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PREPARATION AND CHROMATOGRAPHIC USES OF SURFACE-BONDED SILICONES*

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SUMMARY

Silicones can be synthesized from a variety of pure or mixed monomers on and chemically bonded to silicic surfaces—typically to chromatographic supports. The resulting materials are non-extractable, thermally stable coatings, which perform well in GLC and can be used for some of the more demanding types of analysis.

INTRODUCTION

A great variety of silicones are used in gas–liquid chromatography. Chemical inertness, a high degree of thermal stability, and a wide variety of available structures, are the basic reasons for their use. Silicones have also served in other chromatographic areas, for instance, in reversed-phase paper chromatography. In all of these applications, the silicones are applied to a high surface area and function there as the stationary, liquid phase. It would be most advantageous for a variety of reasons, if these silicones could be chemically bonded to their support. Thus, in liquid–liquid paper or column chromatography (LLC), organic solvents could be used, which would otherwise dissolve the liquid phase. In gas–liquid chromatography (GLC), such materials could be expected to possess superior thermal stability and provide interesting materials for theoretical studies.

Aside from chromatographic applications, the problem of bonding and polymerizing silicones on particles of different surface structures is of considerable interest. In this paper, the bonding of various silicones to materials which contain (or can be treated to contain) free silanol groups, has been investigated. Such materials include various forms of diatomaceous earth (*e.g.* the well-known Chromosorbs® in GLC), silica gels, silica beads (*e.g.* Porasil®), glass beads, etc.

Various chemical reactions have been attempted with such surfaces. However, most of the bonds formed possessed little hydrolytic or thermal stability (for a review,

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see ref. 1). ABEL *et al.*[1] reported on the polymerization of hexadecyltrichlorosilane on a Celite surface and reported use of this material for GLC purposes. The material they obtained possessed good thermal stability, but did not perform well with typical "difficult-to-chromatograph" compounds. MOORE AND DAVISON[2] reported the cross-linking of the silanol groups with polyester acetals to obtain a permanent bond between the solid and the liquid phase.

In GLC, the degree of inertness of the solid support is of prime importance. "Active sites" of the support surface cause the tailing of peaks, irreversible adsorption, variation of retention times with sample size and composition, low column efficiencies and non-linear responses. Because of these undesirable interactions, much work has been done in the methodology of deactivating solid supports (for a review, see refs. 3 and 4). Among other methods of deactivation, supports can be treated with dimethyldichlorosilane (DMCS), hexamethyldisilazane (HMDS), methyltrichlorosilane (MTCS), and similar compounds, which convert the free hydroxyl groups on the surface to silyl ethers.

In the paper by ABEL and co-workers, such active sites (*i.e.* silanol groups) were presumably formed by water on the Celite surface during the course ot polymerization. It is indeed tempting to use these silanol groups to bond the polysiloxanes to the surface and thus achieve both a stable chemical bond between the liquid phase and the solid support, and a deactivation of the solid support.

The apparent question on materials of this sort is, whether the liquid phase is really chemically bonded to the solid support. In our studies, prolonged continuous extraction with various solvents was used as the criterion. The materials were extracted for at least 36 h in a soxhlet apparatus. If solvents as hexane, benzene, ether, chloroform, methylene chloride, ethanol, and methanol, all extracted essentially the same amount, the rest of the liquid phase was supposed to be chemically bonded to the surface. It was considered unlikely that solvents so different in nature, would effect similar percentages of extraction, if the solubility of the liquid phase were the determining factor.

In experiments conducted similar to the method of ABEL and coworkers, liquid phases were obtained which could be completely extracted from the solid support. It was concluded that chemical bonds between the liquid phase and the solid phase either did not form or were broken by subsequent hydrolysis. As could be shown later, the first assumption was the correct one, since later obtained materials with zero extractibility were stable to attempted hydrolysis.

Three considerations were followed in the investigations:

(a) The surface should contain as many silanol groups as possible; therefore, various forms of surface treatment were investigated.

(b) The literature on surface deactivation and our own experiences indicated that dimethyldichlorosilane gives much better results than other, especially larger chlorosilanes (with phenyl or long-chain aliphatic substituents). This is understandable from the ease of hydrolysis of this material and steric requirements. Consequently, we tried to initiate a reaction between the silanol groups of the support and either dimethyldichlorosilane or a similar material. If a great excess of DMCS is reacted with silanol groups, chances are that one chlorine remains for a subsequent reaction with other silicone monomers during polymerization. Thus, the silicone monomer (which is to form the particular liquid phase), is applied to the DMCS-treated support. Then,

during polymerization, the silicone phase is chemically bonded via the DMCS rest to the solid surface. It is quite obvious that the particular conditions of polymerization play an important role in determining the amount of material really bonded to the surface.

(c) Once the polymerization has been achieved, residual or newly formed hydroxyl groups, either on the surface or in the liquid phase, can then be deactivated with a suitable silylation reagent. Some of these reactions are shown in Fig. 1.

