

CHROMSYMP. 073

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

II. DEACTIVATION BY ESTERIFICATION WITH ALCOHOLS AND DEACTIVATION WITH SPECIALLY PREPARED HIGH-MOLECULAR-WEIGHT STATIONARY PHASES

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SUMMARY

Silanol groups present on fused-silica glass capillary column surfaces were readily esterified in the presence of alcohols to form stable, inert, organophilic and hydrophobic alkoxy linkages, which were then easily wetted by a variety of non-polar stationary phases. Such gas chromatographic capillary columns exhibited well deactivated surfaces, good thermal stability and high column efficiencies.

Preliminary studies showed that a new series of appropriately designed and custom-synthesized non-polar and highly polar stationary phases that contain varying degrees of phenyl (up to 50%) or cyanopropyl (up to 98%) substitution, when applied in a single step, efficiently wetted and deactivated the surfaces of fused-silica glass. Then, on exposure to appropriate free-radical generators, these vinyl-containing polymers were readily cross-linked. The characteristics of such columns are considered to be very close to ideal.

INTRODUCTION

Chromatographically, it is now well recognized that the surfaces of untreated fused-silica glass capillary tubing exhibit slight acidic activity. As the metal oxide content of this glass is less than 0.1 ppm, thus ruling out the presence of Lewis acid sites, it is now assumed that this activity is primarily caused by the presence of silanol groups. These appear to be derived from the preponderant and highly reactive, metastable siloxane bridges¹ formed at the high drawing temperatures (2100°C), only to break down to some extent on cooling and contact with water vapor in the air.

As these surfaces were noted to resemble that which is found in certain states of silica gel, deactivation of the glass was attempted by means other than the use of silylating agents, whose reproducibility and overall effectiveness in our hands varied considerably. In this instance, primary and/or secondary alcohols were utilized² in

an attempt to form stable, effective ester linkages with the silanol moieties. Using very simple laboratory procedures for creating different alkoxy linkages by means of hydrogen bonding of free SiOH groups, neutral, well deactivated fused-silica glass surfaces were obtained, which were then easily wetted by commercially available non-polar methyl (OV-101, SE-30) and methyl 5% phenylpolysiloxane (SE-52, SE-54) stationary phases. Such columns also showed good efficiency and thermal stability up to 300°C.

When these commercially available polysiloxane stationary phases containing a higher phenyl content (10–50%) were to be employed, a variety of short-chain diols, including those containing phenyl groups, *e.g.*, 1-phenyl-1,2-ethanediol, were used in an attempt to deactivate the surfaces of the glass. Here too, those alkoxy linkages (estersils²) created by reactions with various glycols (ethylene, triethylene and tetraethylene) also provided reproducible, easily wetted and superbly deactivated surfaces. Particularly when pure tetraethylene glycol was used properly, they exhibited characteristics superior to those noted when Carbowax 20M (containing several classes of polyethylene glycol) was employed for this purpose. The shift in Kováts indices³ was only slightly less discernible, and the columns were stable up to 280°C.

Several observations were of interest here. First, various phenols (with the OH group attached directly to an aromatic ring) that were tried, although capable of forming esters, were not effective in deactivating surfaces. Accordingly, as is well known, as their overall properties differ significantly from those of alcohols, they must be classified as a different family of compounds. Second, the alkoxy surfaces formed from reactions with butanol or the diols could not be wetted by silicone stationary phases containing substantial cyanopropyl substitution. Third, these esterified surfaces were efficiently deactivated and wetted by other non-polar silicone polymers containing groups necessary for elastomer formation. However, in general, when cross-linking of the stationary phase was carried out here, significant surface activity reappeared. In an effort to correct this defect, an attempt has now been made to introduce vinyl groups into the alcohol chain to determine if esters remain intact during covalent bonding to the surface of the glass and the stationary phase.

Finally, during the course of this investigation on the role of alkoxy linkages in decreasing the activity of fused-silica surfaces, it was decided to determine the effect of carrying out other types of reactions with compounds of much higher molecular weight. In this instance, one of a series of α,ω -hydroxymethylsilicone polymers^{4,5} was directly coated on to the *untreated* surface of a fused-silica capillary column. The formation of an efficient, thermally stable, almost completely deactivated surface encouraged us to pursue this line of study further.

