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## ROLE OF SURFACE GROUPS IN AFFECTING THE CHROMATOGRAPHIC PERFORMANCE OF CERTAIN TYPES OF FUSED-SILICA GLASS CAPILLARY COLUMNS. I

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### SUMMARY

Heretofore, experience accumulated during the past two years on the utilization of fused-silica glass for the fabrication of capillary columns for gas chromatography has revealed certain advantages and disadvantages associated with this unique material. Surfaces relatively free of metal oxides, when appropriately coated with certain stationary phases provided excellent columns that were thermally stable and well deactivated. However, it was also noted that the precise chemical nature of the fused-silica glass surface, after drawing at 2100°C, was more complex than anticipated. This was reflected by our inability to coat columns with either very non-polar liquids, *i.e.* squalane, Apiezon L, C<sub>87</sub> hydrocarbon (Kováts) or the highly polar stationary phases (the cyanopropyl silicones).

By carefully surmising the nature of certain of the reactions that may occur on the surface of this glass under different conditions, one is able to utilize this information to extend the number of stationary phases that can be coated on fused-silica glass capillary columns. Accordingly, it has been shown that the selective chemical bonding of the surface layer of the fused silica prior to specific coating provides one with flexibility and versatility in the successful application of many different liquid phases.

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### INTRODUCTION

Approximately two years ago, Dandeneau and Zerenner<sup>1</sup> introduced the use of fused-silica glass tubing for the fabrication of capillary columns for gas chromatographic use. Considerable progress has been made since then in our understanding of certain of the physico-chemical processes that occur on the surfaces of this material which affect chromatographic behavior<sup>2,3</sup>.

Since the metal oxide content of this glass is infinitesimally small (less than 1 ppm) when compared to that found in soda lime and borosilicate glasses (Table I), the minor residual surface activity of fused-silica glass noted in early studies<sup>1,2</sup> cannot be attributed to the presence of Lewis acid sites which not only could react adversely with certain basic moieties in the sample to be chromatographed but could also give rise to some catalysis of the stationary phase and subsequent thermal instability<sup>4</sup>.

TABLE I

METAL OXIDE CONTENT OF VITREOUS SILICA, SODA LIME AND BOROSILICATE GLASSES

Type	Metal oxide content (ppm)										
	<i>Ai</i>	<i>Ca</i>	<i>Cu</i>	<i>Fe</i>	<i>Mg</i>	<i>Mn</i>	<i>Ti</i>	<i>Na</i>	<i>K</i>	<i>B</i>	<i>P</i>
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	—	0.04	0.001	0.01	0.1
High-purity fused silica (synthetic)	0.03	—	0.01	0.03	—	—	—	0.004	0.005	—	—
Regular soda lime glass	3.0%	6.0%			4.0%			16%	0.5%		
Borosilicate glass	2.0%	0.5%						4%		13%	

It has long been known that untoward chromatographic reactions occur when certain solutes come in contact with siliceous surfaces containing an abundance of silanol groups. From the results derived from a series of recent experiments<sup>3</sup>, we came to the conclusion, that while these moieties are, undoubtedly, the major cause of the predominantly acidic residual activity usually noted on fused-silica surfaces, their influence may be considerably decreased by creating an experimental environment which favors a "preponderance" of siloxane bridges which are considered to be either substantially less acidic or neutral in character. From this, it was felt that under the proper conditions, deactivation of these surfaces could be more simply and readily achieved. Once this occurs and the proper surface conditions attained, excellent wettability and the uniform film distribution of a wider number of different stationary phases on the fused-silica glass surface should be readily accomplished.

The following study describes our efforts in this area.

## EXPERIMENTAL

The fused-silica capillary tubing was drawn as previously described<sup>2</sup>. In an effort to decrease those conditions which would favor moderate to intense silanol formation upon cooling and exposure to room air and moisture, the ends of the newly drawn capillary tubing were sealed as soon as they emerged from the draw furnace. The seals were maintained on the unused spooled material at all times. They were broken only prior to the immediate introduction of the material used in the treatment of the surface. The techniques used for selectively treating and deactivating the fused-silica surface prior to coating with a variety of stationary liquids, will be described in future publications (Parts II and III). The stationary phases were applied to the capillary columns by means of either the mercury plug method<sup>5</sup> or the static coating technique<sup>6</sup>.

## RESULTS AND DISCUSSION

As stated previously<sup>3</sup>, the precise ratios of silanol groups to siloxane bridges,

*i.e.* strongly acidic to mildly acidic or neutral sites, existing on the surface at the time of preparing the fused-silica capillary tubing are unknown. Moreover, it is said that such determinations are rather difficult to make experimentally by a simple and convenient method<sup>7</sup> due to the very low surface energy in the capillary tube. A recent study<sup>8</sup> also stresses the usefulness of such a technique if it should come into being. All of this notwithstanding, we do know that at temperatures over 800–1000°C, silanol moieties readily condense. Water vapor is volatilized off and highly strained, very reactive siloxane bridges form. This reaction becomes reversible once again in the presence of much lower temperatures and exposure to room air (and moisture). In an effort to induce empirically more favorable conditions (*i.e.* a preponderance of siloxane bridges instead of silanol groups) for the deactivation and uniform wetting of the fused-silica surfaces when coating with certain types of stationary phases, the ends of the capillary tubing were sealed as they emerged from the furnace (2000–2100°C). After coiling the desired length of tubing, the ends were opened and the column was quickly filled with material used in the initial step of the deactivation process. Under these circumstances (see Fig. 1), in most instances after the deactivation process was completed, we readily obtained a very neutral, easily wettable surface. The silanol moieties that did exist were effectively shielded by the reactive reagent chain and functional groups (R) which were irreversibly bonded to the silicon molecule. If these steps were efficiently carried out, it was most unusual to note signs of an acidic surface. On the other hand, on rare occasions, too vigorous treatment gives rise to a slightly basic surface, something we have not seen before in the handling of fused-silica capillary columns particularly when coated with polar phases such as Carbowax 20M. From Figs. 2–4, we can readily observe examples of those exceptional cases where underreactions or overreactions during the deactivation process gave rise to either slightly acidic or slightly basic surfaces. Fig. 2 depicts the chromatogram obtained on a fused-silica capillary column freshly coated with OV-101. The ratio of 2,6-dimethylphenol (DMP) to 2,4-dimethylaniline (DMA) is 1:0.8 in this test mixture. Note, however, the slightly tailing and diminished DMA peak. DMA, a base, is being adsorbed by the unreacted silanol (acidic) groups still present on the surface. None of the other components show adsorption phenomena. Similar effects (Fig. 3) have been much more commonly observed<sup>2</sup> on improperly prepared acidic fused-silica glass columns or columns deactivated with Carbowax 20M and then subsequently coated with Carbowax 20M. Here, in this case where the DMP:DMA ratio in the polar test

