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## CYANOSILICONES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY. I.

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### SUMMARY

Access to medium-polarity and polar capillary columns would greatly increase the separation power of gas chromatography. A prerequisite for this, however, is that the columns must possess high efficiency, a high degree of deactivation and high thermal stability. A procedure is presented for the preparation of fused silica and soda-glass capillary columns that fulfil these requirements. Efficiency and deactivation are obtained by leaching the capillary followed by silanization at high temperatures using bis(cyanopropyl)cyclotetrasiloxane. Column stability is achieved by *in situ* peroxide-initiated cross-linking in a silicone gum to form a rubber stationary phase.

Three types of phases were synthesized, having 33, 50 and *ca.* 95% cyano substitution. Some tolyl and vinyl substitution was included in order to facilitate cross-linking.

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### INTRODUCTION

Stationary phases for capillary gas chromatography (GC) usually consist of non-polar liquids. The use of polar phases that have the ability to interact selectively with sample components would, however, greatly increase the separation power in our opinion<sup>1</sup>. To achieve this, high demands have to be made on the quality of the polar column. Column efficiency and deactivation should be at the same level as that experienced with non-polar columns. Further, higher temperatures are required for the elution of polar solutes from a polar column compared with a non-polar column, and it is important that a polar column can be used at high temperatures for the separation of substances with high boiling points.

Several methods have been used to achieve column deactivation and the wettability that is necessary when high column efficiency is desired. Deactivation can be achieved by Carbowax treatment<sup>2,3</sup> or silylation at high temperatures<sup>4-8</sup>. Suitable wettability can be obtained by physical surface modification, *e.g.*, deposition of sodium chloride from a sol<sup>9</sup>, or by chemical modification, which involves silylation with reagents carrying the same side-groups as the silicone phase that is to be used<sup>10-12</sup>. We have developed a method in which surface modification is performed

by high-temperature silanization using cyclic siloxanes substituted with special side-groups, *i.e.*, trifluoropropyl<sup>13</sup>, cyanopropyl<sup>14</sup> and phenyl<sup>15</sup>. This method confers both deactivation and wettability upon the capillary surfaces.

Silicone gums give more stable stationary phase films than silicone oils<sup>16,17</sup>. Cross-linked silicone phases (rubber phases), however, offer outstandingly high stability<sup>1</sup>. Some medium-polarity and polar columns coated with such phases have been made. First, columns coated with phenyl<sup>18</sup> and cyanopropyl<sup>19</sup> silicone rubber having cross-links of the type Si-O-Si were prepared. Recently, the use of silicone rubber phases having Si-C-C-Si cross-links has been popular<sup>20-30</sup>. Such phases are easy to prepare and excellent results are generally achieved. Phenyl<sup>28,29</sup> and trifluoropropyl<sup>25</sup> silicone rubber columns have been prepared using this method.

Cyanopropyl(methyl)phenylsilicone OV-225 has been used extensively in packed column gas chromatography, where it has proved to exhibit useful selectivity towards typical solutes. The application of such a phase to capillary column work is also of great interest. Further, phases having higher a degree of cyanopropyl substitution offer useful selectivities, *e.g.*, for the separation of fatty acid methyl esters.

In this paper, we describe a method for the preparation of capillary columns coated with some different types of cross-linked silicone stationary phases containing cyanopropyl, tolyl and methyl substituents.

## EXPERIMENTAL

### *Preparation of bis(cyanopropyl)cyclotetrasiloxane*

The reagent was synthesized by acidic hydrolysis of bis(cyanopropyl)dichlorosilane (Petrarch System, Bristol, PA, U.S.A.) as described earlier<sup>19</sup>. Before use, the identity and purity were monitored by IR spectroscopy, gel permeation chromatography and Si nuclear magnetic resonance spectroscopy.

### *Preparation of cyanosilicone gum phases*

*Basic reversed hydrolysis according to Patnode and Wilcock*<sup>31</sup>. Prepolymers containing 33% cyano-33% tolyl and 50% cyano-25% tolyl were prepared from bis(cyanopropyl)dichlorosilane, methyl(tolyl)dichlorosilane and dimethyldichlorosilane (Petrarch), respectively. Methylene chloride was used as the solvent for these syntheses.

