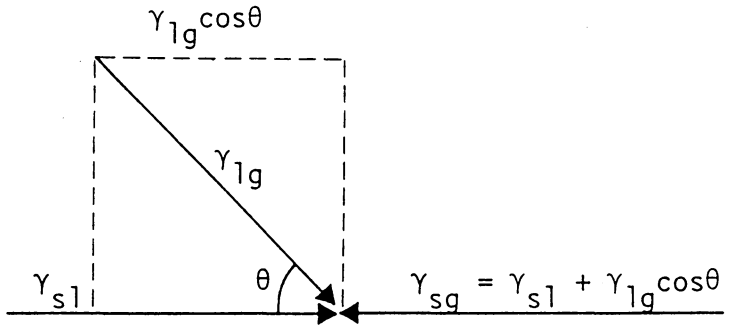


Figure 6: Vector diagram illustrating the balance of the solid-liquid-gas interfacial tensions at equilibrium.

Surface Treatments

Modification of the inner surface of capillary tubing prior to coating with the stationary phase has two primary purposes. The first is to control the activity of the surface active sites such as the metal impurities and silanol groups. The second is to modify the surface properties by physical or chemical means to enhance the wettability of the surface by the stationary phase.

Surface Roughening

One of the earliest techniques used for modifying the inner walls of glass capillary columns was physical roughening. Roughening methods involving surface corrosion are still frequently used for treating soda-lime and borosilicate glasses but due to the extremely thin walls of fused silica they are not generally applicable to this material as the tubing becomes excessively brittle [74]. There are two possible ways to roughen the surface of fused silica. The first would require the drawing of thicker walled tubing which could be etched, but this would cause the fused silica to lose much of its desired flexibility. The second method to increase surface roughness of fused silica would be to deposit microparticulate matter on the inner surface, although few applications have been described.

Increasing the roughness of the surface greatly increases its wettability by the liquid phase. In general, a liquid will spread better on a roughened surface because the surface covered by the liquid releases more energy due to the interfacial forces arising from the increased area under the liquid. The increased wettability has been related to the increased roughness by a roughness factor introduced by Wenzel [75] and further discussed by Cassie [76].

The roughening of the inner surfaces of glass capillary columns has been reported using solutions of ammonia [77], sodium hydroxide [78], hydrofluoric acid [79], hydrochloric acid [80], and several of these solutions in succession [81]. Most of the aqueous procedures deeply attack the glass surface and leave a strongly adsorbing surface.

Gaseous HCl has been used to induce NaCl crystal growth as described in [82] and discussed in detail in [83].

Surface roughening has also been accomplished using hydrogen fluoride gas [84-86] with high concentrations of HF yielding whisker formation on the surface [87]. Sandra et al. [86] have summarized the advantages and disadvantages of whisker surfaces. The main advantages are that with the increased surface area, larger amounts of liquid phase can be accommodated, and therefore larger sample capacities are

obtainable and the presence of the whiskers stabilizes all stationary phases with droplet formation seldom observed. The main drawbacks of these types of treatments, however, are that the whisker surfaces are extremely active and the separation efficiencies of the columns are reduced due to the extremely rough surfaces.

Similar procedures for whisker formation were applied to fused silica capillaries [88] with the result being the formation of holes rather than whiskers.

One of the most successful and often used techniques for surface roughening is the in situ formation of a barium carbonate layer as described by Grob et al. [89,90]. Barium carbonate crystals can be grown on any kind of glass but the structure of the glass influences the shape, size, and distribution of the crystals. Independent work by Schomburg et al. [91] has indicated that the barium carbonate layers lead to the degradation of the stationary phase resulting in increased phase bleeding rates.

Crystalline materials can also be deposited directly on the surface of the capillary column. Sodium chloride crystals have been deposited from an aqueous NaCl solution [92,93]. Carbon black has been deposited by pyrolyzing hydrocarbon gases and liquids inside the column [30] and also by dynamic [94,95] and static coating [96] of columns with a colloidal solution of graphitized carbon black.

Other techniques include the deposition of silanized silicic acid from a suspension of fine particles in the stationary phase [97] and the deposition of a minute amount of silica on the wall of capillary columns by coating the column with a dilute solution of water glass and reacting it with gaseous HCl [98]. Although these techniques have only been reported for composite glass columns, they could be applied to fused silica equally as well.

Recently, novel fused silica columns were prepared by surface modification through controlled doping of the preform [169]. With this method, inorganic dopants are introduced into the glass at the bore of the preform tube from which the capillaries are drawn. The result is the production of capillaries which have specific surface properties but still retain the strength and flexibility characteristic of fused silica. Columns prepared showed novel behavior both as adsorption columns and as columns coated with stationary phases.

Surface Deactivation

The surface roughening methods just described can provide some degree of surface deactivation. The roughening methods involving deposition of particulate matter (NaCl, $BaCO_3$, etc.) physically cover some of the active sites on

the glass surface. For NaCl covered surfaces, the net effect is a column of reduced activity due to the somewhat lower Lewis acidity of sodium compared to other metals present in the composite glass. For $BaCO_3$ treated surfaces, Grob has claimed [90] excellent deactivation in addition to its intended use as a roughening procedure. However, there are several contradictory indications that the barium carbonate layer contributes undesirable activity to the capillary column. It was found earlier by the Grobs [89] that the barium carbonate treatment produced a surface that was slightly basic with the result that acids with pKa less than 6 were difficult to chromatograph. In addition to this, it was found that barium carbonate crystals which were not covered by stationary phase were impossible to deactivate [99]. The most satisfactory columns which were obtained (in terms of activity) were deactivated with Carbowax after the deposition of $BaCO_3$ [89,90]. However, Onuska et al. [100] found that even the Carbowax deactivation was insufficient to prevent the adsorption of propionic acid on the barium carbonate layer.

While these inclusion roughening techniques can, in some circumstances, provide some deactivation for active composite glass columns, they could only increase the activity of fused silica columns. This undoubtedly is the pre-

dominant reason they are not utilized in conjunction with fused silica column preparation.

In addition to physically covering active sites, surface roughening can result in better coverage of the surface by the stationary phase due to the increased wettability. The stationary phase itself can provide some degree of surface deactivation, especially when the more polar phases are used. It is a commonly held belief that the thicker the film of stationary phase, the better the degree of deactivation. However, this has never been proven and from theoretical considerations should not be so since the interactions of the analytes with the surface should be independent of the film thickness (for film thicknesses less than 5 um which are commonly employed). What is commonly observed is an apparent increase in deactivation with thicker films since these columns are typically operated at higher temperatures and/or faster programming rates to compensate for the greater retention resulting from the increased amount of stationary phase. At elevated column temperatures, the affect on peak shape from reversible adsorption will not be as great as noted at lower column temperatures.

Surfactants were used during the infancy of capillary column technology to block active adsorption sites. These surface active agents adhere and form an oriented monolayer

on the inner column wall. The earliest uses involved the addition of surfactants to the liquid phases prior to coating to improve the chromatographic properties of stainless steel columns [101-104]. Various surface active agents have also been utilized in the preparation of glass capillary columns, including trioctadecylmethylammonium bromide (Gas-Quat L) [30,105], sodium tetraphenyl borate (Kalignost) [32], and benzyltriphenylphosphonium chloride (BTPPC) [32,85]. The major disadvantage of the use of surfactants is that since the oriented monolayers are not chemically bound to the surface, they can be displaced by monolayers of other substances leading to a gradual loss of inertness over time. Other drawbacks include the activities of the surfactants toward many classes of sensitive compounds and the possibility of the pretreatment altering the selectivity (polarity) of the stationary phase.

Acid Leaching

The aim of acidic leaching of composite glass surfaces is two fold: to produce a glass surface that consists of almost pure silica by removing the metallic cations which act as Lewis acid sites; and to produce a surface consisting of maximum hydroxylation (surface silanol coverage) as a basis for high density coverage by chemical modification.

If the purpose of acid (or aqueous) treatment is not for removing ionic impurities and only for maximizing hydroxylation (as would be the case for fused silica) the process is termed a hydrothermal treatment rather than leaching, as proposed by Unger [106]. If the leached (or hydrothermally treated) surface is not followed by some treatment to block the surface silanol groups then the net result would be an increase in column activity. Silanol groups can be effectively deactivated by silylation whereas the Lewis acid sites arising from metal oxides cannot.

Early procedures for acid leaching glass capillary columns produced inferior results. Some intensive leaching procedures produced porous columns that were so adsorptive they were only suitable for gas-solid chromatography. It was suggested by Novotny [19] that leaches involving aqueous solutions were detrimental to column performance. Several years later, Novotny et al. [107] and Diez et al. [108] concluded that acidic leaching was useful in removing the active metal cations and improving chromatographic performance. In 1975, Lee et al. [109] reported a two step acid leach for glass columns involving a gaseous HCl treatment followed by washing with a large volume of concentrated formic acid to remove the NaCl crystals formed by the HCl. Schomburg et al. [110] reported a similar procedure except

that the salt crystals were washed out with consecutive rinsings of water, acetone, and ether.

In an extension of their barium carbonate roughening procedure, the Grobs [111] introduced an acidic leach of the column as an important step. This procedure, with few modifications [112], is still advocated and entails a static leach with the column completely filled with a 20% HCl solution.

Rutten et al. [113] have systematically studied the leaching of both soda-lime and borosilicate glass capillary columns. The extracted amounts of all important metal ions were determined by inductively coupled plasma (ICP) spectroscopy as functions of leaching time and temperature with 20% HCl as the leaching solution.

Venema et al. [114] have performed similar experiments only using dynamic leaching with 20% HCl solutions. They concluded that dynamic leaching was preferable to static leaching in regard to the resulting surface adsorptivity. This agrees with earlier findings of Lee et al. [115].

Surface modification of soft glass capillaries by treatment with water vapor has also been reported [116]. The authors claim the water vapor leach results in an accumulation of cations at the surface and a corresponding decrease in the number of silanol groups. As a result,

capillaries are obtained which show good properties for chromatographing strongly basic compounds.

As stated previously, because of the extremely low metal content of fused silica, there is no need for leaching the tubing material to remove Lewis acid sites. However, hydrothermal treatment of fused silica may prove advantageous for increasing the degree of surface hydroxylation. To date, very little information is available on hydrothermal treatments of fused silica. Verzele et al. [88] have reported that fused silica tubing purged with water saturated nitrogen at 350°C for 8 hours followed by silylation produced columns of better inertness than columns prepared without the water treatment. Moseley et al. [117] used a hydrochloric acid hydrothermal treatment although no comparison was made with untreated capillaries. Wright [118] also utilized various HCl treatments of fused silica but each was after a pretreatment with sodium hydroxide with the most effective treatment claimed to be dynamic leaching with 1M NaOH at 100°C followed by hydrolysis with 20% HCl. Increasing the preliminary treatment concentration to 2M NaOH completely dissolved the fused silica. Hydrochloric acid treatment of fused silica has also been reported by Markides et al. utilizing 20% HCl [119,120] and 50% HCl [121] solutions. In these studies, the HCl treatments were deemed

necessary to increase the degree of surface silanol coverage to allow a significant degree of deactivation prior to coating.

Chemical Modification

Chemically replacing surface silanol groups with inert groups is the most effective and practical method for eliminating the activity associated with them. In addition to surface deactivation, the compatibility of the stationary phase with the column wall can be assured by modifying the surface with functional groups identical to those found in the stationary phase. Such similarities are conducive to the wettability of the column wall by the phase and also minimize differences in surface tensions of the liquid phase and the surface as the temperature is raised [122]. This characteristic is of utmost importance since temperature programming is almost always used in capillary column gas chromatography. The surface hydroxyl groups present provide several possibilities for the chemical modification of the glass surface.

In general, the most effective chemical modifications rely on the formation of either Si-O-C bonds or Si-O-Si-C bonds on the surface. Si-C-C bonds are possible but require the chlorination of the silanols followed by further reac-

tion with Grignard reagents [123] or organolithium compounds [123,124]. The limited availability of reagents with different functional groups limits the usefulness of this approach.

The formation of Si-O-C bonds can be accomplished in one of two ways, however, the Si-O-C bond is characterized by fairly low thermostability and ease of hydrolysis which limits its use in surface modification of siliceous column materials [30]. This type of linkage can be formed by first chlorinating the silanol and then reacting with an alcohol. It can also be formed by reaction with organic polymer coatings. This was first reported by Aue et al. [31] for the heat treatment of Carbowax 20M (a polyethylene glycol of 20,000 MW) on a diatomaceous earth support. It was proposed that after heating at 280°C and extracting with hot methanol, the long polyethylene glycol chains were permanently bonded to the silica surface in a nearly monomolecular layer [31,125].

Cronin [126] was the first to apply a non-extractable layer of Carbowax 20M to glass capillary columns by dynamically coating columns with a 2% solution in methylene chloride, sealing the column ends, heating at 280°C for 16 hours, and finally washing the column with methylene chloride followed by methanol. Various related procedures have

since appeared [34,38,97]. Gas phase deactivation with Carbowax 20M has also been used successfully [127]. The first fused silica capillary columns by Dandeneau et al. [66] were also deactivated with Carbowax 20M.

While the exact nature of the bonding of Carbowax to the surface is not known, the actual formation of chemical bonds between the polymer and the silica surface has been verified by diffuse reflectance infrared spectroscopy [128]. Also, the presence of surface hydroxyl groups has been shown to be necessary for the successful bonding of Carbowax 20M [129].

The commonly accepted mechanism [130] for the bonding of Carbowax to siliceous surfaces is that the pyrolysis products of Carbowax include species such as oxirane which are then chemically bound to the glass surface by reaction with surface silanol groups. Such a mechanism is depicted in Figure 7.

Recently, polyethylene glycols of narrower molecular weight distribution, higher purity, and some with higher molecular weight have appeared such as Superox 20M (20,000 MW) and Superox 4 ($4x10^6$ MW). These have also been used for column deactivation with claims made of higher thermal stabilities [131,132]. If the mechanism depicted in Figure 7 is correct then higher thermal stabilities of the deacti-

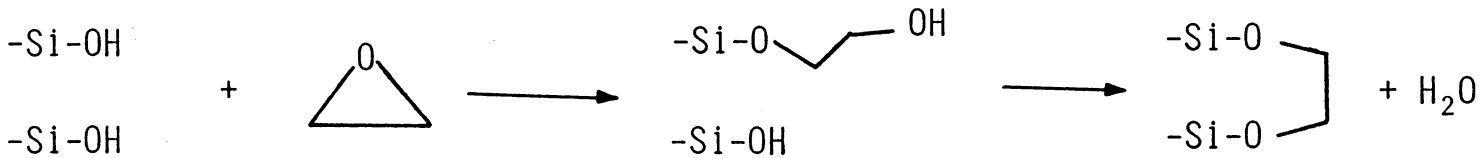


Figure 7: Potential mechanism for the reaction of polyethylene glycols (Carbowax 20M) with surface silanols.

vated layer related to the greater thermostability of the reagent would appear unlikely since the product should be independent of the MW of the initial polyglycol. Improved performance (deactivation and stability) may be attributable to the better film building tendency (i.e.: resistance to droplet formation during heating) of the higher molecular weight material (Superox 4).

Even the thermostabilities of Carbowax 20M deactivated columns are a matter of much controversy. Claims have been made of thermal stabilities above 300°C but there is evidence that Carbowax deactivated columns are not stable for extended periods above 250°C [127,133].

Another drawback to the use of polar polymer deactivations is the tendency for the deactivation layer to influence the polarity of the coated column, particularly with thin films of nonpolar stationary phases [38]. As a result, these Carbowax and Superox type of procedures are still used for the pretreatment of capillary gas chromatographic columns only when the stationary phase is of equal or greater polarity than the polyglycol and the upper temperature limit of the phase itself is less than 250°C.

The most commonly employed and successful methods for chemically modifying the surface of siliceous capillary columns are based on the silylation reaction. Silylation

involves the replacement of surface hydroxyl groups with silyl ether groups forming the Si-O-Si-C linkage. Such chemical modifications are extremely stable due to the strength of the Si-O-Si bond. The second major advantage of silylation is that there are a wide variety of silylation reagents commercially available with constituents covering a wide range of polarity, thus allowing customization of polarity and chemical characteristics of the surface. This approach was first utilized for modification of glass capillary column surfaces in 1962 by Kiselev [134,135] using trimethylchlorosilane (TMCS) as the silylation reagent.

The reaction of TMCS with surface silanols is shown in Figure 8. It has been shown [136,137] by gravimetric and spectroscopic studies that only free hydroxyl groups are involved in this reaction. Hydrogen bonded silanols react to a very small degree, if at all, resulting in "gaps" in the chemically modified surface layer. At lower temperatures, chlorosilanes can be physically adsorbed on the surface of the silica without reacting [138]. As a result, temperatures of 300°-400°C are necessary to ensure the complete reaction of chlorosilanes with available surface hydroxyls [137,138].

A second class of silylating reagents widely used are the disilazanes, with hexamethyldisilazane (HMDS) being typ-

Figure 8: Reaction of chlorosilane (TMCS) with surface silanol.

ical of the class. The net reaction of HMDS with the hydroxyls of the glass surface is depicted in Figure 9. The reaction of HMDS with a silica surface has been determined to follow second-order kinetics [139] which is to say that the reaction of one molecule of HMDS removes two silanol groups. In general, disilazanes are more reactive towards surface hydroxyls than are chlorosilanes since the nitrogen of the disilazane is a much stronger proton acceptor than the chlorine of the chlorosilane [140].

Novotny et al. [141] reported using mixtures of HMDS and TMCS for the silylation of glass capillary columns. Columns were purged with the vapors of a 5:1, HMDS:TMCS solution, ends were sealed and the columns heated to 150°C and held 48 hours. While coating with nonpolar phases was improved by this procedure, it proved to be detrimental in the case of polar phases due to the unsuitable wetting characteristics. In efforts to improve the wettability of the glass surface, a variety of differently substituted silanes were applied [142]. The idea was to silylate the surface with the same functional groups as found in the stationary phase. A modified version of the above procedure has been reported which entails pushing a liquid plug of the 5:1, HMDS:TMCS solution through the column and heating to 200°C [85].

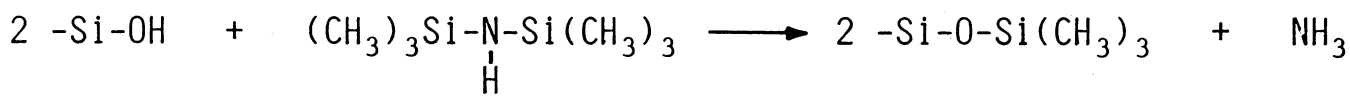


Figure 9: Reaction of disilazane (HMDS) with surface silanols.

High temperature silylation of glass capillary columns was first reported by Welsch et al. [143] with the conclusion that pure HMDS applied as a liquid and heated to 300°C for 20 hours resulted in the most favorable surface silylation.

Grob [144] modified the procedure of Welsch to yield better silylation by heating treated columns to 400°C. Also, other silazanes were suggested [145]: diphenyltetramethyldisilazane, tetraphenyldimethyldisilazane, and triphenylsilylamine to improve the wettability of the surface.

Various siloxanes have also been used successfully in the silylation of capillary columns. Schomburg et al. [91] have described a procedure which forms a nonextractable layer of polymethylsiloxane phase on the glass surface by thermal degradation of the polymer. This type of procedure has been termed PSD (for polysiloxane degradation). It was proposed that during heat treatment (400°-450°C) the polysiloxane partially decomposes with bonding taking place between the decomposition products and the surface silanols. After heat treatment and rinsing, the columns are suitable for coating with the same stationary phase that was used for degradation. Nonpolar polymethylsiloxanes have been used successfully for the deactivation of fused silica tubing, however, intermediate polarity phases (such as OV-17) could

not be successfully applied [88]. Thus the limitation of this technique for fused silica is that apparently it can only be used for the production of nonpolar columns.

Cyclic siloxanes are the most widely used siloxanes for modifying glass capillary surfaces. Cyclic siloxanes were used for silica modification by Aue et al. in nonchromatographic studies [146]. Entirely methylated cyclics were used by Dandeneau and coworkers [147] for the deactivation of fused silica columns for coating with nonpolar phases. The most extensive work with cyclic siloxanes for deactivation has come from Blomberg's group. Trifluoropropylmethyl cyclics were used to deactivate glass columns for coating with a 50% trifluoropropyl methylpolysiloxane [148,149]. More recently, cyclic cyanopropyl siloxanes were synthesized and used to modify the surfaces of glass and fused silica columns for coating with the very polar cyano silicone phases [119-121]. In general, deactivation procedures using cyclic siloxanes entail dynamically coating the cyclic, sealing the column ends, and heating to a temperature of about 400°C and holding 1 to 2 hours.

The probable bonding of cyclic siloxanes to the silica surface is depicted in Figure 10 with octamethylcyclotetrasiloxane (D_4) as an example. When heated, the cyclic siloxane ring is opened by the action of the surface silanols

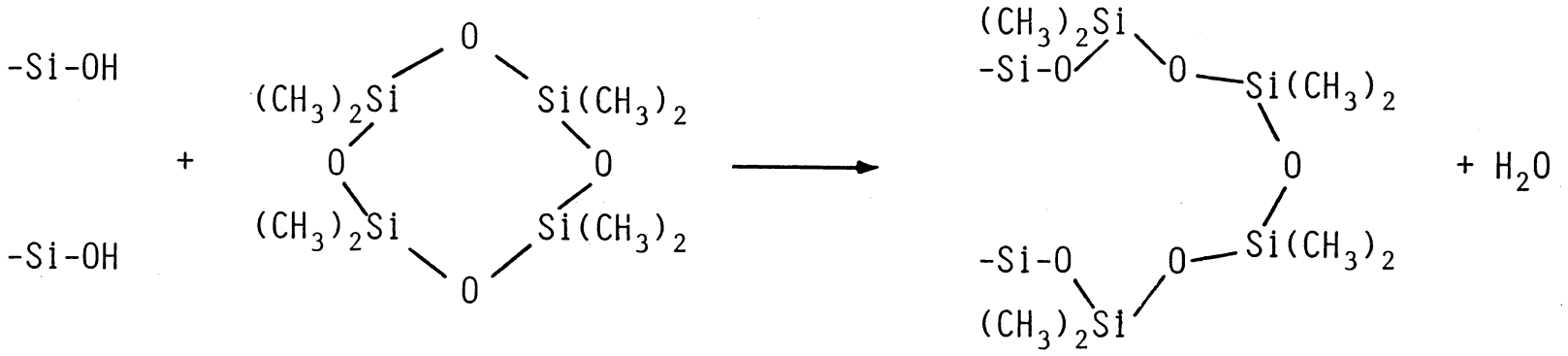


Figure 10: Reaction of cyclic siloxane (D_4) with surface silanols.

and/or traces of water [150]. The number of siloxane links in the chain between bonds to the surface need not be the same as in the starting material since opening of the D_4 rings can result in polymerization. A similar bonding mechanism is likely for the polysiloxane degradation techniques.

Scanning electron microscopy has shown the presence of thin polysiloxane resin films after treatment of glass with trifluoropropyl cyclic siloxanes [151] and after treatment of fused silica with D_4 [152]. This suggests that the success in deactivation with cyclic siloxanes may be due to the formation of a polymeric resin instead of simply the silylation of surface hydroxyl groups.

Difficulty has been experienced in the deactivation of small diameter (less than 0.10 mm ID) fused silica columns for capillary gas and supercritical fluid chromatography. Although the deactivation of narrow bore columns is chemically the same as for larger bore columns, problems can arise due to the blocking of the column during chemical treatment. Schutjes [159] has performed the most extensive study on deactivation of small bore glass and fused silica capillaries. Successful deactivations were obtained using dilute solutions of disilazanes in a volatile solvent. Later work has indicated no difference between the neat disilazane and solutions of the disilazane in the deactiva-

tion of narrow diameter columns [160]. However, the use of neat D_4 was reported to easily plug 50 um ID columns. Hexamethyldisiloxane was found to be a suitable substitute. PSD treatments with nonpolar polysiloxanes were also successful.

The various silylating reagents discussed so far yield different reaction products: chlorosilanes produce HCl; disilazanes produce NH_3; and cyclics yield H_2O as products. It has been suggested that HCl reacts with siloxane bridges on the silica surface to form additional silanol groups. The amount of silanols formed in this way will be more for composite glass columns containing metal oxides than for fused silica. Similarly, water formed can attack the silica surface but contributions to surface silanol coverage should be small.

The generation of water from the cyclic deactivation procedure probably catalyzes the ring opening of the cyclics and facilitates surface coverage. Ammonia, on the other hand, is quite likely to react with the surface of both glass and fused silica by nucleophilic attack on the silica structure generating more reactive surface silanols.

The bonded silyl groups formed are extremely stable and can be heated to 500°C in vacuum or 400°C in air without decomposition [153]. Silylated surfaces produced on treat-

ment with HMDS were shown to be stable to at least 400°C in the presence of water vapor [154].

Recently, deactivation of fused silica capillaries was reported using polyorganohydrosiloxanes. Polymethylhydrosiloxanes were first investigated [155] as potential deactivation procedures that could be carried out at temperatures lower than 400°C. It was found that good deactivations were obtained with temperatures between 250° and 350°C with no advantage seen in using the higher temperature. Both polymeric organohydrosiloxanes and simple organosilicon hydrides were synthesized and used for deactivation [156]. The polymeric hydrosiloxanes contained either 50% phenyl or 50% cyanopropyl and 25% methyl, 25% hydride substitution. Simple hydrosilanes included benzyl dimethylsilane, diphenyl methylsilane, and 1,1,1-triphenyldimethyldisiloxane. Conclusions were that all reagents were good but the polymeric materials yielded somewhat higher total deactivation than the simple hydrosilanes. The proposed reaction of a hydrosilane with a surface silanol is shown in Figure 11.

The degree of surface coverage by silylation is related to the number of silanol groups on the surface. Experiments by Aue et al. [157] showed that larger amounts of silane could be bonded to a solid support which had been previously hydroxylated by acid treatment. A similar conclusion was

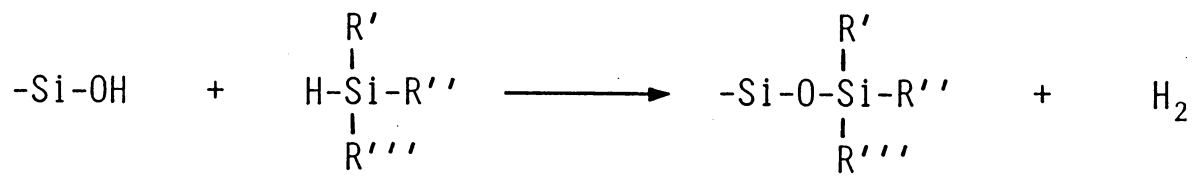


Figure 11: Reaction of hydrosilane with surface silanol.

reached in the preparation of capillary columns [158]. The degree of deactivation and thermostability obtainable by silylation was increased by a maximum density of silanol groups in experiments by Grob [112].

Several other techniques have been reported for deactivation of fused silica. Pretorius et al. have reported two methods: one involving the formation of a thin layer of pyrocarbon [161] and the other involving deposition of a thin film of elemental silicon on the inner surfaces [162].

Pyrocarbon is an allotropic form of carbon that is inert and possesses a moderately high surface energy that makes it wettable by low and intermediate polarity phases. The pyrocarbon layer is formed by filling the column with propane and heating to 1200°C. Thick walled fused silica tubing without the outer polymer sheath was used. The only possibility for applying this treatment to standard thin wall fused silica would be before the polyimide coating is added to the tubing; possibly during the drawing process.

