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REVIEW

PREPARATION OF WALL-COATED OPEN-TUBULAR CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

A capillary column is the heart of a capillary gas chromatographic system. Essentially, it is an open tube, with an inner diameter between *ca.* 10 μm and 1 mm, coated on the inner wall with a liquid stationary phase. To prepare columns from glass, fused silica or other capillary materials, several manipulations are involved, which are still not very well understood and which many workers have studied in detail.

It is generally accepted that raw glass or fused-silica capillary materials need a preliminary hydrothermal treatment, in order to achieve a controlled coverage of silanol groups on the silica surface. Subsequently, the capillaries are deactivated. There are several techniques which aim at deactivating the capillary inner surface with different silanizing reagents under different conditions. Usually temperatures as high as 400°C are necessary for the deactivation treatment. Based on theoretical considerations of the possible distribution of the deactivating groups, and of the knowledge accumulated from investigations on capillary column preparation, most workers agree that it is impossible to get rid of surface active sites completely merely by reactions between reagents and the glass wall surface. A polymer layer is generally

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thought to be necessary to mask the residual active sites. After deactivation of the capillaries, they are usually coated with a stationary phase using a static coating procedure to obtain a high and reproducible column efficiency. Finally, the stationary phase in coated columns is subjected to immobilization, for which purpose several methods are also available.

In recent years it has become a trend that workers heavily involved in the progress of column technology have paid most attention to the preparation of wall-coated open-tubular (WCOT) columns, while techniques for the preparation of support-coated open-tubular (SCOT) and porous-layer open-tubular (PLOT) columns have remained relatively stagnant. Reflecting this trend, this survey is focused on four aspects related to the preparation of the WCOT capillary columns, *viz.*, the capillary material, the pre-treatment (leaching or hydrothermal treatment and dehydration), coating of the capillaries with stationary phases and immobilization of the coated stationary phases.

A broader survey of the evolution, present status and future of open-tubular columns has been made by Ettre[1]. The development of column technology up to 1980 has been excellently surveyed by Lee and Wright[2]. Many aspects described there, such as the theory concerning silica and glass surfaces and various propositions for capillary pre-treatments and dynamic and static coating procedures are still widely accepted. Newer developments including also the immobilization of stationary phases, are surveyed in this paper.

2. CAPILLARY COLUMN MATERIALS

The first capillary ever used for the preparation of capillary columns for gas chromatography was made of stainless steel[3]. During the early days of the development of gas chromatography, some investigators[4,5] reported on the use of metals and plastics as capillary materials. Some workers[6-10] are still interested in the preparation and application of nickel capillary columns. Until fused silica was introduced as a capillary material in 1979[11], glass (soda-lime or borosilicate) had been by far the most popular material for the capillaries. At present, fused-silica capillary columns, owing to their superior mechanical and chemical properties, have become the dominant type in gas chromatography. However, owing to the ease of manufacturing glass capillaries, their lower cost in comparison with fused-silica types and their relative inertness compared with metal capillaries, glass capillaries still share some of the market. It is noticeable that, so far, it is easier to obtain good polar columns from glass than from fused-silica capillaries, because of the difficulties in deactivating the fused-silica surface with polar deactivating reagents.

Desty *et al.*[12] were the first to design and build a capillary drawing machine and they succeeded in coiling glass capillaries immediately after drawing with a metal coiling tube heated electrically to an adequate temperature. In 1975 Desty[13] tried to modify this machine to draw fused-silica capillaries with basically the same principle. However, in doing so the lack of a suitable material for the coiling tube was a limiting factor. It was Dandeneau and Zerenner[11] who invented and patented a method of drawing thin-walled capillaries of high flexibility. This kind of capillary, however, was susceptible to corrosion, and turned very fragile after being corroded. To protect the capillaries, a layer of polymethylsiloxane was coated immediately after drawing.

Later, a polyimide outer coating was applied instead. Polyimide-coated capillaries became very popular and are in common use nowadays. The manufacturing technique for fused-silica capillary has since been adopted worldwide. The polymer outer coating protects the capillary from corrosion, strengthens it mechanically and is thermally stable up to a temperature as high as 350°C, as long as the pre-treatment did not exceed a temperature of 400°C. It is a limiting factor, however, if the capillary has to undergo temperatures persistently higher than 350°C. The polymer outer coating will obviously be damaged if the pre-treatment temperature is higher than 400°C.

More recently, Lipsky and Duffy[14,15] proposed protecting fused-silica capillaries with an aluminium cladding. It is claimed that aluminium-clad capillary columns coated with thin films of thermostable stationary phases could be maintained isothermally at 400–425°C and temperature programmed to 425–440°C. As a result, with proper instrumentation, substances with molecular weights up to 1000–1200 and/or boiling points up to 650–750°C and higher can be analysed. Metal-coated fused-silica capillaries were recently investigated by Hattori and Kojima[16]; apart from the high-temperature stability of the metal coating, it is also claimed that the metal coating allows the application of a unique and simple injection system in which electric heating is applied to a short piece of the column at the inlet.

3. CAPILLARY WALL PRE-TREATMENT

3.1. Aim of and necessity for pre-treatment

To prepare highly efficient, inert and heat-resistant columns, both fused-silica and glass capilllaries have to be subjected to pre-treatments before coating. This aspect has been surveyed extensively and in detail by Lee and Wright[2]. In short, both glass and fused-silica capillary inner surfaces, without adequate treatments, are not satisfactorily wettable, at least not by stationary phases having higher surface tensions. The films coated on such surfaces are usually irregular and unstable and they tend to form droplets, resulting in the deterioration of column efficiency. On fused-silica capillary inner surfaces the weak acidity of silanol groups results in the adsorption of compounds having higher peripheral electron densities, notably strongly basic compounds. The partial ionic character of strained siloxane bridges on the fused-silica surface can function as a proton acceptor in hydrogen bonding interactions, resulting in the adsorption of proton donor compounds. On a glass surface, in addition to the problems caused by silanol groups and strained siloxane bridges, alkali and alkaline earth metal ions[2] cause even more severe problems of adsorptive effects and catalytic activity. The latter also causes the stationary phase to decompose more drastically at higher temperatures, resulting in bleeding of the stationary phases.

For fused-silica capillaries, it was found that there are acidic gases (HCl, NO_2, etc.) inside the capillary, probably formed during the course of manufacture of the capillary material. Capillary column acidity could be reduced in certain batches of fused silica if the capillaries were flushed at room temperature with nitrogen[17–19].

Glass and fused silica are typical hard materials, which might have surface free energies ranging from around 500 to about 5000 dyne cm^{-1} (ref. 20). It would be expected that a coated layer of any type of stationary phase, having a surface tension between 20 and 50 dyne cm^{-1} (see ref. 2), would cause the surface energy of glass or silica to decrease drastically. As a result, the coated layer would be expected to be

very stable, as the restoration of the surface from the coated to the original status, or ridding the silica surface of the coated stationary phase, would require a large amount of energy. However, a monolayer of adsorbed molecules is sufficient to give a high-energy surface the same wettability properties as a low-energy solid having the same surface constitution[20]. To deactivate capillary surfaces (see below) they are invariably subjected to treatments of leaching, dehydration and often to silylating deactivation. Altogether these procedures often result in a surface energy of, for example, ca. 21 dyne cm^{-1} after methylsilylation treatment[21]. Without adequate treatment, the low surface energy of a capillary surface is thought to be the primary reason for the difficulty in coating silica capillaries, resulting in even and coherent layers of polar stationary phases, although phenyl- or cyanosilicones with a cyano substitution of 50% reportedly could be directly applied to fused silica, to obtain columns with reasonable deactivation and fair efficiencies[22].