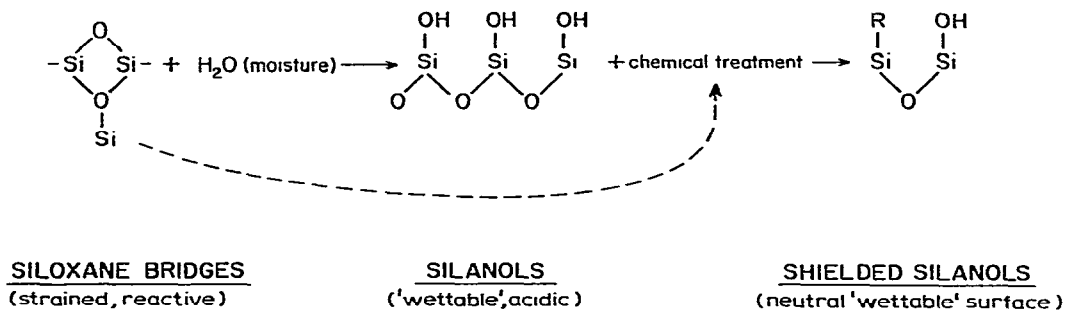


Fig. 1. Chemical reactions taking place on the surface of fused-silica capillary tubing under certain conditions.

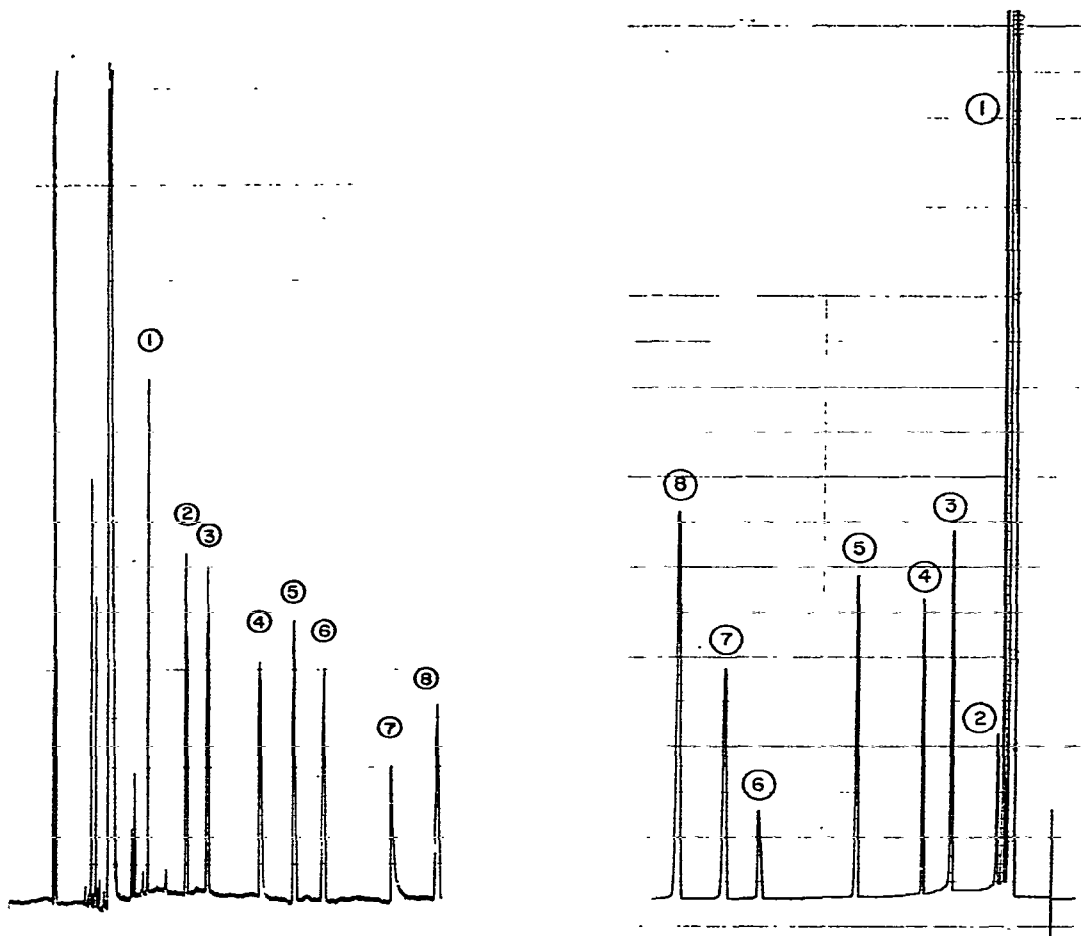


Fig. 2. Chromatogram from fused-silica glass capillary column (50 m) coated with OV-101. "Acidic surface". Temperature, 110°C; pressure, 30 p.s.i. helium. Peak 8, 3077 plates/m at capacity ratio  $k' = 4.0$ . Peaks: 1 =  $C_9$  hydrocarbon; 2 = 2-octanone; 3 =  $C_{10}$  hydrocarbon; 4 = 1-octanol; 5 = 2,6-dimethylphenol; 6 =  $C_{11}$  hydrocarbon; 7 = 2,4-dimethylaniline; 8 = naphthalene.