The elemental silicon layers formed were deposited as very thin films which result in smooth surfaces of high surface energy. These films were produced by the static pyrolysis of monosilane at temperatures between 250° and 500°C. The polyimide coating of fused silica can withstand temperatures up to 450°C for short periods of time in an inert

atmosphere. However, elemental silicon is susceptible to oxidation even at room temperature [163] with traces of water substantially increasing the rate of oxidation to silicon oxide and silicon dioxide [164]. As a result, this technique is more attractive for deactivation of composite glass surfaces than for fused silica. Methods of deactivating the silicon layer have been investigated with silylation being the method of choice [165]. Recent work [166] indicates this procedure is also well suited for deactivation of thin walled nickel capillary columns which were fabricated by electroforming [167].

A cold silanization method has been described for the preparation of medium polarity glass and fused silica capillaries [168]. Silane coupling agents used included methacryloxypropylsilane, triethoxyvinylsilane, glycidoxypropyltrimethoxysilane and the methacrylate of aminoethylaminopropyl(trimethoxy)silane which possess the ability to bond organic polymers to inorganic materials. Claims of excellent deactivation, wettability, and column lifetime were made for treatment with glycidoxypropylmethoxysilane although chromatograms shown cast considerable doubt on the success of deactivation.

Column Coating

Introduction

The main objective in the coating of capillary columns with stationary phase is to deposit the phase in a film of uniform thickness on the wall throughout the entire length of the column. Normally the thickness of the stationary phase film is in the range of 0.1 to 1.0 um although film thicknesses of 5 um and 8 um are not uncommon. The emphasis here is on the uniformity of the coating which is necessary to provide the highest possible separation efficiency. In general, column coating is accomplished by either a dynamic or static procedure. There are several variations of each type and the important ones are discussed in the following section.

Dynamic Procedures

The dynamic coating method was first described in 1958 by Dijkstra and de Goey [170]. In general, this procedure consists of filling 2-15 coils of the column with stationary phase solution and forcing this plug of solution through the column with gas pressure at a slow velocity of approximately 1-2 cm/sec. The result is a thin film of the phase solution being left behind on the column wall. After the plug of liquid is expelled, the gas flow is continued to evaporate the solvent leaving only the stationary phase on the wall.

Such a dynamic procedure most often results in a non-uniform coating due to several factors. As the stationary phase solution travels through the column, the pressure drop of the column decreases (i.e.: the resistance to flow decreases). As a result, the velocity of the coating plug increases resulting in non-uniform film thickness. A buffer column is most often attached to the exit end of the capillary to minimize this effect. A related problem is that during the coating process, some of the coating solution is constantly being consumed (left behind on the wall) which also results in a faster plug velocity and an increasing film thickness.

Depending on the orientation of the column during coating, the deposited liquid may drain from the wall, collecting in the lower portions of the coils [171]. Orientation of the column in a horizontal position helps to minimize the effects of this problem.

After coating, the solvent evaporation under gas flow causes some of the stationary phase to be pushed in the direction of flow; again resulting in thickness non-uniformities [172]. The influence of the drying speed on the quality of dynamically coated columns was investigated [180] with fast drying speeds found to improve efficiency and increase film thickness.

Two additional factors, temperature fluctuations and poor wettability of the column wall, can result in droplet formation and non-uniform stationary phase films but are factors which influence all coating procedures and are not restricted to dynamic coating.

The most significant improvement in the dynamic coating procedure was the introduction of the "mercury plug" technique by Schomburg et al. [34,173]. This technique utilizes a plug of mercury added to the column after the plug of stationary phase solution. Because of mercury's high surface tension, it wipes most of the deposited coating solution from the column wall as it moves through the column. As a result, more concentrated solutions of phase must be used which has an additional advantage in that the deposited films have a greater tendency to resist drainage during the drying step.

Parameters affecting the quality of glass capillary columns prepared using the mercury plug technique have been investigated [181]. It was found that there is an optimum range of coating solution viscosity and velocity within which maximum column efficiency could be obtained.

Various predictions of the film thickness in dynamically coated capillary columns have been made using several mathematical relationships. Novotny et al. [141,174] found

that the film thickness (d_f) is directly proportional to the column radius (r) and the square root of the velocity of the coating plug (u), so that:

$$d_f = \frac{rc}{200}(un/\gamma)^{1/2} \qquad (1)$$

where c, n, and γ are the concentration, viscosity, and surface tension of the coating solution, respectively. This equation is in agreement with the Fairbrother-Stubbs equation [175]. Guiochon [176] suggested the equation:

$$d_f = \frac{1.34rc}{100}(un/\gamma)^{2/3} \qquad (2)$$

would be more applicable to capillary column coating.

Bartle [177] used experimental results to compare these two equations and found that equation (1) was the most adequate except in the case of thin films of low solution viscosities, in which case equation (2) was better suited. Alexander and Lipsky [178] verified the validity of these equations for the mercury plug method.

Several techniques have been proposed for determining the average film thickness in dynamically coated capillary columns. The value of d_f can be calculated from coating

solution volume differences before and after coating [11,179] or from the weight of stationary phase that can be rinsed from the column [64]. Another technique has been described [179] that entails monitoring the shortening of the coating plug over a given column length. Film thickness can then be calculated knowing the concentration of the solution, the volume of solution consumed and the internal column diameter.

Static Procedures

Golay [6] is credited with developing the static coating procedure in the late 1950's. However, for the next 10 years or so, the dynamic technique was almost exclusively used until a comparison of the two techniques was published by Bouche and Verzele [182]. In this study, it was shown that coating efficiencies were higher for static coating than for dynamic coating. The general static coating procedure involves filling the column with a dilute stationary phase solution in a volatile solvent, sealing one end of the column, connecting the other end to vacuum and evaporating the solvent under reduced pressure. The most significant advantages of this type of procedure are that the film thickness is uniform and can be accurately calculated from the equation:

$$d_f = \frac{r}{2\beta} \qquad (3)$$

where r is the column radius and β is the phase ratio (ratio of open volume to liquid phase volume) of the column. For accurate determination of the phase ratio from a weighed amount of stationary phase, the liquid phase density must be known. A tabulation of several liquid phase densities has been published [183]. Since most of the stationary phases useful for preparing capillary columns have densities very close to 1, an entirely adequate approximation for the film thickness is:

$$d_f = 1/2rc \qquad (4)$$

where d_f is the film thickness in micrometers, r is the column radius is millimeters, and c is the concentration of the stationary phase solution in parts per thousand (wt./vol.).

Various static coating procedures have been discussed in detail [182-186]. The most important considerations are that the coating solution be free of particulate matter and that no air or vapor bubbles exist in the column after it is filled, especially at the end closure. Earlier procedures recommended filling the column by suction. Grob [187] advocated the use of pressure to fill the capillaries with the

primary advantage being the reduced time necessary to fill the column and the elimination of gas bubble formation in the liquid during the filling process. When reduced diameter columns are being coated, high pressure has to be used to fill the columns with the coating solution. Several devices have been designed to accommodate high pressure filling of columns [159,188,189].

As with all coating procedures, the column should be thermostated during the solvent evaporation step so as to minimize uneven coating due to the deposition of the phase in the form of bands. A water bath at room temperature is usually sufficient except when coating long columns or columns of small internal diameter. In such cases it is desirable to have a thermostated water bath at higher temperatures to reduce the solvent evaporation time. The best arrangement to maintain constant above ambient temperatures is to use a double water bath, with the outer bath temperature controlled by a thermostat and the columns isolated from this area in an inner bath [179,185].

The static coating of small diameter columns at elevated temperatures has been described [189]. Columns evacuated isothermally at temperatures ranging from 23° to 80°C showed no differences in efficiency while coating times were reduced by 75% on going from 23° to 80°C. Other work by the

same authors used mixed coating solvents to shorten the evacuation time in the coating procedure [190].

With the goal of shortening evacuation time for coating small diameter columns or for standard diameters with thick films, liquid butane was recently reported as a coating solvent [191]. Comparisons were made between columns coated with butane and pentane solvents with no differences noted in column performance. Evacuation times were reduced by as much as 88% below that needed for pentane.

The static procedure is considered to be the most reliable coating technique and has remained essentially unchanged in the last 25 years. Its major disadvantage is that it is relatively time-consuming; not only for small diameter columns as previously mentioned, but also for standard dimension columns. As an example, short, 10 meter columns (0.25 mm ID) require about 5 hours to evaporate methylene chloride and about 3 hours to evaporate pentane, even when thermostated at 30°C. In addition to the aforementioned techniques for shortening coating times, a new procedure has been developed from theoretical evaluation of the coating process [192-194]. This technique is called "free release static coating".

Static coating procedures generally require the evacuation of solvent at reduced pressures. The free release

method accomplishes solvent evaporation with the column exit at atmospheric pressure (no vacuum applied) and elevated temperature [192] and also even at lower temperatures [194]. The technique entails drawing one end of the column to a hair-like fibre; filling the column with coating solution; sealing the exit end with a flame (bubble formation not critical); attaching a so-called "damping column" to the open end of the capillary; and placing the column into a thermostated bath (up to 90°C) with only the hair-like sealed end protruding into the room air. As a result, coating speed is increased dramatically. Columns 10 meters in length were coated in less than 1 hour. One apparent disadvantage of the technique is that the speed of evaporation is critically dependent on the solvent composition. This technique presents an interesting area for further research.

The characteristics desired for the coating solvent in any static coating procedure limit the number of good choices. The solvent should be volatile (to minimize the time needed for coating), should produce stable solutions, and should dissolve the phase in all proportions (so the phase does not precipitate as its concentration increases during solvent evaporation). The most popular solvents for static coating are methylene chloride and pentane. Methylene chloride has excellent solvating properties and high

volatility and is suitable for use with a large number of stationary phases with a range of polarities. Pentane is recommended for coating the more nonpolar phases because solvent evaporation can be accomplished in about half the time needed for methylene chloride [184].

Grob [249] recommended using only freshly prepared solutions of stationary phase since columns coated with stored solutions occasionally showed excessive activity. It was originally thought that possibly some HCl release from methylene chloride was responsible for partial degradation of the liquid phase. This was partly the reason for their switching to pentane. However, the same behavior was noted with pentane solutions. Ten years earlier, Bouche and Verzele [182] had reported difficulty with chloroform solutions that had been stored for several days. Similarly, it has been recently reported [195] that a stationary phase underwent further polymerization when stored (in absence of solvent) in soft glass bottles. The use of Teflon or acid-washed Pyrex bottles was recommended for phase storage.

End Sealing

Sealing one end of a capillary column for static coating is a theoretically simple yet experimentally demanding procedure. The necessary attributes of an end seal are that

it can be formed with no vapor bubbles between it and the liquid plug in the column, and it can withstand the vacuum applied for the duration of the solvent evaporation step (typically 3-12 hours). In addition to these requirements, there are several other characteristics that are highly desirable. These include a minimum amount of manipulation required, rapid sealing of the closure technique, and the ability for one sealing technique to be used for all solvents, stationary phases, column materials, and column internal diameters.

The literature reveals a large number of descriptions of "rapid" and "simple" sealing techniques with some decidedly more "rapid" and "simple" than others. Early workers used a plug of water glass (sodium silicate solution) to seal columns [182-184]. Other procedures include cements [196], adhesives [185,197,198], household glue [199], silica gums [64], methacrylate glue polymerized by a spray reagent [200], paraffin wax [201-203], and the mechanical attachment either of plugs [198,204,205] or of tubing which can be clamped [206,207]. The article by Grob [207] also contains a review of mechanical closure techniques.

Stationary Phases

Introduction

Numerous stationary phases have been used for packed column GC, however, only a small proportion have been used successfully with capillary columns. Stationary phases developed especially for capillary chromatography are now being produced which have higher viscosities and greater purities; properties which are required for producing efficient, inert, and thermally stable capillary columns. A list of commercially available phases most commonly used for capillary column preparation is given in Table 5. As is evident, polysiloxanes account for the majority of phases with polyethylene glycols making up the largest minority. Several reviews which have appeared recently include stationary phases used in capillary GC [208], capillary column technology [151], and a comprehensive review of polysiloxanes used in GC [209].

Stationary Phase Stability

For capillary columns to remain efficient throughout their useful operating temperature range, it is necessary that the stationary phase remain stable as a thin, homogeneously deposited film. Although highly stable columns can be readily prepared with nonpolar stationary phases, the pro-

Table 5. Commercially available stationary phases commonly used for capillary GC.

Name	Chemical nature	Temperature range (°C)	Polarity
Squalane	C_{30} alkane	-50-100	0
SF-96, OV-101	Methylsilicone oil	0-200,0-260	205, 229
SE-30, OV-1	Methylsilicone gum	20-350	217, 222
SE-52, OV-73	5% phenyl, methyl silicone gum (OV-73 is 5.5% phenyl)	20-350	334, 401
SE-54	1% vinyl, 5% phenyl methyl silicone gum	20-350	337
OV-1701	7% phenyl, 7% cyanopropyl methyl silicone gum	20-325	789
OV-17	50% phenyl methyl silicone oil	20-250	884
OV-17 (gum)	1% vinyl, 50% phenyl methyl silicone gum	20-300	---
OV-215	50% trifluoropropyl, 1% vinyl, methyl silicone gum	20-275	1545
OV-225	25% cyanopropyl, 25% phenyl, methyl silicone	50-250	1813
Superox 4	Polyethylene glycol gum	50-300	2238
Superox 0.1	Polyethylene glycol gum	50-280	2301
Carbowax 20M	Polyethylene glycol gum	60-250	2308
Superox 20M	Polyethylene glycol gum	50-300	2309
Silar 5CP	50% cyanopropyl, 50% phenyl, silicone oil	50-275	2428
Silar 10CP	100% cyanopropyl silicone oil	50-275	3682

cess is not so simple when using the more polar phases. More difficulty arose with the use of fused silica as substrate since many phases of moderate to fairly high polarity showed lower efficiencies and lower stabilities when coated on the fused silica than on glass surfaces. It was originally assumed that this difficulty arose due to lower surface energy of the fused silica which was insufficient for the efficient spreading of the more polar phases. However, wettability studies comparing glass and fused silica [210] have shown that clean, freshly drawn, untreated glass, fused silica, and quartz all have high critical surface tensions greater than 50 dynes/cm which is higher than the surface tension of one of the most polar stationary phases known, 1,2,3-tris(cyanoethoxy)propane (surface tension = 49 dynes/cm at 25°C). The ability to efficiently coat more of the polar phases on glass than on fused silica is due to the relative ease in roughening the glass surface, increasing both its wettability and film stability for a wider range of phase polarities and viscosities. As discussed earlier, roughening of fused silica is not generally successful and other solutions to this problem are necessary.

A very important factor in the stability of stationary phases coated on any capillary column is the viscosity of the deposited film. Nonchromatographic studies have shown

that the tendency for film disruption is inversely proportional to the film viscosity [211,212] which agrees with the long-standing observation that viscous gum phases coat more efficiently and have higher temperature stabilities than less viscous phases. A recent chromatographic study [213] has also concluded that capillary coating efficiencies and stabilities correlate with the viscosities of the stationary phases.

The nonpolar (methyl) polysiloxane phases show little viscosity dependence on temperature. However, the more polar polysiloxanes show a rapid decrease in viscosity at elevated temperatures [214] which results in lower film stabilities. The temperature-viscosity relationship of methyl and methylphenyl polysiloxanes and mineral oil is illustrated in Figure 12.

The low temperature dependence of the viscosity of methyl polysiloxanes has been related to the chemical structure of the polysiloxane molecule [215]. The molecule is believed to possess a helical conformation (in the absence of solvents) over a wide range of molecular weight. Increasing the temperature has two counterbalancing effects on the siloxane chain. The addition of thermal energy will tend to cause an increase in the mean intermolecular distance while at the same time, the helices will tend to

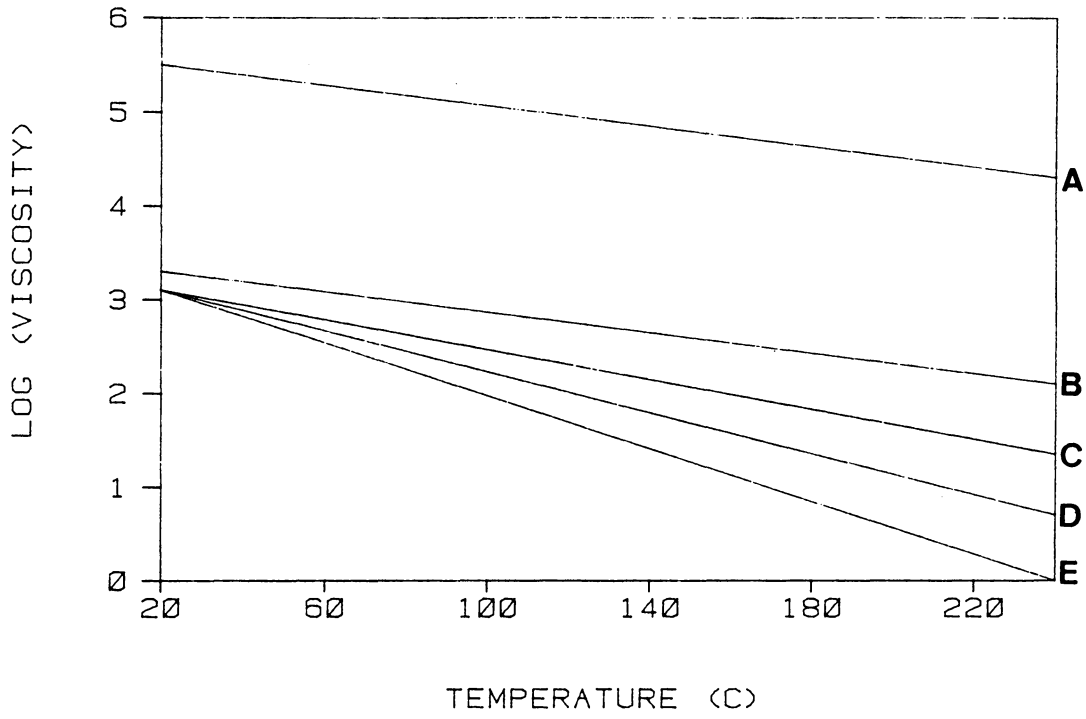


Figure 12: Temperature/viscosity relationship of several polysiloxanes and mineral oil: (A) high viscosity methylpolysiloxane similar to OV-1, (B) medium viscosity methylpolysiloxane similar to OV-101, (C) medium viscosity, low phenyl content methylphenylpolysiloxane, (D) medium viscosity, high phenyl content methylphenylpolysiloxane similar to OV-17, and (E) medium viscosity mineral oil. (From ref. 214)

expand, reducing the intermolecular distance. It is this expansion of helices opposing the increase of intermolecular distance which is proposed to keep the net intermolecular distance, and thus the viscosity, fairly constant with changes in temperature [213]. The presence of bulky substituents in the more polar polysiloxanes (phenyl, cyanopropyl, etc.) distorts the regular helical expansion and bond distance. The net result is a greater viscosity dependence on temperature.

Stationary Phase Immobilization

There are essentially two ways to reduce this dependence of viscosity (and film stability) on temperature, but in many cases the two are related. One way is to synthesize high viscosity polysiloxane gums either by preparing higher molecular weight linear materials or by introducing a slight degree of cross-linking in the polymer chain. Further film stability can also be obtained by cross-linking the stationary phase inside the capillary column. Cross-linking greatly reduces the tendency for the phase to lose viscosity during temperature programming and it also produces a film that is more resistant to wash-out by solvents. The advantages of the enhanced film stability obtained from cross-linking (or immobilization) have been reviewed by Grob et al. [216] and Blomberg [151].

Chemically, there are two approaches to produce cross-linked siloxane stationary phases: the formation of either Si-O-Si bonds or Si-C-C-Si bonds. The second approach results in carbon-carbon bonds which are usually formed between methyl groups attached to silicon atoms.

Grob [217] was the first to attempt to produce a cross-linked coating in conjunction with bonding to the support (glass) surface. Nonextractable coatings were produced by the in situ polymerization of polyolefins with boron trifluoride. Surface bonding was achieved by treating the glass surface with thionyl chloride and reacting the Si-Cl produced with hydroxyl terminated polymers and organolithium groups. This work was discontinued because the coating was insufficiently thermostable which has since been attributed to the use of unleached glass surfaces [218].

In 1976, Madani and coworkers [219] addressed the issue of immobilization by a new approach. They prepared methyl and methylphenyl polysiloxane prepolymers, coated them on the capillary wall and polymerized them in situ using ammonia gas at elevated temperatures [220].

The in situ polymerization of hydroxyl terminated prepolymers can be accomplished by the use of silicon tetrachloride as was first introduced by Blomberg et al. [221] and modified since [222] for glass and later applied to fused silica by Lipsky and McMurray [223].

Application of any of these techniques leaves Si-O-Si crosslinks in the polymer backbone. Various problems have been associated with this approach even though thermal stability is excellent, owing to the strength and stability of the siloxane bonds formed. Some of the problems included increased column activity due to residual silanol or alkoxy groups left in the phase and lowered column efficiency due to the extremely high levels of crosslinking (10-50% depending on prepolymer chain length) which hinders gaseous diffusion.

The cross-linking of polysiloxanes to form insoluble rubbers by means of free radical initiation of Si-C-C-Si bond formation is well understood and has been used in the rubber industry for years [214,224]. However, this type of cross-linking was first used in conjunction with capillary column preparation relatively recently. The earliest reports of the use of peroxides to initiate cross-linking of polysiloxane stationary phases were by the Grobs [216,218,225], Sandra et al. [226], and Blomberg et al. [227]. Various peroxides have been used, including t-butyl peroxide (TBP), benzoyl peroxide (BP), 2,4-dichlorobenzoyl peroxide (DCBP), and dicumyl peroxide (DCP). Dicumyl peroxide is presently the most commonly used initiator for silicone immobilization in capillary columns since it is consid-

ered to yield decomposition products that will not influence the stability of the phase. BP is unsuitable since one of its major decomposition products is benzoic acid which catalyzes silicone degradation [151]. A similar problem is encountered with DCBP which decomposes to form 2,4 dichlorobenzoic acid. The decomposition products of BP and DCBP can be incorporated into the stationary phase to some extent which can change the phase polarity and column activity [228]. Similar difficulties can arise with any free radical initiator with more serious problems stemming from the initiators with the more polar functional groups. As a result, other sources for free radical generation have been studied. The mechanism for free radical cross-linking of polysiloxanes is shown in Figure 13.

Gamma radiation has been investigated for suitability as a cross-linking initiator by a number of workers. Early work showed encouraging results in terms of phase nonextractability and column inertness for glass columns [229] and various glasses, including fused silica [230]. Subsequent work by Hubball et al. [231-235] also looked encouraging and as a result, a series of fused silica capillary columns cross-linked by gamma irradiation from a ^{60}Co source became commercially available. However, it was found that gamma radiation was less effective in cross-linking the more

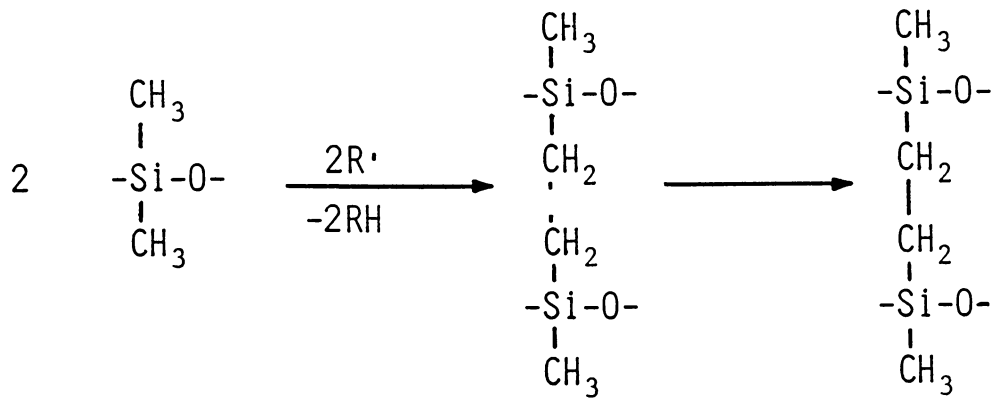


Figure 13: Mechanism for free radical cross-linking of polysiloxanes.

polar phases, that the polyimide outer coating of fused silica is deteriorated which leads to excess column brittleness [232], and the gamma radiation affects the activity and wettability of the inner fused silica surface [235]. As a result, radiation induced cross-linking is not as "clean" as it was first thought to be. This method of preparing immobilized phases is still attractive for labs having access to a radiation source, especially if working with glass capillaries. The successful immobilization of nonpolar polysiloxane phases (standard and thick films), intermediate polarity polysiloxanes, and the polar polyethylene glycol type phases has recently been reported using glass capillaries [236-238].

A second, and more viable alternative to the use of peroxides for free radical induced immobilization is the use of azo compounds. Several azo compounds were investigated and found to be adequate for stationary phase cross-linking. The most successful compounds were found to be azo-t-butane (ATB), azo-t-octane (ATO), and azo-t-dodecane (ATD) [239].

Other alternatives for in situ polysiloxane immobilization include heat-curing and curing initiated by ozone. Hydroxyl terminated polysiloxanes can be heat-cured forming Si-O-Si crosslinks by a mechanism that involves H_2O elimination. However, Blomberg [240] found it difficult to obtain

a defined termination of such a reaction. Bradshaw et al. [241] recently reported the spontaneous cross-linking of methyl-2-phenylethyl polysiloxane at 260°C in the absence of any initiator. A mechanism by which the 2-phenylethyl groups could facilitate cross-linking was not proposed.

Immobilization initiated by ozone is a well known method but is of limited industrial importance since the method is restricted to the curing of thin polymer sheets because of the slow diffusion of ozone in the polymer [151]. However, for stationary phase films, the technique is well suited. Excellent results have been reported for the curing of intermediate polarity polysiloxanes at 150°C [242,243].

The column coating and cross-linking procedures differ slightly depending on the nature of cross-linking initiator used. Peroxides and azo compounds that have a low vapor pressure at room temperature (DCP, BP, DCBP, ATO, ATD) can be doped directly into the stationary phase solution and the column coated in the normal way. However, for the initiators that have a high vapor pressure at room temperature (ATB and TBP) the columns are coated first and then saturated with the vapors of the initiator. In both cases, cross-linking is generally accomplished by sealing both column ends and heating the column to the curing temperature and holding for a specified period of time. Data which

indicate the reactivity of several free radical initiators are listed in Table 6 [228]. Decomposition temperatures listed are temperatures at which half the amount of initiator is decomposed after 15 minutes.

The initial efforts to stabilize some phenyl-containing polysiloxanes by free radical cross-linking met with limited success [216,218]. With a large proportion of methyl groups replaced by phenyl groups, the probability of two methyl radicals forming and combining is reduced. As a result, there is a need to incorporate functional groups into the polymer which cross-link more readily than methyl groups. Vinyl groups have typically been used since lower levels of initiators are needed to achieve similar cross-linking levels as compared to methyl groups alone [244]. Polysiloxanes containing 50% and 70% phenyl substitution and between 1% and 4% vinyl groups have been synthesized and cross-linked [245]. Vinyl groups have also been used by Blomberg and coworkers for immobilization of phenyl and cyanopropyl containing polysiloxanes [246,247].