To increase the surface wettability by the stationary phases, numerous methods have been proposed for roughening the glass inner surface. For example, the glass surface could be roughened by gaseous hydrogen chloride etching[23], by sodium chloride deposition and by covering with fine silanized silica powder[24] or silicic acid suspension (DUDOX colloidal silica)[25]. It was also proposed to cover the capillary inner surface with a layer of carbon by pyrolysis[26-28] or with a layer of barium carbonate[29,30] or to treat the capillary surface with hydrogen fluoride[31-33] or 2-chloro-1,1,2-trifluoromethylethyl ether[34,35]. A roughening treatment is generally believed to have some advantages. At present however, it is not common for roughening capillary surfaces.

Alternative methods for changing glass or metal capillary inner surfaces are simply to precipitate silicon[8,36], silicon carbide[37] or polyimide[38] on the capillary inner wall. Recently, Anthony et al.[39] proposed a modified chemical vapour deposition process for imparting specific surface properties to glass or fused-silica capillaries.

After pre-treatments such as flushing of fused-silica capillaries, and the subsequent hydrothermal treatment, in addition to leaching–dehydration treatment of glass capillaries, and deactivation of both kinds of capillaries or covering their inner surface with various substances, the capillary inner surface should be readily compatible with the stationary phase to be coated. The intermediate deactivation layer should shield all the negative effects of the impurities in capillary materials, of surface silanol groups, of strained Si–O–Si bonds and so on, resulting in perfectly neutral columns; at the same time, the deactivating layer prevents the impurities and surface silanol groups from affecting the thermal stability of the stationary phase.

3.2. Hydrothermal treatment of fused silica and leaching–dehydration treatment for glass capillaries

For fused-silica capillaries, hydrothermal treatment (this term, originally proposed by Unger[40], implies hydroxylation of the surface at higher temperatures) prior to further deactivation[41,42] is predominant, because at present the most successful deactivating procedures for siliceous materials rely on an even coverage of the surface with silanol groups of suitable density. Owing to the high temperatures involved in the manufacture of fused-silica capillaries, the density of silanol groups on its surface is reported to be low (0.2 silanol groups per nm^2, compared with 4.3 per nm^2 on a

fully hydroxylated silica surface[43] and is stated to be insufficient for deactivation[42].

Hydrothermal treatment has been shown to be especially necessary for the coating of polar stationary phases[44]. Most workers use hydrochloric acid of different concentrations as reagents. Ogden and McNair[42], however, treated fused-silica capillaries with nitric acid of different concentrations, and found that the best deactivation could be obtained by treating fused-silica capillaries with 20% nitric acid at 200°C, after subsequent silylation. The reason was suggested to be the most complete coverage of the treated surface by silanol groups. Schutjes et al.[45] simply rinsed fused-silica capillaries with a dilute solution of hydrofluoric and nitric acids before a brief rinse with dilute hydrochloric acid and water. After dehydration by flushing the capillaries with nitrogen at elevated temperatures and subsequent deactivation, columns of acceptable quality were obtained.

For glass capillaries, by far the most popular pre-treatment is to change their inner surface into more or less pure silica. Rutten et al.[46] made extensive studies of the leaching and dehydration of glass capillaries. Leaching of the capillaries can be carried out statically[46-48] or dynamically[50-53] with dilute hydrochloric acid. Desalination can also be achieved by treating the glass surface with gaseous hydrogen chloride[23,54], sulphur dioxide[56], ammonia solution[57] and water vapour[58]. Among the numerous procedures proposed, leaching with acids appears to be the most commonly applied method for pre-treating glass capillaries.

Lee and Wright[2] elucidated the mechanism of acid leaching in more detail. It has been demonstrated that at a pH below about 7, glass is hydrolytically decomposed. Some of the Si–O–R bonds on the glass surface (R being an alkali or alkaline earth metal ion) are cleaved and converted to Si–OH bonds, so a surface gel is formed. This type of process is generally thought to be diffusion controlled, with the amount of alkali extracted being proportional to the square root of time[59]. This might be verified by the data shown in Table III in ref. 51. By depth profiling analysis, it was shown that in the leaching of both soft and hard glasses, both the alkali and alkaline earth metal ion contents decrease from the bulk to the surface; the contents of the ions in a certain layer decrease in the course of leaching, until these ions disappear in the top layers after prolonged leaching.

There are different opinions about the best way of leaching. Lee and Wright[2] stated that during prolonged dynamic leaching without boiling of the leaching solution, the capillary surface is not roughened excessively and that the reactive cations diffuse more effectively from the glass matrix into the leaching solution. They also suggested that under static conditions it is possible that boron ion re-precipitation could take place. Alkali and alkaline earth metal ions extracted from the surface were also thought to re-precipitate. Wright et al.[52] found that dynamic leaching not only removed boron and other detectable impurities, but also carbon contamination. However, Grob and Grob[48] stated that they had been unable to obtain a constant column quality by dynamic leaching. Venema and co-workers, who had also proposed dynamic leaching[53], later pointed out that leaching of a glass capillary dynamically at lower temperatures (e.g., 50°C) resulted in less satisfactory deactivation by HMDS[60].

The excessive moisture that remains in the capillaries after leaching is subsequently removed by dehydration. Again, there are different methods of dehydration. Grob and Grob[48] suggested dehydrating of the leached surface under vacuum at

300°C for 2–3 h, while Lee and Wright[2] proposed a longer, milder treatment, that is, overnight treatment with a carrier gas flow at about 100°C and subsequently for a few hours at 150°C to remove undesirable residual water. It was stated that to prevent "excessive surface dehydroxylation" the temperature should not be above 150°C. The topic of leaching and dehydration (hydrothermal treatment for fused-silica capillaries) has been extensively studied by Rutten et al.[46].

In general, the hydrothermal treatment of fused-silica capillaries and leaching–dehydration treatments of glass capillaries are intended to provide a desired number of silanol groups evenly distributed on the surface, on which the deactivating groups can be anchored. For glass surfaces, metal ions will also be removed. However, many different recipes result in different levels of inertness of the treated capillaries, and even with a given method the resulting surface silanol group coverage is prone to vary, owing to some unknown factors that may be changed inadvertently. These facts indicate that these treatments are not yet completely understood or well defined.

3.3. Deactivation

Subsequent to hydrothermal or leaching–dehydration treatments, the capillaries have to be further deactivated. In the history of capillary deactivation, different methods have been proposed and practically evaluated. For instance, the surface silanol groups were chlorinated and then reacted with alcohol[61] in order to change the original silanol groups into ether groups, or with organometallic compounds[61,62] to form Si–C–C bonds. However, these methods are no longer in use.

Aue et al.[63] discovered that after heat treatment at 280°C and subsequent exhaustive extraction with methanol, a thin film of Carbowax 20M deactivated diatomaceous earth support material very well. Based on their discovery, Cronin[64] proposed deactivating the capillary inner surface by coating a layer of Carbowax 20M on it and heating the sealed capillary at 280°C for 16 h. Different methods of Carbowax deactivation have been proposed[65,66]. Aue and Younker[67] and Cronin[68] showed that this treatment resulted in well deactivated surfaces with very low bleeding. However, there was disagreement about the thermal stability of the Carbowax deactivation layer. Some investigators have shown[66,69] that it is not stable for extended use above 250°C. Grob and Grob[29] claimed that strongly polar polyethylene glycol deactivated surface is "poorly wettable by apolar phases". Blomberg and Wännman[70], however, found such a surface to be very compatible with SP-2100 and OV-101. Interestingly, Franken et al.[65] and de Nijs et al.[66] have shown that this observed difference could be explained by the thickness of the deactivation layer. A very thin Carbowax deactivation layer seems to be compatible with non-polar stationary phases, whereas a thicker deactivation layer shows characteristics of a polar stationary phase. To the best of our knowledge, as long as the analytical temperatures are not too high, Aue et al.'s deactivation method results in very good columns, and it is still applied nowadays.