A prepolymer containing a high degree of cyano substitution was prepared from bis(cyanopropyl)dichlorosilane. A methyl(vinyl)cyclopentasiloxane was synthesized according to Kantor *et al.*<sup>32</sup> and the rings thus obtained were opened by refluxing in butanol. To facilitate subsequent cross-linking<sup>33</sup>, 1.7 mol-% of this opened methyl(vinyl)siloxane was included in the reaction mixture. Further, 0.5 mol-% of 1,4-dimethyl-1,1,4,4-tetrachlorodisilylethylene (Petrarch) was added in order to introduce a slight degree of cross-linking in the prepolymer as suggested by Peaden *et al.*<sup>28</sup>. The synthesis was carried out in acetonitrile.

Prepolymers were prepared by the slow addition of an excess of 6 *N* ammonia solution to the silane mixtures with vigorous stirring at 0°C under an atmosphere of nitrogen.

*Polymerization of the prepolymer.* Polymerization was carried out in two steps, the first at 210°C for 30 min using sodium silanolate as a catalyst, the second at 110°C

for 10 min using ammoniumhydroxide as catalyst<sup>33,34</sup>. Only the latter of these steps was necessary when polymerizing prepolymers synthesized with dimethyltetrachloro-disilethylene. The reactions were performed with stirring under an atmosphere of nitrogen. Gums prepared in this manner were dissolved and purified by washing with dilute hydrochloric acid, followed by water, to remove catalyst residues. Finally, after drying the gums with calcium sulphate, residual silanol groups were capped by reaction with 1,3-divinyltetramethyldisiloxane (Petrarch) in refluxing acetonitrile for 6 h under an atmosphere of nitrogen.

#### Column preparation

Two types of capillaries were used, AR-glass (Glaswerk Wertheim, Wertheim am Main, G.F.R.) and fused silica (Chrompack, Middelburg, The Netherlands), I.D. 0.22 mm. AR-glass capillaries were leached with 20% hydrochloric acid, principally according to Grob *et al.*<sup>35</sup> as described earlier<sup>26</sup>. Fused silica was leached with 20% hydrochloric acid at 100 or 250°C for 12 h, rinsed and dried as described for AR-glass<sup>26</sup>.

The leached capillaries were coated dynamically with a 20% (w/v) solution of the cyclic cyanosiloxane in methylene chloride at a constant rate of 20 mm/sec. During such dynamic coating, a buffer capillary was connected to the end of the capillary. Immediately after the coating plug had left the column, the flow of dry nitrogen passing through the column was drastically increased, and the evaporation of the solvent was allowed to proceed for 6 h<sup>36</sup>. The capillary was then evacuated by attaching both ends to a small vacuum pump, and the ends were carefully sealed with a micro-flame. The sealed capillary was heated in an oven to 395°C at a rate of 5°C/min and the final temperature was maintained for 1.5 h, after which the oven was allowed to cool slowly to room temperature. One end of the column was opened under the surface of methylene chloride, thus forming a plug with which the column was rinsed using nitrogen. Finally, the column was dried by flushing with dry nitrogen.

Of the stationary phases used, some were synthesized in our laboratory and some were obtained from other sources. OV-225 and an experimental polymer, OV-225/vinyl, were obtained from Chrompack. Silar 10C was obtained from Applied Science Labs. (State College, PA, U.S.A.).

After dissolving the stationary phase in a suitable solvent (Table I), 5% of dicumyl peroxide (Merck, Darmstadt, G.F.R.), calculated from the amount of stationary phase, was added to the coating solution if the phase was to be cross-linked. Before filling the column, the coating solution was filtered and centrifuged; only freshly prepared solutions were used. Coating with a stationary phase was performed by the static method and with the column immersed in a horizontal position in a water-bath. The coated column was opened under an atmosphere of dry nitrogen, *ca.* 60 sec before the vacuum was disconnected, and was then directly flushed with dry nitrogen for 30 min.

The gum phases were cross-linked *in situ* by dynamic curing in a GC oven, programmed from 40 to 170°C at a rate of 5°C/min, the final temperature being maintained for 40 min. During the curing, the column was rinsed with a slow stream of dry hydrogen (0.1 ml/min). After curing, the column was rinsed with 5 ml of methylene chloride and conditioned in a gas chromatograph programmed at 1°C/min to 250°C.