As the polarity of the polysiloxane increases further, vinyl groups lose effectiveness for facilitating cross-linking. Tolyl groups have been incorporated instead of vinyl groups to enable immobilization of a 50% tolyl polysiloxane and various cyanopropyl polysiloxanes [246,247] and polysi-

Table 6. Reactivity data of various free radical generators.

Free radical generator	Activation energy (kcal/mole)	Decomposition temperature* (°C)
2,4-dichlorobenzoyl peroxide (DCBP)	28.1	87
dibenzoyl peroxide (BP)	29.9	109
di-t-butyl peroxide (TBP)	37.5	160
dicumyl peroxide (DCP)	38.0	142
azo-t-butane (ATB)	43.0	187

*temperature for $t_{1/2}$ = 15 min.

loxanes with up to 90% cyanopropyl substitution (10% tolyl) [248]. However, because of their high reactivity, tolyl groups are easily oxidized by peroxides during curing and the use of other free radical initiators is essential.

III. CAPILLARY GAS CHROMATOGRAPHIC METHODOLOGY

Performance Evaluation

Introduction

In general, the three most important criteria for evaluating capillary columns are the separation efficiency, inertness, and temperature stability of the column. There are numerous methods commonly employed for evaluating these criteria. In the following sections the various techniques for column performance evaluation will be discussed.

Separation Efficiency

The resolution or degree of separation between chromatographic peaks is related to two factors: the efficiency of the column and the selectivity of the stationary phase. Because of the limited efficiencies of packed gas chromatographic columns, a large number of selective stationary phases have been developed over the years to enable the separation of closely related molecules. However, because of the very high efficiencies obtainable with capillary columns, fewer selective phases are needed and resolution is usually increased by increasing column efficiency.

There are several approaches for evaluating the efficiency of a chromatographic column. These are usually some variation of the concept of theoretical plates. This concept is a carryover from distillation processes and since there are no discrete "plates" in a chromatographic column, it is an artificial concept. The definition of a theoretical plate is one equilibrium between the mobile phase and the stationary phase. As a result, the larger the number of "equilibrations" that exist, the greater the efficiency of the column. In reality, due to the dynamic nature of gas chromatography, this equilibrium is never established in any part of the column. The resulting non-equilibrium is the major cause of band spreading in the chromatographic process. The performance of capillary columns has been reviewed by several authors [11,19,250].

As stated previously, the most commonly used expressions for evaluating column efficiency utilize the theoretical plate concept. The number of theoretical plates (N) is given by the expression:

$$N = 16\left[\frac{t_r}{w_b}\right]^2 \qquad (1)$$

where t_r is the retention time of the component of interest and w_b is the peak width at the base. In most cases there

is some uncertainty in determining this width at the base and other expressions can be derived which utilize the peak width at other locations. The most often used expression for number of theoretical plates utilizes the peak width at one-half the peak height, resulting in:

$$N = 5.545\left[\frac{t_r}{w_{1/2h}}\right]^2 \qquad (2)$$

Since the retention time of the peak is directly proportional to the column length, the number of theoretical plates will also depend on column length. In order to express the column efficiency irrespective of column length, another term is often used; the height equivalent to one theoretical plate or HETP:

$$HETP = \frac{L}{N} \qquad (3)$$

where L is the column length.

The number of theoretical plates is dependent upon the capacity factor (k) of the peak where k is determined by the expression:

$$k = \frac{t'_r}{t_m} \qquad (4)$$

where t_m is the retention time of a non-retained solute (the gas holdup time) and t'_r is the adjusted retention time ($t'_r = t_r - t_m$). The earlier the elution of the peak (smaller k) the higher the number of theoretical plates [12]. With capillary columns, t_m (which is not related to the partitioning process) can be rather large which results in relatively large numbers of theoretical plates.

In an attempt to overcome this problem, several other expressions have been proposed to better express the true separation efficiency of the column. The most popular of these is the number of effective theoretical plates (N_{eff}) proposed by Purnell [251]:

$$N_{eff} = 16\left[\frac{t'_r}{w_b}\right]^2 = 5.545\left[\frac{t'_r}{w_{1/2h}}\right]^2 \qquad (5)$$

The effective plate number can also be obtained from the capacity factor and N from the expression:

$$N_{eff} = N\left[\frac{k}{k+1}\right]^2 \qquad (6)$$

As is obvious from this equation, the number of effective plates also depends on the capacity factor, as does N. When measuring efficiency of any column, a peak with capacity

factor greater than 2 should be used [252] since the higher the capacity factor, the smaller the influence on the measured separation efficiency. Also, the component used along with its capacity factor should be specified when reporting column efficiencies.

More recently, the number of theoretical plates at infinite capacity (N_{inf}) has been introduced [282]. The main advantage of this concept is that it is more independent of the capacity factor (k) than other expressions used.

Another widely used method for describing column efficiency is the comparison of measured plate numbers with theoretically predicted plate numbers. The coating efficiency (CE) has been defined as the ratio of theoretical plate height to experimental plate height under optimum conditions [11,182]:

$$CE = \left[\frac{H_{theor}}{H_{exp}} \right]_{min} \tag{7}$$

The theoretical plate height is usually obtained from the simplified Golay-Giddings equation [253]:

$$H_{theor} = r\left[\frac{11k^2 + 6k + 1}{3(k + 1)^2} \right]^{1/2} \tag{8}$$

where r is the column radius. A more general treatment of the coating efficiency which does not neglect the effects of resistance to mass transfer in the liquid phase (which is generally neglected for thin stationary phase films) and the pressure drop across the column has been discussed by Cramers et al. [254]. A more accurate determination of coating efficiency can be made if the diffusion coefficients of the solute in the mobile and stationary phases are known.

Another useful concept for describing chromatographic column efficiency is that of the separation value which has been described in detail by Ettre [225]. The separation value is an approximation for the number of peaks that will fit between the two peaks used for the calculation. The two components used for the measurement are generally members of a homologous series; alkanes and fatty acid methyl esters are the most common. Two terms for the separation value were simultaneously introduced: the effective peak number by Hurrell and Perry [256] and the Trennzahl, or separation number, by Kaiser [257]. The only difference between the two is the degree of resolution specified for the fitted peaks. The Trennzahl (TZ) is calculated from the equation:

$$TZ = \frac{t_{r2} - t_{r1}}{w_{1/2h2} - w_{1/2h1}} - 1 \qquad (9)$$

where the subscripts 1 and 2 refer to the elution order of the specified peak pair. Other approaches have been described more recently [258,259].

The problem with the separation number concept is that it is very dependent on the peak pair selected. The Grobs have reported [260] a preference for fatty acid methyl esters rather than alkanes as standards because of their more similar retentions and capacities on different stationary phases. It was also found [260] that there was no significant difference between TZ values obtained under isothermal or temperature programmed conditions.

Several authors [261-263] have criticized this method of column efficiency determination based on the finding that the magnitude of the separation number varied directly with partition ratios and inversely with column temperature. In response, Grob and Grob [264] argued that column resolution, which is a practical measure of separation efficiency, is also dependent on temperature and is directly related to the separation number (TZ) measurements. In spite of these criticisms, the separation number is, in general, no more dependent on chromatographic conditions than other methods of efficiency evaluation. The important consideration is that for the comparison of any two columns to be meaningful, the columns must be tested in exactly the same manner.

In addition to the chromatographic conditions discussed previously, there are additional parameters that affect column efficiency: the sample capacity and the choice of carrier gas and carrier gas velocity.

The anti-Langmuir type isotherm resulting from overloading the column with sample results in peak shapes that are classified as either "fronting" or "leading." Fronting peaks are characterized by a longer response time between the baseline and the peak maximum than from the apex back to the baseline. Such a peak shape results in reduced column efficiency. The maximum sample size has been defined by Keulemans [265] to be the amount injected into the column that results in no more than 10% reduction in column efficiency.

The influence of the carrier gas on column efficiency is related to the average linear gas velocity ($\bar{u}$) through the column, which can be calculated from the column length (L) and the gas holdup time:

$$\bar{u} = \frac{L}{t_m} \qquad (10)$$

The relationship between $\bar{u}$ and column efficiency was investigated in the 1950's by several workers; most notably, by van Deemter et al. [266] for packed columns and Golay

[267] for capillary columns. The resulting mathematical expression for capillary columns involved two complex terms which are related to various basic processes in the column during the passage of sample molecules. These terms summarize the effect of the longitudinal gaseous diffusion (B) and the so-called resistance to mass transfer related to the diffusion process in the gas (C_g) and liquid (C_ℓ) phases. The equation describing this complicated relationship is commonly called the Golay equation and in its simplified form is:

$$HETP = B/\bar{u} + (C_g + C_\ell)\bar{u} \qquad (11)$$

The Golay equation has been further refined by Giddings [253] but the simplified expression remains unchanged.

The relationship expressed by the Golay equation can be represented graphically by a hyperbola and is usually called a van Deemter curve. van Deemter curves representative of a capillary column operated with nitrogen, helium, and hydrogen carrier gases are shown in Figure 14. The gas velocity corresponding to the minimum of the curve (i.e.: where HETP is the smallest) is termed the optimum average carrier gas velocity ($\bar{u}_{opt}$). At velocities below the optimum, the B term in equation 11 is dominant and small changes in the gas

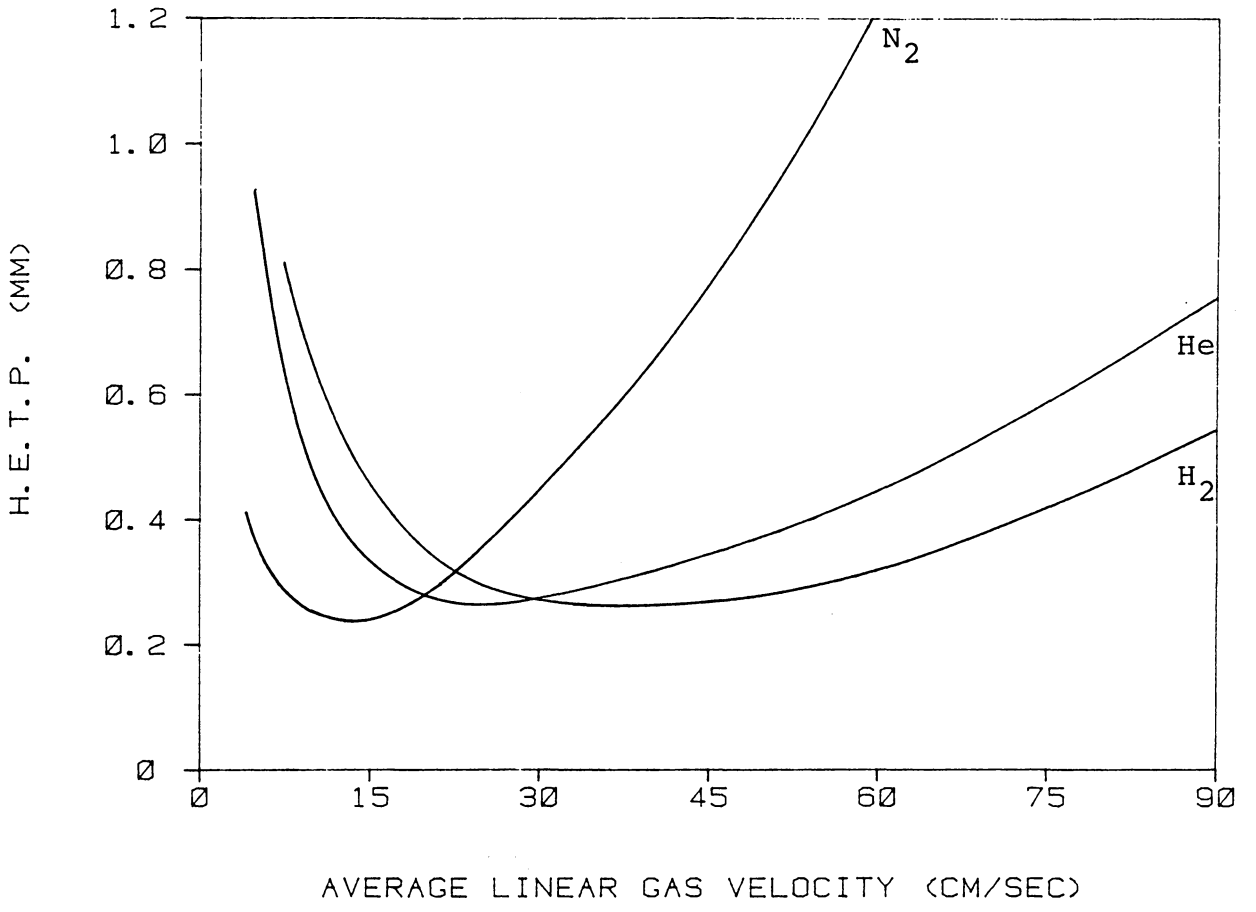


Figure 14: Effect of carrier gas on capillary column efficiency.

velocity result in substantial changes in column efficiency. On the other hand, at velocities above the optimum, the (C_g + C_ℓ) term is dominant and much smaller efficiency changes result from gas velocity changes.

The two most important characteristics of the van Deemter curve are the location of the optimum velocity and the slope of the ascending portion of the curve at higher gas velocities; both of which are very dependent on the choice of carrier gas. In general, for a given column, the optimum velocity will be higher with a low density carrier gas (e.g., hydrogen) than with a high density gas (e.g., nitrogen). On the other hand, the maximum column efficiency ($HETP_{min}$) will be slightly better with the high density carrier gas.

With regard to the slope of the ascending part of the van Deemter curve after $HETP_{min}$, the smaller the slope, the greater the gas velocity that can be used without greatly reducing the column efficiency. The highest possible velocity that can be used for a given separation is the most desirable since the retention time will be lowered according to the equation:

$$t_r = \frac{L}{\bar{u}} (k + 1) \qquad (12)$$

The ascending portion of the curve approaches linearity and can be approximated mathematically by the C term of equation 11:

$$HETP \approx (C_g + C_\ell)\bar{u} \qquad (13)$$

In other words, the slope of the van Deemter curve is equal to the $(C_g + C_\ell)$ term, i.e.: the sum of the resistance to mass transfer in the gas and liquid phases. Because of the relationship between density and diffusivity, this resistance is lower for the lower density gases as is the slope of the curve. What this means is that hydrogen can be operated at about 4 times the velocity of nitrogen with minimal reduction in column efficiency. Consequently, hydrogen is, in general, much preferred over nitrogen as carrier gas for capillary gas chromatography. In many instances (mostly due to safety regulations) helium is used as a compromise.

Inertness

The degree of column inertness is one of the most important criteria for assessing the quality of capillary gas chromatographic columns. The inertness of the column (especially fused silica) is usually directly related to the success of the deactivation treatment applied to the tubing. Proper deactivation, as mentioned previously, is essential

for assuring compatibility between the stationary phase and the column wall. This compatibility is required to keep the liquid phase distributed as a thin film within the column. As a result, the degree of deactivation influences the inertness as well as the efficiency and thermal stability of the coated column.

In evaluating column inertness, several potential column influences must be considered; including both reversible and irreversible adsorption and the catalytic degradation of the analyte. Reversible adsorption is the simplest process to detect as it results in non-Gaussian chromatographic peaks which tail. The process of irreversible adsorption often results in symmetrical peaks but of reduced height or area and can be a very difficult process to identify. In severe instances the entire sample band may be completely adsorbed. Catalytic degradation also occurs and is most often evidenced by skewed peaks of reduced response and, in many cases, the appearance of additional peaks due to degradation products. A variety of test procedures have been described to evaluate the influence of these phenomena; some of the most successful of which are described below.

Methods for characterizing the extent of reversible adsorption usually center on some measure of the shape or symmetry of a chromatographic peak. The simplest techniques

for doing this require the determination of either an asymmetry factor or a tailing factor. An asymmetry factor as defined by Goretti and Liberti [268] is:

$$A = \frac{a + b}{(a + b) - (a - b)} \qquad (14)$$

where a and b are the widths of the baseline segments formed by dropping a perpendicular through the peak maximum bisecting the baseline. The concept of a tailing factor was defined by McNair and Bonelli [269] as a percentage by the relationship:

$$TF = \frac{a}{b} \times 100 \qquad (15)$$

where a and b are the segments as above except as measured at 10% of the peak height above the baseline. More sophisticated computer assisted numerical methods for describing asymmetric peaks have been described in detail by Cooke [270].

Although a tailing peak is usually indicative of column adsorptive processes, a symmetrical peak does not necessarily indicate a lack of column adsorption. Grob et al. [260] have argued convincingly that peak shape alone is not suffi-

cient for detecting adsorption since adsorption can also cause a broadened Gaussian-shaped peak, a symmetrical peak of reduced area, or even a skewed peak of correct area but with increased retention. In accordance with this, it was proposed that a method for determining any of these causes of peak distortion would be the measurement of peak height as a percentage of that expected for complete and undistorted elution. Integration of peak areas is necessary to distinguish between reversible and irreversible adsorption. Such a test also lends a certain degree of quantitative information to column inertness testing.

A test mixture has been described by the Grobs [260,271] which utilizes this concept. This mixture and the detailed procedure reported [260,271] for its use have become widely accepted in column inertness testing. Some of the major reasons attributing to its widespread acceptance are:

1. The test consists of a single temperature programmed chromatographic run which saves considerable time that would be needed for optimizing separate isothermal runs.
2. The mixture contains all compounds necessary to judge the four basic aspects of column quality: adsorptive activity, acid/base characterization, separation efficiency, and film thickness.

3. Essentially the same mixture can be used regardless of the polarity of the stationary phase.
4. The chromatographic conditions are standardized so as to make results comparable, not only for columns of different dimensions and phase polarity, but more importantly, for columns produced in different laboratories.

The test components included in the mixture are listed in Table 7. The various constituents are each chosen to provide a certain type of information. The hydrocarbons are included to test the integrity of the chromatographic instrumentation (leaks, poor injection, etc.) and to serve as reference compounds. The purpose of the aldehyde is to detect specific aldehyde adsorption other than by hydrogen bonding. Alcohols are usually more sensitive to adsorption by hydrogen bonding interactions (surface silanols and siloxane bridges) than most other functional groups. 1-octanol is used because it is well retained resulting in good sensitivity to adsorption and the diol is included as a more rigorous test because of the dihydroxyl functionality. The dimethylaniline and dimethylphenol are present to enable acid/base surface characterization of the column; the ethylhexanoic acid and dicyclohexylamine serve the same purpose in a more stringent way. The fatty acid methyl esters are

Table 7. Composition of the comprehensive test mixture according to Grob. Test mixture I contains all substances except (C_{12}) and is recommended for polar stationary phases. Test mixture II, in which (al) and (C_{11}) are replaced by (C_{12}), is recommended for nonpolar stationary phases.

Test substance	Concentration (ng/ul)
decane (C_{10})	47.8
undecane (C_{11})	48.3
dodecane (C_{12})	48.9
nonanal (al)	69.4
1-octanol (ol)	61.7
2,3-butanediol (D)	105.6
2,6-dimethylaniline (A)	56.9
2,6-dimethylphenol (P)	53.9
2-ethylhexanoic acid (S)	67.2
dicyclohexylamine (A_m)	56.7
methyl decanoate (E_{10})	67.2
methyl undecanoate (E_{11})	65.6
methyl dodecanoate (E_{12})	63.9

used to permit the calculation of the separation efficiency of the column in addition to monitoring the film thickness (or more importantly, a change in film thickness over time).

The procedure for interpreting the test chromatogram is illustrated in Figure 15. Quantitative information is obtained by drawing a smooth curve that just touches the tops of the alkane and methyl ester peaks. For a "perfect" column, all other peak heights would just reach this curve (called the "100% line"). The extent of a particular interaction is then assessed by the percent reduction in peak height for the given analyte. Separation efficiency is calculated from one or both pairs of fatty acid methyl ester homologs. The film thickness is monitored by observing the elution temperature of methyl dodecanoate under standard conditions of carrier gas flow velocity and temperature programming rate.

The apparent inertness of a capillary column is very dependent on the amount of analyte introduced into the column and the column temperature during analysis. The degree of interaction between analyte and active column sites is dependent on the number of active sites in the column. If high sample loads are used then the relative amount of adsorption will be diminished resulting in a false appraisal of column quality. In general, low nanogram levels of

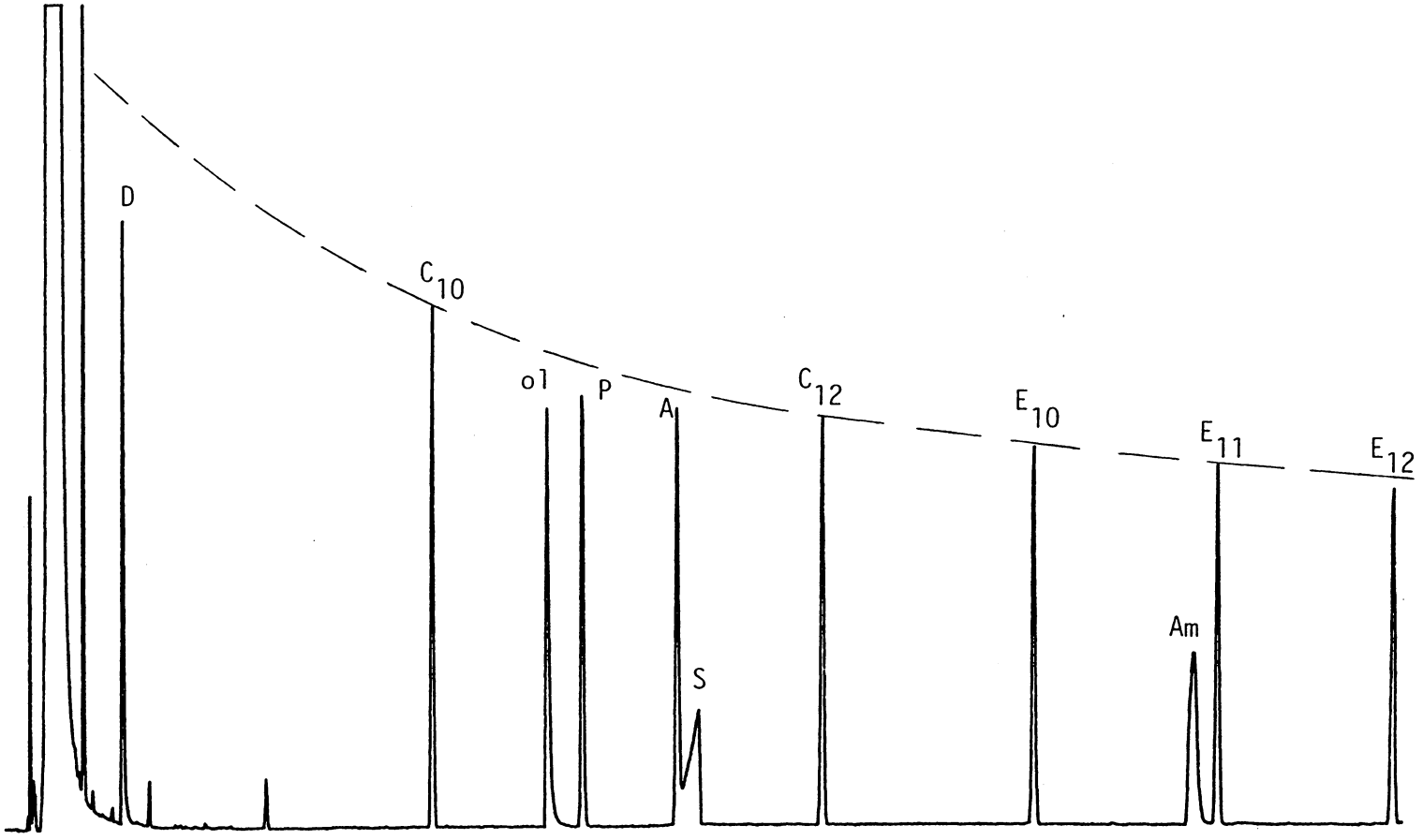


Figure 15: Test chromatogram obtained on column coated with dimethylsiloxane stationary phase illustrating the Grob comprehensive test mix II.

material should be chromatographed so as to enable the operation of the chromatograph at high sensitivity levels. Schomburg [272] has evaluated the dependence of irreversible adsorption on the amount of analyte injected.

The choice of column temperature is often overlooked in the testing of chromatographic columns. Tests at high isothermal temperatures should be avoided since compound retention is lowered resulting in less time for adsorptive influences to occur. Also, adsorption interactions are reduced at higher temperatures which results in minimized peak tailing. It has been demonstrated by Grob et al. [260] that an active column producing a skewed peak for 1-octanol at 50°C produced a much more symmetrical peak for the 1-octanol at 105°C. This indicates the necessity of operating either at low isothermal temperatures or temperature programming from low starting temperatures at slow programming rates to obtain a true evaluation of column inertness.

The catalytic activity of a column is an inertness defect that is often difficult to diagnose but can be confirmed rather easily. Such catalytic influences can be distinguished from those arising from adsorption by chromatographing several solutes of differing functionalities at different temperatures. A very simple experiment based on the direct dependence of catalytic losses and the inverse

dependence of adsorptive losses on temperature has been described by Grob [273]. The test solutes used include n-eicosane as a reference, the trimethyl silyl ether of octadecanoic acid which is sensitive to decomposition but not adsorption, and n-octadecanol-1 which is thermally stable but easily adsorbed. Several injections are made at various temperatures and the ratios of the peaks are monitored. As the column temperature is increased, the relative peak area for the alcohol will increase if adsorption is occurring and the relative peak area for the silyl ether will decrease if catalytic activity is present.

The initial testing of capillary tubing prior to coating with the stationary phase can be an invaluable aid in the preparation of capillary columns as it can often be difficult to determine which attributes of final column quality are traceable to the support surface and which others to the coating. Various procedures for testing uncoated capillaries have been described [133,274-277]. The intermediate surface testing procedure described by Schomburg [133] is one of the more informative. This method requires the use of a coated capillary which elutes various test probes with perfect symmetry to which the tubing to be tested (either coated or uncoated) is connected. The change in peak symmetry or relative response after passing through the test

capillary is then used as an indication of surface activity in the test piece.

Thermostability

The temperature stability of a coated capillary column is one of its most important characteristics since most columns are used with temperature programming. The stationary phase should remain deposited as a thin, homogeneous film on the inner wall and not physically rearrange to form droplets or chemically rearrange (decompose). In addition to this, the deactivation layer (if any) also needs to be stable to the same operating temperature as the liquid phase since a disruption of the deactivation layer will lead to phase film disruption.

The loss of stationary phase from the column that gives rise to an increased baseline is usually termed "column bleed." The amount of phase bleed formed in a given period of time depends on such factors as the type of stationary phase, column temperature, the nature and area of the support surface, and the stationary phase film thickness.

The deterioration of the stationary phase results from essentially two processes: one related to the composition of the stationary phase and the other due to catalytic effects of the surface. The first process, related to the

composition, includes dependence on molecular weight, viscosity, and purity of the phase. As the temperature of the column is increased, a point is reached where the liquid phase exhibits a significant vapor pressure and begins to migrate through the column. This effect is minimized by using stationary phases with high molecular weights, narrow molecular weight distributions, and the cross-linking of the phase in the column. Also, at elevated temperatures the polymeric chains can thermally rearrange, forming lower molecular weight segments. Such a process can be catalyzed by a variety of impurities found in the stationary phase; most notably, metal impurities or traces of residual polymerization catalyst.