Currently, the most popular deactivation techniques are various kinds of silylation. On silylation, the surface silanol groups are substituted by silyl ether groups. Kiselev[71] and Kiselev and Shcherbakova[72] were the first to report the silylation of a glass capillary surface. The reagent they used was trimethylchlorosilane (TMCS). By studying the silylated silica surface by gravimetric and spectroscopic methods,

Davydov et al.[73] and Armistead and Hockey[74] showed that only the free surface hydroxyl groups, i.e., hydroxyl groups which are separated from adjacent groups by more than 3.1 Å, and which are therefore incapable of hydrogen bonding[73,75,76], are involved in silylation reactions. It was stated that when hydroxyl groups are hydrogen-bonded, they react little, if at all, with deactivating reagents[73,74]. This point of view was supported by Hair and Hertl[77], judging from the results of vapour-phase silylation and surface IR spectroscopy, and also by Mauss and Engelhardt[78] and by Berendsen and De Galan[79]. On the other hand, Snyder and Ward[80] stated that bonded silanol groups are more reactive. They suggested that the two bonded silanol groups exert a concerted effect on reacting chlorosilane molecules; the proton of one bonded silanol group and the oxygen atom of the other simultaneously attract the chlorine atom and the silicon atom in the chlorosilane molecule, respectively. They reasoned that this concerted effect facilitated the reaction between bonded silanol groups and the silanization reagents. Anthony et al.[81] further reasoned that carbonyl groups, having a dipole moment, could be adsorbed preferentially at bonded silanol groups by a similar mechanism. This effect was used by the authors to probe the water and silanol groups on the fused-silica surface.

free surface hydroxyl groups

hydrogen-bonded surface hydroxyl groups
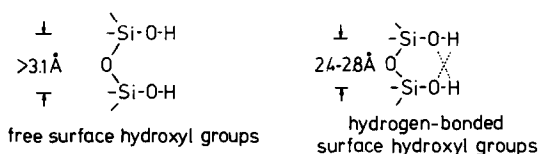
    In addition to treatments with methylchlorosilanes (DMCS and TMCS), some workers applied silylation methods that make use of two other chlorine-substituted organosilanes, viz., allyl- and phenyltrichlorosilane and a 5:1 mixture of hexamethyldisilazane and trimethylchlorosilane[82-85]. Efforts were made to increase the polarity of the deactivating groups attached on the glass capillary inner surface, in order to increase its wettability by polar stationary phases. The silylated surface was oxidized by nitrogen dioxide or air, and oxidized statically or dynamically with oxygen at 160°C for 24 h[83]. To some extent, this oxidation improved the wettability of the glass capillary surface by the polar stationary phase dinonyl phthalate. In an attempt to obtain a deactivated surface which could be adaptable to different stationary phases, chlorodimethyl-[3-(4-chloromethylphenyl)butyl]silane was made to react with the surface silanol groups; subsequently, the chlorine atoms in the 4-chloromethyl groups were substituted with the same groups as in the selected stationary phase[84]. It was stated that the modification of glass capillary surfaces with a "cyano monolayer" increased their wettability by cyano-substituted stationary phases, resulting in stable and homogeneous films instead of the commonly observed droplets.

    Welsch et al.[86] treated the raw glass capillary surface with various reagents at different temperatures for different times. They found that the best result was obtained by treatment with pure hexamethyldisilazane for about 20 h at temperatures approaching 300°C. Their discovery showed the importance of a higher treatment temperature in the deactivation of glass surfaces by silylation.

    More recently, several investigators suggested treating glass or fused-silica cap-

illaries with different high-temperature silylation (HTS) methods. Among these HTS treatments are excellent methods known as the PSD (alkylpolysiloxane degradation) treatment[87-89] and persilylation (with disilazanes)[48,90-94]. Blum and Grob[95] proposed deactivation at 370°C for 8 h with a mixture of the stationary phase XF-1150 (polysiloxane with 50% each of cyanoethyl and methyl groups) and diphenyltetramethyldisilazane (DPTMDS). They showed that the deactivated surface obtained can be coated successfully with stationary phases of medium polarity. Moser et al.[96] recently proposed a two-step deactivation method for glass capillaries, the first step with triphenylsilylamine for good wettability and the second with DPTMDS to improve the inertness of the capillaries. With fused-silica capillaries flushed with 5 column volumes of 1% hydrochloric acid and then dried under a nitrogen flow at higher temperatures and deactivated with DPTMDS, Ahnoff and Johansson[97] prepared good capillary columns with stationary phases having 5-33% phenyl substitution.

As to the manipulation of the deactivation, Lee et al.[51] and Wright et al.[52] preferred to silylate under dynamic gas-phase conditions; however, this dynamic deactivation method does not appear to be dominant at present.

Fused-silica surfaces were also suggested to be efficiently deactivated by HTS treatment with D_4 (octamethylcyclotetrasiloxane)[98-101] and tri- or tetracyclosiloxanes with phenyl, diphenyl, trifluoropropyl and cyanopropyl substituents. The reagents proposed were methyl(trifluoropropyl)cyclosiloxanes[102,103], bis(trifluoropropyl) cyclosiloxanes[103,104], hexaphenylcyclotrisiloxane[104,105], methylphenylcyclosiloxane[106], bis(cyanopropyl)cyclosiloxanes[103,104,107-109] and cyanopropyl(methyl)cyclosiloxanes[108,109]. A disiloxane, bis(cyanopropyl)tetramethyldisiloxane, was also used for deactivation of capillary surfaces[110].

Making use of the HTS technique, Schutjes et al.[111] specifically studied the deactivation of very narrow-bore capillaries (50 μm) and obtained columns of very low activity.

Although in practice there are well established techniques for deactivating silica surfaces and also leached and dehydrated glass surfaces), it is felt that some fundamental aspects of the deactivating reaction are yet to be understood. Apart from such basic problems as whether it is isolated or bonded (bridged) silanol groups that are more reactive, there are different opinions on the reasons why an HTS-treated surface is considerably more inactive than a low-temperature-treated surface. Godefroot et al.[94] postulated that it is far easier for a trimethylsilyl group, acting as a "leaving" group, than for a proton in a hydroxyl group to undergo elimination with a nearby hydroxyl group. As a result, the elimination of the organosilyl group could probably occur at a much lower temperature of 300-400°C, forming Si-O-Si bonds, while the elimination reaction between two silanol groups should occur at 500-800°C. Berendsen et al.[112] reported the decomposition of an organosilyl-bonded surface at a temperature as low as 310°C, with cleavage of Si-O-Si(R3) linkages as part of the result. Some other investigators[94,113,114] shared the opinion that siloxane bridges thus formed contributed to the remarkable inertness of the HTS-treated glass capillaries. Welsch and Frank[115] observed that "normal" silylation, together with formation and cleavage of siloxane bridges, led to an extremely low coverage of silanol groups on the surface. They also observed the conversion of DPTMDS to polyfunctional agents, which made possible the coverage of the surface with doubly anchored short siloxane or silazane chains, causing better deactivation.

By studying the pyrolysis of the silylated silica, Hansson and Trojer[116] found that under the conditions applied, cleavage of Si–O–Si bonds could not be detected. Rutten and co-workers[117,118] studied HTS with fused silica (Cab-O-Sil) as a model material by means of ^{29}Si and ^{13}C cross-polarization magic-angle-spinning NMR. They explained the inertness of the HTS-treated surface mainly by the formation of doubly or triply anchored organosilyl groups on the surface rather than the formation of siloxane bridges. Reiher[119] derived a reaction model, and tried to explain nearly all HTS effects.

Many workers have proposed that during high-temperature silanization deactivation, a polymer layer, which masked the active sites on the surface, was formed on the capillary inner wall. This layer was thought to help in attaining a high inertness[19,31,60,88,120,121]. Aue and Wickramanayake[120] were the first to point out that the disproportionation of the deactivating silanyl reagents, forming two or three functional silanyl compounds, plays a role in the formation of the masking polymer layer. It might be speculated that three functional siloxane species were responsible for the formation of a more rigid, two- or three-dimensional network of high polymers, which covers the active sites on the column wall better. The high temperature involved in the deactivation may be necessary only for the disproportionation of the deactivation reagents and/or for the polymerization of the polyfunctional silanyl species to form the proper deactivation layer.