EXPERIMENTAL

Blank fused-silica capillary columns were flushed with nitrogen for 30 min prior to deactivation procedures. All alcohols employed were of analytical-reagent grade and were kept free from moisture. They ranged from C₁ to C₁₀ and were representative of primary, secondary and tertiary types. The diols were ethylene glycol, triethylene glycol, tetraethylene glycol and styrene glycol (1-phenyl-1,2-ethanediol). They were applied to the surface of fused-silica tubing by either the dynamic or static techniques. With reference to the former, the liquids in neat form or in

solutions in concentrations up to 45% in pentane or dichloromethane were forced through the capillary tubing with nitrogen by means of a mercury plug (2 cm/sec). Concentrations of 0.20-1.2% in pentane or dichloromethane were used for static coating.

Following the initial step of the deactivation procedure, traces of solvent were removed by passing nitrogen through the capillary tube for 2 h at 60°C. With nitrogen still flowing, the glass coil was brought back to room temperature. The ends were placed under vacuum for 15-30 min and then carefully sealed. The temperature of the capillary column was increased at the rate of 2°C/min to 300°C, where it remained for 12-15 h. After the column had cooled, the seals were broken and the column was purged with nitrogen for 1 h after being brought to 110°C. When tetraethylene glycol was used to esterify the surface, after the column had cooled it was then carefully rinsed with 5-10 ml of dichloromethane or methanol and then blown dry with nitrogen at 110°C.

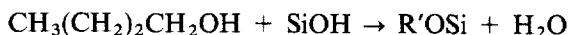
A commercial stationary phase, OV-101 (Ohio Valley Co.), or a custom-made polysiloxane diol was applied by the dynamic technique. Commercial gum phases (SE-30, SE-54) and specially synthesized high-molecular-weight polysiloxane compounds with differing degrees of phenyl and cyanopropyl substitution⁴ were coated on to capillary columns by the static method.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the adsorption of certain of the polar components of the test mixture when batches of untreated fused-silica glass capillary tubing were coated directly with the usual commercially available non-polar stationary phases SE-30 (methylsilicone) and SE-54 (5% methyl-, 1% phenylvinylsilicone).

When an alcohol, in this instance butanol, was used to esterify and deactivate the surface, prior to coating with the same phases, excellent chromatograms were obtained. It can be seen in Figs. 3 and 4 that the surface activity has been effectively neutralized, and a uniform, efficient and thermally stable film (up to 300°C) was produced.

Apparently, as first noted with silica², the alcohol moiety reacts with the OH groups of silanols under favorable conditions to form butoxy groups (estersils), which on a fully esterified surface are remarkably stable, organophilic and hydrophobic:



Similar results were generally obtained with C₄-C₁₀ primary alcohols. However, the general overall impression was that the straight-chain 1-butanol and 1-decanol were the easiest to work with and seemed to provide esters with the best overall chromatographic properties. The influence of the size and shape of other branched alkyl groups on the surfaces of fused-silica glass will be the subject of another report, particularly as preliminary studies confirmed the observations that branched "bushy" groups² or "brushes"⁶ cover a larger surface area than that noted with a straight-chain group.

It should be noted that when butanol or decanol (but not the diol) is employed in ester formation, some activity problems may be encountered unless adequate pre-