The second process, that of surface catalytic effects, is related to the nature of the tube surface. Composite glass surfaces containing alkaline and acidic additives can lead to the degradation of the phase. Coleman [278] has shown that both alkaline and acidic surfaces lead to the decomposition of silicone oil stationary phases which is consistent with the observation by Schomburg et al. [279] that borosilicate glass columns exhibited better temperature stability than soda-lime glass columns due to the lower alkali content. A detailed study of bleed rate of a methyl polysiloxane on various types of pretreated borosilicate and

soft glass columns has also been reported by Schomburg et al. [91]. Grob et al. [218] also reported increased thermal stability of methyl polysiloxanes on leached glass surfaces. Studies by Venema and coworkers [280,281] have related the stability of various stationary phases to the presence of specific compounds either present in the glass or used for surface roughening. Barium carbonate, metal chlorides, and aluminum oxide were found to have the strongest detrimental effect on stability while sodium chloride and several other metal oxides showed little effect. For reasons related to purity, fused silica capillary columns are more thermostable than either type of composite glass (leached or not).

IV. FUSED SILICA SURFACE WETTABILITY AND DEACTIVATION

Introduction

The increasingly widespread acceptance of fused silica as the capillary column material of choice has been accompanied by greater demands being placed on the performance (i.e.: efficiency, inertness and reproducibility) of the analytical column. The overall quality of the column is a complex function of many variables including the activity of the raw fused silica tubing, the nature of any surface deactivation treatment applied, the choice of stationary phase and the quality of the coating, and the initiator used (if any) for cross-linking the stationary phase inside the column.

As discussed in earlier sections, the initial attainment of a smooth, homogeneous stationary phase film is dependent upon the ability of the phase to completely wet the inner surface of the capillary wall. The importance of this wettability was first suggested by Farre-Rius et al. [101] who used the concept of a Zisman plot [283] to determine the critical surface tensions of various tube materi-

als. Since that time several workers have used this approach to determine the degree of wetting of glass surfaces by stationary phases [142,284-288]. The capillary rise technique has been used for the characterization of actual capillaries made of glass [142,210] and fused silica [210,235].

Because of the relatively high surface energy of fused silica, most stationary phases will wet the surface, however, columns coated without deactivation of the surface most often show undesirable activity for sensitive analytes. Efforts to deactivate the surface while maintaining or enhancing surface wettability have been at the forefront of capillary column research for many years now.

Chemical modification of fused silica is presently the most satisfactory approach for both deactivating and modifying the wettability of the surface. Such modification usually occurs through the surface silanol groups by the formation of silyl ether groups. The success of such procedures requires an even distribution of these surface hydroxyls to allow the formation of a continuous deactivating layer. Because of the extremely high temperatures (1800°C-2200°C) necessary for drawing, the surface of the fused silica is nearly completely dehydroxylated [289].

In this chapter, results are presented of various attempts to reproducibly maximize the surface silanol concentration of fused silica. Treatments giving rise to maximal surface hydroxylation were used in conjunction with a wide variety of deactivation procedures. These surfaces were characterized by the use of the capillary rise method to obtain data for the construction of Zisman plots. Silylating reagents with substituents covering a wide range of polarity were used and compared in terms of the critical surface energy of treated tubing. Different classes of silylating reagents containing methyl substituents were used and compared as to the relative surface coverage obtained. Also, differing degrees of residual column activity was traced to the choice of cross-linking initiator used. Consistent with the high degree of surface coverage demonstrated with several reagents, highly efficient and inert capillary columns were prepared which produced chromatograms free from both reversible and irreversible adsorption of nanogram levels of alcohols, amines, and acids.

Theory of Wettability

The theory of wetting at the solid-liquid interface is discussed in detail by Shaw [290] and Adams [291] and summarized [210] elsewhere; only the salient features are presented here.

From the balancing of the three interfacial tensions that were shown in Figure 5 (Chapter 2), an equilibrium expression is obtained:

$$\gamma_{sg} = \gamma_{s\ell} + \gamma_{\ell g} \cos\theta \qquad (1)$$

where, again, γ_{sg} is the surface tension of the solid in equilibrium with the vapor of the wetting liquid; $\gamma_{\ell g}$ is the surface tension of the wetting liquid in equilibrium with its vapor; and $\gamma_{s\ell}$ is the surface tension of the solid in equilibrium with the wetting liquid.

Rearranging (1) gives the so-called Young's equation, (2):

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{s\ell}}{\gamma_{\ell g}} \qquad (2)$$

Young's equation holds only if the solid is partially wet by the liquid; it fails if the solid is completely wet ($\cos\theta = 1$) or if the solid is not wet at all ($\cos\theta < 0$). The cosine

of the contact angle (θ) can thus be used as a direct measure of the surface wettability.

The determination of θ (or $\cos\theta$) for liquids in contact with the inner surface of fused silica capillary tubing can be made accurately by the technique of capillary rise since fused silica is inherently straight.

A capillary tube of radius r is shown immersed in a liquid of density ρ in Figure 16. If the liquid at least partially wets the tube, the liquid rises. It continues to rise until the force due to the surface tension which is pulling the liquid upward is counterbalanced by the downward pull of the force of gravity. The height of rise of liquid in the capillary is represented by h and is measured from the surface of the liquid to the lowest point of the meniscus. Only the vertical component of the upward force is effective in causing the liquid to rise up the capillary so that the upward force is $2\pi r\gamma_\ell \cos\theta$. The downward force is given by $\pi r^2 h\rho g$ where g is the acceleration of gravity. As before, at equilibrium these forces must balance so that:

$$2\pi r\gamma_\ell \cos\theta = \pi r^2 h\rho g \qquad (3)$$

or

$$\cos\theta = \frac{h\rho gr}{2\gamma_\ell} \qquad (4)$$

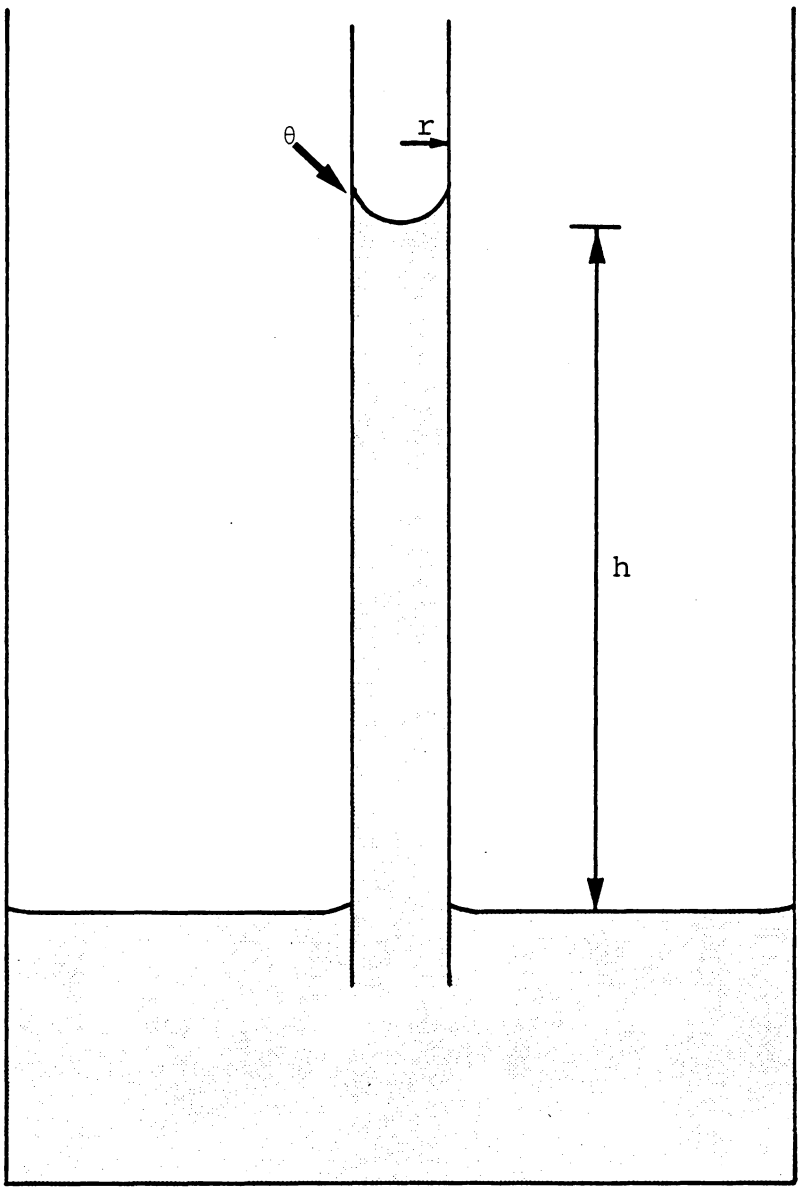


Figure 16: Diagram of capillary rise experiment showing fused silica capillary immersed in a reservoir of liquid.

The exact solution for capillary rise [291] includes a correction for the deviation of the meniscus from sphericity and would use the density difference ($\Delta\rho$) between the liquid and the surrounding vapor instead of simply the liquid density. Good discussions of experimental aspects of the capillary rise method have appeared in the literature [292,293].

A useful parameter for characterizing the wettability of solid surfaces is that of the critical surface tension (or critical surface energy), γ_c, as proposed by Zisman and coworkers [283,294]. Critical surface energies are obtained from plots (Zisman plots) of $\cos\theta$ vs. γ_ℓ for various liquids. In most cases, these plots are linear and can be extrapolated to zero θ ($\cos\theta = 1$). The γ_ℓ value corresponding to $\cos\theta = 1$ was proposed by Zisman to be characteristic of the particular solid and was designated the critical surface tension. The significance of the critical surface tension is that, in general, liquids with $\gamma_\ell \leq \gamma_c$ will completely wet the surface while liquids with $\gamma_\ell > \gamma_c$ will wet the surface incompletely. The concept of the critical surface energy is used to quantify the degree of wettability of fused silica both before and after a variety of chemical modifications.

If the solid surface under investigation is heterogeneous, i.e.: composed of two types of material, then the observed contact angle for the composite surface is given by:

$$\cos\theta_{obs} = \sigma_1\cos\theta_1 + \sigma_2\cos\theta_2 \qquad (5)$$

assuming the heterogeneities are effectively averaged and σ_1 and σ_2 are the fractional areas of each type of material with their respective contact angles (θ_1 and θ_2). The slopes of the Zisman plots can be used to determine the relative coverage of the two surface types if $\theta = 0$ for one of the surface structures and γ_c is the same for both the heterogeneous surface under study and a surface comprised of entirely type 1 structures, as has been described by Bartle et al. [210]. For this limiting case, if $\theta_2 = 0$ for the bare silica surface then the magnitude of $\cos\theta_{obs}$ will decrease as σ_1 increases. As a result, the relative degree of surface coverage of the type 1 groups on two surfaces can be assessed from the ratio of the slopes of the two Zisman plots by the relationship:

$$\sigma_1 = \frac{\cos\theta_{obs} - 1}{\cos\theta_1 - 1}$$

$$\sigma_1 = \frac{\text{slope of Zisman plot for heterogeneous surface}}{\text{slope of Zisman plot for type 1 surface}} \quad (6)$$

This type of approach is used to assess the relative surface coverage of fused silica by different classes of silylating reagents carrying the same functional groups; the more negative the slope, the higher the relative surface coverage.

Experimental

Materials and Reagents

Fused silica capillary tubing was obtained from Polymicro Technologies, Inc. (Phoenix, AZ, U.S.A.). All solvents were 'Baker Resi-Analyzed' grade and the hydrochloric and nitric acids were 'Baker Instra-Analyzed' grade from J.T. Baker Chemical Co. (Phillipsburg, NJ, U.S.A.).

Deactivating reagents used were: trimethylchlorosilane (TMCS), hexamethyldisiloxane, octamethylcyclotetrasiloxane (D_4), octamethylcyclotetrasilazane, tetravinyltetramethylcyclotetrasiloxane, (3,3,3-trifluoropropyl) methyl siloxanes (mixed cyclics, F_3/F_4), octaphenylcyclotetrasiloxane (Ph_4), and tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane from Petrarch Systems (Bristol, PA, U.S.A.); hexamethyldisilazane (HMDS) and hexamethylcyclotrisiloxane (D_3) from Ald-

rich Chemical Co. (Milwaukee, WI, U.S.A.); SF-96 (a dimethyl polysiloxane) and Carbowax 20M (a polyethylene glycol) from Foxboro/Analabs (North Haven, CT, U.S.A.); Superox 20M and Superox 4 (both polyethylene glycols) from Alltech/Applied Science (Deerfield, IL, U.S.A.); and diphenyltetramethyldisilazane (DPTMDS) from Fluka Chemical Corp. (Hauppauge, NY, U.S.A.).

The stationary phase, OV-73 (a 5% phenyl, methylpolysiloxane gum) and the capillary butt connector (Valco 1/32" zero dead volume union) were obtained from Chrompack, Inc. (Bridgewater, NJ, U.S.A.). The stationary phase, OV-1701 (a 7% cyanopropyl, 7% phenyl methylpolysiloxane) was purchased from American Scientific Products (Columbia, MD, U.S.A.).

Dicumyl peroxide from Pfaltz & Bauer, Inc. (Waterbury, CT, U.S.A.) and azo-tert-butane from Fairfield Chemical Co. (Blythewood, SC, U.S.A.) were used as cross-linking initiators.

The comprehensive test mixture II (according to Grob) was obtained from Fluka Chemical Corp. (Hauppauge, NY, U.S.A.).

Capillary Rise

The capillary rise method was used to measure the advancing contact angle of methanol/water mixtures on the various fused silica surfaces at a temperature of 25° ± 1°C. The surface tensions and liquid densities of the mixtures used are listed in Table 8. Approximately 15 ml of solution was placed in a 100 ml color comparison tube and supported on a ring stand. A thermometer was placed through one hole of a 3-hole #6 rubber stopper, a right-angle 1/4" open glass tube placed through another hole, and a 1/8" Swagelok union was threaded through the third hole and the entire assembly was fitted in the top of the comparison tube. Sections of fused silica were held in place in the 1/8" union with a 1/8" x 0.4 mm graphite reducing ferrule. Frontal illumination against a white background allowed easy location of the meniscus in the capillary. The level of the surface of the liquid in the color comparison tube and the height of rise of the meniscus in the fused silica capillary were each measured to ±0.01 cm with a cathetometer. After each measurement, the wetted portion of the capillary was removed so as to minimize hysteresis effects on the following measurement.

Table 8. Surface tensions (γ_ℓ) and densities (ρ) of the methanol/water mixtures used in the capillary rise experiments. [Source: CRC Handbook of Physics and Chemistry, 59th ed., CRC Press, Boca Raton (1979].

Composition ($MeOH/H_2O$)	γ_ℓ (dynes/cm)	ρ (g/ml)
100/0	22.1	0.792
90/10	24.9	0.820
75/25	28.3	0.859
70/30	29.7	0.872
60/40	32.6	0.894
50/50	34.9	0.916
25/75	45.8	0.962
20/80	51.6	0.967
10/90	58.5	0.982
0/100	72.0	1.000

Hydrothermal Treatment

Fused silica capillaries were flushed with 1 column volume of either water, 20% hydrochloric acid, or 20% nitric acid with nitrogen pressure and the column ends sealed in a flame. The capillaries were then placed in an oven and heated to various temperatures and held for 10 hours. After heat treatment, the water treated capillaries were rinsed with a column volume of water; the HCl treated capillaries were rinsed with a column volume of 1% HCl; and the HNO_3 treated capillaries were rinsed with a column volume of 1% HNO_3. All capillaries were then rinsed with a column volume of methanol and dehydrated at 225°C for 90 minutes under nitrogen flow.

Column Deactivation

To accomplish deactivation, a plug of the deactivating reagent was pushed through the column with nitrogen. Reagents which are liquids at room temperature were used neat with the column ends flame sealed immediately after expelling the reagents. Solid reagents were dissolved in either methylene chloride or pentane and dynamically coated with the column ends sealed after 30 minutes of drying under nitrogen flow at 25°C for pentane and 40°C for methylene chloride solutions. The tubing was then placed in an oven

and heated at 10°C/minute to various final temperatures and held for various lengths of time. Tubing to be heated above 350°C was wrapped in a protective jacket of aluminum foil and purged with nitrogen prior to heating. After cooling to room temperature, excess reagent was removed by rinsing the columns with methylene chloride and drying at 100°C with nitrogen flow. Individual conditions for each reagent are noted with the wettability results in Table 9.

Column Coating

Solutions for static coating the capillaries were always freshly prepared by dissolving OV-73 in pentane at a concentration of 0.004 g/ml (to produce a film thickness of 0.25 um in a 0.25 mm ID column). Columns were placed in a doubly insulated water bath thermostated at 30°C and filled with the coating solution by nitrogen pressure.

The exit ends of the capillaries were sealed with paraffin wax in the following way. After filling the column with coating solution, the inlet end was raised above the level of liquid in the reservoir and a small section of column (ca. 30 cm) was filled with nitrogen. As the last drop of solution was still forming on the column exit end, this end was submerged in a vial containing iso-octane and the inlet end removed from the pressurized vial. Next, the vial

containing the iso-octane was pressurized causing the column of liquid to reverse its previous direction and move about 10 cm. The nitrogen pressure on the vial of iso-octane was released and the iso-octane vial quickly replaced with a vial containing molten paraffin wax and repressurized. The total column of liquid would move another 5-10 cm before the wax would begin to harden and flow would stop. The vial of wax was removed and the original inlet end of the column (the end that now contains about a 10 cm air gap) was connected to the vacuum line. While observing the meniscus, the vacuum line was opened and the meniscus would begin to move smoothly towards the wax-sealed end. A rapid movement of the entire liquid plug in the direction of vacuum would indicate a failure of the seal or the presence of bubbles somewhere in the column and is termed "breakthrough". Although such a sealing procedure may sound complex, it can be accomplished in less than 2 minutes and the wax seal hardens immediately and is ready for evacuation. During the course of this study, no column breakthrough was ever observed when using this end-sealing technique.

Cross-linking

Stationary phase cross-linking was achieved by the use of either dicumyl peroxide (DCP) or azo-t-butane (ATB) as the free radical initiator. Because DCP is a solid, it is added to the stationary phase solution prior to coating the column. DCP was added to the coating solution from a 2% (wt/vol) solution in toluene to give 1% total by weight (wt DCP/wt OV-73). Dynamic curing of the phase was accomplished by mounting the columns in an oven with a low flow of carrier gas and programming the oven temperature from 40°C to 170°C at 5°C/min and holding at 170°C for 60 min. After curing, the columns were programmed to 300°C at 2°C/min and held 10 hours for conditioning. Columns were rinsed with 5 ml pentane followed by 5 ml methylene chloride followed by 5 ml methanol. Test chromatograms were run before and after solvent rinsing to determine the amount of phase washout by measuring the reduction in the capacity factor (k) of n-dodecane at 100°C. Phase washout was calculated from:

$$\frac{(k_1 - k_2)}{k_1} (100) = \% \text{ washout} \qquad (10)$$

where k_1 and k_2 are the capacity factors before and after rinsing, respectively.

Since ATB is a volatile liquid, it cannot be added to the coating solution prior to coating. As a result, the columns were first statically coated with phase and then the coated columns were saturated with ATB vapors by bubbling nitrogen through ATB in a vial and passing the ATB vapors through the column. Columns were purged with ATB vapors for 1 hour at room temperature, the ends sealed and the columns programmed to 220°C and held 1 hour. Column conditioning, rinsing and percent washout determination were the same as for DCP.

Column Evaluation

Column evaluations were performed on a Hewlett-Packard Model 5880A gas chromatograph with split injection and flame ionization detection. Chromatographic data was simultaneously processed with the 5880A GC Terminal and stored on floppy disks using a Perkin Elmer Model 3600 Data Station so as to allow replotting of chromatograms on a Hewlett-Packard Model 7225A Graphics Plotter.

The inertness of the final columns was tested with several mixtures including the comprehensive Grob test mix II, primary alkyl amines, and a mixture of alkaloid drugs containing methadone HCl, cocaine HCl, codeine, and morphine.

Results and Discussion

In utilizing the contact angle approach for characterizing fused silica surfaces, there are several characteristics that must be emphasized. First of all, the critical surface energy need not be independent of the probe liquids used and the data obtained from Zisman plots using different liquids should not be quantitatively compared. This is apparent from a comparison of surfaces 5 and 6 (Table 9). Data for surface 5 were obtained using a homologous series of alkanes while that for surface 6 resulted from the use of methanol/water mixtures. Since methanol/water mixtures cover a wider range of surface tension than the alkanes, they were used throughout.

Secondly, any data point for which $\cos\theta = 1$ cannot be used in the construction of the Zisman plot since γ_c must be obtained from extrapolation. Also, the extrapolation to γ_c should be kept short and in the linear region.

The advancing contact angles were used throughout in obtaining the data from capillary rise experiments. Because of potential problems with selective adsorption, the advancing angle is usually considered more reliable than the receding angle [76]. The time needed for the height of rise in the capillaries to equilibrate was dependent upon the composition of the probe liquid mixture: the higher the

Table 9. Summary of critical surface energy (C.S.E.) determinations for various deactivation reagents and conditions.

	DEACTIVANT	F.S. PRETREATMENT	TEMP(°C)/TIME(hr)	C.S.E. (dynes/cm)	SLOPE ($\times 10^{-3}$ cm/dyne)
1	none	none		28–48	
2	none	(a) water followed by methanol rinse		44	
3	none	(b) HNO_3/200°/10 hr		46	
4	D_4*	(a)	400°/1.5	23	-35
5	D_4*	(b)	400°/1.5	21	-37
6	D_4	(b)	400°/1.5	21	-68
7	D_3*	(a)	410°/2	23	-49
8	D_3	(b)	400°/1.5	21	-9
9	hexamethyldisiloxane	(b)	400°/1.5	21	-73
10	TMCS	(b)	400°/1.5	21	-53
11	TMCS	(a)	150°/0.5	25	-38
12	SF-96	(b)	400°/1.5	20	-73
13	HMDS	(b)	400°/1.5	20	-77
14	octamethylcyclotetrasilazane (2% in pentane)	(b)	400°/1.5	20	-80
15	tetravinyltetramethylcyclotetrasiloxane (10% in pentane)	(a)	390°/1.5	22	-54
16	F_3/F_4	(b)	400°/1.5	22	-54
17	DPTMDS	(a)	400°/10	25	-40
18	DPTMDS	(b)	400°/10	26	-58
19	Ph_4 (10% in $MeCl_2$)	(a)	400°/1.5	29	-49
20	tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane (2% in $MeCl_2$)	(b)	280°/16	32	-24
21	cyclic mixture**	(b)	400°/1.5	28	-46
22	polysiloxane***	(b)	400°/1.5	21	-65
23	Carbowax 20M (2% in $MeCl_2$)	(b)	280°/16	43	-8
24	Superox 20M (2% in $MeCl_2$)	(b)	280°/16	44	-16
25	Superox 4 (0.25% in $MeCl_2$)	(b)	280°/16	34	-14

*measured with homologous series of alkanes

**7% tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane, 7% Ph_4, 2% tetravinyltetramethylcyclotetrasiloxane, and 84% D_4—2% in $MeCl_2$

***7% cyanoethyl, 7% phenyl, 1% vinyl, 85% methyl polysiloxane—2% in pentane

water content (higher γ_ℓ) the longer the equilibration time. In most cases, solutions containing less than 50% water reached an equilibrium height within a minute or so. When using 100% water, equilibration times often exceeded 30 minutes. As a result, water was used only sparingly as a probe.

As mentioned previously, the exact solution for capillary rise takes into account a correction for the deviation of the meniscus from sphericity. For capillaries of 0.25 mm ID, this correction would have added only about 0.004 cm to the actual height measured and in all measurements here it was neglected. This factor, along with a small error encountered by not being able to locate the level of the surface of the liquid when sighting through the glass reservoir can be corrected for by applying calibration measurements on capillaries of identical diameters with liquids which completely wet the surface [210,235]. Values obtained directly from equation 4 differed by less than 0.01 in $\cos\theta$ from those obtained using calibration and thus calibration was deemed not necessary.

The linearity of all the Zisman plots reported in this study was quite good; correlation coefficients were 0.990 or better for all plots except for surface 8 which had a correlation of 0.98. Critical surface energies and the slopes of

the Zisman plots are given in Table 9. Actual data points used in the construction of the Zisman plots are listed in Appendix A.

As seen from the first entry, the critical surface energy of the raw fused silica is widely variable with values ranging from 28 to 48 dynes/cm. The majority of pieces tested were determined to have energies in the low to mid 40's. These values are lower than those found by Bartle et al. [210] who measured surface energies for some freshly drawn tubing to be greater than 72 dynes/cm. It is known [295] that clean glass is a high energy surface, but as a result of this high energy, the glass surface can easily be converted to a lower energy surface through adsorption and hydration [296,297]. Such processes can certainly occur during the handling and storage of the fused silica and are proposed as the probable cause for these discrepancies in wettability. The fused silica used in this study was not freshly drawn; in many cases it had been stored by the manufacturer over 6 months prior to being shipped and was stored after receipt for as long as 1 year before all of a particular lot was used. No attempt was made to correlate surface energy with shelf life since the exact storage conditions of the material were unknown. Although the manufacturer claims that all tubing was purged with nitrogen immediately after

drawing and stored with sealed ends, several rolls of material were received over the course of this work which had one or both ends open.

The cause of variation in surface energy can also manifest itself in the degree of chromatographic activity of coated columns. Figure 17 shows a comparison of three 10 meter columns made from fused silica cut from the same roll of stock. Columns A and B were coated with no pretreatment and not cross-linked while column C was subjected to intense hydrothermal treatment (HNO_3/200°C/10 hr) followed by deactivation with D_4 prior to coating and cross-linked with ATB. All chromatograms were obtained isothermally at 200°C with H_2 carrier gas at 50 cm/sec (measured at 200°C). The injector temperature was 200°C; the detector temperature was 325°C; and 1 ul was injected with a split ratio of 20:1. Note the wide variation in peak symmetries, areas, and number of peaks. The alkaloid drugs are compounds which are very difficult to chromatograph (especially at the nanogram level) due to their very polar and basic nature.