Four probable explanations as to the higher inertness of HTS-treated silica surface have been cited above: the cleavage of organosilyl groups and the subsequent formation of Si–O–Si bonds, the doubly/triply anchored organosilyl groups on the surface, the doubly anchored siloxane/silazane chains or the coverage of the surface by a thicker deactivation layer. It is not so easy to decide which of them or combination of them contributed to the inertness of HTS-treated capillaries. The relative positions of atoms or groups of atoms on the silica surface, their interactions and the possible interactions between them and the attacking reagents are greatly relevant to the deactivating reactions of fused-silica capillaries. In order to understand the deactivating reaction well, the ambiguity concerning the factors mentioned above should be removed as much as possible.

Fused silica, however, is amorphous by nature and it cannot be analysed by X-ray diffraction or by surface techniques, such as ESCA. As a result, one has to take the knowledge obtained from crystal silica as the starting point to build a model based on this knowledge to study the structure of the fused-silica surface[79]. As the density and refractive index of amorphous silica are close to those of cristobalite and tridymite, it is thought that the structures of these crystal forms of silica can provide probable models for amorphous silica.

Accepting the structure of tridymite as the model for the silica surface (Fig. 1), taking the O–Si bond length as being the average of the Van der Waals radii of O and Si atoms (0.140 and 0.195 nm, respectively) and the steric distribution of the respective atoms, it can be calculated that the distance between surface Si atoms is 0.547 nm. A hydroxyl group is attached on top of each of the surface Si atoms with the bonds parallel with each other. This theoretically estimated value of the distance between surface silanol groups agrees very well with the value obtained by NMR measurement of the silica surface[122]. According to this calculated distance between silanol groups, their density can be calculated to be 3.9 per nm^2. The experimentally
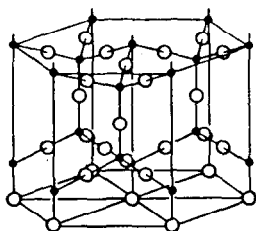
Fig. 1. Crystal structure of β-tridymite, open circles, oxygen atoms; closed circles, silicon atoms.

measured value of tridymite surface hydroxyl group density is 4.6 per nm^2 (ref. 79).

It is well documented that during the heating of the hydrated silica surface at increasing temperatures, the concentration of the residual SiOH groups decreases continuously (ref. 122, p. 639). However, according to the tridymite model of the silica surface, it would be difficult to form a new Si–O–Si bond on the basis of two previous silanol groups. The sheer distance between the neighbouring silanol groups, which at 0.547 nm is 63% longer than the sum of the two Si–O bond lengths, makes it difficult to form new Si–O–Si bonds. What is more, according to the model, originally the Si–O(H) bonds are parallel with each other, so by assuming the formation of Si–O–Si bonds from these Si–O(H) bonds by elimination of water molecules, one has to accept either extremely distorted bond angles or less distorted bond angles with bonds even longer than mentioned above, or, in other words, severely distorted tetrahedra. Although it has been stated that the Si–O–Si angle is easily deformed and the formation of slightly distorted tetrahedra is possible[2], in view of the whole silica surface, assuming a tridymite-like structure, it seems very difficult to arrange nearly all of the new O–Si–O bridges formed by elimination of silanol (and also organosilyl) groups, to cause an extremely low coverage of silanol groups.

It has been proposed that the most likely mechanism of dehydration of the silica surface is the migration of protons via strained oxygen bridges, rather than the migration of hydroxyl groups (ref. 122, p. 640). To the best of our knowledge, however, how to arrange the newly formed Si–O–Si bridges by dehydration, without the difficulties arising from the tridymite model of silica surface, remains an open question.

Judging from what has been stated above, it is probably difficult to explain the higher inertness of the HTS-treated silica surface merely by assuming organosilyl groups as leaving groups, catalysing the formation of Si–O–Si bridges. Actually, if the formation of Si–O–Si bridges was the main cause of high inertness, considering the low silanol concentration on the fused-silica capillary surface, it would have been possible to achieve high inertness simply by silylating surface silanol groups on the fused-silica capillary walls without hydrothermal treatment.

From a geometrical point of view, the explanation that the formation of doubly or triply anchored organosilyl groups results in higher inertness is possible, and so is the explanation that the higher inertness is caused by coverage of the surface with doubly anchored short siloxane or silazane chains. However, it has been found that the unmodified hydroxyl groups interact with solute molecules, even though they are shielded by organosilyl groups. After a chain length of about four carbon atoms, this

long-range effect becomes negligible[123]. It is our opinion that probably silylation of most of the surface silanol groups and subsequent coverage of the inner surface by a suitable thickness of a deactivating polysiloxane layer, either caused by polymerization of di- and trifunctional silanyl species produced from deactivating reagents under HTS treatment or caused by other treatments, is the best way to deactivate fused-silica capillaries.

Recently, by Xu and Vermeulen it was proposed to treat fused-silica with D_4 (octamethylcyclotetrasiloxane) in the presence of oxygen at high (450°C[124]) or lower (320°C[125]) temperatures. It was suggested that at higher temperatures, oxygen would oxidize D_4 into tri-functional silanyl species, which would copolymerize with fragments from D_4 to form a three-dimensional, rigid siloxane polymer deactivation layer (Fig. 2) on the fused-silica capillary surface, shielding the remaining active sites better. This so-called high-temperature aerobic silylating deactivation (high-temperature ASD) results in a relatively thick deactivation layer on the capillary surface (73 nm), so that the treated capillaries without the coating of stationary phase act as columns with thin films on their surface. The coated columns showed very low activity against basic samples such as decylamine. Later, tri-functional silanyl reagents such as methyl- and phenyltriethoxysilane were added into D_4 to deactivate fused-silica capillaries in the presence of oxygen (low-temperature ASD). It was found that there were thicker layers on treated capillaries, the layer thickness being roughly proportional to the amount of oxygen that had been sealed into the capillary. Good deactivation was reported for columns prepared with low-temperature ASD-treated capillaries[125].

Other types of compounds were also tested for the deactivation of the inner surface of capillaries. Traitler[126] showed that it is possible to coat medium-polarity stationary phases such as Carbowax onto surfaces cold-treated with compounds such as γ-glycidoxypropyltrimethoxysilane, methyl 4-trimethoxysilylpropylamino-ethylaminobutyrate, γ-methacryloxypropyltris(2-methoxyethoxy)silane and vinyl-triethoxysilane.

Recently, methyl-, phenyl- and cyanopropylsiloxanes containing silylhydride groups have been synthesized and applied to deactivate the capillary surface at lower temperatures. The resulting columns were evaluated, good results being reported by various workers and the columns were proved to be sufficiently inert for many applications when the amounts of sample available were not below 1 ng per component[43,127,128,129].

For the deactivation of the fused-silica surface, it is noticeable that on the basis of a study of the surface groups[130], Lipsky and McMurray[17,131,132] proposed to
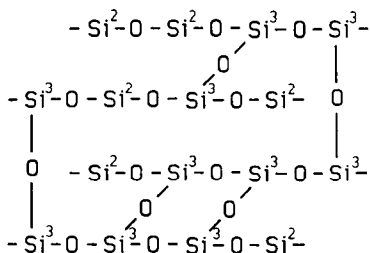
Fig. 2. Segment of three-dimensional siloxane polymer; the numerals 2 and 3 denote di- and trifunctional silanyl groups, respectively.

deactivate the fused-silica capillary surface with specially prepared, high-molecular-weight, OH-ended stationary phases. Blum[133-135] and Grob and Grob[136] reported on the positive effect of hydroxyl-terminated polysiloxane stationary phases (such as the medium-polarity phases OV-1701-OH, OV-31-OH, OV-61-OH and OV-17-OH and the apolar phases PS-347.5 and PS-086) on the inertness of the columns ultimately obtained. An increased thermostability of the coated stationary phases was observed, which was attributed to a more inert support surface resulting in less catalytic destabilization of the phases. The more inert surface in turn was attributed to the elimination of residual surface silanols by condensation reactions with the phases. Grob and Grob[136] further stated their basic idea that inertness should not be correlated with the incidence of silanol groups in the column as a whole, but more specifically with the silanol groups on the column wall surface.