TABLE I  
CHARACTERISTICS OF SOME TYPICAL CAPILLARY COLUMNS COATED WITH CYANOSILOXANES

Glass	Stationary phase	Substituents	Coating solvent	Silicone viscosity	Capacity ratio, <i>k</i> (naphthalene)	HETP (mm)	UTE* (%)	Kovats retention index at 90°C		MAOT** (°C)	Proportion extractable after curing, %
								Octanol	Naphthalene		
AR	33-CN	33% cyanopropyl, 33% methyl, 33% tolyl	Methylenechloride	Rubber	15	0.30	75	1383	1564	300	45
FS	33-CN			Rubber	13	0.22	91	1389	1556	300	47
AR	OV-225	25% cyanopropyl, 50% methyl, 25% phenyl	Methylenechloride	Fluid	25	0.71	33	1466	1616	225	—
AR	OV-225/vinyl			Rubber	17	0.30	77	1493	1646	230	0
FS	OV-225/vinyl			Rubber	15	0.24	84	1488	1645	250	21
AR	50-CN	50% cyanopropyl, 25% methyl, 25% tolyl	Methylenechloride	Gum	13	0.28	81	1495	1678	300	—
FS	50-CN			Rubber	11	0.50	40	1485	1661	300	35
AR	95-CN	ca. 95% cyanopropyl, vinyl	Acetonitrile-diethyl ether (3:2)	Gum	20	0.41	59	1648	1817	300	—
FS	95-CN			Gum	21	0.54	40	1605	1831	300	—
AR	Silar 10C	100% cyanopropyl	Ethylacetate	Fluid	14	0.22	111	1651	1875	275	—
FS	Silar 10C			Fluid	17	0.27	75	1617	1833	275	—
FS***	Silar 10C			Fluid	20	0.46	44	1622 <sup>§</sup>	1812 <sup>§</sup>	275	—

\* UTE = Utilization of the theoretical best efficiency.

\*\* MAOT = Maximum allowable operation temperature.

\*\*\* Leached at 250°C.

§ Measured at 80°C.

## RESULTS AND DISCUSSION

Dimethyl- and methyltolylidichlorosilanes are more reactive than bis(cyanopropyl)dichlorosilane; this may give rise to inhomogeneous prepolymers. "Reversed hydrolysis", *i.e.*, with water added to a mixture of halosilanes, was employed as this type of hydrolysis is considered to facilitate the formation of homogeneous silicones<sup>33</sup>. Further, the synthesis was performed under basic conditions, which gives rise to relatively long prepolymer chains. Homogeneous silicones can also be obtained by synthesis via cyclic intermediates as described by Grassie and co-workers<sup>37-39</sup>.

The use of two catalysts in the polymerization step was found experimentally to give high polymer viscosity. For gums having *ca.* 95% cyano substitution, only ammonium hydroxide was required to yield gums of sufficient viscosity. The syntheses of the cyanosiloxane gums were checked by IR spectroscopy of the products.

Leaching of AR-glass capillaries serves several purposes, *e.g.*, to remove metal ions from the surface, to produce a barrier that hinders metal ions from diffusing from glass bulk to surface, to even out differences between glass batches, to hydroxylate the glass surface in order to make efficient silanization possible and, when polar silanizing reagents are to be used, to facilitate even wetting of the glass with these reagents. The aim of the silanization is to achieve a high degree of capillary deactivation and, when polar stationary phases are used, good wettability. Wettability is, however, obtained only on surfaces that have a high and even coverage of silanization moieties. Such a coverage cannot be achieved on non-treated fused silica capillaries. It seems that a fused silica surface contains too few silanol groups to be sufficiently modified by silanization. Further, the necessary even distribution of silanizing reagents could not be attained on untreated fused silica. Fused silica capillaries were therefore leached at 250 and 100°C. When silanized and coated with Silar 10C, capillaries leached at 250°C showed slightly better elution of amines than capillaries leached at 100°C; the efficiency was, however, higher for capillaries leached at 100°C (Table I); 100°C was chosen as being a suitable leaching temperature for fused silica.

It should also be pointed out that a fused silica surface might easily be contaminated; leached glass vessels, high-purity chemicals and freshly prepared solutions were therefore used in such a leaching procedure.

For the successful performance of the cyano modification, three critical requirements must be fulfilled. First, the silanizing reagent must be deposited as an even film along the length of the capillary. Glass areas not covered with reagent would not be silanized, as the reagent does not evaporate during the heat treatment in the capillary. Wettability is achieved on leached capillaries and the formation of an even film of reagent is ensured by a carefully performed dynamic coating. Second, no air or solvent residues should be present in the capillary during silanization, otherwise non-extractable discoloured residues might be formed in the capillary. Column performance is adversely affected by the presence of such residues. Third, the reaction time and temperature should be carefully controlled.