Such inconsistencies in the surface energy and chromatographic performance of untreated fused silica indicate the need for a pretreatment of the fused silica to enable reproducible column performance and inertness. Simply rinsing the fused silica was effective in reducing the wide varia-

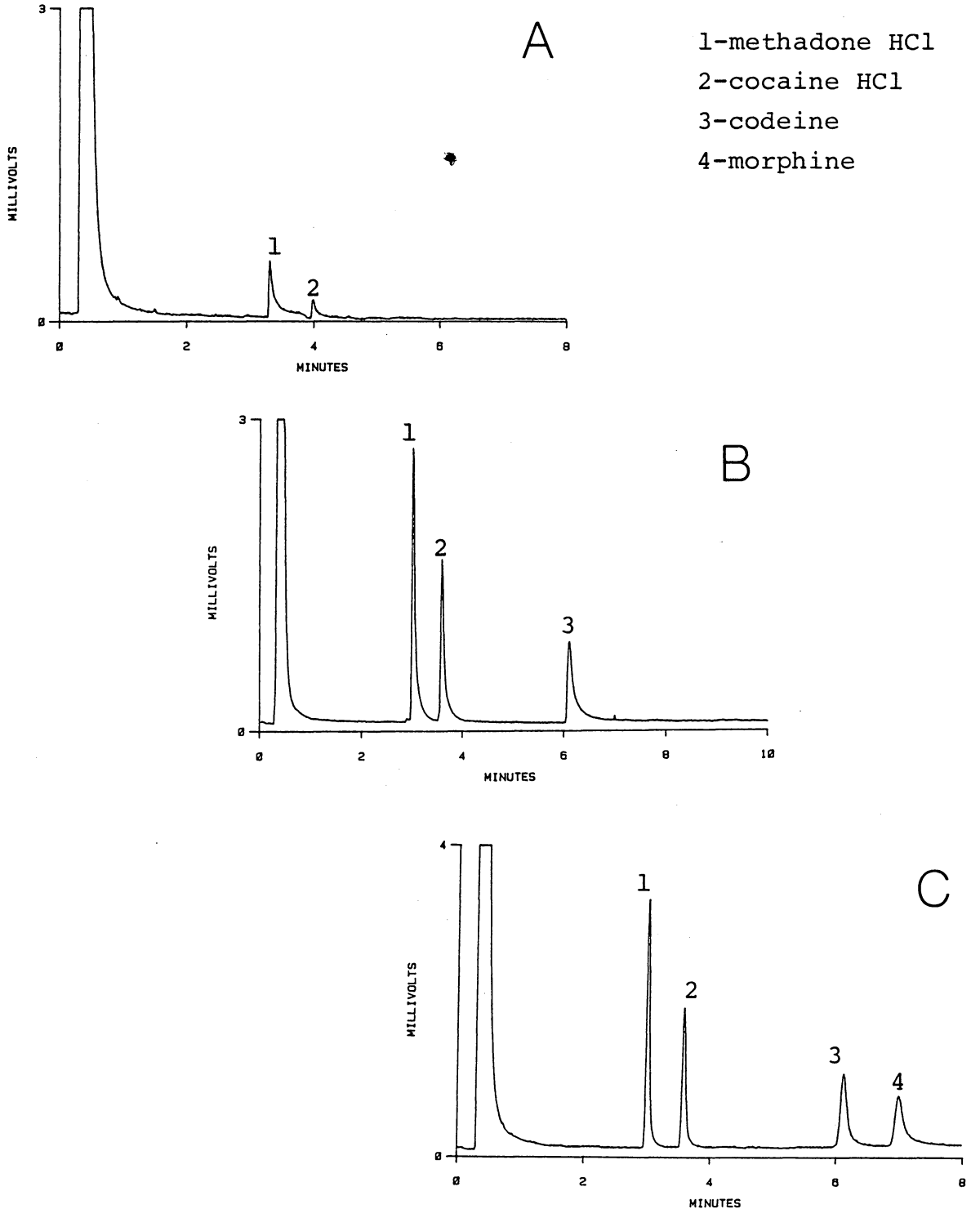


Figure 17: Chromatograms of alkaloid drugs (20 ng each). Columns A and B were coated on untreated surfaces while C was hydrothermally treated and deactivated. For details, see text.

tions in the measured critical surface energy (surface 2) but still showed insufficient deactivation as evidenced by surfaces 4, 7 and 11 and also noted by others [121]. The incomplete deactivation of surfaces 4, 7, and 11 is evident from the critical surface energy. The critical surface energy of a methylated surface should be 20-21 dynes/cm [283].

Consequently, more rigorous methods were investigated to pretreat the fused silica surface with the intention of maximizing the surface silanol coverage: these hydrothermal treatments include the use of water, 20% hydrochloric acid, and 20% nitric acid.

A simple, yet reliable technique was needed to assess the extent of surface hydroxylation without having to evaluate coated columns. The concept of intermediate surface testing as described by Schomburg [133] and further discussed by Grob [275] was found to be ideally suited. Also, a test probe was needed which would be sensitive to surface hydroxyl groups. Since it is well known that alcohols are sensitive to hydrogen bonding sites characteristic of silanol groups, 1-octanol was used.

The test procedure required a coated capillary column that could elute the 1-octanol with perfect symmetry (i.e.: no reversible adsorption). A 10 m x 0.25 mm ID fused silica

column coated with OV-1701 (film thickness = 0.3 um) was prepared which gave undistorted elution of the 1-octanol. This column served as the pre-column to which the test capillaries were attached by means of a 1/32" zero dead volumn union. To ensure that the capillary connection was not responsible for any peak distortion, 1 m was cut from the 10 m OV-1701 column and reconnected to the 9 m piece and re-evaluated (9+1 m OV-1701).

The calculation of a tailing factor was used to quantify the degree of reversible adsorption. A chromatogram of 1-octanol on the 9+1 m OV-1701 column illustrating the calculation of the tailing factor is shown in Figure 18. Chromatograms for calculating tailing factors were obtained isothermally at 80°C with H_2 carrier gas at 50 cm/sec (measured at 40°C). Injector temperature was 225°C; detector temperature was 325°C; and 1 ul was injected with split ratio of 20:1. To calculate the tailing factor, a line was drawn perpendicular to the baseline through the peak maximum. Next, a line was drawn parallel to the baseline which intersects the peak at 10% of its height above the baseline. The ratio of the trailing segment (B) to the leading segment (A) was defined as the tailing factor (TF). A perfectly symmetrical peak would have TF = 1.00; a leading (or fronting) peak would have TF less than 1; and a tailing peak

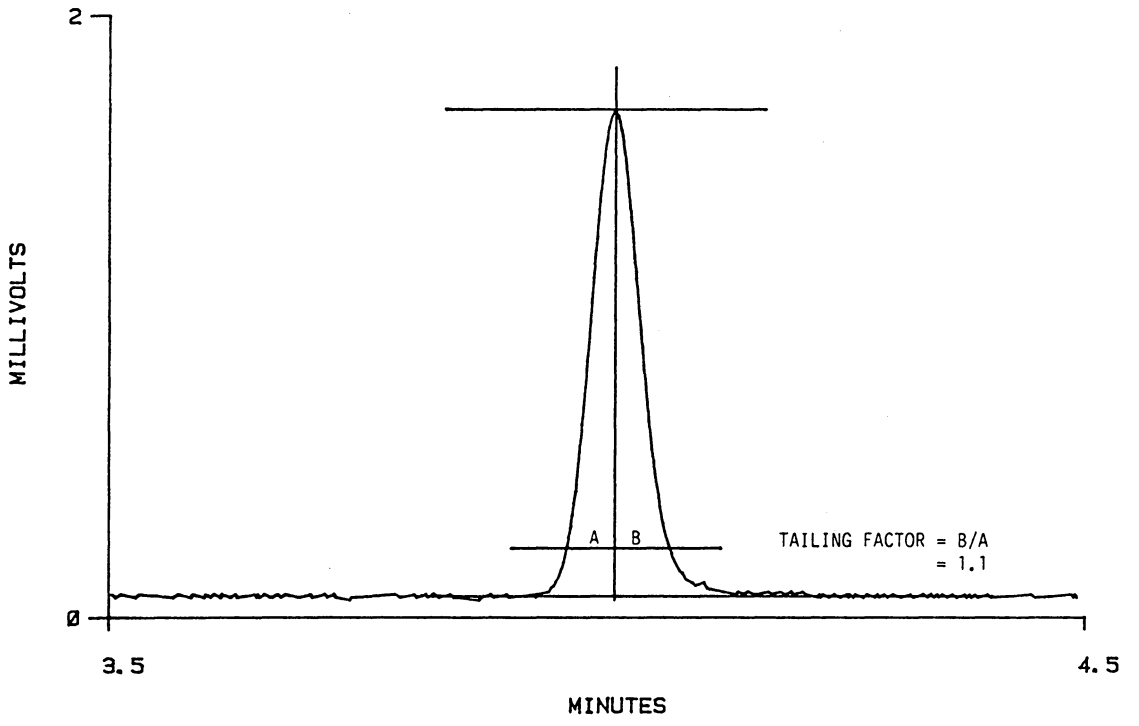


Figure 18: Chromatogram of 1-octanol (2.5 ng) illustrating the tailing factor calculation.

would have TF greater than 1. The results of an investigation into the amount of 1-octanol that should be injected (so as not to overload the column) is summarized in Table 10. Sample weights of 10 and 5 ng overloaded the column as is evidenced by tailing factors less than 1. However, 2.5 ng was not so large as to result in fronting peaks and was used throughout. The tailing factor of the 9 m OV-1701 column (1.13) is indistinguishable from that of the 9+1 m OV-1701 column (1.15) which verifies the integrity of the capillary connection. Each value reported is the average of 3 injections.

The various hydrothermal treatments were performed on 1 meter pieces of fused silica capillary tubing and were connected to the 9 m OV-1701 test column in the same way. The results of these hydrothermal treatments are summarized in the plot in Figure 19. All data points are the average of 5 injections. Chromatographic conditions were the same as described for Figure 18.

From this analysis, there is no appreciable difference between water and 20% HCl in hydroxylating the fused silica surface; there is an almost identical linear increase of the tailing factor with temperature for the 10 hour treatments. However, there is a substantial increase in the tailing factor for the 150°C and 200°C treatments with 20% HNO_3. The

Table 10. Tailing factor as a function of amount of 1-octanol injected.

Amount of 1-octanol on column	Tailing factor
10.0 ng (9m OV-1701)	0.89
5.0 ng (9m OV-1701)	0.95
2.5 ng (9m OV-1701)	1.13
2.5 ng (9+1m OV-1701)	1.15

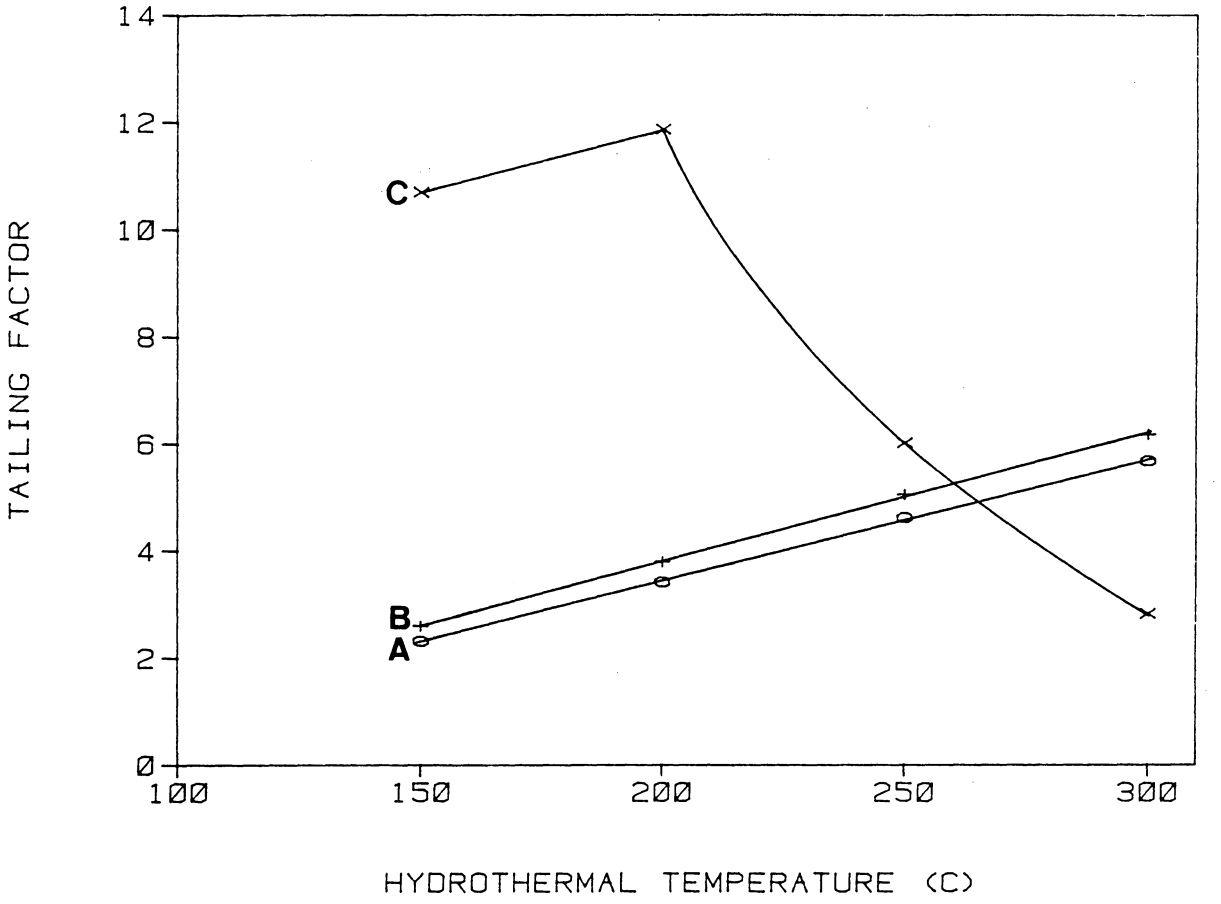


Figure 19: Evaluation of effect of various hydrothermal treatments on asymmetry of 1-octanol peak. Curve A - water, B - 20% HCl, C - 20% HNO_3.

dramatic reduction of the tailing factor with nitric acid at temperatures above 200°C was first thought to be a failure in the reproducibility of the measurements. However, subsequent treatment and measurement of two additional capillaries for each set of conditions reproduced the original set of data within 5% and proved this was not the case.

This sharp reduction in surface silanol coverage is attributable to the decrease in surface area of the fused silica. Hydrothermal treatment of porous silica with steam by Ohmacht and Matus [302] as functions of temperature and time has shown more than a 60% reduction in surface area on going from a 10 hour treatment at 180°C to a 10 hour treatment at 250°C. Treatment of the silica with steam for 10 hours at 280°C resulted in an 85% reduction in surface area. This reduction of surface area is caused by increasing the porosity of the silica. A reduction in surface area of the fused silica would account for the reduction in column activity due to the reduced number of sites available for reversible adsorption with 1-octanol. Accordingly, the increase of surface hydroxylation and decrease of surface area of the fused silica are concurrent processes. For all the hydrothermal treatments with water and HCl and the HNO_3 treatments at or below 200°C, the rate of hydroxylation is greater than the rate of surface area reduction. Only in

the presence of the 20% nitric acid at temperatures in excess of 200°C does a rate reversal occur.

The greatest degree of surface hydroxylation (largest tailing factor) that could be reproducibly obtained resulted from the treatment of the fused silica with 20% HNO_3 at 200°C for 10 hours. Figure 20 shows a chromatogram of 1-octanol on a 1 meter piece of this tubing connected to the 9 meter OV-1701 pre-column. The remaining conditions were the same as described for Figure 18. Determination of the critical surface energy of tubing treated in this way yielded a value of 46 dynes/cm (surface 3).

Capillary tubing was subjected to this HNO_3/200°C/10 hr treatment and subsequently deactivated with various silylating reagents to evaluate the degree of success of deactivation for the nitric acid treated columns as compared to untreated capillaries.

Equations 5 and 6 can be used to compare the relative surface coverage for surfaces that have the same critical surface energy. Comparing the extent of methylation for various deactivating reagents by this approach shows that for surfaces with critical surface energies of 21 dynes/cm (surfaces 6, 8, 9, 10) the relative degree of coverage decreases in the order hexamethyldisiloxane>D_4>TMCS>>D_3. For surfaces with critical surface energies of 20 dynes/cm

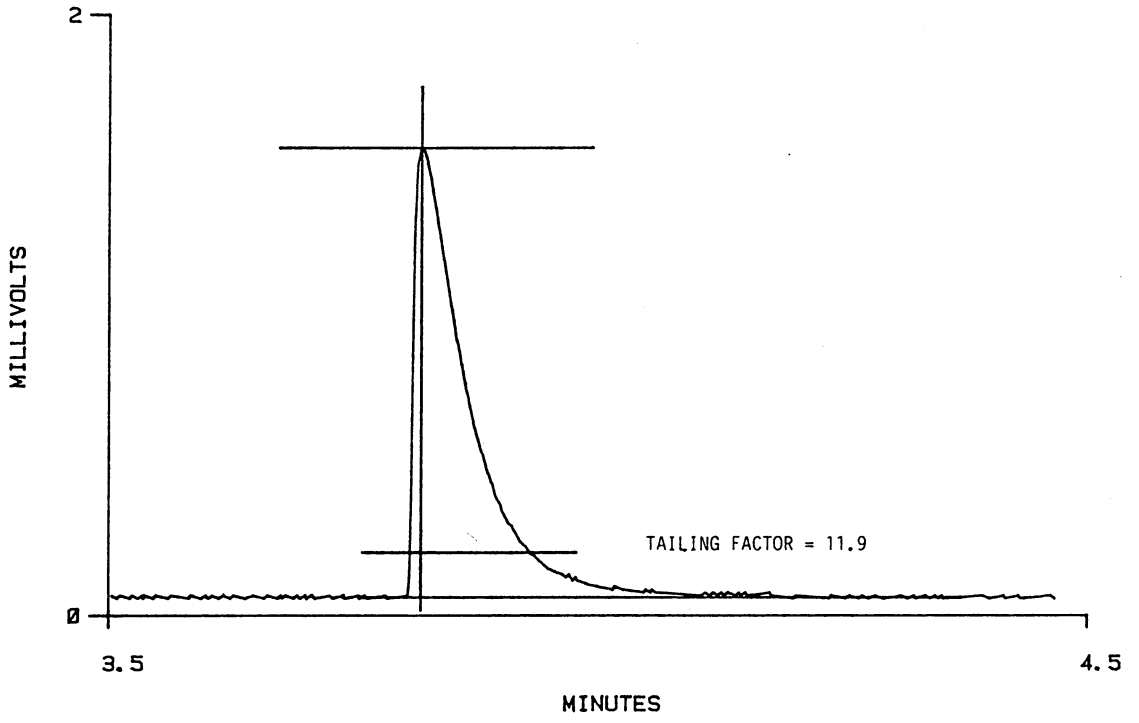


Figure 20: Chromatogram of 1-octanol (2.5 ng) on test capillary hydrothermally treated with nitric acid at 200°C.

(surfaces 12-14) the degree of coverage decreases in the order octamethylcyclotetrasilazane>HMDS>SF-96. It should be noted (with the exception of D_3) that the differences among any of these are not large and most are adequate for a high degree of surface coverage. The only treatment which failed to give a high degree of surface coverage was the D_3 (surface 8). Summarizing all the methyl silylation treatments, it appears that the silazanes (surfaces 13, 14) provide the highest degree of surface coverage followed by the siloxanes (with the exception of D_3; linears followed by cyclics, surfaces 6, 9, 12) followed by the chlorosilane (surface 10). The Zisman plot for a nitric acid treated surface silylated with D_4 is shown in Figure 21.

Surfaces 4, 5; 7, 8; and 10, 11 cannot be included in the above comparison based on the Zisman plot slopes since the critical surface energies are not the same. At first glance, this might appear to be a failure of equations 5 and 6. However, this is not the case since in obtaining 6 from 5 it was assumed that the surface contained only two types of surface structures; one that was completely wet ($\theta_2 = 0$) and one that was incompletely wet (θ_1). The values of γ_c obtained for surfaces 4, 7, and 11 are indicative of more than two types of surface structures present on the fused silica. Therefore, equation 5 must be expanded to include at least one additional term:

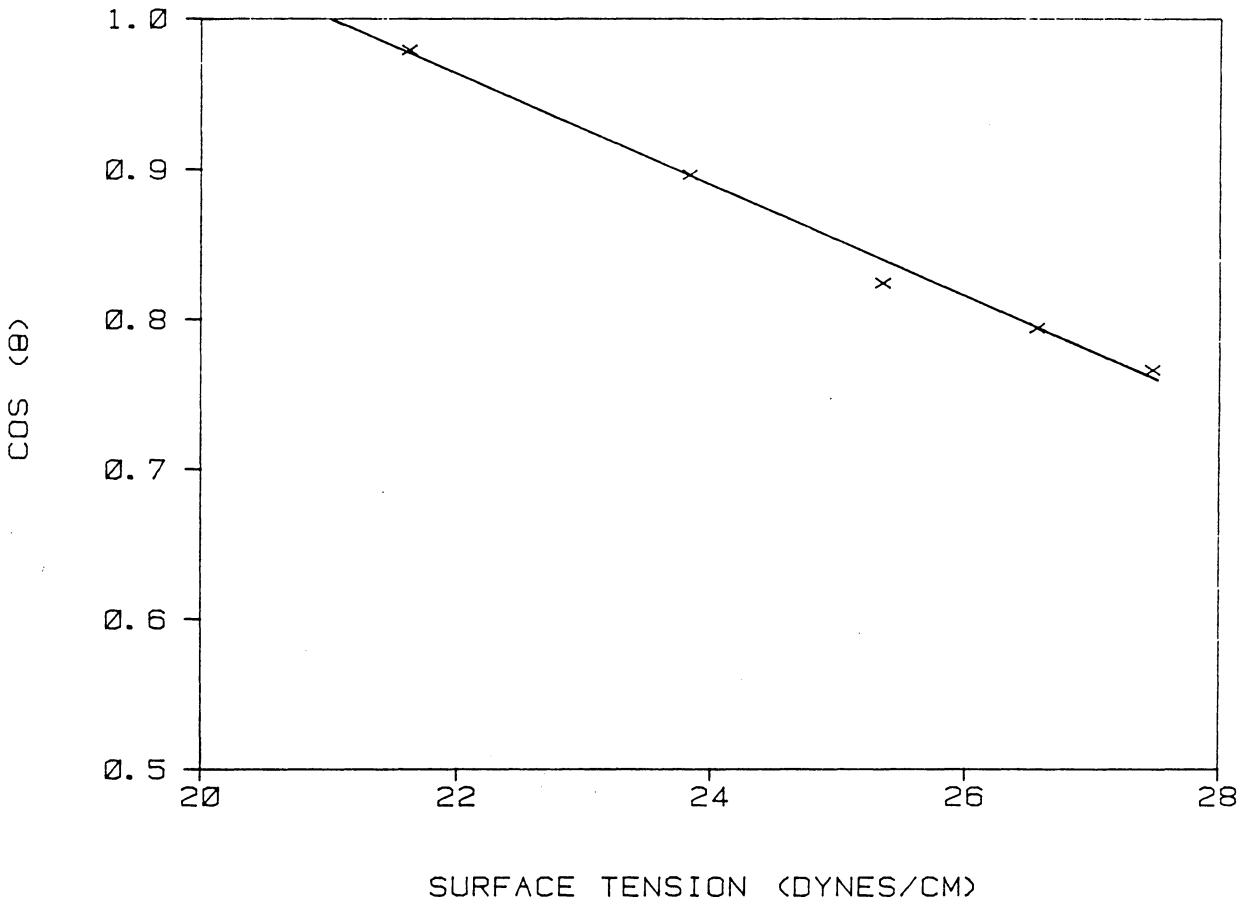


Figure 21: Zisman plot for fused silica hydrothermally treated with nitric acid and deactivated with D_4.

$$\cos\theta_{obs} = \sigma_1\cos\theta_1 + \sigma_2\cos\theta_2 + \sigma_3\cos\theta_3 \qquad (8)$$

where σ_3 is now the fractional area occupied by the type 3 surface and θ_3 is the contact angle characteristic of this surface. To probe the methylated surfaces, methanol/water mixtures were used which covered the range of 22-30 dynes/cm. If σ_1 is arbitrarily assigned to be the fractional area occupied by methyl groups (γ_c = 21 dynes/cm) it is obvious that each of the probe liquids used will incompletely wet σ_1. If σ_2 is the fractional area occupied by the bare silica surface (which in reality is composite but is homogeneous and is treated as a single entity, $\gamma_c \geq 45$ dynes/cm) each of the probe liquids used completely wets σ_2. If σ_3 were completely wet by the range of liquids used, then equation 6 would still hold. Therefore, the surface energy of the structure giving rise to σ_3 must lie within the range of the surface tensions of the probe liquids used (22-30 dynes/cm) resulting in incomplete wetting of this type surface by at least one of the liquids. In cases such as this, the success of deactivation must be judged by the value of γ_c and not the slope of the Zisman plot. Whatever the surface structure is that gives rise to this phenomenon, the water and methanol rinses were not sufficient to remove it

whereas the 20% nitric acid treatment was. As a result, this type of hydrothermal treatment is needed not only for maximizing the extent of hydroxylation of the surface, but also for cleaning it.

The extent of surface deactivation with trimethylchlorosilane and D_4 is compared in Figure 22. Chromatogram A was obtained on fused silica that was rinsed with water and methanol and deactivated with TMCS (surface 11); chromatogram B was obtained on similarly rinsed fused silica and D_4 deactivated (surface 4); and chromatogram C was obtained on fused silica treated with HNO_3/200°C/10 hr followed by D_4 deactivation (surface 6). The remaining conditions were the same as described for Figure 17. The slight degree of surface coverage with TMCS is evidenced by the appearance of the morphine peak (compared to untreated surfaces in Figure 17). Obviously, D_4 is the better silylating reagent and the hydrothermally treated surface is superior to the rinsed one, as evidenced by the increased peak response (and relative response morphine/codeine) noted in chromatogram C.

Further evidence for the high degree of deactivation obtained as a result of the nitric acid hydrothermal treatment prior to deactivation is shown in Figure 23 with chromatograms of a series of primary alkyl amines. These compounds are some of the most difficult to chromatograph on

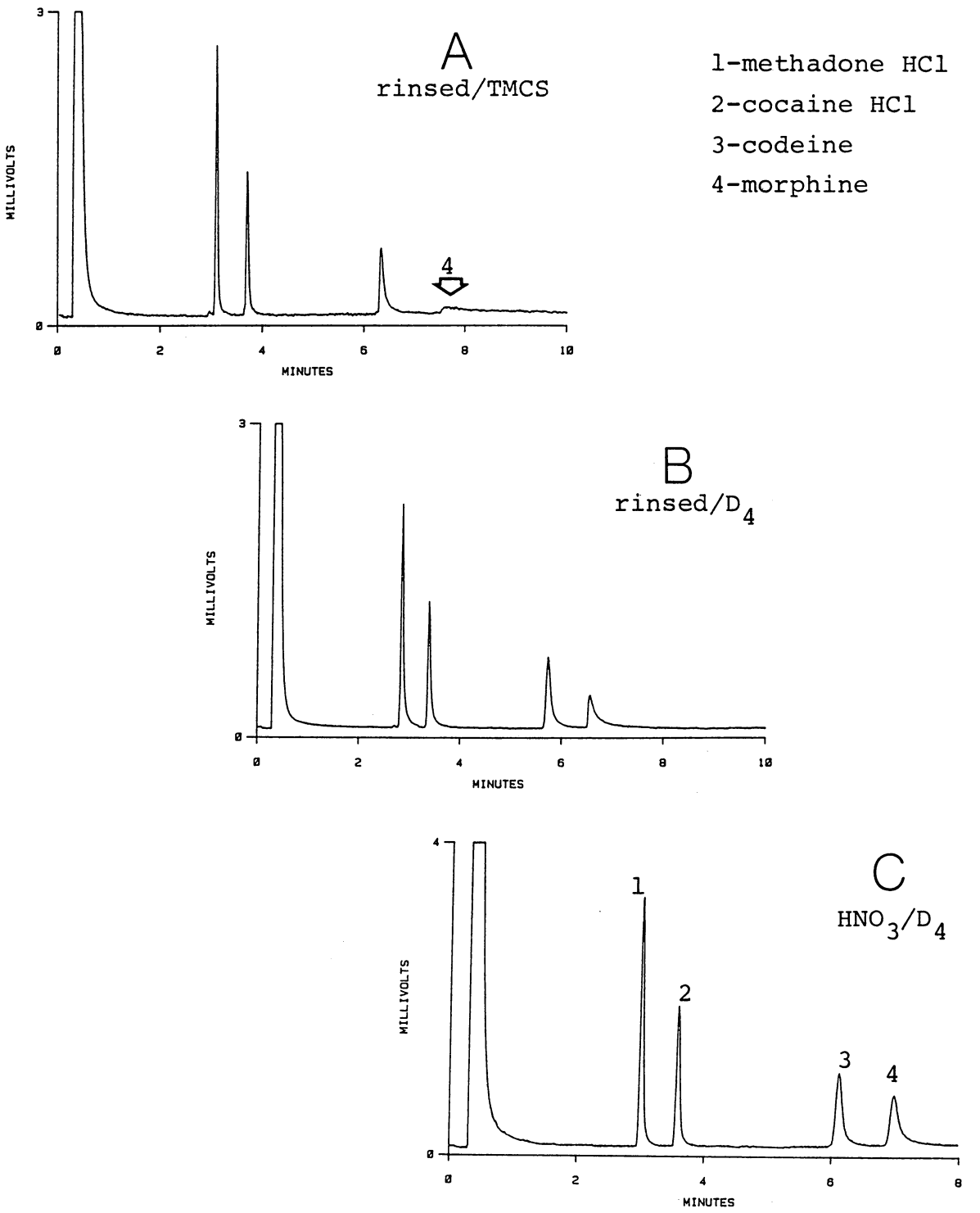


Figure 22: Chromatograms of alkaloid drugs (20 ng each) illustrating relative degree of deactivation. Column pretreatment conditions are noted beside each chromatogram. For details, see text.