This idea appears to conform with the discovery by Colenutt and Clinch[137] that oxidation of the stationary phase OV-17 coated on a column at 340–380°C by passing a stream of air through the column improved the column inertness. It is likely that the oxidation of stationary phase results in a certain number of hydroxyl groups, which attach to the polysiloxane framework instead of some of the organic groups in the composition of the stationary phase. Those hydroxyl groups might appear closely adjacent to the column wall surface, and might condense with the surface hydroxyl groups, thereby improving the column inertness. The hydroxyl groups which are not adjacent to the column wall surface do not appear to contribute to the activity of the column.

Up to now, to deactivate capillary surfaces with silylation reactions, higher treatment temperatures have been thought to be necessary in order to obtain satisfactory deactivation, although Lee and co-workers for the first time showed that it is possible to deactivate the silica surface with polyorganohydrosilanes at relatively low temperatures (at 250–350°C with methylhydrosilanes[127], at 300–350°C with phenylhydrosiloxane[128,129] and, to obtain the best deactivation, at 350°C with cyanopropylhydrosilane[44].

4. COATING OF CAPILLARY COLUMNS

After pre-treatments (leaching and dehydration for glass capillaries and purging and hydrothermal treatment for fused-silica capillaries), the capillaries are ready to be coated. In order to obtain the highest possible column efficiency, a homogeneous coating layer is necessary. Roughly classified, there are two coating techniques: dynamic and static. The first coating method ever proposed was Golay's static coating[3]. Almost immediately afterwards, the dynamic method was proposed by Dijkstra and De Goey[138].

4.1. Dynamic coating

In the dynamic coating procedure, several percent of the capillary length is first filled with a solution of the stationary phase to be coated and the solution plug is then pushed through the capillary at a velocity of approximately 1–2 cm s^{-1} with the pressure of an inert gas, generally nitrogen. As a result, a thin film of the solution is left behind on the capillary wall. After coating, the capillary is flushed for some time with inert gas and the solvent is then evaporated, leaving a thin coating of the stationary phase on the column inner wall.

Owing to the simplicity of the dynamic coating method, it used to be widely applied for the coating of glass capillary columns. However, coating with this method is complicated by various potential problems that cause non-uniform stationary phase films. Lee and Wright[16] studied a number of these problems in detail and numerous investigators have dealt with these problems (e.g., refs. 85 and 139–143).

Many solutions have been proposed for reducing the negative effects caused by these problems, such as to control the coating speed and temperature[141], to control the concentration of the coating solution[144] and to control the solvent volatility[145] and the rate of solvent evaporation[140]. Stabilization of the coating speed during the entire coating process was achieved by using a flow restriction device[146], and also a syringe pump attached to the capillary, operating in the withdrawal mode, with gas pressure applied to another end of the capillary[147,148]. Finally, the dynamic coating technique was significantly improved by the "mercury plug" method of Schomburg and co-workers[23,149], who proposed applying a mercury plug immediately after a plug of stationary phase solution which was more concentrated than that in the conventional dynamic coating procedure. As the mercury and the coating solution plugs were pushed forward by gas pressure, owing to the high surface tension of mercury, most of the coating solution was wiped out of the surface, leaving a thin and even film behind. This film, owing to the higher viscosity of the coating solution, resisted drainage during coating and evaporation of the solvent.

Notwithstanding all these refinements, it is still more difficult to obtain the highest possible column efficiency with a dynamic coating procedure. Moreover, it is more difficult to predict and to control the film thickness of the ultimate stationary phase layer. Several equations have been proposed for calculating the film thickness from known parameters[150–155] and to determine it experimentally[86,140,141,144,154–162].

4.2. Static coating

In contrast to dynamic coating, static coating has commonly been thought to provide the most efficient columns[163,164]. It was even reported that the column efficiency obtained could be higher than that which would be expected from existing theory[165]. Another advantage of static coating is that the mobile to stationary phase ratio is known accurately and therefore, knowing the density of the stationary phase, the film thickness can be determined accurately[166]. With these two major advantages, not surprisingly, static coating has attracted the attention of many column manufacturers.

As first developed by Golay[3] in 1956–58, the static coating procedure consisted of filling the capillary with a solution of the stationary phase, pulling the capillary through a heated zone to evaporate the solvent (through an open end of the capillary). This method was subsequently improved by Horváth[167]. Later in the evolution of the static coating method, it was further improved in two directions. In the first, based on the work of Horváth[167] and others[161,168], the evaporation of the solvent was carried out by pulling the capillary, filled with the liquid phase solution, through a heated zone, for example, a thermostatically heated oven, thereby evaporating the solvent[169–174]. It was stated[172,174] that by heating the entering capillary abruptly with a high-energy density inlet arc, the interior column wall is subjected to a rigorous cleaning treatment and to a continuous spray of the liquid aerosol suspended in

high-temperature, high-velocity solvent vapour at high pressure. This may result in a more intimate contact between the column wall and the liquid phase and, consequently, in higher column quality.

In the second approach, capillaries were coated statically in a simpler way, in which the solvent was evaporated by applying a vacuum to one end of the capillary after being filled with the stationary phase solution and sealed at the other end[175]. Among those investigators who contributed to the development of this coating method, Schutjes et al.[111] studied particularly the coating of narrow-bore capillaries.

In another reported static coating method[176], the capillary was first filled with a solution of stationary phase, the solution was subsequently frozen and the solvent evaporated in vacuo. Successful coating was reportedly obtained.

Among various static coating methods, the second attracted most investigators, about 20 papers having been reported on various details of different procedures[144,166,177-193]. It was found important that the coating solution is dust free and degassed to eliminate bumping (i.e., the breakdown of the coherence of the bulk of the coating solution) during the solvent evaporation step, and that no air or vapour bubbles should exist in the column. Sealing of the end of the capillary, where no bubble is allowed to exist, was found to be critical, as any leakage there will result in failure of the coating.

With the static coating procedure the mobile to stationary phase ratio is equal to the concentration of the coating solution at the coating temperature, hence the thickness of the stationary phase layer can be calculated with the following equation:

$$1/4 \, \pi \, d_c^2 c \; = \; \pi \, d_c \, d_f \tag{1}$$

where d_c is the inner diameter of the capillary, c the coating solution concentration at the coating temperature and d_f the film thickness. Hence

$$c \; = \; 4 \, d_f/d_c \tag{2}$$

The concentration c obtained is expressed in v/v terms. In order to prepare solutions on a w/v basis, the density of the stationary phase must be known. A number of stationary phase densities can be found in ref. 166.

The main disadvantage of the static coating procedure proposed by Bouche and Verzele[175] is that it is time consuming. For example, an Apiezon column (70 m × 0.6 mm I.D.; solvent, benzene) was coated in 10 days[175]. More recently, Kong and Lee proposed coating statically at higher temperatures[194] and with more volatile solvents such as isopentane or its mixtures with other solvents[195], in order to accelerate coating. The coating efficiencies of the resulting columns were found independent of the coating temperature applied. Highly efficient columns were prepared successfully and relatively rapidly with stationary phases whose polarities extended up to that of Carbowax. Vacuum was applied to facilitate the vaporization of the stationary phase solvent.