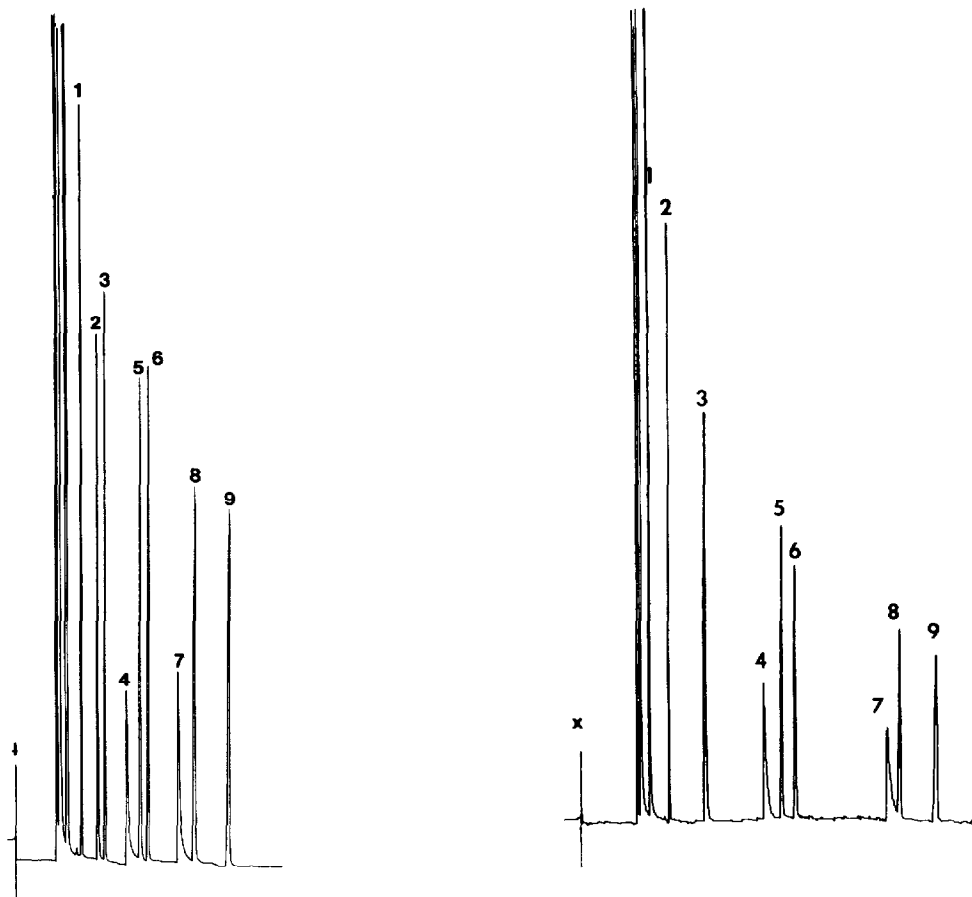


Fig. 1. Chromatogram obtained with 15 m \times 0.25 mm I.D. fused-silica glass capillary column, coated directly with OV-101 without prior deactivation of the surface. Temperature, 100°C; pressure, 12 p.s.i. (helium); chartspeed, 60 cm/h. Peaks: 1 = C₉; 2 = 2-octanone; 3 = C₁₀; 4 = 1-octanol; 5 = 2,6-dimethylphenol; 6 = C₁₁; 7 = 2,4-dimethylaniline; 8 = naphthalene; 9 = C₁₂.

Fig. 2. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica glass capillary column, coated directly with SE-54 without prior deactivation of the surface. Temperature 100°C; pressure, 18 p.s.i. (helium); chartspeed, 60 cm/h. Peaks 1-9 as in Fig. 1, except peak 5 is C₁₁ and peak 6 is 2,6-dimethylphenol.

cautions are taken when the static method is then used to coat the stationary phase on a surface where the reaction was not taken to completion. These phenomena usually were not noted when the dynamic technique was employed by utilizing the mercury plug method for coating with dilute or highly concentrated solutions of stationary phase liquids.

The results of the esterification of the glass surface with tetraethylene glycol (TEG) are shown in Fig. 5. Here, the esterified surface was coated with the commercial stationary phase OV-17 (50% methyl-, phenylmethylsiloxane). An efficient, uniform film was produced that was stable up to 270-280°C. However, the presence of the TEG ester here caused a moderate shift in the C₁₃ band toward the front. This was not seen when a custom-synthesized high-molecular-weight 50% methyl-, phe-