Fig. 3. Chromatogram from fused-silica glass capillary column (25 m  $\times$  0.009 in.) coated with Carbowax 20M. "Acidic surface". Temperature, 130°C; pressure, 14 p.s.i. helium. Peaks: 1 =  $C_{12}$  hydrocarbon; 2 = 2-octanone; 3 = 1-octanol; 4 =  $C_{16}$  hydrocarbon; 5 = naphthalene; 6 =  $C_{18}$  hydrocarbon; 7 = 2,4-dimethylaniline; 8 = 2,6-dimethylphenol.

sample is 1:1, once again, the slightly acidic surface interacts significantly with the DMA component of the test sample. It has been our experience, that once this occurs on a Carbowax 20M film, and the column is exposed to either mild temperature cycling and/or small amounts of oxygen present in carrier gas cylinders (if oxygen scrubbers are not used), complete film breakdown inevitably occurs in a matter of days. These phenomena are not seen with Carbowax 20M fused-silica glass columns whose surfaces have been made neutral or basic prior to coating with the stationary liquid. In Fig. 4, from the chromatogram obtained from a Carbowax 20M column,

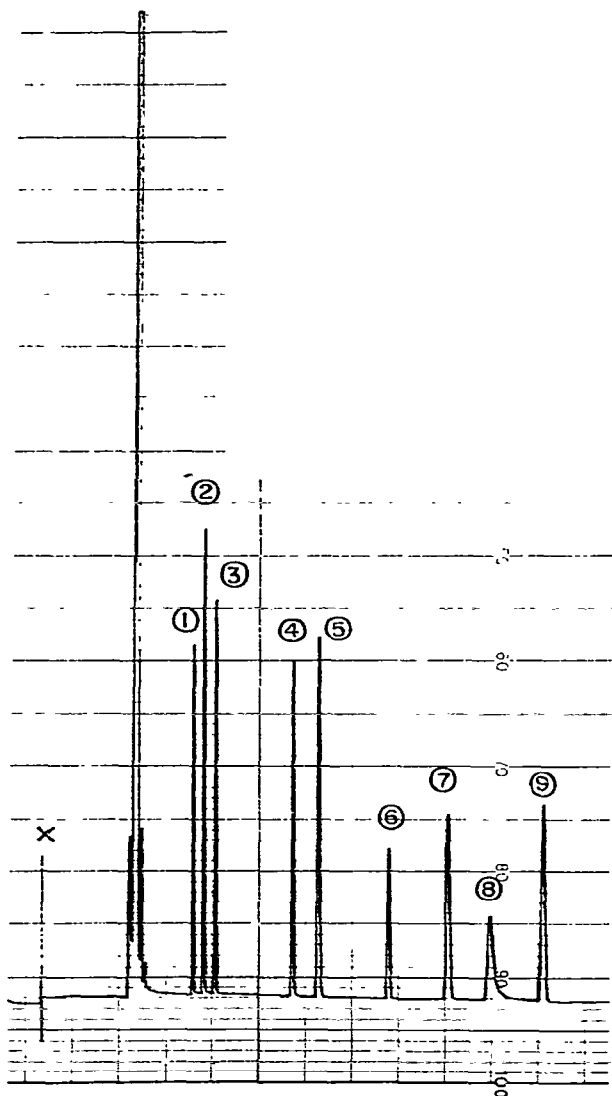


Fig. 4. Chromatogram from fused-silica glass capillary column (25 m) coated with Carbowax 20M. "Basic surface". Temperature, 140°C; pressure, 18 p.s.i. helium. Peaks: 1 =  $C_{15}$  hydrocarbon; 2 = 1-octanol; 3 = cyclooctanone; 4 =  $C_{17}$  hydrocarbon; 5 = naphthalene; 6 =  $C_{18}$  hydrocarbon; 7 = 2,4-dimethylaniline; 8 = 2,6-dimethylphenol; 9 =  $C_{19}$  hydrocarbon.

one can observe the slightly "tailing" and diminished DMP band. Here, the slightly basic surface is adsorbing the acidic DMP component of the test sample.

With added experience, a neutral, uniformly wettable fused-silica glass surface became the rule rather than the exception. Moreover, we observed that by selectively bonding the surface layer prior to the application of the final stationary phase, one was provided with much greater flexibility and versatility, in the successful use of a wider variety of stationary liquids than could be had with that technique whereby one bonds

the stationary phase directly to the surface of the fused-silica glass capillary tubing<sup>9</sup>. In this latter instance, today, this reaction can only be carried out with a few non-polar phases.

At present, by utilizing this system, OV-101, OV-1, SE-30, SE-52, SE-54, OV-3, OV-7, OV-11, OV-17, Dexsil 300, Dexsil 400, Carbowax 20M and free fatty acid phase (FFAP) have been successfully coated onto this type of glass column.

Uniformly distributed films readily yielding 3000 theoretical plates or more, per meter, excellent deactivation and thermal stability are typical characteristics of these uniquely flexible fused-silica glass columns. The following chromatograms very clearly illustrate these outstanding attributes and are representative of what has been accomplished thus far by utilizing this approach.

Figs. 5 and 6 are typical chromatograms obtained from surface-treated fused-silica glass columns coated with the non-polar silicones OV-101 (methyl silicone) and SE-54 (5% phenyl, 1% vinyl, methyl silicone). With most non-polar phases, films usually varying in thickness from 0.1–0.5  $\mu\text{m}$ , can be readily placed on these surfaces.