At about the same time, the static coating procedure was studied in more detail on the basis of theoretical considerations[196] (Fig. 3). In a static coating process, heat from outside the capillary being coated is transferred to the meniscus, i.e., the surface where stationary phase solvent is evaporating; the solvent vapour, whose pressure is

higher than that at the orifice of the capillary, flows through the coated capillary to the outlet. There are two most important, competing restricting factors governing this process: mass (solvent vapour) transfer out of and heat transfer into the capillary. According to Poiseuille's law,

$$\frac{dV}{dt} = \frac{\pi d_c^4 (P^2 - P_0^2)}{256 L \eta_v P_{atm}} \tag{3}$$

where P and P_0 are the pressure at the meniscus and the outlet of the capillary, respectively, η_v is the viscosity of the solvent vapour and, P_{atm} is atmospheric pressure. From eqn. 3, it can be seen that the solvent vapour flow-rate (dV/dt) through the capillary is proportional to the term $P^2 - P_0^2$, and inversely proportional to L, the distance between the meniscus and outlet of the capillary. It can be shown further that

$$\frac{dL}{dt} = \frac{273.16 d_c^2 (P^2 - P_0^2) M}{64 \cdot 22400 T_c L \eta_v d_1 P_{atm}} \tag{4}$$

where dL/dt is the coating speed, M the molecular weight of the solvent, T_c the coating temperature and d_1 the density of the solvent. In conventional static coating, P is usually low and hence the coating speed dL/dt is usually low, especially when
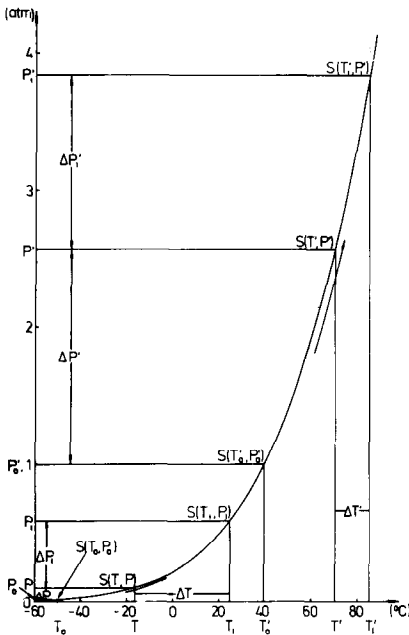

Fig. 3. Temperature-pressure correlation of vapour of pentane in equilibrium with pure liquid. T (T'), P (P') = temperature and pressure, respectively, at the coating solution front; P_0 (P_0'), T_0 (T_0') = pressure and temperature at column outlet; P_1 (P_1') and T_1 (T_1') are the respective equilibrium pressure and temperature. Unprimed parameters denote conventional static coating and primed parameters at higher temperature and pressure.
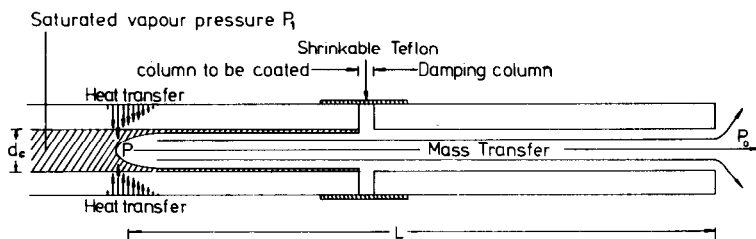
Fig. 4. Illustration of free release static coating process.

the capillary to be coated is long or has a small inner diameter. When a higher coating temperature is used, however, the term $P^2 - P_0^2$ can be much larger even though P_0 is higher. At higher coating temperatures, however, the difference between the saturated vapour pressure at the bulk of the coating solution (P_1) and P is larger. This may cause a greater possibility of bumping. In theory, this was suggested to be avoidable by increasing the restriction to mass transfer, thereby increasing P and decreasing $P_1 - P$ accordingly.

Based on these theoretical considerations, the so-called free release static coating (FRSC) procedure was proposed by Xu and Vermeulen (Fig. 4)[196]. With this procedure, coating of both normal and narrow-bore capillaries was performed at a temperature higher than the normal boiling point of the stationary phase solution and solvent vapour was released freely into atmosphere without evacuation, a damping column was attached to the column to be coated to increase the restriction to the mass transfer. This procedure has been demonstrated to be suitable for the coating of various stationary phases[196,197]. The coating speed was found to be high and relatively constant throughout the coating process (Table 1) while the advantages of the static coating procedure —high coating efficiencies of the resulting columns and exactitude of the coated film thickness— were retained. With special, very volatile solvent mixtures such as those composed of n- or isobutane and other solvents, coating of capillary columns could be performed rapidly at lower, even ambient temperatures. On the other hand, coating with higher $P^2 - P_0^2$ values facilitates the preparation of long, narrow-bore columns[198]. The importance of the choice of the stationary phase solution in a coating process and some other factors involved (the

TABLE 1

FREE RELEASE STATIC COATING SPEED OF A GLASS CAPILLARY DURING PROCESS

Column: I.D. 300 μm, O.D. 620 μm. Coating solution: 50 mg OV-101/10 ml n-pentane–acetone (3.5: 1.0, v/v). Damping column: 40 m. Degassing temperature: 90°C; coating temperature: 85°C.

Coils coated	Coating speed (cm min^{-1})
0	16.2
10	15.9
20	15.4
30	15.1
40	15.0
50	14.4
60	13.9

resulting coating speed, the occurrence of bumping and the solubility of the stationary phase) were discussed in detail. It was stated that an appropriate choice of stationary phase solvents (or mixtures of solvents) safely may result in much higher coating speeds. If the deactivation of the capillary inner surface is good and uniform, the occurrence of bumping phenomena may in principle be avoided by using a damping column[199]. Table 2 gives the relevant physical parameters of some of the common solvents.

As heat is transferred into the capillary just around the meniscus, the depth of the meniscus was suggested to govern the amount of heat that transfers into the capillary, to evaporate the solvent at a rate that the coating speed indicates. Based on the balance of the heat that transfers into the capillary around the meniscus and the heat needed to evaporate the solvent, a physical model was proposed for calculating the depths of the menisci from experimental data for coating speeds from the coating process of a 130-μm glass capillary with various mixtures of pentane and acetone. It was found that, by addition of polar solvents to an alkane solvent, the depth of the meniscus changed. Coating with solvent mixtures whose compositions were within certain ranges would result in much higher coating speeds than with pure alkane solvents[200] (Fig. 5).

Recently, Wooley et al.[201] studied a number of factors involved in the static coating of phenyl- and biphenyl-substituted polysiloxane stationary phases. Trichlorofluoromethane, diethyl ether and benzene were selected as coating solvents. It was stated that trichlorofluoromethane was the preferred coating solvent for phenyl- and biphenyl-substituted polysiloxanes. From a toxicological point of view, however, it should be noted that this solvent is hazardous.

A new method for coating small-diameter columns with polymeric stationary phases was recently proposed by Dluzneski and Jorgenson[202]. The narrow-bore capillaries (I.D. 5 or 10 μm) were first filled with a saturated solution of stationary phase in a selected solvent mixture. By quickly lowering the temperature, owing to the decrease in the solubility of the stationary phase with temperature, it was precipitated on to the capillary surface.

Clearly, the Dluzneski and Jorgenson method is the most rapid for coating capillary columns. Without taking into account the time required to fill the capillaries before coating and draining the solvent off the coated columns after the coating, the coating time is independent of the column length and inner diameter. However, they used the coated columns in LC analysis and coating efficiencies measured gas chromatographically were not given. With respect to the coating efficiencies, the static coating procedure usually gives better results. When a higher pressure is applied at the meniscus, such as in the free release static coating procedure, the coating speed can be high, whereas the high coating efficiencies typically obtained with a static coating procedure are retained.