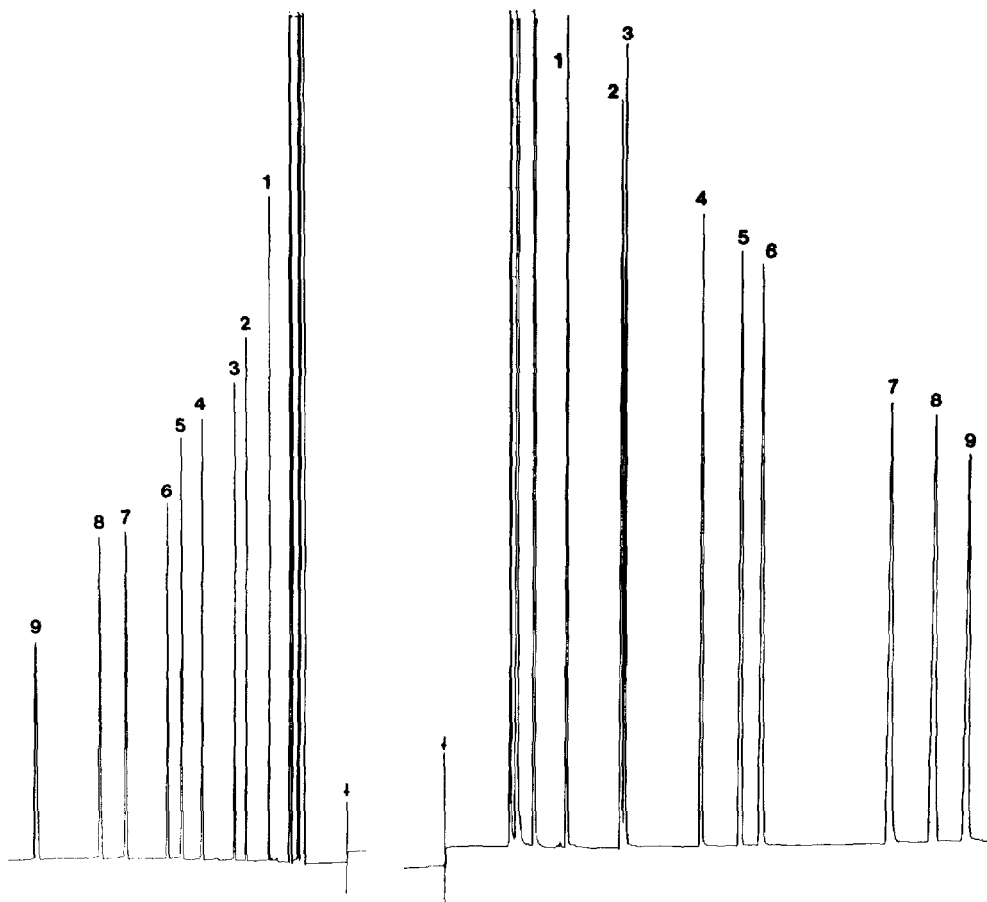


Fig. 3. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica capillary column, deactivated by esterification with butanol, coated with OV-101. Temperature, 90°C; pressure, 18 p.s.i. (helium); chart-speed, 60 cm/h. Peaks as in Fig. 1.

Fig. 4. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica capillary column, deactivated by esterification with butanol, coated with SE-54. Temperature, 90°C; pressure, 14 p.s.i. (hydrogen); chart-speed, 120 cm/h. Peaks as in Fig. 2.

nylpolysiloxane polymer was directly applied to the surface of a fused-silica capillary column¹.

Fig. 6 shows the chromatogram obtained from a column coated with a specially prepared high-molecular-weight diol polysiloxane polymer. This semi-viscous material was coated dynamically on to an untreated 0.25-mm I.D. fused-silica glass capillary column, the solvent removed, the ends of column were sealed and the column was heated to 325–350°C overnight. The column was allowed to cool to room temperature, the sealed ends were removed and the column was conditioned by slowly raising the temperature to 300°C. An efficient, thermally stable methylpolysiloxane column (Fig. 6) was produced, which in the exceptional case had an almost completely deactivated surface. With experience, in most instances completely inert surfaces were routinely obtained. Apparently, under these circumstances, it is plausible