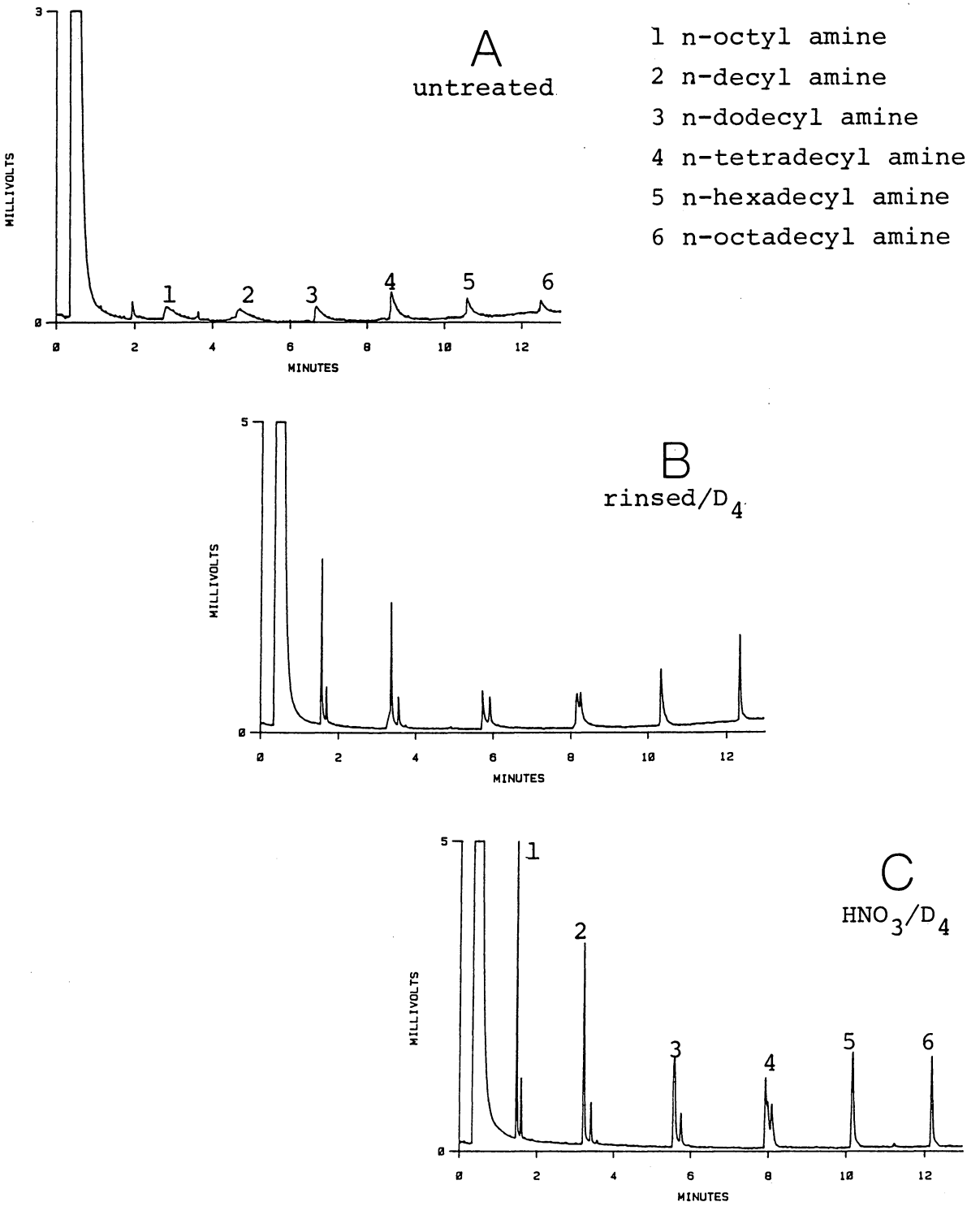


Figure 23: Chromatograms of primary alkyl amines (10 ng each) illustrating relative degree of deactivation. Column pretreatment conditions noted beside each chromatogram. For details, see text.

fused silica capillary columns because of their basicity (amine group) and their good retention (alkyl chain) and the slightly acidic nature of the fused silica surface. All columns were 10 m x 0.25 mm ID fused silica coated with 0.25 um film thickness of OV-73. Injector and detector temperatures were 225°C and 325°C, respectively. The oven temperature was programmed from 80°C to 210°C at 10°C/min with H_2 carrier gas at 50 cm/sec (measured at 40°C) with a 1 ul injection split 20:1. Chromatogram A on the untreated surface is typical of the activity of bare (i.e.: undeactivated) fused silica. Chromatogram B (surface rinsed with water followed by methanol and D_4 deactivated) is a dramatic improvement with resolution obtained between the amine and alkane impurities for the octyl through tetradecyl amines. While the amine peaks still show a slight degree of tailing in chromatogram C (hydrothermally treated with HNO_3/200°C/10 hr and D_4 deactivated), the exceptional quality of the column is evident from the nearly doubled peak response and the flat baseline at the higher temperature near the end of the run (resulting from the increased stationary phase film stability).

The surface energy of chemically modified fused silica can be increased from the 20-21 dynes/cm characteristic of methyl groups by the use of deactivating reagents with more

polar functional groups. Also, compatibility between the tubing surface and the stationary phase can be ensured by using deactivants with functional groups similar or identical to those of the phase. As an example, surface 16 was deactivated with (3,3,3-trifluoropropyl) methyl cyclic siloxanes resulting in a fused silica surface with a critical surface energy of 22 dynes/cm which is compatible with the trifluoropropyl containing stationary phases such as OV-210 and OV-215.

Higher surface energies are obtainable by utilizing deactivants with phenyl substituents. The entirely phenyl substituted cyclic tetramer (Ph_4) yielded a critical surface energy of 29 dynes/cm (surface 19). Diphenyltetramethyldisilazane (surfaces 17,18) is an excellent silylating reagent for introducing some phenyl substitution onto the surface. The conditions used here for the fused silica are analogous to those developed by the Grobs [145] for glass. As expected, the surface which was acid treated prior to deactivation was superior to the rinsed surface. This reagent has also been used successfully with OV-73 as the liquid phase with only a 90 minute hold at 400°C.

Recently there has arisen some controversy over the use of DPTMDS in improving the wettability of glass and fused silica surfaces. Rutten et al. [298] have claimed that

silylation with DPTMDS at a temperature of 400°C yields a surface identical to that formed when HMDS is used due to the loss of phenyl groups from DPTMDS. The results presented here clearly demonstrate the increased wettability resulting from silylation with DPTMDS at 400°C (surface 18) over HMDS (surface 13), at least with fused silica as the substrate. These quantitative results are in agreement with the recent qualitative studies of Grob and coworkers [299,300].

The most polar cyclic siloxane used for chemical modification of the fused silica surface was tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane (surface 20). A reaction temperature of 280°C for 16 hr resulted in good deactivation with a critical surface energy of 32 dynes/cm.

The Carbowax pyrolysis procedure of Cronin [126] was studied and compared with identical treatments for Superox 20M and Superox 4 (surfaces 23-25). Superox 20M and Superox 4 are specially synthesized polyethylene glycols of molecular weight 20,000 and 4 million, respectively. Their reputed advantages over the Carbowax polyethylene glycols lie in their narrower molecular weight distribution and higher purity, resulting in better temperature stability. The Carbowax 20M and Superox 20M both gave very high critical surface energies making these surfaces wettable by all

stationary phases commonly used for fused silica capillary column coating. However, the temperature limit of a Carbowax 20M or Superox 20M pretreated column would become either that of the deactivation layer (about 250°C) or that of the stationary phase, whichever were lower. Also, the polarity of polyethylene glycol pretreated columns coated with the more nonpolar phases would be affected by the polar deactivation. For these reasons, the polyethylene glycol type deactivating procedures are not commonly used. There is a current interest in the use of these materials for the deactivation of fused silica columns for supercritical fluid chromatography (SFC) where the increased mobile phase strength in SFC (a supercritical fluid) as compared to GC (an inert gas) would minimize the observance of column polarity changes and where column temperatures would rarely exceed 150°C. Preliminary results with Carbowax 20M deactivation coupled with a cross-linked film of OV-1701 for SFC were quite encouraging [301].

Because of its higher molecular weight, Superox 4 possesses a higher temperature limit than the lower molecular weight polyethylene glycols. However, treatment of fused silica with Superox 4 does not yield a surface with as high a surface energy as either the Carbowax 20M or Superox 20M. Solutions of Superox 4 used for dynamically coating the

capillaries for deactivation were necessarily more dilute than the Carbowax 20M and Superox 20M solutions due to the very high viscosities of the Superox 4 solutions.

The final deactivation comparison to be made is between the use of an intermediate polarity stationary phase for polysiloxane degradation type deactivation versus a mixture of cyclic siloxanes. The stationary phase was synthesized utilizing cyclic siloxanes as the starting materials by a procedure described in the next chapter. The phase was 7% cyanoethyl, 7% phenyl, 1% vinyl, 85% methyl polysiloxane; the mixture of cyclics used for deactivation was prepared to give equivalent percentages of each functional group from tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane, tetravinyltetramethylcyclotetrasiloxane, Ph_4, and D_4. As seen from a comparison of surfaces 21 and 22, the use of the cyclic mixture yielded a fused silica surface of moderately high energy which produced a stable and efficient column when coated with the phase. The polysiloxane degradation of the polymeric phase yielded a surface with very low energy (equivalent to methylation with a relatively high surface coverage) which could not be coated efficiently with the same stationary phase. A similar phenomenon was noted for the attempted polysiloxane degradation of OV-17 (50% phenyl methyl polysiloxane) on fused silica by Verzele et al. [88].

In addition to the activity of the column material, the choice of initiator used for cross-linking can contribute to the final activity of the column. Initial experiments with nitric acid hydrothermal treatments followed by D_4 deactivation and using dicumyl peroxide as initiator were somewhat disappointing.

Through subsequent experiments, the residual activity of the column was traced to the dicumyl peroxide. Columns treated identically in all respects except using azo-t-butane as initiator showed excellent inertness. Figure 24 shows chromatograms of the Grob test mix II on a column which was untreated and not cross-linked (A), and two columns which were HNO_3/200°C/10 hr treated and D_4 deactivated with one using DCP as initiator (B) and the other using ATB as initiator (C). Columns were temperature programmed from 40°C to 130°C at 5°C/min with H_2 carrier gas at 50 cm/sec (measured at 40°C). The injector and detector temperatures were 250°C and 325°C, respectively, with an injection volume of 1 ul split 20:1. In chromatogram A, notice the severe tailing of the alcohol peaks (1, 3) and the tailing of the free acid (5); all indicative of reversible adsorption on the active surface silanols. Also note the complete disappearance (irreversible adsorption) of the dicyclohexylamine (9) due to interactions with the acidic silanols and the

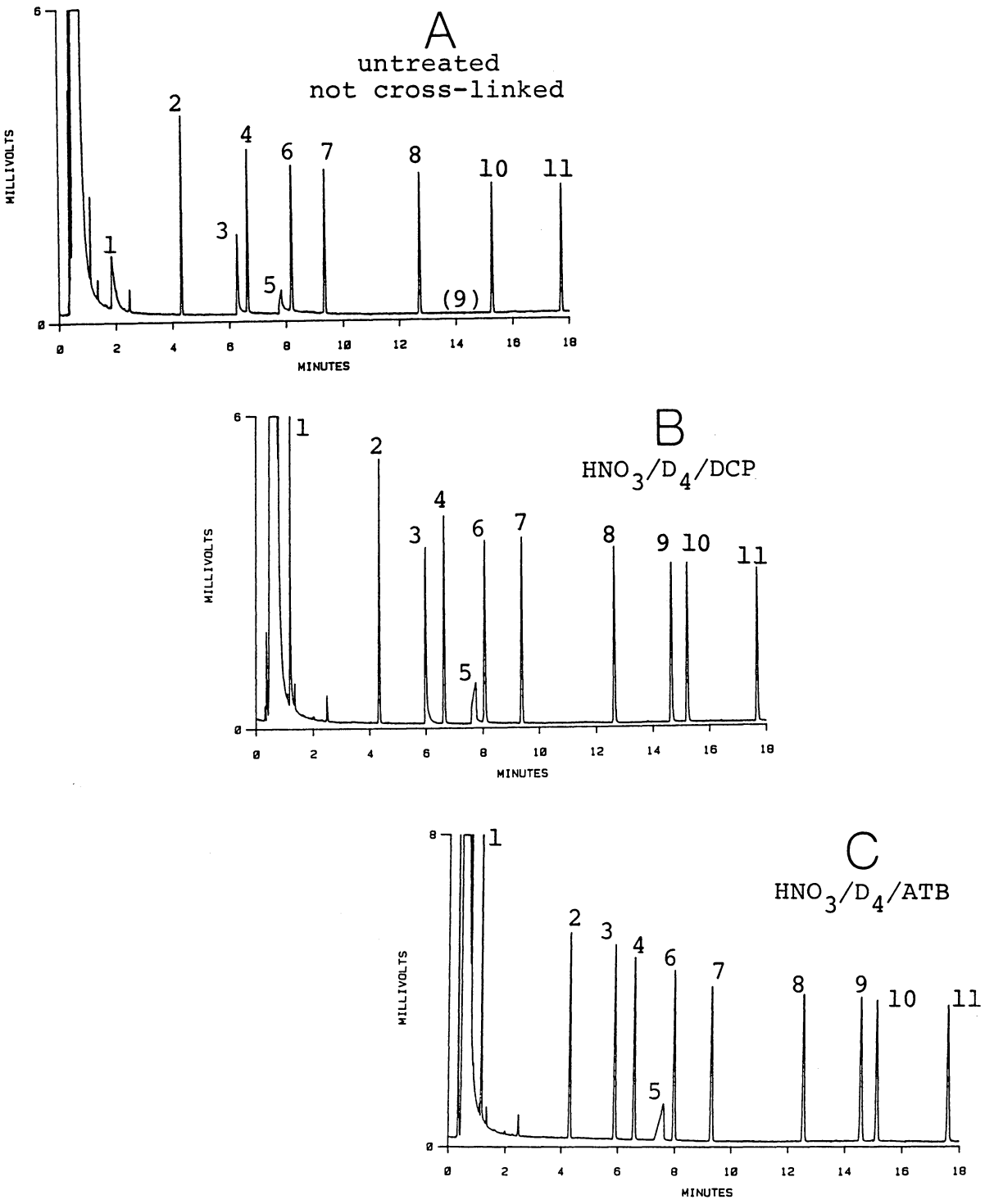


Figure 24: Chromatograms of the Grob comprehensive test mix illustrating column inertness. Preparation conditions noted beside each chromatogram. Peak identifications and amounts listed in Table 11. For details, see text.

Table 11. Peak identification and amount injected for chromatograms of Grob comprehensive test mix II in Figure 24.

Peak number	Identity	Amount injected (ng)
1	2,3 butanediol	2.7
2	n-decane	1.4
3	1-octanol	1.8
4	2,6 dimethylphenol	1.6
5	2-ethylcaproic acid	1.9
6	2,6 dimethylaniline	1.6
7	n-dodecane	1.5
8	methyl decanoate	2.1
9	dicyclohexylamine	1.6
10	methyl undecanoate	2.1
11	methyl dodecanoate	2.1

siloxane bridges of the fused silica surface. While chromatogram B is a dramatic improvement, the alcohol peaks still exhibit tailing in addition to slight height reductions of the aniline (6) and amine peaks. The residual activity of columns prepared using DCP as the source of free radicals for the initiation of cross-linking can be attributed to the decomposition products formed. The major decomposition products of dicumyl peroxide are cumyl alcohol and acetophenone, which if incorporated into or adsorbed onto the stationary phase, would result in increased column polarity (for nonpolar phases) and a reduction in column inertness. Azo-t-butane, on the other hand, decomposes to isobutane, isobutene, and nitrogen; all of which are volatile, nonpolar and easily removed from the column during conditioning. Any incorporation of the hydrocarbon products into the phase results in no detectable change in column polarity or inertness. As a result, chromatogram C shows perfect elution (symmetry and height) of all the components of the test mix except for the free acid. The reduced height and the fronting shape of the acid peak are expected due to the nonpolar nature of the stationary phase used (OV-73) and the limited solubility of the acid in the phase resulting in column overload. However, there is no peak tailing evident which is indicative of a lack of reversible adsorption and exami-

nation of the integrated area counts showed no evidence of irreversible acid adsorption.

ATB and DCP were equally effective in initiating cross-linking of the OV-73 stationary phase. Percent washout from both types of columns ranged between 2 and 5%.

Finally, an evaluation of the thermostability of variously treated columns was performed. The importance of the deactivation layer in determining the maximum allowable operating temperature of a column is illustrated by the plot in Figure 25. All columns were 10 m x 0.25 mm ID fused silica coated with 0.25 um film thickness of OV-73 after the indicated pretreatment and crosslinked with DCP. After curing and conditioning, each column was temperature programmed from 175°C to 325°C at 5°C/min with hydrogen carrier gas at an average linear velocity of 50 cm/sec (measured at 100°C). Each column was programmed 4 times with the final run used for comparison. As expected, the HNO_3/200°C/10 hr treated column followed by D_4 deactivation (A) showed the lowest column bleed as the temperature increased to 325°C. The rate of column bleed increases markedly in going from the rinsed, deactivated surface (B) to the untreated surface (C) to the Carbowax 20M deactivated surface (D). The high bleed resulting from the Carbowax treated column is due to the lack of thermal stability of the polyethylene glycol layer.

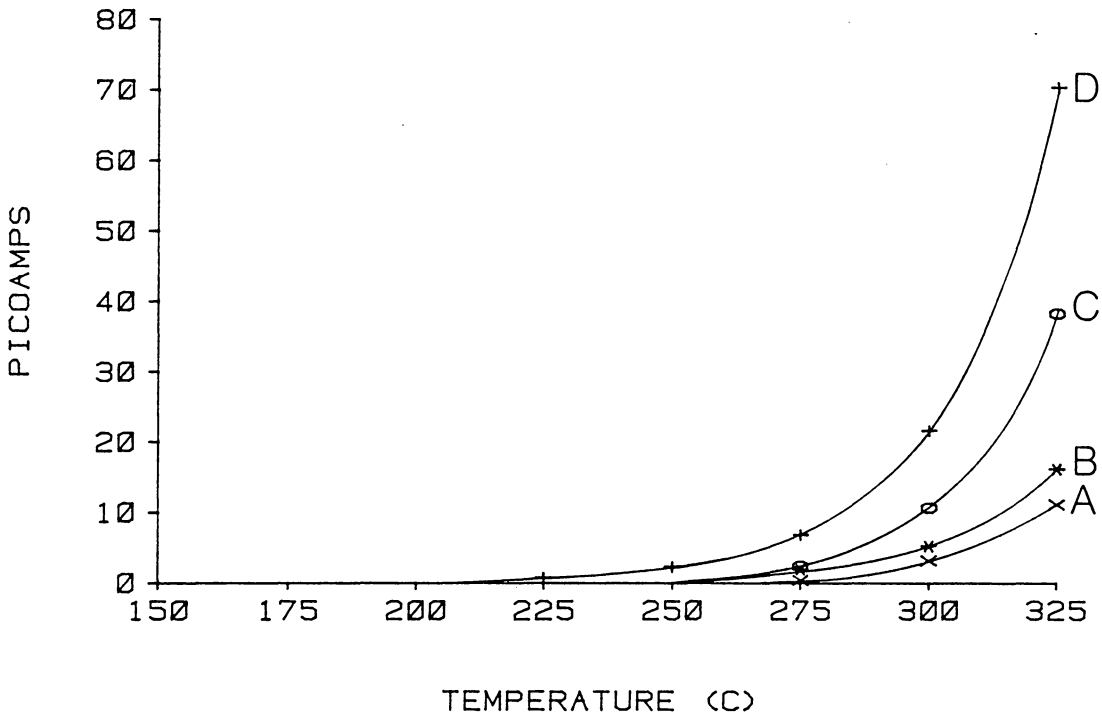


Figure 25: Affect of fused silica pretreatment on column thermostability. (A) hydrothermally treated and D_4 deactivated, (B) rinsed and D_4 deactivated, (C) untreated, and (D) Carbowax 20M deactivated.

The relative bleed rate of the phase from the other surfaces is explainable by the relative phase film stability obtained on the deactivated surfaces with the high degree of surface coverage obtained after the nitric acid treatment resulting in the most compatible surface.

Conclusions

The activity and wettability of raw fused silica capillary tubing was found to be widely variable which places severe limitations on the reproducibility of column deactivation and inertness. Hydrothermal treatment of the fused silica with nitric acid was proven to be very effective for cleaning and maximizing the silanol coverage of the surface. The capillary rise method was used to obtain contact angle data on the untreated fused silica and fused silica treated with a variety of deactivating reagents. This contact angle data was used in the construction of Zisman plots which allowed quantitative characterization of the wettability of the surfaces by their critical surface energies. The choice of cross-linking initiator was also found to be important in producing capillary columns with maximum inertness. Azo-t-butane was shown to be preferable to dicumyl peroxide in the preparation of nonextractable stationary phase films capable of chromatographing low nanogram levels of sensitive ana-

lytes such as alcohols, amines and free acids with no adsorption. The thermal stability of the final column has also been related to the success of the deactivation procedure. The maximum surface coverage obtained by nitric acid hydrothermal treatment and high temperature silylation is necessary for providing the utmost compatibility between the stationary phase film and the capillary column wall.

V. SILOXANE STATIONARY PHASE SYNTHESIS

Introduction

The thermal stability and inertness of stationary phases used in gas chromatography are both very dependent on such characteristics of the phase as the molecular weight, molecular weight distribution, purity, and the endgroups present on the polymer chain. High molecular weights and narrow molecular weight distributions are desirable since these properties increase the viscosity of the stationary phase film resulting in the reduced tendency to rearrange and form droplets or bubbles as the column temperature is increased. The most undesirable impurities that are often present in the phase are traces of metals (or metal oxides) picked up from the handling of the material (through glassware, etc.) or the presence of residual polymerization catalyst (acid or base) or polymerization by-products. These types of impurities, in addition to active chain ends such as -Cl and -OH, can cause excess column activity (reversible and irreversible adsorption) as well as the depolymerization of the phase. Because of the inherent inertness of the fused silica tubing material and the potential for further

reducing the column activity by hydrothermal treatment and silylation, there is a need to produce stationary phases with comparable performance characteristics in terms of molecular weight control and purity levels.

Further demands are placed on the stationary phase characteristics when attempting to prepare stable, efficient capillary columns with phases other than the methyl silicones (i.e.: the more polar ones). The foremost desirable characteristic is the ability to cross-link the phases inside the column resulting in stable, nonextractable stationary phase films. The phase nonextractability becomes the primary concern when using capillary columns with mobile phases other than inert gases; the current enthusiasm in supercritical fluid chromatography (SFC) with open tubular columns is a prime example.

Polysiloxane Synthesis

In the synthesis of siloxane stationary phases for gas chromatography, the starting materials most often used are dichlorosilanes. The initial step of such a procedure, the hydrolysis of the dichlorosilanes, produces a mixture of cyclosiloxanes and chlorine and hydroxyl end-blocked linear polysiloxanes. Such a process is represented in Figure 26. If given sufficient time to reach equilibrium, virtually all

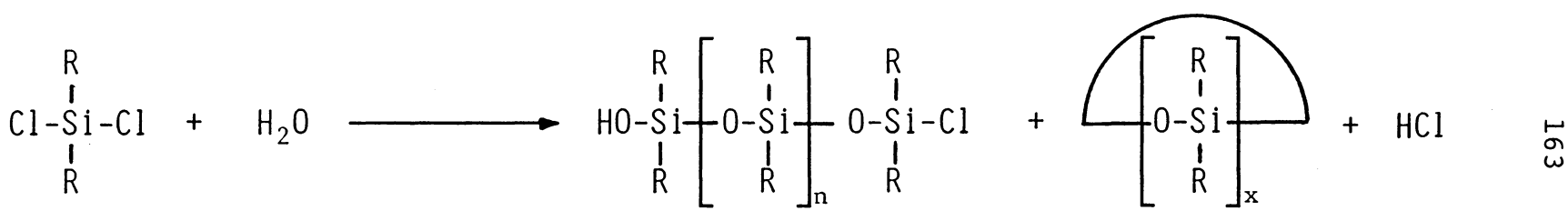


Figure 26: Hydrolysis of dichlorosilanes.

SiOH and SiCl species are removed leaving predominantly siloxane (Si-O-Si) links and HCl. As an example, the weight ratio of cyclic to linear siloxanes resulting from the hydrolysis of dimethyldichlorosilane is about 1:1 with ca. 80% of the cyclic fraction being octamethylcyclotetrasiloxane (D_4) [303]. To this mixture, a catalyst is added which causes siloxane bond redistribution and results in higher molecular weight polysiloxanes, with the primary driving force being the ring-opening polymerization of the cyclics. The common practice of adding the chlorosilanes to a water miscible solvent before hydrolysis leads to a higher proportion of cyclics due to dilution which favors intramolecular condensation rather than chain extension. After hydrolysis, the siloxanes are removed from the HCl solution by partitioning them into a water immiscible solvent with successive water extractions. This process, although effective in removing the majority of HCl, cannot remove traces of the acid which could be adsorbed onto the siloxanes, especially the more polar ones.

These traces of HCl have several undesirable affects. First of all, the adsorbed HCl could affect the polarity of the stationary phase and adversely affect the overall inertness of the column. Secondly, HCl from hydrolysis can cleave organic groups from silicon with vinyl, phenyl, and

possibly cyano groups being most susceptible. A third deleterious affect is the possible formation of amide groups in cyano containing polysiloxanes as detected by Jones et al. [304]. And finally, the molecular weight of the linear siloxanes is governed by equilibria with species capable of forming end-blocks at the chain ends. When utilizing hydrolysis of chlorosilanes, -OH and -Cl are two such potential end-blockers.