5. IMMOBILIZATION OF STATIONARY PHASES

Immobilization of the stationary phases by in situ cross-linking and bonding on the surface after static or dynamic coating of capillaries is one of the significant advances in the evolution of column technology. By immobilization the stationary phase is physically stabilized and, as a result, it can resist the strain caused by me-

TABLE 2

FREE RELEASE STATIC COATING SPEEDS OF VARIOUS PURE SOLVENTS AT 85°C WITH SOME OF THE PHYSICAL CONSTANTS CONCERNED

H_{vap} = heat of vaporization; d_1 = density; MW = molecular weight; H_v/V = H_{vap} per unit volume; γ = surface tension; η = viscosity. For conditions of the coating, see ref. 199. Physical data cited from ref. 199.

| Solvent	Boiling point (°C)	H_{vap} (cal mol^{-1})	d_1 (g cm^{-3})	MW	H_v/V (cal cm^{-3})	γ (85°C) (dyne cm^{-1})	η (85°C) (g cm^{-1} s^{-1})	Coating speed (cm min^{-1})
Diethyl ether	34.51	6946.2	0.7138	74.12	66.9	9.5	0.13	10.5
Pentane	36.07	6595.1	0.6262	72.15	57.2	9.1	0.14	13.6
Dichloromethane	40.0	7572.3	1.3266	84.93	118.3	17.4	0.27	5.3
Acetone	56.2	7641.5	0.7899	58.08	103.9	16.3	0.19	4.6
Chloroform	61.7	7500.5	1.4832	119.38	93.2	19.3	0.33	3.4
Methanol	64.96	8978.8	0.7914	32.04	221.8	16.1	0.27	1.8
n-Hexane	68.95	7627.2	0.6603	86.18	58.4	11.7	0.19	4.2
Carbon tetrachloride	76.54	7628.8	1.5940	153.82	79.0	18.2	0.47	<1.0
Ethyl acetate	77.06	8301.1	0.9003	88.12	84.8	16.1	0.25	2.1
Ethanol	78.5	9673.9	0.7893	46.07	165.7	16.8	0.42	<1.0
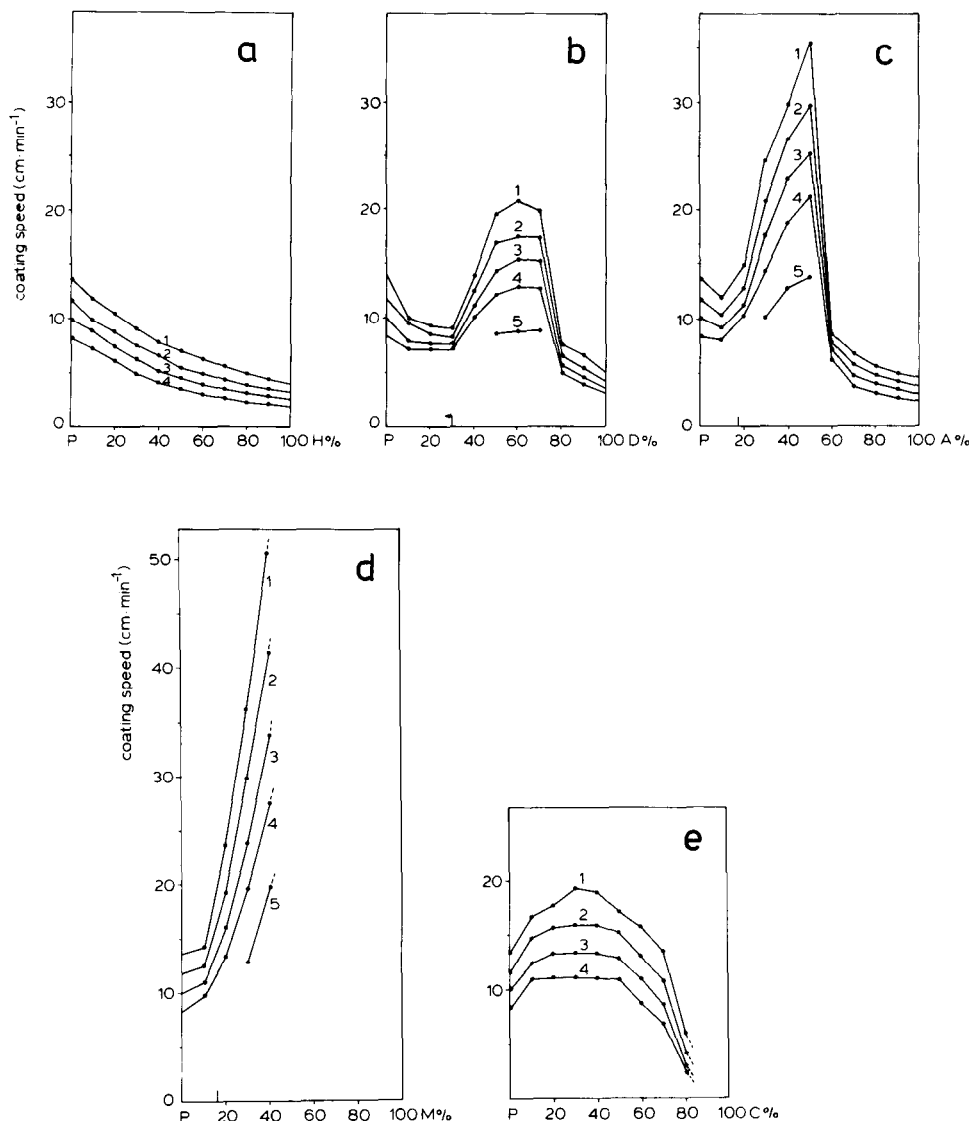
Fig. 5. Free release static coating speed *vs.* composition of mixtures of pentane with other solvents (a, hexane; b, dichloromethane; c, acetone; d, methanol; e, chloroform) at different temperatures. 1, 85°C; 2, 80°C; 3, 75°C; 4, 70°C; 5, 60°C. For details, see ref. 199.

chanical vibration, high temperatures and the injection of polar solvents and solutes[15,19,203]. Such stabilization is particularly advantageous for polar and for thick films of stationary phases. It has been reported[204] that after immobilization and re-silylation of the stationary phase, chemical stability of the stationary phases is increased to some extent.

Madani and co-workers were the first to propose the *in situ* synthesis of cross-linked methyl-[205], ethyl- and methylphenyl-polysiloxanes[206], and various mixtures

of methyl- and phenyl-polysiloxanes[207,208] by base-catalysed reactions with ammonia as the catalyst. In addition to the stabilization of the stationary phases they managed to tailor a given polarity by pre-selecting the ratio of phenyl to methyl groups[207]. Blomberg and co-workers developed other cross-linking techniques, *viz.*, base-catalysed cross-linking of α,ω-hydroxypolymethyl- (or -cyanoethyl- or -cyanopropyl-) siloxanes. α,ω-Hydroxypolysiloxanes from di- and trichloromethylsilane mixtures[209,210] and from dichlorodimethylsilane[211,212] and cyanoethyl- (or cyanopropyl-) substituted siloxanes[213] have been tested. Silicon tetrachloride was also tested as an immobilization reagent[101,110]. Verzele *et al.*[214] showed that the silanol-terminated silicones can be gummified. First studied by Lipsky and McMurray[16] and Geeraert and Sandra[215], this method has attracted more attention recently[133,136]. The effects of this method on the quality of the columns obtained were reported to be excellent.

Currently, immobilization of the stationary phases is mostly realized by free radical initiation (with peroxides[98-100,105-109,204,216-223], azo compounds[98,109,222-224], radiation from ^{60}Co[86,108,224-226] and ozone[106,227]). Free radical initiation was first proposed by Grob *et al.*[216], dibenzoyl peroxide being proposed as a "standard" radical initiator. In the early days there were applications of this compound (*e.g.*, ref. 217). It was soon found[19,218], however, that as a result of the desired reaction it decomposes to give benzoic acid, which in turn catalyses siloxane degradation. Dicumyl peroxide was found to be a better reagent. More recently, Grob and Grob[204,219,220] studied perxide-initiated immobilization in more detail. Using dicumyl peroxide as the immobilization reagent, they found that vinyl groups in the stationary phase molecules favour the immobilization. As a result, less peroxide was found to be required for the reaction. Immobilization of phenyl-[99,106,107,221-223] and cyanopropyl-[19,228] containing silicone phases can be achieved by incorporating vinyl or tolyl groups in the stationary phase molecules. In addition to dicumyl peroxide, *tert.*-butyl peroxide has also given good results[98,101].