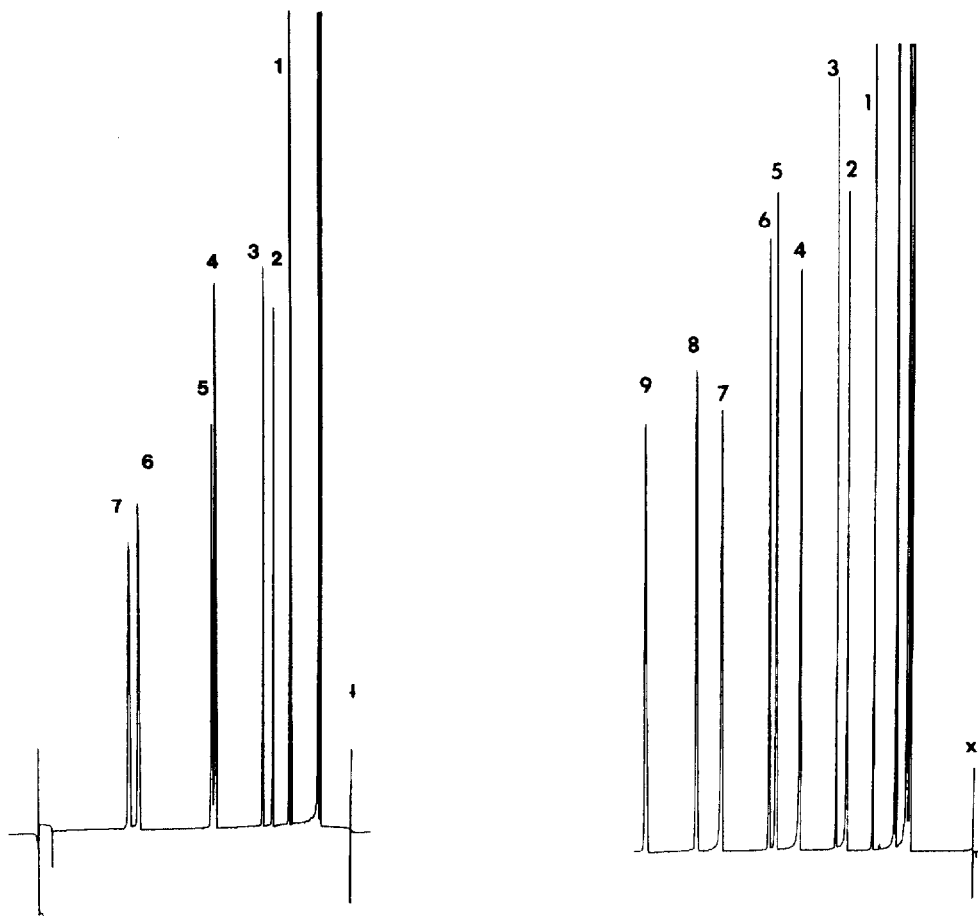


Fig. 5. Chromatogram obtained with 15 m \times 0.25 mm I.D. fused-silica glass capillary column, deactivated by esterification with tetraethylene glycol and then coated statically with OV-17. Temperature, 100°C; pressure, 13 p.s.i. (helium); chartspeed, 60 cm/h. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = C₁₂; 4 = 2,6-dimethylphenol; 5 = C₁₃; 6 = 2,4-dimethylaniline; 7 = naphthalene.

Fig. 6. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica glass capillary column with a high-molecular-weight polysiloxane diol polymer coated directly on to the untreated surface. Temperature, 100°C; pressure, 18 p.s.i. (helium); chartspeed, 60 cm/h. Peaks as in Fig. 1; the only sign of activity is the presence of slight tails on peak 2 = 2-octanone, peak 4 = 1-octanol and peak 7 = 2,4-dimethylaniline. The peak ratios are excellent.

to believe that with heat the OH groups of this particular silicone polymer readily condensed with the slightly acidic surface silanol groups, which may have acted as a catalyst in this reaction. In contrast to relatively short-chain alcohols or diols, in this instance, the siloxane linkage to the glass surface involved a very long-chain silicone polymer. Here, a stable, uniformly distributed cross-linked polymeric film with all the chromatographic properties of the methylsilicones, OV-101, SE-30 or OV-1, was produced on surfaces that now appeared to be neutral. Hence there was no need to go through the usual second step, namely, coating with the conventional stationary phase.