Some vinyl substitution in a silicone gum greatly facilitates cross-linking when dicumyl peroxide is used as an initiator<sup>33</sup>. The cross-linking reaction may, however, be hindered for steric reasons, *e.g.*, by the presence of phenyl or cyanopropyl groups. To avoid such hindrance, we attempted to incorporate vinyl groups into the gums as

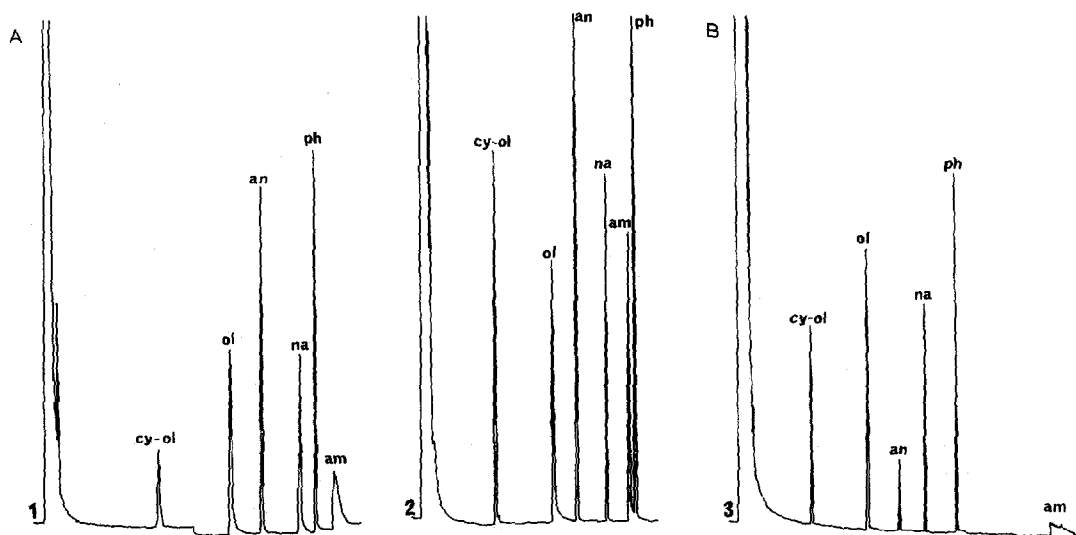


Fig. 1. Gas chromatograms (flame-ionization detector, FID) of a test mixture on different capillary columns. Initial temperature 40°C, programmed at 7°C/min. Peaks: cy-ol = cyclohexanol; ol = octanol; an = aniline; na = naphthalene; ph = phenol; am = dicyclohexylamine. Columns: 1 = OV-225 on AR-glass; 2 = OV-225/vinyl, cured on AR-glass; 3 = 33CN, cured on fused silica. Each peak corresponds to *ca.* 1 ng of substance. Column lengths: 1 and 2 = 10 m; 3 = 15 m.

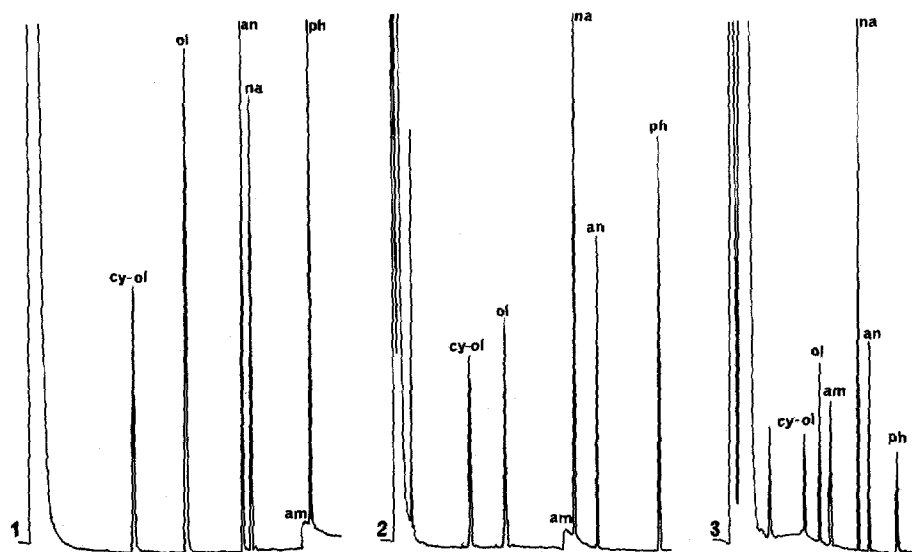


Fig. 2. Gas chromatograms (FID) of a test mixture on different capillary columns. Conditions and peaks as in Fig. 1. Columns: 1 = 50CN, cured on fused silica; 2 = Silar 10C on fused silica; 3 = Silar 10C on AR-glass. Column lengths: 1 and 2 = 10 m; 3 = 22 m.