Chromatograms procured from columns coated with Carbowax 20M and

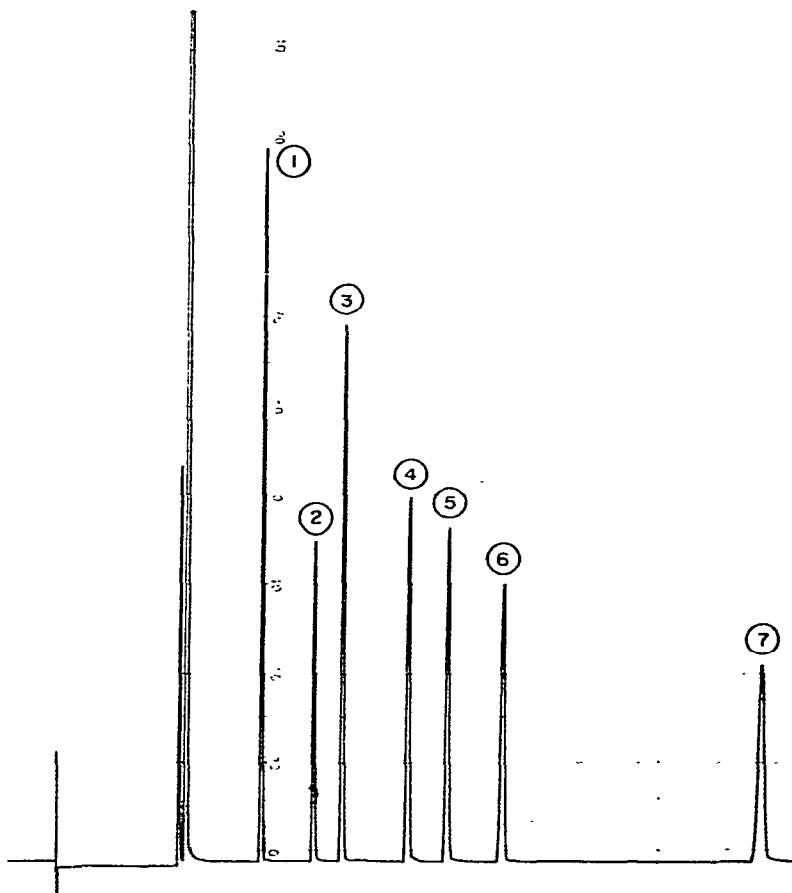


Fig. 5. Chromatogram from fused-silica glass capillary column (25 m) coated with OV-101. Temperature, 110°C; pressure, 18 p.s.i. helium. Peaks as in Fig. 6.

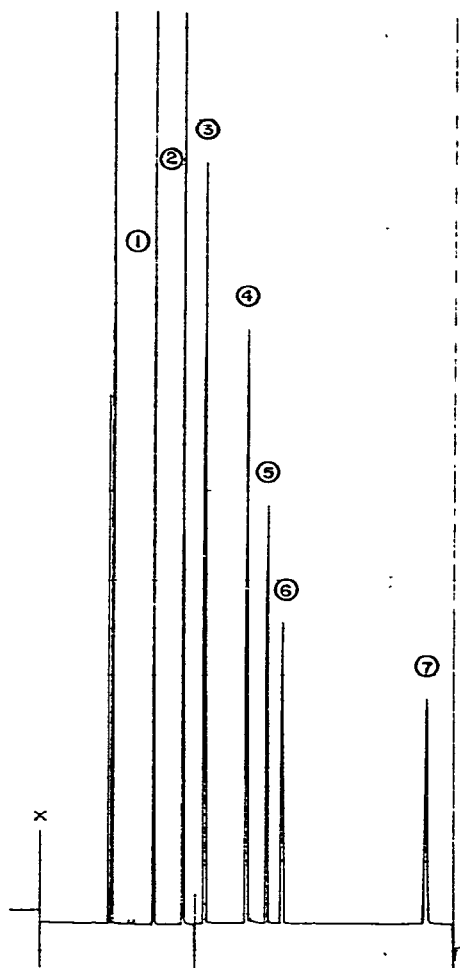


Fig. 6. Chromatogram from fused-silica glass capillary column (50 m) coated with SE-54. Temperature, 110°C; pressure, 28 p.s.i. helium. Peak 7, 3200 plates/m at  $k' = 4.58$ . Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = 2,4-dimethylaniline; 5 = naphthalene; 6 =  $C_{12}$  hydrocarbon; 7 =  $C_{13}$  hydrocarbon.

FFAP are seen in Figs. 7 and 8. Neutral surfaces and stable films provided one here with long lived columns. Very minor differences in relative retention times of certain of the test sample solutes are observed on the two medium polarity columns. These changes are more substantial when complex mixtures of either *cis-trans* methyl esters of fatty acids or certain essential oils are analyzed on both phases, making them versatile and valuable additions to the analyst's collection.

For reasons, some of which still may be obscure at this point in time, the addition of substantial quantities (10 to 50%) of the polar phenyl group to the non-polar methyl silicone backbone provided difficulties to most investigators attempting to coat fused-silica glass capillary columns with a variety of the slight to medium polarity methyl phenyl silicone phases. Most of the methods heretofore employed by

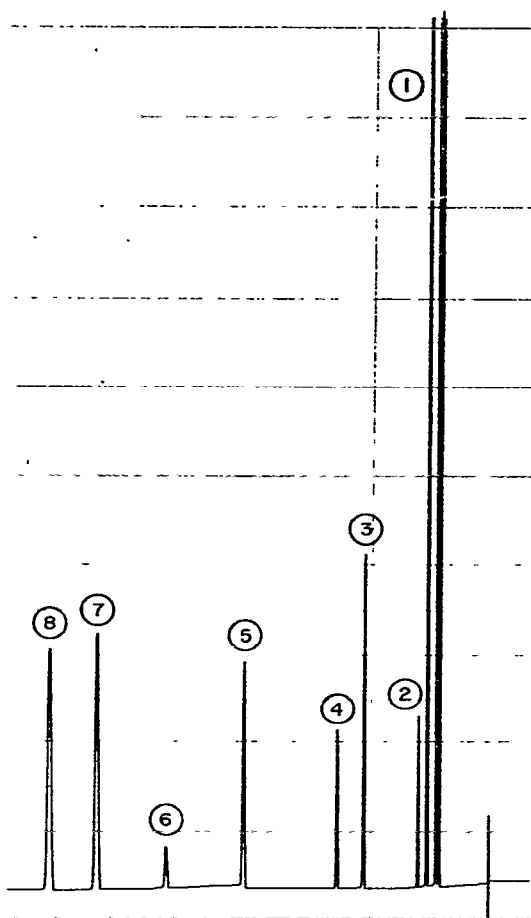


Fig. 7. Chromatogram from fused-silica glass capillary column (25 m) coated with Carbowax 20M. Temperature, 140°C; pressure, 18 p.s.i./helium. Peaks as in Fig. 3.