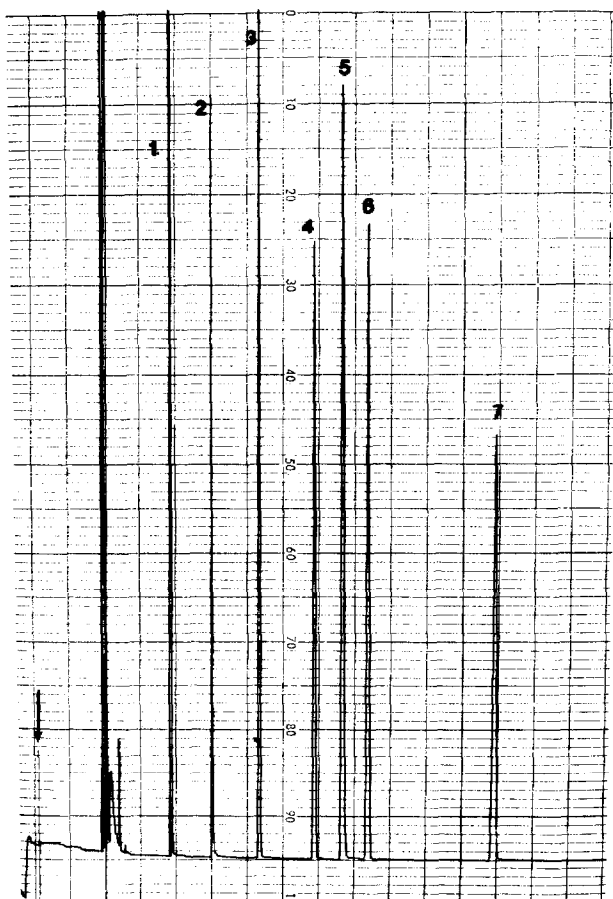


Fig. 7. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica glass capillary column with high-molecular-weight vinyl-containing 20% methyl-, phenylpolysiloxane polymer, coated directly on to the untreated surface. Temperature, 110°C; pressure, 20 p.s.i. (helium); chartspeed, 60 cm/h; film-thickness, 0.25 μ m. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = C₁₂; 5 = 2,4-dimethylaniline; 6 = naphthalene; 7 = C₁₃.

This result prompted us to investigate again⁷ two areas of interest. The first involved those factors which govern the successful wetting of the fused-silica glass surface by a wide range of non-polar and polar polymeric films, and the second those reactions which may be responsible for the structural changes involving either the binding or the effective covering of the silanol groups, thus leading to the neutralization of the slightly acidic surface of fused-silica glass. Obviously, interest here too centered around the fascinating possibility of greatly extending the ability to "neutralize" the surface and coat efficiently this very versatile glass with a wide variety of different polymeric films in a single step.

When it was first observed³ that certain commercially available stationary phases (particularly silicone polymers with substantial phenyl or cyanopropyl substitutions) could not be properly wetted on the surface of fused-silica glass, we at

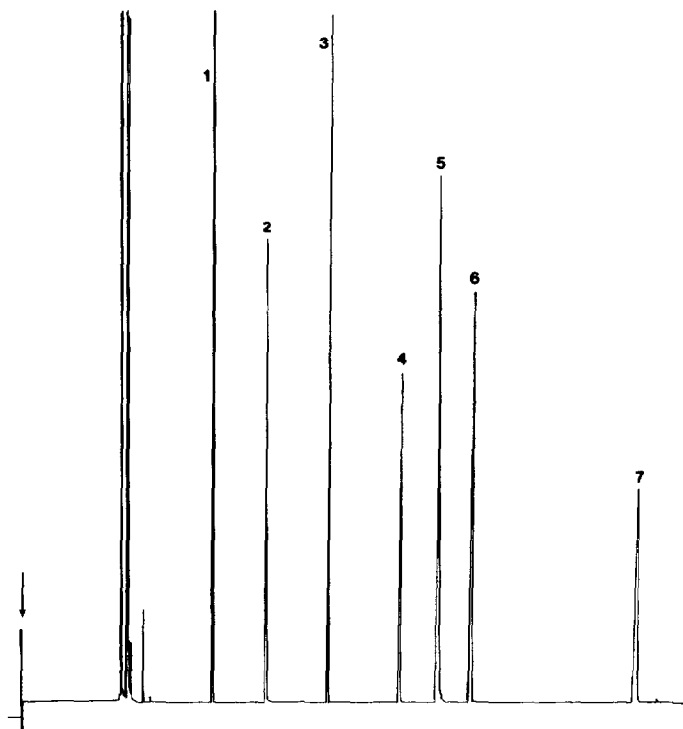


Fig. 8. Chromatogram obtained with same column as in Fig. 7, except length = 100 m and film-thickness = $0.1 \mu\text{m}$. Temperature, 110°C ; pressure (hydrogen), 45 p.s.i.; chartspeed, 60 cm/h. Peaks as in Fig. 7; 3800 plates/m for naphthalene at $k = 3.6$.

that time improperly assumed that this effect was due to the relatively low surface energy of this particular type of untreated glass. Accordingly, we then postulated that these surfaces had to be altered by either physical or chemical means in order to increase the surface energy to the level where these materials can readily wet this altered surface. Later, when studies⁸ by contact angle measurements revealed the relatively high surface energies of 50–72 dyn/cm for fused-silica glass, we still found difficulty in reconciling our laboratory experience with these data. With time, however, it appeared that both sets of laboratory observations were valid, but certain assumptions were inappropriate. Evidence was mounting in our laboratory to make us believe that those specific commercial stationary phases used in our studies, *i.e.*, OV-3, OV-7, OV-11, OV-17 (10–50% methyl-, phenylsiloxanes) and SP-2340 and Silar 10C (75–100% cyanopropylmethylpolysiloxane), did not possess the appropriate physical chemical properties for effective use with fused-silica surfaces. They were relatively low-molecular-weight liquid polymers and, in these instances, the particular intermolecular forces between the stationary phase molecules and the existing surface moieties on fused-silica glass were less than the forces between the molecules of the stationary films themselves. This resulted in droplet formation with all its consequences. When certain physico-chemical modifications were made in some of the specially prepared high-molecular-weight silicone polymers used in cross-linking experiments⁴ on fused-silica glass, it was noted for the first time that, for example,