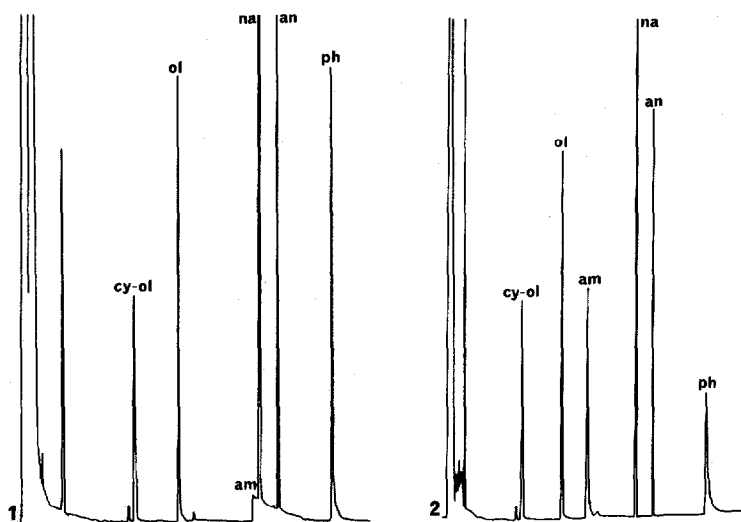


Fig. 3. Gas chromatograms (FID) of a test mixture on different 10-m capillary columns. Conditions and peaks as in Fig. 1. Columns: 1 = 95CN, on fused silica; 2 = 95CN, on AR-glass.

methyl(vinyl)siloxane segments rather than single methyl(vinyl)siloxane units. A further possibility for facilitating cross-linking of silicone gums containing bulky groups is to incorporate tolyl groups. Gums containing bulky groups, however, require relatively large amounts of peroxide to be cross-linked even when vinyl or tolyl groups are present. This might lead to some adsorptive column activity when using a static

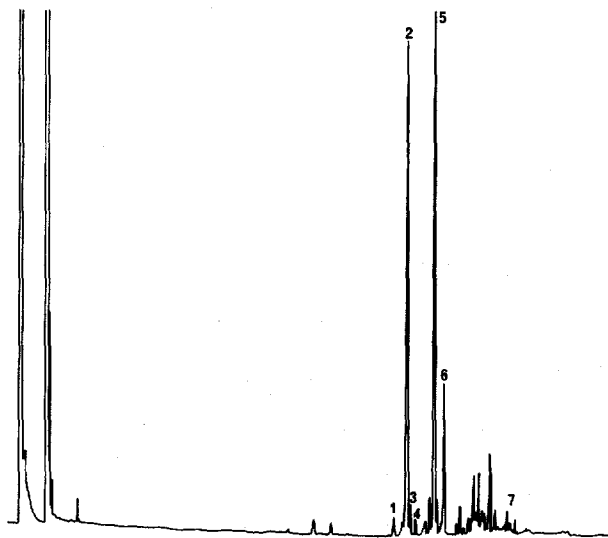


Fig. 4. Gas chromatogram (FID) of a sample containing methylated fatty acids obtained from tall oil. Column: 10-m fused silica, coated with 95CN cyanosilicone gum. Initial temperature 110°C, programmed at 5°C/min. Peaks: 1 = 18:0; 2 = 18:1<sup>9</sup>; 3 = 18:1<sup>11</sup>; 4 = 18:2<sup>5,9</sup>; 5 = 18:2<sup>9,12</sup>; 6 = 18:3<sup>5,9,12</sup>; 7 = 20:3.

curing method<sup>25</sup>. Such an effect was not observed when curing under so-called dynamic conditions.

OV-225 is considered unsuitable for capillary columns, as low efficiency and thermal stability are obtained with this phase (Table I). OV-225/vinyl is an experimental polymer that can be cured. High efficiencies were obtained when using this phase, but the thermal stability was as for OV-225. Silar 10C is a relatively viscous fluid that is satisfactory for coating the silanized capillaries. The home-made phases gave columns with high efficiencies and high thermal stabilities; the column activity is demonstrated in Figs. 1–3. The lowest adsorptive activity was experienced with Silar 10C and the home-made phases. A special merit of the rubber stationary phases is their high general durability; they can thus withstand vast amounts of solvents, even water. Further, they are more resistant towards alkaline samples than corresponding silicone gums.

The utility of the cyanosilicone gum stationary phases is demonstrated by the separation of fatty acid methyl esters in Fig. 4.

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