others as well as ourselves for this purpose, inevitably gave rise to "bead" formation. From this, we can only conclude that in this instance, those techniques used in preparing the surface (one with a relatively low surface energy to begin with), did not significantly alter its surface energy. In all probability, the intermolecular forces between the methyl phenyl silicone molecules and the existing surface moieties were less than the forces between the molecules of the stationary liquids themselves, resulting in droplet formation and all its consequences. Conversely, with the present techniques of selectively tailoring the chemical bonding of the surface prior to coating with a specific phase or class of phases, it must be assumed that a significant increase in surface energy occurs. Thus, the resultant stable and uniformly distributed methyl phenyl silicone films that were formed in this case, were due to the fact that the intermolecular forces between the new surface molecules and those of the methyl phenyl silicones were now greater than the forces between the liquid phase molecules themselves.



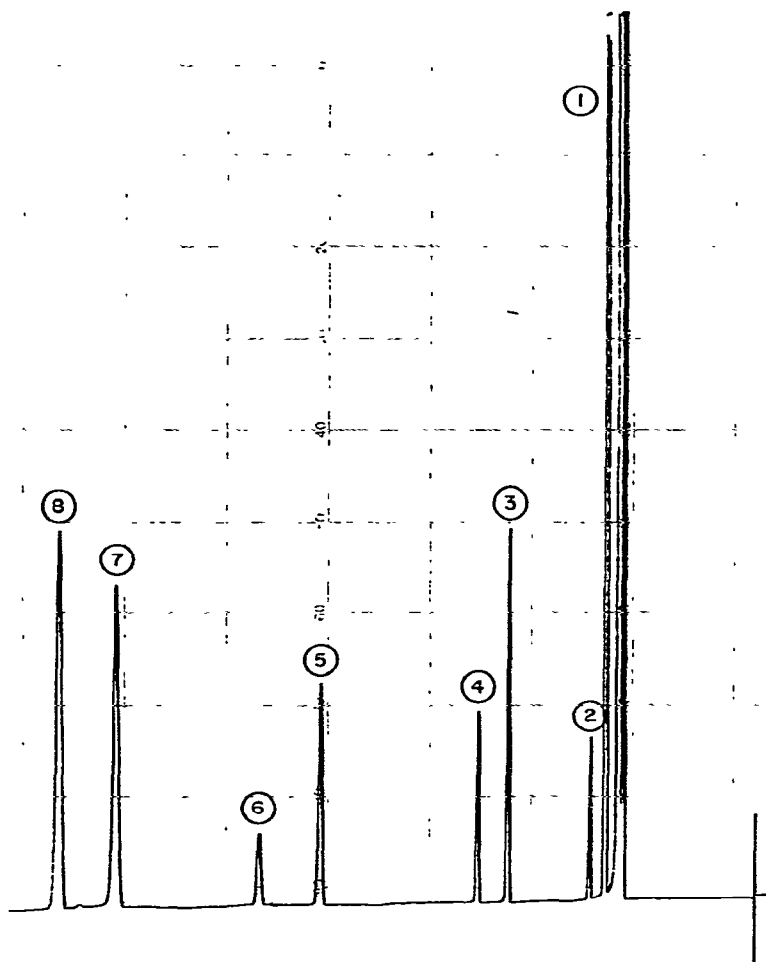


Fig. 8. Chromatogram from fused-silica glass capillary column (25 m) coated with FFAP. Temperature, 140°C; pressure, 18 p.s.i. helium. Peaks as in Fig. 3.

Figs. 9–12 represent chromatograms from columns coated with OV-3 (10% phenyl methyl silicone), OV-7 (20% phenyl methyl silicone), OV-11 (35% phenyl methyl silicone) and finally OV-17 (50% phenyl methyl silicone). Since considerable differences exist in the retention index units,  $\Delta I$  (McReynolds), this is reflected in the relative order of elution of the test sample components on the different phases here (Table II). Generally, as the phenyl content of the stationary phase is increased, modest polar effects become more apparent and the general selectivity of the phase is increased. Again from careful perusal of these chromatograms, it is obvious that excellent film distribution and deactivation has been achieved here.

Similar success was noted with another series of phases possessing unusual structural characteristics, the Dexsils, which again, in the past have been difficult to deactivate and efficiently coat on to various glasses used in the fabrication of capillary