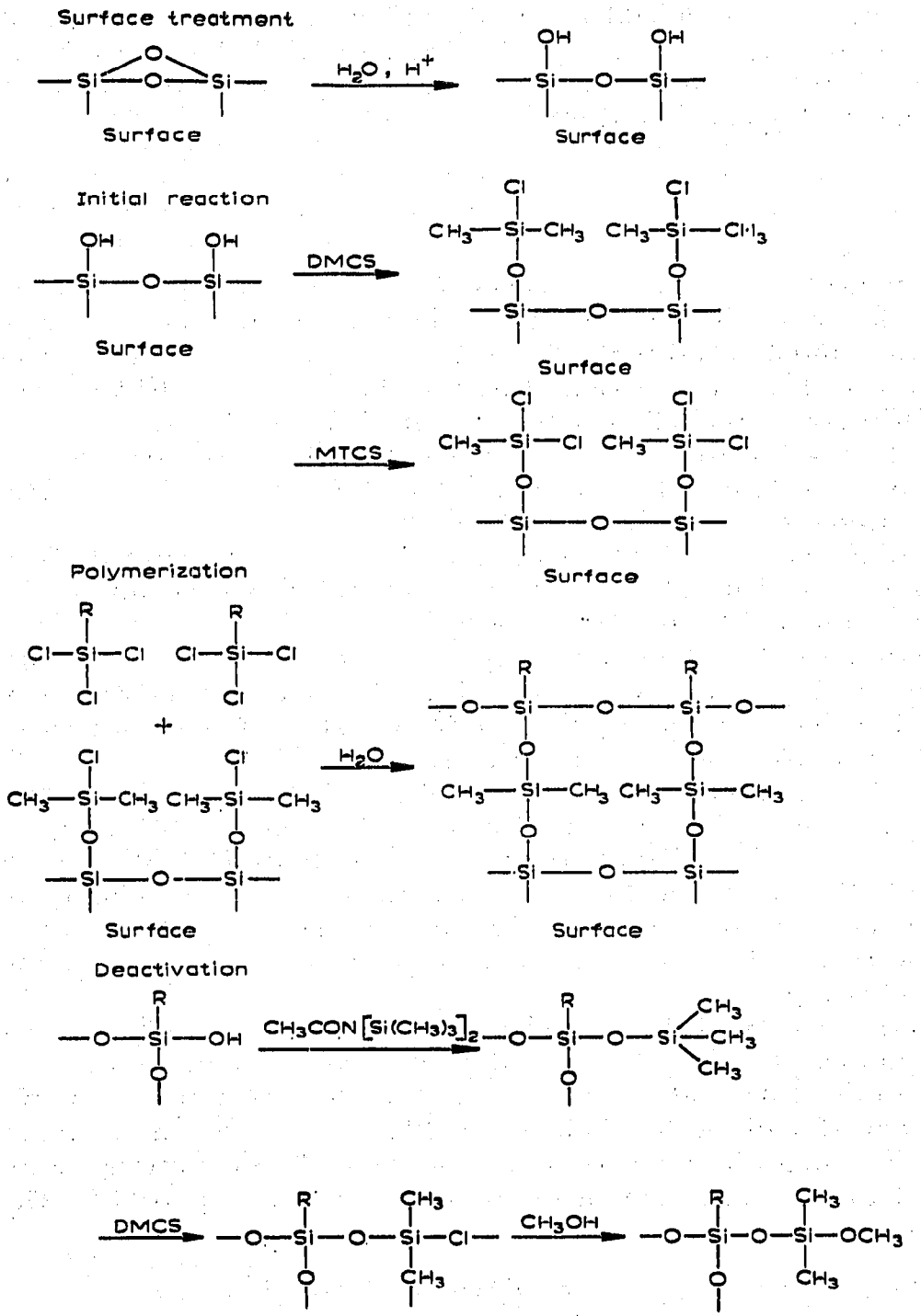

Fig. 1. Typical assumed reactions.

For chromatographic purposes, the obtained materials were expected to show the following qualities:

(i) Their chromatographic behavior should be similar to that of liquid silicones applied to solid supports in a manner common in GLC column preparation. However, the bonded liquid phase should be completely unextractable with any organic solvent and should have considerable thermal stability, at least as good as that of a comparable, commercial silicone.

(ii) The bonded liquid phases should be obtainable from a variety of silicone monomers in a variety of loadings on a variety of solid substrates. The capability to use various silicone monomers would enable the chromatographer to "tailor" a column exactly to his needs in polarity and relative retention.

EXPERIMENTAL

Activation of silicic surfaces

The "activity" of surfaces after various types of treatment was judged solely by the amount of chemical bonding obtainable, *i.e.*, the amount of non-extractable polymer under otherwise similar conditions. Other methods of characterization as determination of chemisorbed water, titration of hydroxyl groups[5], or I.R. were not attempted. In several test series, the following treatments were employed:

(1) Estimate the number of free hydroxyl groups possible on the surface and add twice the amount of water necessary to generate them. Keep at 65° overnight.