Richter *et al.*[223] found that high percentages of peroxide may result in oxidation of tolyl groups. Therefore, they recommended azo-*tert.*-butane (ATB) as a cross-linking initiator[98,109,222,223]. ATB can be simply applied by carrying through the column with an inert gas after coating with a stationary phase. In this way the column can be tested before curing. Kuei *et al.*[229] and Lee *et al.*[230] reported on the application of ATB for the immobilization of polarizable polysiloxane stationary phases containing biphenyl-, naphthyl- and phenoxyphenyl groups. Richter *et al.*[224] reported the use of some other azo compounds, such as azocumene, -cyclohexane, -2,2'-bis(2-methylpropionitrile) (AIBN), -*tert.*-octane (ATO) and -*tert.*-dodecane (ATD) for this purpose. Among the azo compounds used as immobilizers, probably ATB and ATO are the best.

Schomburg *et al.*[87] and Bertsch *et al.*[225] reported almost simultaneously on the immobilization of stationary phases by means of radiation. Lakszner and Szersy[231] reported on the immobilization of layers of the stationary phase PS-255 up to a thickness of 9 μm with radiation from ^{60}Co. Immobilization by means of radiation has the advantages of involving no substances that may react with the stationary phase or catalyse the degradation of the stationary phase added to the column; this facilitates the control of the cross-linking reaction. However, the necessity to have a special radioactivity facility is the main drawback of this immobilization technique.

It was stated[19] that with ozone as the immobilization reagent the stationary phases SE-33, SE-54, OV-215 and two methyl (tolyl)silicone gums (33 and 50% tolyl) were cured at room temperature. SE-30, OV-1707, SE-52 and a cyanopropyl(methyl)-tolylsilicone gum (33% CN) were ozone-cured at 150°C[232]. Ozone was also used to cure tolyl- and phenyl-containing gums[105,106,109]. It was found that the presence of tolyl groups in the molecules of stationary phases facilitated immobilization: polysiloxane phases containing phenyl-, cyanopropyl- and tolyl groups could be immobilized, but without the presence of tolyl groups the immobilization of the stationary phases was not possible.

Different techniques of immobilization were compared by Markides et al.[109]. These techniques were classified into those resulting in Si–O–Si linkages and those resulting in Si–C–C–Si linkages. The performance of the methyl polysiloxane stationary phase cross-linked with the two techniques was compared[100].

Polyethylene glycol stationary phase was first reported to be immobilized by De Nijs and De Zeeuw[233]; however, no description of the procedure was given. Sandra et al.[234] reported that a polyol stationary phase, RSL-310, could be immobilized by dicumyl peroxide (DCUP). Traitler et al.[235] reported on immobilizing Carbowax 20M with γ-glycidoxypropyl(trimethoxy)silane, DCUP and dibutyltin dilaurate, for columns to be used up to 300°C. Buijten et al.[236] suggested treating polyethylene glycol (PEG) 40M with methylvinylcyclosiloxane and DCUP, or conditioning the column at 150°C after coating and then treating it with ethylene oxide. It was stated that the former treatment resulted in columns that could be used up to 300°C and the latter up to 260°C. Etler and Vigh[237] immobilized CP-wax 51 and Superox-6 with the joint action of DCUP and gamma radiation, obtaining 65% immobilization. Bystricky[238] immobilized polyol phase with 40% DCUP, and 93–97% of the stationary phase was reportedly immobilized. Martinez de la Gandara et al.[239] claimed that DCUP applied by a second coating can be used to immobilize Carbowax. Morandi et al.[240] reported on the immobilization of PEGs with a two-step technique: reaction with trichloromethane and allyl alcohol, and immobilization with dilauroyl peroxide. Russo et al.[241] immobilized PEG stationary phases on a carbon black layer on glass capillaries using DCUP.

Blum[134] proposed cross-linking the hydroxyl-terminated stationary phase OV-240-OH with a so-called trifunctional cross-linker, dimethyltetramethoxydisiloxane; after coating, a parallel condensation of the stationary phase with the silanol groups of the glass surface was thought to be feasible. As a result, fully immobilized, inert, thermally stable highly polar columns were reportedly obtained. This technique was completed with methylation of the remaining acidic sites with an ethereal solution of diazomethane after immobilization. Higher inertness was shown to be obtained by the additional methylation, but the maximum working temperature decreased by about 40°C after the methylation. Similarly, polyethylene–polypropylene glycol ether copolymers were reportedly coupled with methyltrimethoxysilane under the catalysis of trifluoroacetic acid[242] and N,N,N′,N′-tetrakis(polyethylene–propylene glycol ether)ethylenediamine coatings[243] were coupled with γ-glycidoxypropyltrimethoxysilane. Columns with high separation efficiency and inertness and an extended range of application were shown to be obtained. Janák et al.[244] reported that the upper working temperature of a propylene glycol, Ucon LB-550-X, was increased by 40–50°C by treating the coated film with gaseous hydrogen chloride, the column

efficiencies and the polarity of the stationary phase not being affected. It was stated that during this treatment, catalysed coupling of polypropylene glycol chains and their accidental thermally initiated cross-linking through methyl radicals might take place. However, the film could be washed away by dichloromethane; apparently, it was not sufficiently immobilized.

It was stated recently[131] that non-polar high-molecular-weight, partially cross-linked polysiloxane applied to the untreated surface of fused-silica capillary tubing could be further cross-linked to an extent of 85–95% by condensation through heating without the cross-linkers. So-called trifunctional cross-linkers were reported to immobilize hydroxyl-terminated polysiloxane coatings more successfully[134]. David et al.[245] pointed out that a choice had to be made between degree of immobilization and maximum selectivity of hydroxyl terminated cyanopropylsilicones cured by free-radical cross-linking. From his experience, Schomburg[246] suggested that the presence of vinyl groups within the silanol-terminated polysiloxane chain allows for thermal immobilization at much lower temperatures (down to 200°C). This also makes possible the immobilization of phenyl- and cyanopropyl-substituted siloxanes without immobilizers, although highly phenyl- or cyanopropyl-substituted polysiloxanes are more difficult to immobilize. Schomburg also reported that the hydroxyl-terminated polysiloxane can be cross-linked using oligosiloxane additives containing several SiOH groups. Blomberg and co-workers[247,248] also immobilized hydroxyl-terminated siloxane–silarylene copolymers with thermal curing without radical initiators.

Benecke and Schomburg[249,250] reported on the immobilization of polymeric chiral stationary phases such as XE 60–L-valine–(S)- and XE 60–L-valine–(R)-α-phenylethylamide, with cross-linking reagents such as ATB and dicumyl peroxide. The cross-linking was most successful with ATB as the initiator. The enantioselectivity of the chiral phases did not change on complete cross-linking.

6. CONCLUSIONS

Although column technology has already had a history of more than 20 years, it is still full of vigour in its development. We are convinced that there are good reasons for this vigour. For one thing, up to now, the analysis of, e.g., underivatized amines still is not free from the problem of adsorption, which not only causes peak tailing but also loss of sample components by adsorption or catalytic decomposition. It has been shown, however, by a capillary column supplier that it is possible to prepare methylsilicone columns on which underivatized amines can be chromatographed at an initial temperature of 50°C and a temperature programming rate of 5°C/min, resulting in very slightly tailing peaks. It seems to us that in order to reach higher inertness of the deactivated capillary inner surface, a better understanding of the reactions involved, the structure of the silica surface and its change after the various treatments is crucial. Coating of narrow-bore and long columns, which are necessary for supercritical-fluid chromatography (SFC) and high resolution, high-speed gas chromatographic (GC) analysis, is another problem. The recent progress made in column manufacturing techniques appears to be promising. It is possible that by increasing the quality of deactivation and by the application higher pressures at the meniscus, long, narrow-bore columns can be coated with the free release static

coating (FRSC) procedure rapidly and almost without failures. In response to the desire for practical analysis, new kinds of stationary phases are being proposed continuously. In all of its aspects, capillary column technology is being further developed to obtain columns with even higher inertness, higher temperature resistance, an even wider range of polarities and wide ranges of other characteristics such as sample capacity (film thickness), so that it will be better adapted to the increasingly critical demands of GC and SFC analysis.

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