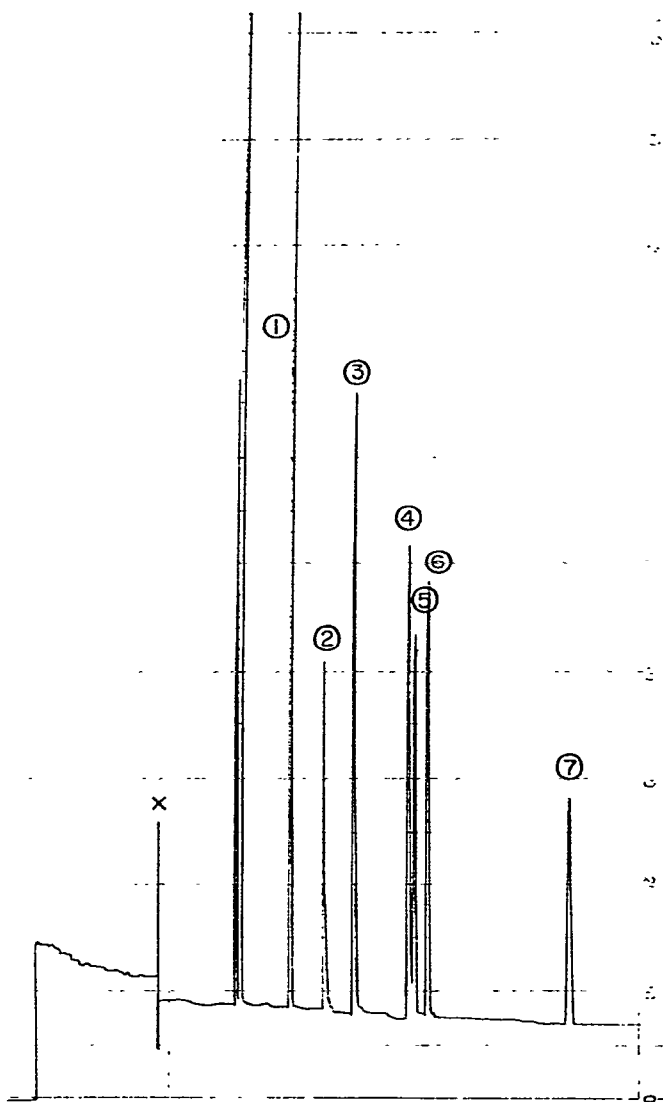


Fig. 9. Chromatogram from fused-silica glass capillary column (25 m) coated with OV-3 (10% phenyl methyl silicone). Temperature, 110°C; pressure, 18 p.s.i. helium; chart speed, 1 cm/min; sample, test mixture. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = 2,4-dimethylaniline; 5 = C<sub>12</sub> hydrocarbon; 6 = naphthalene; 7 = C<sub>13</sub> hydrocarbon.

columns. Chromatograms obtained from fused-silica glass capillary columns prepared with Dexsil 300 (a methyl siloxane-carborane polymer, mol.wt. 16,000–20,000), and Dexsil 400 (a methyl phenyl siloxane-carborane polymer, mol.wt. 12,000–16,000) are shown in Figs. 13 and 14. Once more, substantial differences in the order of elution of the solutes of the test mixture are noted (Table III). With an increase in polarity due to the presence of the phenyl moiety in Dexsil 400, the naphthalene component has moved toward the front and the order of emergence of

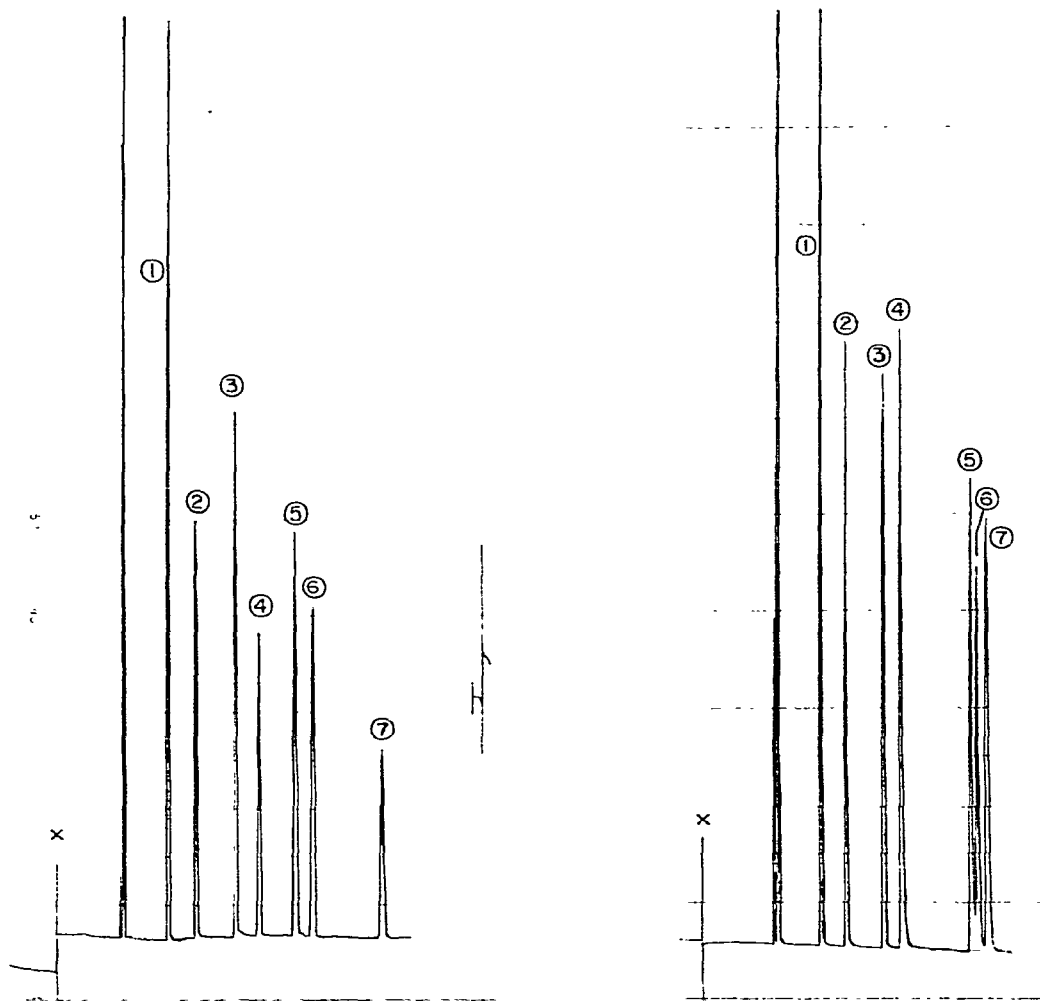


Fig. 10. Chromatogram from fused-silica glass capillary column (25 m) coated with OV-7 (20% phenyl methyl silicone). Temperature, 110°C; pressure, 17 p.s.i. helium; chart-speed, 1 cm/min; sample, test mixture. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = C<sub>12</sub> hydrocarbon; 5 = 2,4-dimethylaniline; 6 = naphthalene; 7 = C<sub>13</sub> hydrocarbon.