To circumvent these problems, it is obviously desirable to avoid HCl in the synthesis procedure. One way to avoid HCl is by forming methoxysilanes from the chlorosilanes as the first synthetic step as has been exploited recently by Lee and coworkers [304-307] and Markides et al. [120]. A second and simpler method is to utilize cyclic siloxanes as starting materials. This approach has additional advantages in that HCl gas is never encountered in the procedure and by using only trace amounts of catalyst the molecular weight of the linear polymer can be made very high. The only possible endgroups present are those introduced by the catalyst unless an end-blocker is intentionally added. The only stationary phases commercially available that utilize cyclic starting materials are homo polymers of (3,3,3-trifluoropropyl) methyl siloxane obtained from (3,3,3-trifluoropropyl) methylcyclotrisiloxane (F_3) [209].

In this chapter, results of the use of mixtures of commercially available cyclic siloxanes as starting materials for the synthesis of stable, high molecular weight intermediate polarity polysiloxanes suitable for use in capillary gas and supercritical fluid chromatography are presented.

Supercritical Fluid Chromatography (SFC)

The use of supercritical fluid mobile phases for chromatography is a concept that is not new but is just now beginning to receive widespread attention, due in part to both the recent developments in gas chromatography and the technical difficulties in establishing open tubular column liquid chromatography as a routine analytical technique. SFC, however, should not be regarded as a potential replacement for either gas or liquid chromatography; it simply is a technique complementary to both. SFC can be used to separate molecules that are unsuitable for gas chromatographic conditions due either to the lack of thermal stability or sufficient vapor pressure. As a complement to high pressure liquid chromatography (HPLC), SFC can offer higher separation efficiencies, shorter analysis times, and a broader range of easily interfaced detectors (flame ionization detector, mass spectrometer, etc.). In addition, the higher densities characteristic of supercritical fluids as compared

to gases leads to solute solubility in the mobile phase and mobile phase selectivity as important parameters in the chromatographic process; parameters which are also important in HPLC but are mostly nonexistent in GC.

With currently available technology, SFC with both packed and capillary (open tubular) columns is possible and is being used. Essentially, the choice of either packed or open tubular column is based on the ultimate complexity of the sample to be chromatographed. Because of the open column, longer column lengths can be used with capillary columns and higher total separation efficiencies are obtainable than with packed columns. On the other hand, packed columns are more attractive for shortening the analysis times of fairly simple mixtures (as compared to HPLC) and for higher sample capacities. It is far beyond the scope of this work to present an in-depth discussion of supercritical fluid chromatography or the advantages and disadvantages of packed and capillary columns. Several recent articles are available which review these topics [308-310]. For the sake of continuity, a brief description of the important parameters in SFC is included below.

A supercritical fluid is a gas which has been heated to a temperature above its critical temperature (meaning the fluid cannot be liquefied, no matter how high the pressure)

while being compressed by a pressure above its critical pressure (meaning the fluid cannot exist in the gaseous state, no matter how high the temperature). Under these conditions the gas is converted to a dense fluid with a single phase which possesses solvent properties that are different from either the gaseous or liquid phases. The unique properties of this supercritical fluid are what give it its intermediate position between gases and liquids as mobile phases in chromatography. Representative values for the most important of these properties are summarized in Table 12.

The main parameters controlling solute retention in GC and HPLC are the column temperature and mobile phase composition, respectively. The chromatographic techniques employed for maximizing solute resolution in the shortest time which are based on these parameters are temperature programming (GC) and gradient elution (HPLC) although temperature programming has recently been shown to be advantageous with microbore liquid chromatographic columns [311]. The analogous controlling parameter in SFC is generally the density of the mobile phase, although temperature has also been shown to play a significant role in certain circumstances [312]. As a result, the programming mode applicable to SFC is density programming which can be accomplished by

Table 12. Comparison of gaseous, supercritical, and liquid mobile phases.

	GC	SFC	HPLC
Diffusion coefficient (cm^2/sec)	10^{-1}	10^{-4}	10^{-5}
Density (g/cc)	.001	0.8	1
Viscosity (g/cm-sec)	10^{-4}	$5x10^{-4}$	10^{-2}

either programming the pressure upwards, the temperature downwards, or a combination of the two.

Table 13 lists the properties of several commonly used supercritical fluid mobile phases. Of these, carbon dioxide (CO_2) is very popular due to its many practical advantages, including a near ambient critical temperature, minimal interference with a variety of detectors, and its nontoxic and nonflammable nature. By programming the pressure up to 340 atm (5000 psi), densities of 0.95 g/cc are obtained (temperature = 35°C) resulting in excellent mobile phase solvating properties.

For reasons of instrument design and hazard considerations, CO_2 and pentane are the most widely used SFC mobile phases. Since neither of these fluids is very selective, there is a strong need for developing alternative stationary phases to maximize the differential solubility between the stationary and mobile phases. As these mobile phases are both essentially nonpolar, the availability of immobilized stationary phases with different selectivities (i.e.: different from the nonpolar methyl polysiloxanes) that can withstand the increased solvent strength of the supercritical mobile phases is vital to the widespread acceptance of SFC.

Table 13. Physical properties of common supercritical fluid mobile phases.

	Normal boiling point (°C)	Critical point data		
		T_c(°C)	P_c(atm)	d_c(g/cc)
n-pentane	36.3	196.6	33.3	0.232
carbon dioxide	-78.5*	31.3	72.9	0.448
nitrous oxide	-89.0	36.5	71.4	0.457

*sublimation point

Experimental

Materials and Reagents

Fused silica capillary tubing (0.25 mm and 0.10 mm ID) was obtained from Polymicro Technologies, Inc. (Phoenix, AZ, U.S.A.). Silane and siloxane starting materials were dimethyldichlorosilane, diphenyldichlorosilane, methylvinyldichlorosilane, trimethylchlorosilane, octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane (Ph_4), tetramethyltetravinylcyclotetrasiloxane, 1,3-divinyltetramethyldisiloxane from Petrarch Systems, Inc. (Bristol, PA, U.S.A.), and tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane from Silar Laboratories, Inc. (Scotia, NY, U.S.A.). Tetramethylammonium hydroxide (TMAH, 20% in methanol) from Sigma Chemical Co. (St. Louis, MO, U.S.A.) was used as polymerization catalyst. The stationary phase, OV-1701, was obtained from American Scientific Products (Columbia, MD, U.S.A.). Azo-tert-butane (ATB) from Fairfield Chemical Co. (Blythewood, SC, U.S.A.), dicumyl peroxide (DCP) from Pfaltz & Bauer, Inc. (Waterbury, CT, U.S.A.), and azobisisobutyronitrile (AIBN) from Dynamics Corp. (S. Plainfield, NJ, U.S.A.) were used as cross-linking initiators.

Polysiloxane Synthesis

Chlorosilane Procedure. (25% phenyl, 1% vinyl, methyl polysiloxane). A mixture of 4.71 g dimethyldichlorosilane, 3.17 g diphenyldichlorosilane, and 0.15 g methylvinyldichlorosilane was added to 6 ml acetonitrile to which 6 ml water was then added. The siloxane oligomers formed were extracted with 6 ml methylene chloride and washed with successive 10 ml aliquots of water until the water layer was neutral to litmus. The methylene chloride layer was transferred to a 3-neck, 100 ml round bottom flask and the solvent removed at 37°C under nitrogen flow. TMAH (500 ppm) was added and the flask placed in an oil bath at 100°C with the contents stirred under argon for 2 hours. The temperature was raised to 150°C and held 3 hours (still under argon) to destroy the catalyst. After cooling, 3 ml methylene chloride and 500 ul TMCS were added and stirred for 1 hour to affect endcapping. Low molecular weight material was removed by dissolving the polymer in methylene chloride and adding an equal volume of methanol, causing higher molecular weight material to precipitate. This fractionation was repeated several times, after which the polymer was dried under vacuum at room temperature.

Cyclic Siloxane Procedure. (25% phenyl, 1% vinyl, methyl polysiloxane). A mixture of 5.76 g Ph_4, 5.29 g D_4,

and 0.19 g tetramethyltetravinylcyclotetrasiloxane was added to 10 ml toluene in the 3-neck reaction flask. TMAH (500 ppm) was added and the flask contents stirred at 100°C under argon for 24 hours. Destruction of catalyst, endcapping, fractionation, and drying were the same as described for the chlorosilane procedure.

Modified Cyclic Procedure.

A. (60% phenyl, 1% vinyl, methyl polysiloxane)

A mixture of 7.99 g Ph_4, 1.88 g D_4, and 0.13 g tetramethyltetravinylcyclotetrasiloxane was added to 10 ml toluene in the reaction flask. To this mixture, 100 ppm TMAH and 0.037 g 1,3-divinyltetramethyldisiloxane were added and the mixture stirred for 12 hours under argon at 100°C.

B. (7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane)

A mixture of 1.79 g tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane, 1.57 g Ph_4, 6.45 g D_4, and 0.19 g tetramethyltetravinylcyclotetrasiloxane was added to the reaction flask along with 100 ppm TMAH and 0.037 g 1,3-divinyltetramethyldisiloxane and stirred at 100°C for 12 hours under argon. After 12 hours at 100°C, both A and B were heated to 150°C and held 3 hours to destroy the catalyst. Fractionation and drying were the same as for the chlorosilane procedure.

The reaction flask was cleaned prior to each use by filling with methylene chloride and stirring for 1 hour and then rinsing with several aliquots of methanol, followed by several aliquots of dilute (10%) hydrofluoric acid. The flask was then flushed with large quantities of water, rinsed with acetone and dried at 110°C for 1 hour.

Stationary Phase Characterization

Gel Permeation Chromatography (GPC). GPC was carried out on two columns connected in series. Both columns were 25 cm x 7 mm ID packed with 10 micron LiChrogel (polystyrene/divinylbenzene copolymer) particles. The first column (PS-400) and the second column (PS-1) had exclusion limits of about 400,000 and 1,000, respectively and were donated for this study by E. M. Science (Gibbstown, NJ, U.S.A.). The mobile phase was HPLC grade methylene chloride from J. T. Baker Chemical Co. (Phillipsburg, NJ, U.S.A.) and was pumped at 1.0 ml/min with a MACS 100 (E. M. Science) reciprocating piston pump. Dual detection was accomplished with a Varian UV detector, Model 5000, at 254 nm and a Waters differential refractive index detector, Model R401, connected in series. The UV detector response was monitored with a Hewlett-Packard Model 3390A digital electronic integrator while the RI trace was recorded on a strip chart

recorder. Since all polysiloxanes used contained phenyl groups, the UV response was used to quantitate molecular weight distributions. The column oven on a Varian Model 5020 HPLC was used for thermostating the columns at 30°C.

Molecular weight calibration was performed with polystyrene standards (Waters Associates, Milford, MA, U.S.A.) in the range of 600 to 233,000. Standards and samples were prepared at a concentration of 2% in methylene chloride and filtered through Millex-SR 0.5 um filter units (Millipore Corp., Bedford, MA, U.S.A.). Injection volume was 100 ul.

Spectrometric Analyses. IR spectra were recorded on a Perkin Elmer Model 710B spectrophotometer by pressing a thin film of each polymer between two sodium chloride plates and scanning from 4000 to 600 cm^{-1}.

NMR spectra were recorded on a Bruker WP-270 SY MHz spectrometer. Solutions for ^{1}H NMR were 10% in deuterated chloroform from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.). Solutions for ^{29}Si NMR were 20-25% in deuterated chloroform with 0.02 g/ml chromium acetylacetonate added as a relaxing agent. Tetramethylsilane (TMS) was added to solutions for the ^{29}Si NMR as an internal standard. Instrument conditions used for the recording of NMR spectra are listed in Table 14.

Table 14. NMR spectrometer conditions.

	^{1}H	^{29}Si
Number of scans	10	1100
Line broadening	none	2.0
"01" (middle of window)	4416 Hz	-5000 Hz
Sweep width	4000 Hz	16129 Hz
Pulse width	4.0 us	6.5 us
Spectrometer frequency	270 MHz	53.671 MHz
Sample spinner	18 Hz	18 Hz

Differential Scanning Calorimetry (DSC). Glass transition temperatures of the polysiloxanes were obtained from DSC using a Perkin Elmer DSC-4 differential scanning calorimeter. Samples were approximately 20 mg each and were scanned at 20°C/min in a helium atmosphere.

Fused Silica Column Preparation

All columns (both the 0.25 mm and the 0.10 mm ID) were coated with film thicknesses of 0.25 um of the stationary phase on an untreated surface as described in the previous chapter.

Preliminary testing of the cross-linking of the 25% phenyl, 1% vinyl, methyl polysiloxane (from cyclics) with DCP and AIBN was done in vial tests in the following way. Small glass vials were cleaned, dried, and accurately weighed to ±0.0005 g. Solutions of stationary phase in methylene chloride were doped with various levels of each initiator by addition from toluene solution. Five hundred microliters of each solution (phase concentration of 20 mg/ml) was pipetted into each glass vial and the solvent removed from the vials under reduced pressure at room temperature. All vials containing the same cross-linking initiator were grouped together in specially made metal containers that could be purged with an inert gas (nitrogen) during

curing. The vials containing DCP were heated in an oven from 40° to 160°C at 10°C/min and held 60 min, then programmed at 10°C/min to 180°C and held an additional 60 min. Vials containing AIBN were programmed from 40° to 80°C at 10°C/min and held 3 hours. After cooling, each vial was again carefully weighed to determine the amount of phase in each vial. Next, 1 ml of methylene chloride was pipetted into each vial and allowed to stand undisturbed for 1 hour, after which time the methylene chloride was carefully poured out and the vials were redried in a vacuum oven at room temperature and then reweighed. The percentage of phase extracted was calculated from:

$$\% \text{ washout} = \frac{\text{original wt. - wt. after washout}}{\text{original wt.}} (100) \qquad (1)$$

Conditions giving rise to successful cross-linking in the vials were used to cross-link some of the coated columns while others were cross-linked with ATB as described in the previous chapter. The success of cross-linking in the columns was evaluated by reduction in the capacity factor (k) of n-dodecane at 100°C after extraction with methylene chloride and supercritical CO_2.

Stationary Phase Polarity Determination

The polarity of the synthesized phases was determined by measuring the retention index (R.I.) for each of the first five members of the McReynolds' series (benzene, 1-butanol, 2-pentanone, nitropropane, and pyridine) according to the formula:

$$\text{R. I. of B} = (100)\frac{\text{Log[B-Z]/[A-Z]}}{\text{Log[C-Z]/[A-Z]}} + (100 \times \text{C\# of A}) \qquad (2)$$

where A, B, and C represent the retention times of the lower hydrocarbon, the component of interest, and the higher hydrocarbon, respectively, and Z is the gas holdup time (i.e.: retention time of methane). Retention data were obtained with the columns held isothermally at 50°C.

The McReynolds' constants "b" and "r" were calculated from the following relationships:

$$b = \frac{t_{r(\text{dodecane})} - t_{r(\text{decane})}}{200} \qquad (3)$$

$$r = \left[\frac{t_{r(\text{dodecane})}}{t_{r(\text{decane})}}\right]^{1/2} \qquad (4)$$

Retention data for these calculations were obtained isothermally at both 75° and 100°C.

Gas Chromatography

Column evaluations were performed on a Hewlett-Packard Model 5890A gas chromatograph with split injection (ratio 200:1) and flame ionization detection. Helium was used as carrier gas at an average linear gas velocity of 33 cm/sec (measured at 50°C). Peak retention times were measured to one one-thousandth of a minute with a Hewlett-Packard Model 3390A digital electronic integrator.

Supercritical Fluid Chromatography (SFC)

The instrumentation for SFC consisted of an ISCO Micro LC500 syringe pump (operated in constant pressure mode) with CO_2 as the mobile phase. A Perkin Elmer Sigma 2000 gas chromatograph was used for thermostating the column and also for flame ionization detection. The injector consisted of a Rheodyne sample valve with a 0.5 ul internal sample loop. An SFC splitter from Scientific Glass Engineering (Melbourne, Australia) was inserted between the sample valve and the column with a split ratio set at about 30:1. Pressure restriction between the column and the FID was accomplished by connecting a 2 cm x 0.005 mm ID piece of fused silica to

the column end. Chromatographic data was simultaneously processed with a Perkin Elmer LCI-100 Laboratory Computing Integrator and stored on floppy disks using a Perkin Elmer Model 3600 Data Station. Stored chromatograms were replotted on a Hewlett-Packard Model 7225A Graphics Plotter.

Results and Discussion

Bases that catalyze the polymerization of cyclic siloxanes include hydroxides, alcoholates, phenolates, and siloxanolates of the alkali metals; the siloxanolates and fluorides of quarternary ammonium and phosphonium bases; and organoalkali metal compounds. It is believed that all catalysts form the siloxanolate anion in situ [303]. After polymerization is complete, the activity of the catalyst must be destroyed so as to produce a heat-stable polymer. Tetramethylammonium hydroxide was chosen as the polymerization catalyst because of the ease of catalyst deactivation. TMAH is considered to be a "transient catalyst" since at temperatures above 120°C it decomposes to form trimethylamine and methanol. The amine decomposition product does not catalyze polymerization and is easily removed from the polymer because of its volatility.

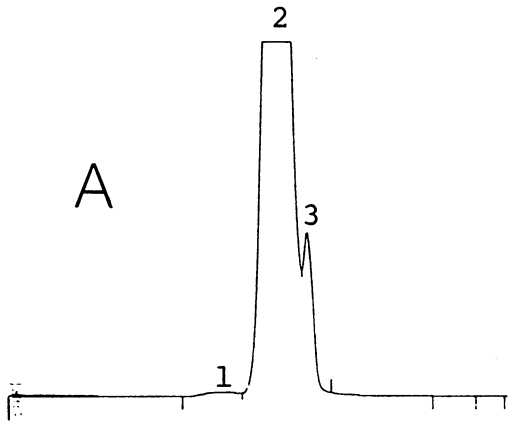
Following the synthesis of each polymer, the success of each fractionation step was monitored by GPC to determine

the number of fractionations necessary to remove the majority of lower molecular weight materials (linears and cyclics). The removal of the lower molecular weight fractions is often the most significant difference between stationary phases sold for general use and those sold specifically for capillary use. Table 15 shows a comparison of average molecular weights for three commercial polysiloxanes and those synthesized in this study. OV-17 showed only 91% of a very low molecular weight fraction. This combined with the inability to effectively cross-link this material are the primary factors that preclude its use for coating capillary columns. The molecular weight profile of OV-1701 by GPC shows a bimodal distribution with a small portion (23%) of the mixture being a very high molecular weight gum. However, the majority of the OV-1701 phase (69%) is of only moderate molecular weight (62,000). The chromatographic performance of OV-1701 in terms of thermal stability could undoubtedly be improved by narrowing the molecular weight distribution. The OV-73 stationary phase (used in the previous chapter) showed a very high molecular weight (gum) with good purity (97%). Gel permeation chromatograms along with reports for each of these are shown in Figure 27.

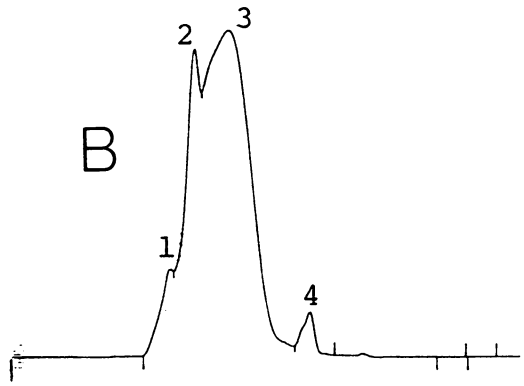
The polysiloxanes that were synthesized here were subjected to methylene chloride/methanol fractionations until

Table 15. Average molecular weights for polysiloxanes determined by GPC.

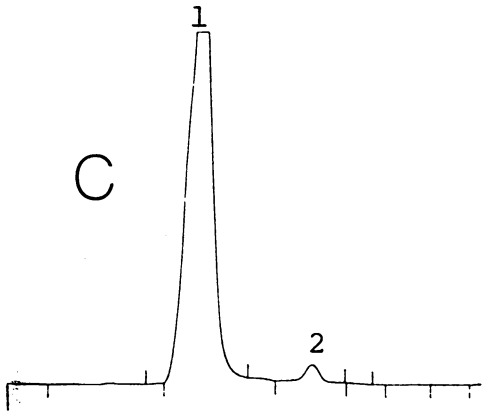
	PHASE	M_n	PURITY
	OV-73	>1,000,000	97%
	OV-17	3,100	91%
	OV-1701 (bimodal)	>1,000,000	23%
		62,200	69%
(A)	25% phenyl/1% vinyl methyl polysiloxane (from dichlorosilanes)	7,000	97%
(B)	35% phenyl/1% vinyl methyl polysiloxane (from cyclics)	14,100	97%
(C)	60% phenyl/1% vinyl methyl polysiloxane (from cyclics)	29,000	99%
(D)	7% cyanoethyl/7% phenyl/1% vinyl methyl polysiloxane (from cyclics)	217,900	99%



	%
1	0.5
2	91.2
3	8.3



	%
1	5.3
2	23.1
3	68.9
4	2.7



	%
1	97.5
2	2.5

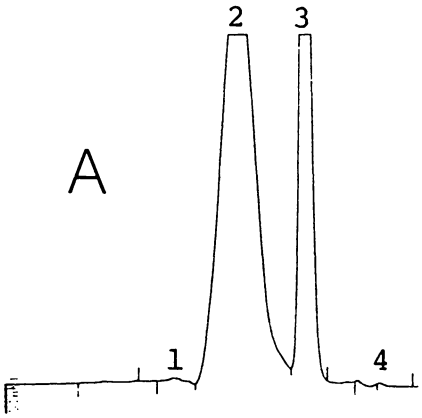
Figure 27: Gel permeation chromatograms of commercial polysiloxanes. (A) OV-17, (B) OV-1701, and (C) OV-73.

the desired purity level was obtained. In general, 4 to 5 fractionations were necessary to obtain greater than 97% purity of the desired molecular weight fraction.

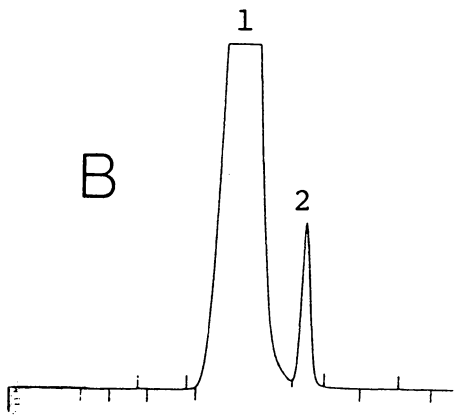
Figure 28 shows three chromatograms illustrating the affect of the methanol precipitations on siloxane C from Table 15. Chromatogram A is of the reaction mixture after the decomposition of the catalyst at 150°C for 3 hours. The higher molecular weight material of interest constitutes only 61% of the mixture. Chromatogram B was run after the second methylene chloride/methanol fractionation. The percentage of the desired fraction is now about 93%. Five fractionations resulted in the composition represented in chromatogram C, with the desired fraction over 99% of the total sample.

Figure 29 shows chromatograms illustrating the same process with siloxane D from Table 15. Chromatogram A is the reaction mixture after catalyst destruction showing about 82% of the higher molecular weight fraction. Chromatogram B was obtained after the first methanol precipitation (90%) and chromatogram C after the fourth and final fractionation (99%).

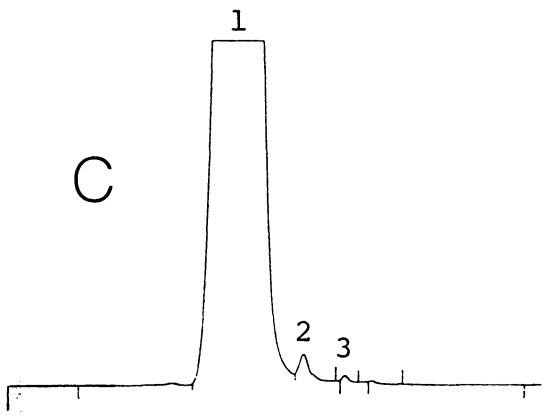
One major difference in the synthesis procedures between siloxanes A, B, and C, D is that the procedures for siloxanes A and B used TMCS as the end-blocker while the



	%
1	0.4
2	60.9
3	38.6
4	0.1

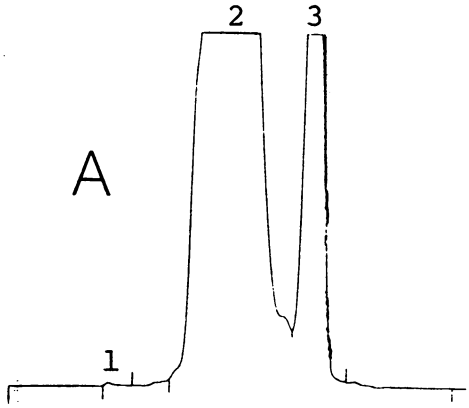


	%
1	93.1
2	6.9

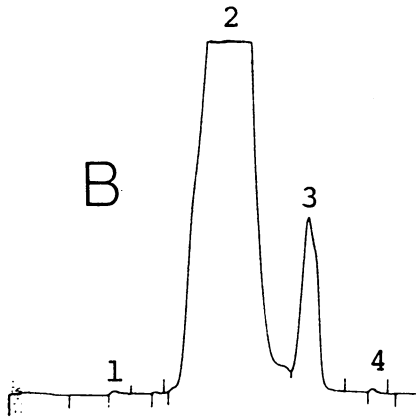


	%
1	99.4
2	0.5
3	0.1

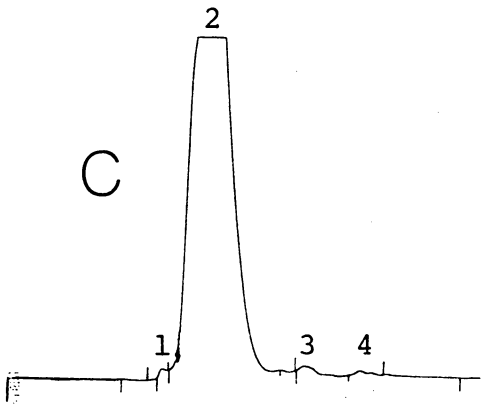
Figure 28: Gel permeation chromatograms of 60% phenyl, 1% vinyl, methyl polysiloxane. (A) reaction mix, (B) after second fractionation, and (C) after fifth and final fractionation.



	%
1	0.1
2	81.5
3	18.4



	%
1	0.1
2	90.3
3	9.5
4	0.1



	%
1	0.1
2	98.9
3	0.6
4	0.4

Figure 29: Gel permeation chromatograms of 7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane. (A) reaction mix, (B) after first fractionation, and (C) after fourth and final fractionation.

procedures for siloxanes C and D used 1,3-divinyltetramethyldisiloxane as the end-blocker. The TMCS was added to the mixture at the end of the procedure to replace the active chain ends with trimethylsilyl groups. Such an endcapping procedure will also add trace quantities of HCl to the reaction mixture from the silylation reaction. With one of the primary reasons for utilizing cyclic starting materials being the elimination of HCl in the procedure, an alternate procedure for endcapping was desired. As a result, the molecular weight of the last two entries in Table 15 was controlled by the use of a disiloxane as end-blocker added to the starting materials before polymerization. In addition to eliminating the formation of HCl, this procedure also simplifies the synthesis process and maximizes the reproducibility of the end-blocking step. The ratio of amount of end-blocker to starting material used governs the equilibrium molecular weight of the final polymer. In the procedures used here, a disiloxane with a vinyl group on each end was used to aid in the cross-linking of the final polymer inside the columns.

The compositions of the synthesized materials were determined by integration of the ^{1}H NMR spectra and the results summarized in Table 16. Good agreement was found between the NMR integrations and the mole % charged for each

Table 16. Compositions of polysiloxanes from ^{1}H NMR integration.