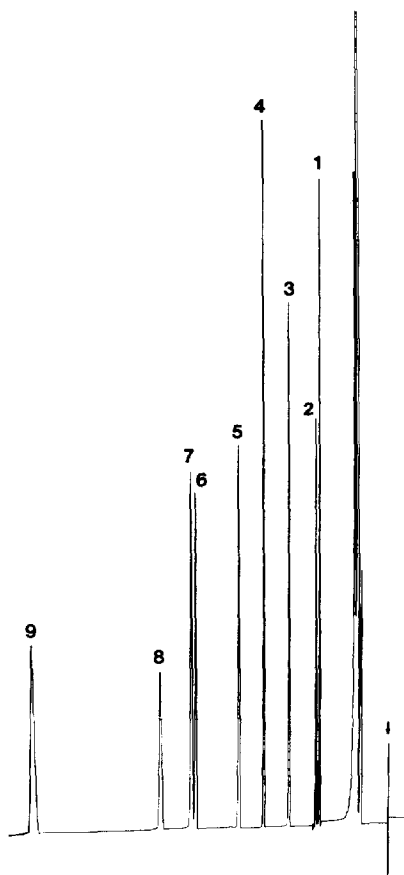


Fig. 9. Chromatogram obtained with 25 m \times 0.25 mm I.D. fused-silica glass capillary column with a specially prepared high-molecular-weight vinyl-containing methylpolysiloxane with 75% cyanopropylmethyl substitution, coated directly on to the untreated surface. Temperature, 110°C; pressure, 18 p.s.i. (helium); chartspeed, 60 cm/h. Peaks: 1 = C₁₂; 2 = cyclooctanone; 3 = 1-octanol; 4 = C₁₆; 5 = naphthalene; 6 = 2,6-dimethylphenol; 7 = 2,4-dimethylaniline; 8 = C₁₈.

those made with high phenyl or cyanopropyl substitution (biscyanopropyl as well as cyanopropylmethyl) not only wet very well but also gave rise to well deactivated surfaces⁷.

Some early results of this study are shown in Figs. 7 and 8. The particular material used to coat these fused-silica columns directly in a single step by the static technique without prior deactivation procedures was a specially synthesized high-molecular-weight, viscous, vinyl-containing methylpolysiloxane polymer with 20% phenyl substitution. The deactivation was almost perfect for both the 25M and the thin-film 100M columns. The only imperfection was a barely perceptible tail on the peaks representing octanol and 2,4-dimethylaniline.

Similarly, a very highly polar fused-silica glass capillary column was obtained by the single-step direct application of one of a series of specially prepared high-molecular-weight vinyl-containing methylpolysiloxanes with, in this instance, 75% cyanopropylmethyl substitution⁷. Fig. 9 again shows that another very efficient, thermally stable film (270°C) was produced on a completely deactivated surface. Both

the highly substituted phenyl- and cyanopropylmethylpolysiloxane stationary phases were easily cross-linked after exposure to appropriate free-radical generators (azobis-*tert.*-butane). However, difficulties in vulcanization were encountered when high percentages of the bis-cyanopropyl moiety were present. More extensive details of this study will be presented elsewhere⁹.

Thus, about 4 years after the dramatic announcement of the use of flexible fused-silica glass tubing for capillary column gas chromatography¹⁰, preliminary evidence from our laboratory now leads us to believe that fused-silica surfaces can be expeditiously coated by an ever increasing variety of properly designed non-polar and highly polar stationary phases. Thus, upon fruition, when all parameters used to assess the quality of these capillary columns and the ease of their fabrication are taken into consideration, they may become the "ideal" capillary columns for a long time to come.

ACKNOWLEDGEMENT

This work was supported in part by Contract DE-AC02-76-EVO2958. A010, U.S. Department of Energy.

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