Fig. 11. Chromatogram from fused-silica glass capillary column (25 m) coated with OV-11 (35% phenyl methyl silicone). Temperature, 110°C; pressure, 17 p.s.i. helium; chart speed, 1 cm/min; sample, test mixture. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = C<sub>12</sub> hydrocarbon; 4 = 2,6-dimethylphenol; 5 = 2,4-dimethylaniline; 6 = C<sub>13</sub> hydrocarbon; 7 = naphthalene.

DMP and DMA has been reversed when compared to that seen with Dexsil 300, OV-17 and OV-101.

Finally, due to the very high surface tension of exceedingly useful very polar stationary phases such as the cyanopropyl silicones (OV-225, OV-275, Silar 5C and 10C), these materials have been very difficult to coat on the usual soda lime or borosilicate glass capillary columns without encountering droplet formation. Success

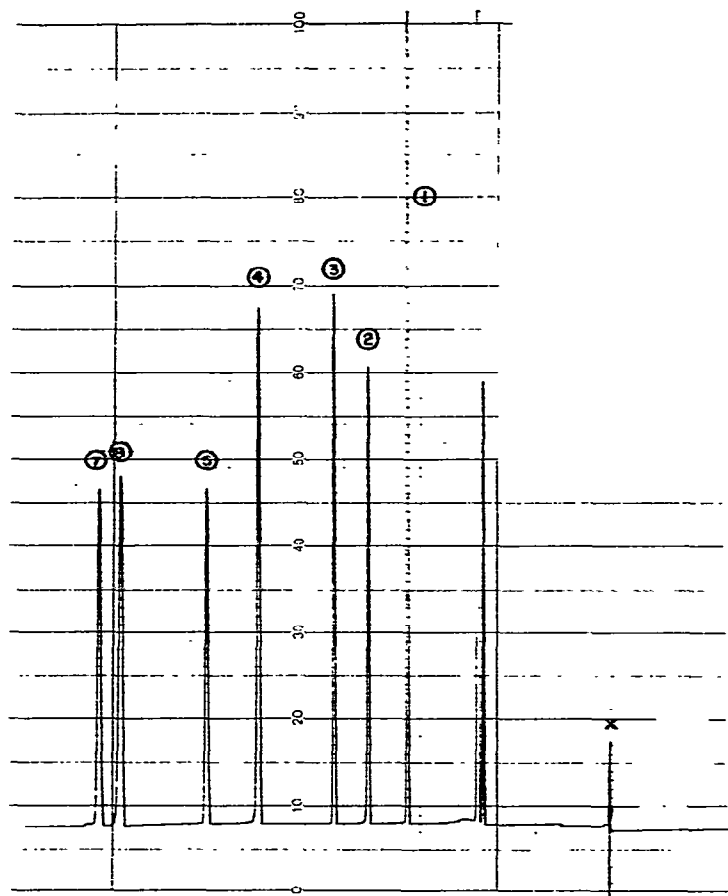


Fig. 12. Chromatogram from fused-silica glass capillary column (25 m) coated with OV-17 (50% phenyl methyl silicone). Temperature, 110°C, pressure, 17 p.s.i. helium; chart speed, 1 cm/min. Peak 7, 3850 plates/m at  $k' = 3.25$ . Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 =  $C_{12}$  hydrocarbon; 4 = 2,6-dimethylphenol; 5 =  $C_{13}$  hydrocarbon; 6 = 2,4-dimethylaniline; 7 = naphthalene.

was only achieved when soda lime glass capillary tubing was treated with gaseous HCl<sup>10</sup>. While most observers contend that this effect was primarily due to the "roughening" of the surface brought about by the deposition of a matrix of NaCl crystals, recent experiences in the treatment of a wide variety of glass surfaces make us cast some doubt upon this prevailing concept. Another explanation may be in order here. It is felt that under these circumstances, strong acids such as HCl, hydrolyze surface sodium silicates to silicic acid and NaCl. The resultant liberated, hydrolyzed forms of silicic acid (silanol groups) are strongly polar and can effectively interact with very polar liquids and are thus readily wetted.

From all of this, it becomes apparent that no single technique can be used for the preparation of the surface of a unique glass such as fused silica—which would enable one to effectively coat it with a wide range of liquid phases and in particular, those that represent both extremes in polarity. Careful attention to the selection of the

TABLE II

## ORDER OF ELUTION OF TEST MIXTURE ON FUSED-SILICA GLASS CAPILLARY COLUMNS COATED WITH PHENYL METHYL SILICONES

Temperature, 110°C.

<i>OV-17 (50% phenyl)</i>	<i>OV-11 (35% phenyl)</i>
1. 2-Octanone	1. 2-Octanone
2. 1-Octanol	2. 1-Octanol
3. C <sub>12</sub> Hydrocarbon	3. C <sub>12</sub> Hydrocarbon
4. 2,6-Dimethylphenol	4. 2,6-Dimethylphenol
5. C <sub>13</sub> Hydrocarbon	5. 2,4-Dimethylaniline
6. 2,4-Dimethylaniline	6. C <sub>13</sub> Hydrocarbon
7. Naphthalene	7. Naphthalene
<i>OV-7 (25% phenyl)</i>	<i>OV-3 (10% phenyl)</i>
1. 2-Octanone	1. 2-Octanone
2. 1-Octanol	2. 1-Octanol
3. 2,6-Dimethylphenol	3. 2,6-Dimethylphenol
4. C <sub>12</sub> Hydrocarbon	4. 2,4-Dimethylaniline
5. 2,4-Dimethylaniline	5. C <sub>12</sub> Hydrocarbon
6. Naphthalene	6. Naphthalene
7. C <sub>13</sub> Hydrocarbon	7. C <sub>13</sub> Hydrocarbon

appropriate surface conditions compatible with the stationary phase to be employed would do much to hasten further progress in this area. It is hoped that something like three to four variations in the basic technique of surface treatment would do much in accomplishing this goal.