PHASE	METHYL	PHENYL	VINYL	CYANO
A	73%	26%	1%	--
B	64%	35%	1%	--
C	44%	55%	1%	--
D	83%	8%	1%	8%
OV-1701	86%	7%	--	7%

polymer except for the 25% phenyl polysiloxane obtained from cyclics which appears to be 10% higher in phenyl content than expected. This is attributed to ineffective stirring during polymerization which did not allow full reaction of the starting materials. Since no end-blocker was added to the starting materials, the reaction mix became very viscous in a short period of time. Another significant advantage then, of adding the disiloxane endcapper to the starting materials is that there is a significant reduction in the viscosity early in the reaction which allows for more complete mixing of the starting materials and also allows the proper equilibrium composition to be reached. Since the rate of polymerization of the phenyl cyclic is greater than that of the methyl cyclic [303], the incomplete mixing is capable of resulting in the higher phenyl content.

Another potential problem with the use of mixtures of cyclic siloxanes is also related to the fact that the rate of anionic polymerization will differ for the different cyclic siloxanes. It is known [303] that cyclics with vinyl and phenyl substituents will begin polymerization before the D_4 (assuming all are in solution). Because of these rate differences, copolymerization of two or more different cyclics will often yield a random copolymer only after extended periods of equilibration. Alternatively, a copo-

lymer can be made by polymerizing a co-cyclic; however, such co-cyclics are often difficult to make. Recently [120], this approach has been used to prepare polysiloxanes containing substantial cyano substitution. These same authors [120] have claimed that "a more homogeneous polymer can be obtained from mixed substitution along the units in the cyclic siloxane." This should not be the case if the reaction mixture utilizing homo-cyclics is allowed to reach equilibrium since all siloxane bonds in the structure are equally as vulnerable to attack by the active chain ends. However, the main questions now become how long this equilibration will require and how to go about determining sequencing in the polymer chain.

Determination of the sequencing in a siloxane polymer is a topic that has not received much attention in the literature. The problem has been approached here from two directions. The first involved the determination of the glass transition temperature (T_g) of the polymer and the second relied on the signal splitting in the ^{29}Si NMR spectrum of each polysiloxane.

The presence of two glass transition temperatures has been attributed to the presence of two types of blocky structures in copolymers containing acrylonitrile and butadiene units [313] and also in polysulfone systems by Ward et

al. [314]. By analogy, if the polysiloxane materials synthesized here from cyclic starting materials contained significant blocky regions of dimethyl and diphenyl siloxanes, one might expect there to be two T_g's; one representative of the dimethyl blocks and the other representative of the diphenyl blocks. T_g determination by DSC for all polysiloxanes synthesized showed only one well defined transition in the subambient temperature region. These transition temperatures are summarized in Table 17 with the DSC traces of OV-1701 and siloxane D reproduced in Figure 30. The glass transition temperatures for these two materials are indistinguishable. The T_g for siloxane C was very high (-8°C) which is undoubtedly the reason for the poor chromatographic performance of this phase noted at temperatures from 40° to 150°C.

The existence of a single glass transition, however, is not to be construed as meaning the sequencing in the polymer is not blocky. Therefore, a more critical test of sequencing was employed. ^{29}Si NMR has been shown to offer valuable information on the framework of silicones by observing the signal splittings in the spectra of methyl-phenyl siloxane copolymers [315,316]. These authors were the first to assign the signal splittings of monomer sequences up to the pentad level. However, the equations derived are only valid

Table 17. Glass transition temperatures of polysiloxanes obtained from DSC.

PHASE	T_g (°C)
A	-63
B	-52
C	- 8
D	-91
OV-1701	-94

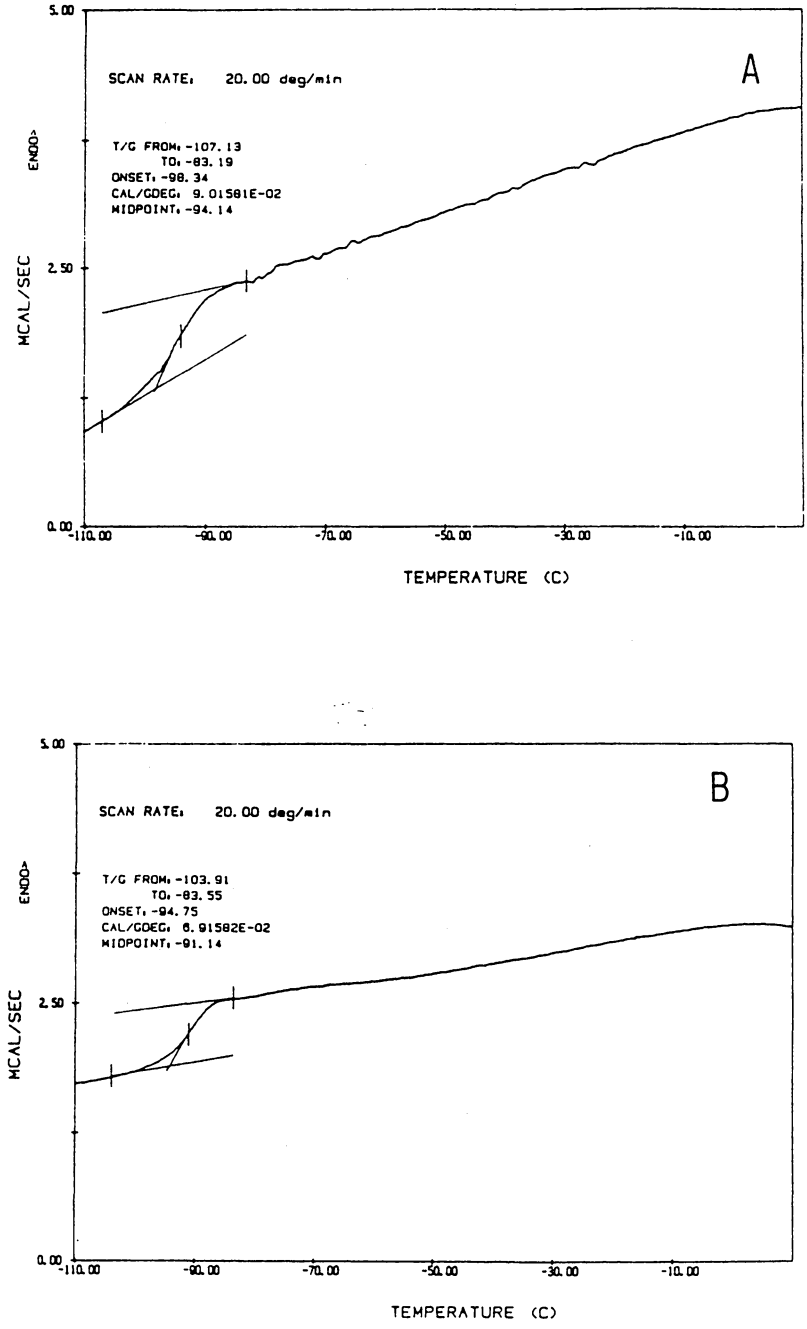


Figure 30: DSC traces for two cyano containing polysiloxanes. (A) 7% cyanopropyl, 7% phenyl, methyl polysiloxane (OV-1701) and (B) 7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane.

for a 50/50 ratio of methyl and phenyl groups. Using the same concepts, another series of equations has been derived by Brandt et al. [317] which is valid for siloxane copolymers with other than a 50/50 ratio of methyl and phenyl groups. ^{29}Si NMR spectra were obtained for the three methyl-phenyl polysiloxanes (one from dichloro, A, and two from cyclic starting materials, B and C). Analysis of the splitting patterns shows that for all three siloxanes there is a tendency for a statistical distribution of methyl and phenyl groups, i.e.: there is no evidence of blocky structures in either of the materials synthesized from the cyclic siloxanes. The spectrum of siloxane B is shown in Figure 31. The silicon-dimethyl region is -19 to -23 ppm and the silicon-diphenyl region is -46 to -50 ppm.

The conclusion to be drawn from these results is that the necessary time needed for randomization is on the order of hours, with 12 to 24 hours being adequate. This is in agreement with work done by McGrath and coworkers on methyl-phenyl siloxanes that shows a tendency for blocky structures to exist with reaction times less than 6 hours but not existing after equilibration for more than 6 hours [318].

The ability for these phases to be cross-linked was evaluated in several ways. For siloxane B, a preliminary

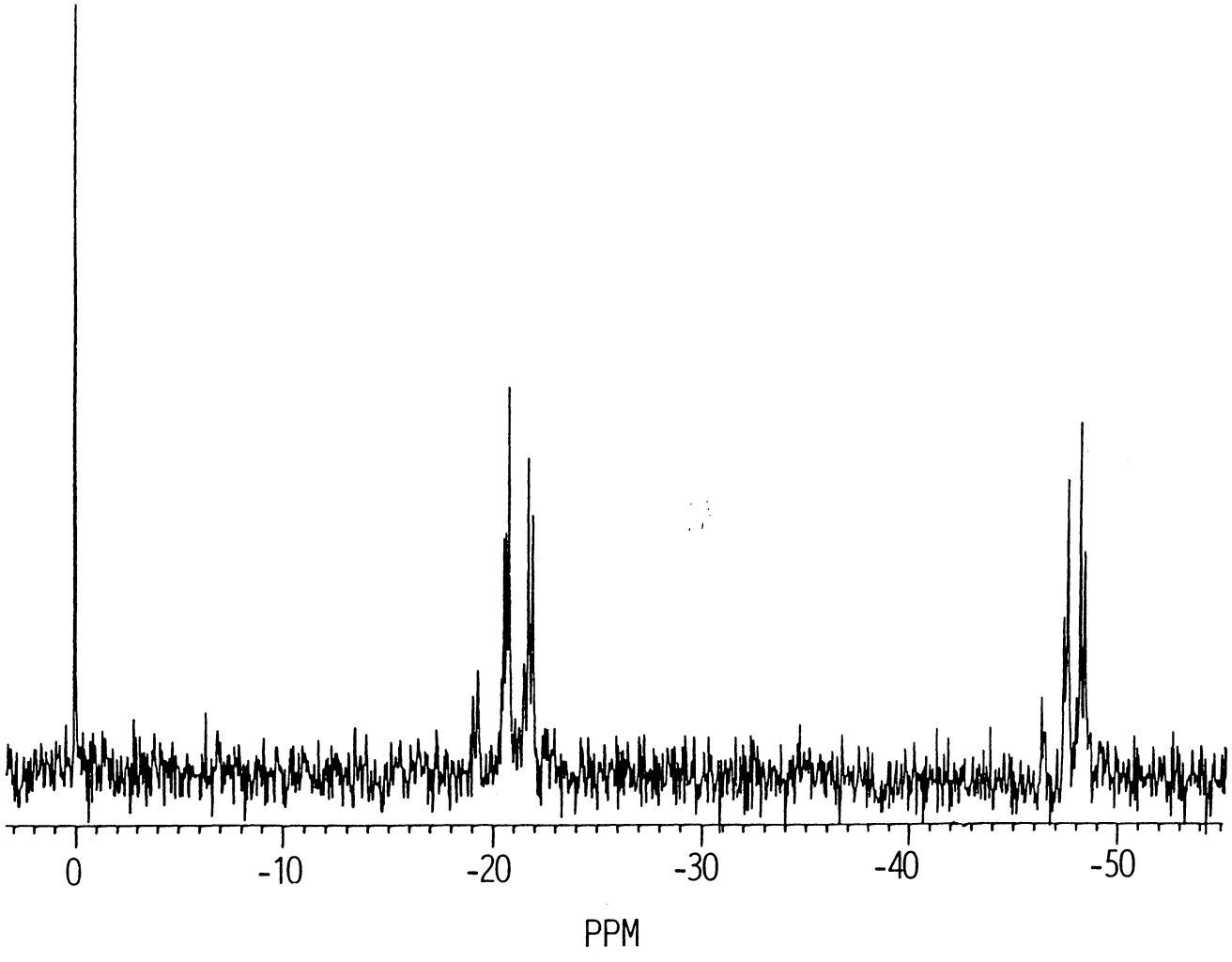


Figure 31: ^{29}Si NMR spectrum of 35% phenyl, 1% vinyl, methyl polysiloxane.

series of vial tests were performed to assess the degree of cross-linking obtainable by DCP and AIBN. The results of these tests are summarized in Table 18. AIBN was of interest since it: is known for its ease of generation of free radicals, has a low decomposition temperature ($t_{1/2}$ = 1.3 hours at 80°C), generates relatively inert decomposition products, has a low vapor pressure (can be doped into the phase solution prior to coating), and is readily available commercially. AIBN was used for cross-linking a 5% phenyl methyl polysiloxane by Wright et al. [288] but its use was discontinued due to a discoloration of the polymer. This could well be attributed to the procedure used in that the curing was done in an air atmosphere at 150°C and the possible oxidation of the cyano groups of the initiator. Later work done by the same group reported the inability to cross-link similar phases under more controlled conditions [239]. Other workers [319] reported successful siloxane immobilization with AIBN when added at relatively high levels (10% by weight). In the work presented here, AIBN could not be used to initiate cross-linking of the 35% phenyl containing polysiloxane even when added to the phase at a 15% level. On the other hand, only 0.5% DCP was needed to render the same polysiloxane insoluble.

Table 18. Results of cross-linking siloxane B in vial tests with DCP and AIBN.

% DCP added	% washout	% AIBN added	% washout
0	85	0	88
0.5	6	1	91
1	6	5	92
5	6	10	90
		15	89

One observation was made during the course of the vial tests which probably accounts for this difference. After adding the phase and AIBN to the vials and removing the solvent, a faintly visible, semicrystalline ring was noted on the glass vial at the level the liquid had previously occupied. This could be attributable to the limited solubility of AIBN in the polysiloxane solution. If the initiator were not evenly distributed in the polymer film during curing, there would be an ineffective degree of cross-linking. Due to the polarity of the nitrile group in the initiator and the polarity of the phenyl containing siloxanes, this precipitation would be expected to occur more readily, however, with the 5% phenyl containing phase reported earlier than with the 35% phenyl containing phase synthesized here. Nevertheless, as a result, AIBN was ruled out as a suitable cross-linking initiator. Results of cross-linking experiments with OV-73 and DCP by the vial tests are given in Table 19 for comparison.

The ability for 0.5% DCP to effectively cross-link siloxane B was confirmed in coated columns with no appreciable phase loss occurring (less than 5%) after rinsing with methylene chloride and supercritical CO_2 (density of 0.3 g/cc). Successful cross-linking of this phase and siloxane A was also accomplished by using ATB with an average of 2%

Table 19. Results of cross-linking OV-73 in vial tests with DCP.

% DCP added	% washout
0	88
0.5	87
1	8
3	0
5	0

phase loss after rinsing coated columns with 12 column volumes of methylene chloride.

The remaining phases synthesized and OV-1701 were subjected to cross-linking with ATB. Siloxane C averaged 2% phase loss and siloxane D and OV-1701 each averaged 3% phase loss when coated in 0.25 mm ID columns, cross-linked, rinsed with 12 column volumes of methylene chloride and conditioned for 10 hours at 275°C. Siloxane D coated in a 0.10 mm ID column and subjected to the same conditions showed no phase loss after methylene chloride washing or after extensive use with supercritical CO_2 as the mobile phase (over 50 hours with densities ranging from 0.3 to 0.9 g/cc). A supercritical fluid chromatogram of free fatty acids obtained from the saponification and acidification of coconut oil on the 10 m x 0.10 mm ID column coated with siloxane D is shown in Figure 32.

The most commonly used method for characterizing the polarity of stationary phases in gas chromatography is the calculation of Kovats' retention indices for the first five probes of the McReynolds' series [320] and reporting the sum of these indices. This was done for each of the phases synthesized here and also for OV-1701 and the results are tabulated in Table 20. The listed retention index for each compound is the average of 3 injections at 50°C. All columns

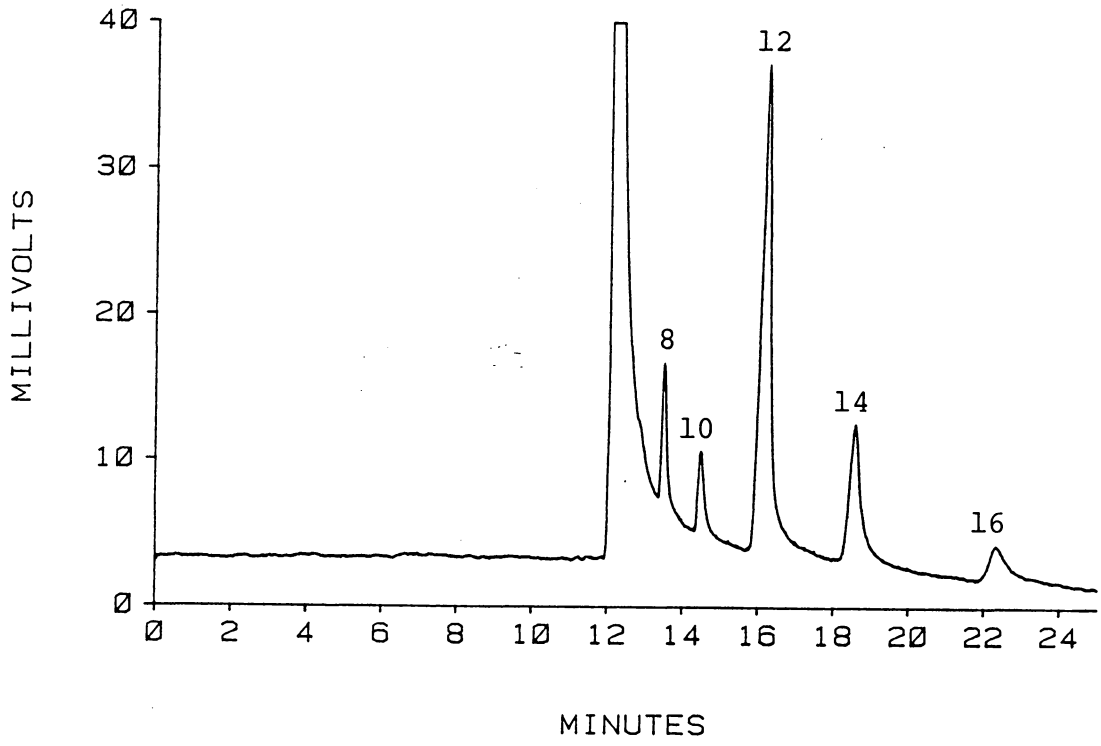


Figure 32: Supercritical fluid chromatogram of free fatty acids from coconut oil. Conditions: Column - 10m x 0.10 mm ID fused silica coated with 0.25 um film thickness of siloxane D. CO_2 mobile phase, isothermal at 100°C and isobaric at 2000 psi (density of 0.3 g/cc), Split ratio 30:1, flame ionization detection. Peaks identified by alkyl chain length (all are saturated).

Table 20. Retention indices of polysiloxanes.

PROBE	SILOXANE A	SILOXANE B	SILOXANE D	OV-1701
Benzene	723.6	747.8	712.7	700.0
1-Butanol	728.2	746.0	773.6	763.3
2-Pentanone	764.1	785.5	775.2	763.3
Nitropropane	841.3	871.4	870.4	851.8
Pyridine	886.2	920.6	847.9	828.3
$\Sigma(I)$	3943.4	4071.3	3979.8	3906.7

were 10 m x 0.25 mm ID coated with 0.25 um film thicknesses on untreated fused silica and cross-linked with ATB. For interpreting polarity from the index values, the higher the number, the greater the retention for the particular analyte. The higher overall phase polarity is indicated by a higher sum of all five retention indices. As is seen from the table, siloxane D is more polar than OV-1701 which is expected due to the higher CN/CH_3 ratio in siloxane D (cyanoethyl vs. cyanopropyl). Additional information for comparing these two phases is given by the McReynolds' constants "b" and "r". These constants obtained for both phases at 75° and 100°C are listed in Table 21. A comparison of "b" and "r" values indicates the preferred phase for separation of the members in a homologous series of compounds. Accordingly, OV-1701 would be expected to give slightly improved separations for any series of homologous compounds due to the higher "b" and "r" values. This is also expected due to the higher CH_3/CN ratio for OV-1701.

The increased polarity of siloxane B over siloxane A is due to the greater amount of phenyl substitution for B as was shown in Table 16.

A comparison of the thermal stability of siloxane D and OV-1701 is illustrated by the curves in Figure 33. After coating each with a 0.25 um film thickness on 10 m x 0.25 mm

Table 21. McReynolds' constants "b" and "r" for two cyano-containing polysiloxanes.

	siloxane D		OV-1701	
	75°C	100°C	75°C	100°C
"b"	0.0293	0.0088	0.0333	0.0100
"r"	1.93	1.57	1.94	1.60

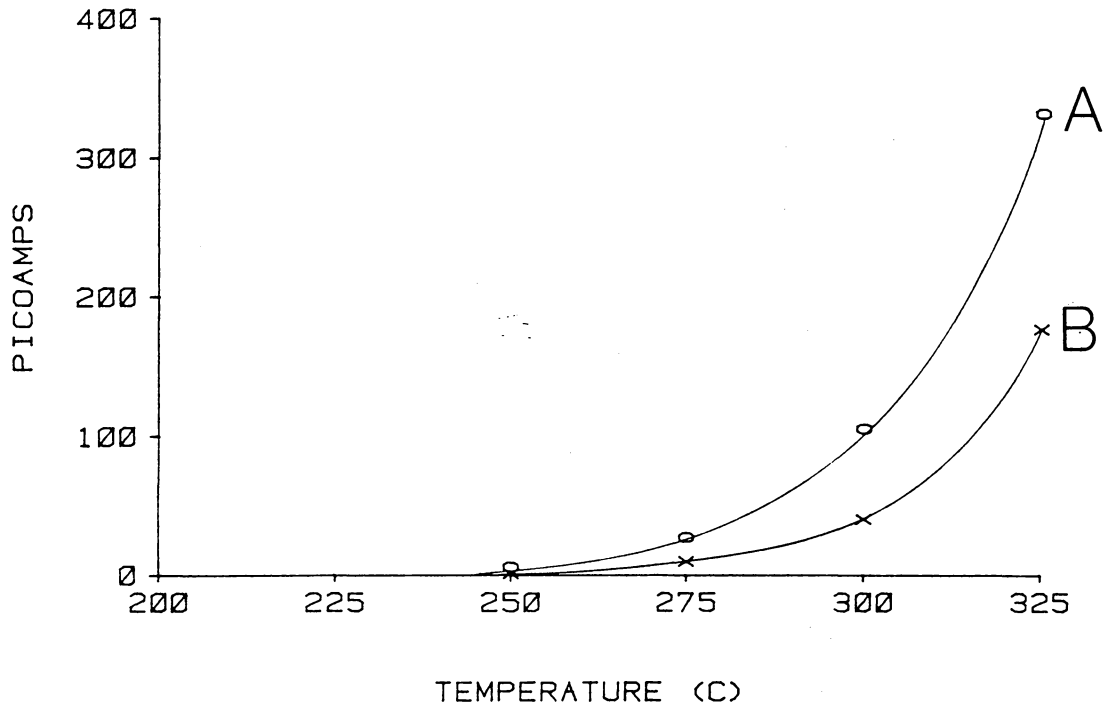


Figure 33: Comparison of thermostability for two cyano containing polysiloxanes. (A) 7% cyanopropyl, 7% phenyl, methyl polysiloxane (OV-1701) and (B) 7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane.

ID untreated fused silica, cross-linking with ATB, rinsing with 12 column volumes of methylene chloride, and conditioning at 275°C for 10 hours, each column was programmed 4 times from 175° to 325°C at 5°C/min with an average linear carrier gas (H_2) velocity of 50 cm/sec (measured at 100°C). In each case the final chromatographic run was used for comparison. As is evident, siloxane D has a higher degree of thermal stability than the commercial OV-1701. This difference should be due to the differences in molecular weight distributions noted in Table 15.

Conclusions

Polysiloxane synthesis using mixtures of commercially available cyclic siloxanes was found to be a viable alternative to the use of dichlorosilanes in the production of intermediate polarity stationary phases containing cyanoethyl and phenyl groups. The main advantages of this type of procedure are: no HCl is encountered during any step of the synthesis which eliminates deleterious affects on the phase and simplifies the procedure, and the addition of a disiloxane endcapper to the starting materials allows simpler and better molecular weight control of the final polysiloxane while eliminating trace HCl that would be introduced via chlorosilane endcapping and also keeping the

reaction mixture viscosity to a minimum. A new liquid phase, 7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane was synthesized and shown to be more polar than OV-1701 with higher temperature stability, easily cross-linked and suitable for use in supercritical fluid chromatography.

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APPENDIX A

Zisman Plot Data (methanol/water mixtures)

	cos θ									
	% methanol	100	90	75	70	60	50	25	20	10	0
surface # (Table 9)	surface tension (dynes/cm)	22.1	24.9	28.3	29.7	32.6	34.9	45.8	51.6	58.5	72.0
1									.979	.900	.814
1								.937		.815	.644
2									.932	.919	.800
3									.950	.910	.796
6		.886	.713	.469							
8		.982	.962	.922							
9		.945	.759	.498							
10		.930	.781	.602							
11			.989	.861	.810						
12		.818	.622	.366							
13		.879	.625	.398							
14		.882	.602	.381							
15			.834	.666		.417					
16		.976	.832	.636	.578						
17			.993	.842	.785	.684					
18				.861	.786	.613					
19					.986	.823	.732				
20						.963	.938	.653			
21					.905	.795	.660				
22		.954	.743		.457						
23								.980	.926	.880	
24								.965	.896	.767	
25							.989	.829	.752		

Zisman Plot Data (n-alkanes)

	cos θ				
	n-alkane	C-8	C-10	C-12	C-14	C-16
surface # (Table 9)	surface tension (dynes/cm)	21.6	23.8	25.4	26.6	27.5
4			.949	.899	.853	
4			.955	.892	.834	.788
4			.966	.916	.852	.808
5		.982	.899	.827	.797	.769
7			.970	.907	.841	.795

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DEACTIVATION AND PREPARATION OF FUSED SILICA OPEN TUBULAR COLUMNS FOR GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY

by

Michael Wayne Ogden

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Chemistry

(ABSTRACT)

The activity and wettability of raw fused silica capillary tubing was found to be widely variable which places severe limitations on the reproducibility of column deactivation and inertness. Hydrothermal treatment of the raw fused silica with nitric acid was proven to be very effective for cleaning and maximizing the degree of silanol coverage of the surface. The capillary rise method was used to obtain contact angle data for untreated fused silica and fused silica treated with a variety of deactivating reagents. This contact angle data was used in the construction of Zisman plots which allowed quantitative comparison of the wettability and degree of surface coverage obtained with the different deactivants. The thermal stability of the final column was related to the success of the deactivation procedure. The choice of cross-linking initiator was also found to have an affect on column inertness.

In the synthesis of intermediate polarity polysiloxane stationary phases, mixtures of commercially available cyclic siloxanes were shown to be a viable alternative to the use of dichlorosilanes as starting material. The main advantages were the simplification of the synthesis procedure, simpler and better molecular weight control of the polymer, and the elimination of HCl as a by-product of both the polymerization and endcapping steps. A new stationary phase, 7% cyanoethyl, 7% phenyl, 1% vinyl, methyl polysiloxane was synthesized and found to be more polar than OV-1701 with higher temperature stability, easily cross-linked, and suitable for use in supercritical fluid chromatography.