TABLE III

## ORDER OF ELUTION OF TEST MIXTURE ON FUSED-SILICA GLASS CAPILLARY COLUMNS COATED WITH CERTAIN STATIONARY PHASES

Temperature, 110°C.

<i>OV-101</i>	<i>OV-17</i>
1. 2-Octanone	1. 2-Octanone
2. 1-Octanol	2. 1-Octanol
3. 2,6-Dimethylphenol	3. C <sub>12</sub> Hydrocarbon
4. 2,4-Dimethylaniline	4. 2,6-Dimethylphenol
5. Naphthalene	5. C <sub>13</sub> Hydrocarbon
6. C <sub>12</sub> Hydrocarbon	6. 2,4-Dimethylaniline
7. C <sub>13</sub> Hydrocarbon	7. Naphthalene
<i>Dexsil 300</i>	<i>Dexsil 400</i>
1. 2-Octanone	1. 2-Octanone
2. 1-Octanol	2. 1-Octanol
3. 2,6-Dimethylphenol	3. Naphthalene
4. C <sub>12</sub> Hydrocarbon	4. C <sub>12</sub> Hydrocarbon
5. 2,4-Dimethylaniline	5. 2,4-Dimethylaniline
6. Naphthalene	6. 2,6-Dimethylphenol
7. C <sub>13</sub> Hydrocarbon	7. C <sub>13</sub> Hydrocarbon

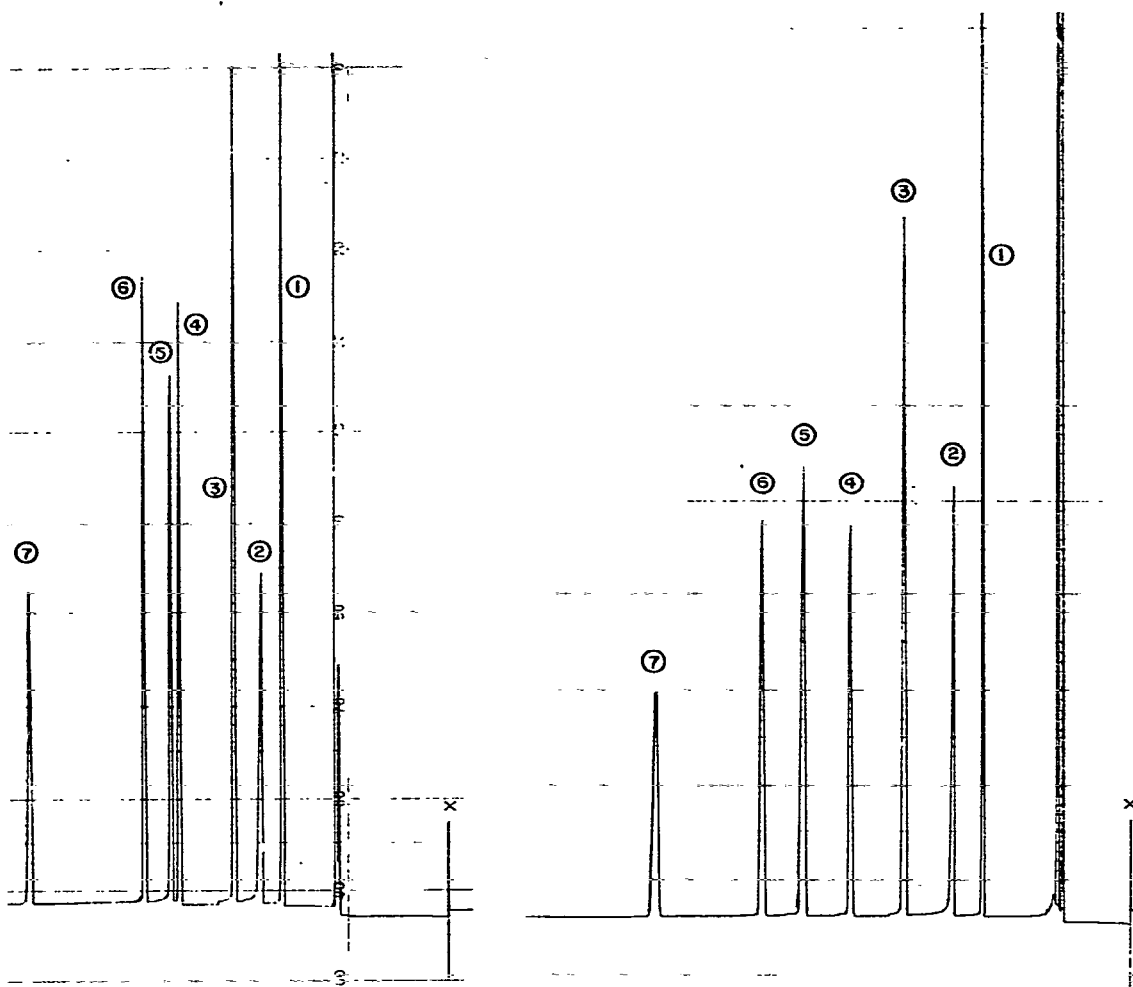


Fig. 13. Chromatogram from fused-silica glass capillary column (25 m) coated with Dexsil 300. Temperature, 110°C; pressure, 18 p.s.i. helium; chart speed, 1 cm/min. Peak 7, 3815 plates/m at  $k' = 3.0$ . Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 =  $C_{12}$  hydrocarbon; 5 = 2,4-dimethylaniline; 6 = naphthalene; 7 =  $C_{13}$  hydrocarbon.

Fig. 14. Chromatogram from fused-silica glass capillary column (25 m) coated with Dexsil 400. Temperature, 110°C; pressure, 18 p.s.i. helium. Peak 7, 3000 plates/m at  $k' = 6.4$ . Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = naphthalene; 4 =  $C_{12}$  hydrocarbon; 5 = 2,4-dimethylaniline; 6 = 2,6-dimethylphenol; 7 =  $C_{13}$  hydrocarbon.

#### ACKNOWLEDGEMENT

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