(2) Use a similar amount of conc. HCl, treat as above.

(3) Cover the material with conc. HCl, reflux for 4 h, wash with distilled water until neutral. Wash three times with acetone, put the material into a vacuum desiccator over silica gel, evacuate and keep at 80° overnight.

(4) Cover the material with dilute NaOH, reflux for 15 min–1 h, wash with distilled water. Suspend in dilute HCl, wash with distilled water until neutral, dry as in treatment No. 3. For materials easily dissolved in NaOH (porous silica beads), the NaOH was calculated to dissolve 5 % of the material.

(5) Use treatment No. 3, suspend in a solution of 5 % MTCS in toluene, reflux for 1 h, wash with toluene, then with water until neutral. Add KOH solution up to pH 10, wash with water to neutral, bring pH to about 4 with dilute HCl. Wash with acetone three times. Dry as in treatment No. 3. This treatment aims at making more and easier accessible silanol groups on the surface. An alternate approach (5a) is to suspend in DMCS and treat as in treatment No. 5. Suspend in dry toluene, add the silicone monomer(s), and polymerize

(6) Heat the material (Chromosorbs only) at 550° overnight. This treatment was used to *minimize* the number of silanol groups and provide reference materials.

Since the major aim of this study was to obtain a material suitable for GLC, the surface treatment experiments were conducted predominantly on Chromosorbs (G and W, "acid-washed", ranges from 60/80 to 120/140 mesh). These materials were also easy to handle and to test, and were therefore used as model supports for the various surface treatments.

Initial reaction

Pour the activated samples into a solution of MTCS or DMCS in toluene, stir

and reflux for 4 h. (The chlorosilanes should be present in great excess and atmospheric moisture should be excluded.) Remove most of the solution in vacuum, resuspend in dry toluene.

Polymerization

Add the calculated amount of silicone monomer(s), evaporate to dryness in a fluted flask on a rotary evaporator, using a 65° waterbath and oil pump vacuum, leave for an additional 30 min. (This procedure cannot be used for highly volatile monomers.) Polymerize in fluidized bed in air at optimized settings of temperature, water content of the carrier gas, and time of polymerization.

General polymerization conditions. The wide variety of liquid and solid phases used in this procedure demands quite a variety of different conditions to obtain optimal results in each case. During a run, the attained degree of polymerization can be judged from small samples taken from the fluidized bed, which are suspended in water and tested for evolved HCl.

The water content of the air stream must be known. To show the effect of different water contents, a small stream of water-saturated air was added to the main (dried) air stream and the water content calculated from flow, temperature, and pressure readings.

The temperature of the polymerization was set anywhere between ambient and 150° by preheating the air stream. The lower limit is generally determined by time considerations, the upper limit by the volatility of the silicone monomer.

In this paper, the "per cent loading" is always calculated as 100 times the ratio of weight of silicone monomer (*e.g.* $C_{18}H_{37}SiCl_3$) over the total weight of silicone monomer plus solid support. For comparison with commercial phases, this loading is corrected to represent the polymer (*e.g.* $(C_{18}H_{37}SiO_{3/2})_n$) rather than the monomer.

Extraction

Continuous soxhlet extractions for 36 h or Goldfisch extractions (Fisher Scientific Co., St. Louis, Mo.) for 15 h with widely disparate solvents were performed on all new materials. Once a particular phase had been tested with various solvents, subsequent samples were extracted only with benzene (compare Table I). The values obtained were considered reasonably accurate if: (a) the weight loss of the polymeric material and weight gain in the receiver concurred within 10% relative; and (b) similar amounts were extracted by several organic solvents.

Deactivation

If necessary for a specific purpose, the obtained materials can be further deactivated (Fig. 1). A typical procedure is to silylate with a 3% bis(trimethylsilyl)acetamide–*o*-xylene mixture in a closed tube with teflon-lined screw cap at 145° for 2 h (use safety precautions), and rinse with dried benzene several times. Suspend in dry methanol, let stand for 1 h and then soxhlet-extract with methanol (anhydrous condition) for 4 h.

Testing

All materials with reasonable extraction values (< 5% of theoretical loading) and some others were tested in a gas chromatograph, with selected mixtures of typi-

cally difficult-to-analyze compounds, *viz.* ethanol, acetonitrile, butanol, dimethylformamide, aminoethanol, phenol, hexanoic acid, bromonaphthalene, tri-*n*-butylphosphate, and others (Figs. 2 and 3).

Such test chromatograms can reveal a great deal about the success of the polymerization. For instance, inhomogeneity of the coating, residual "active sites", etc., can give rise to asymmetrical peaks, non-bonded material of low molecular weight will

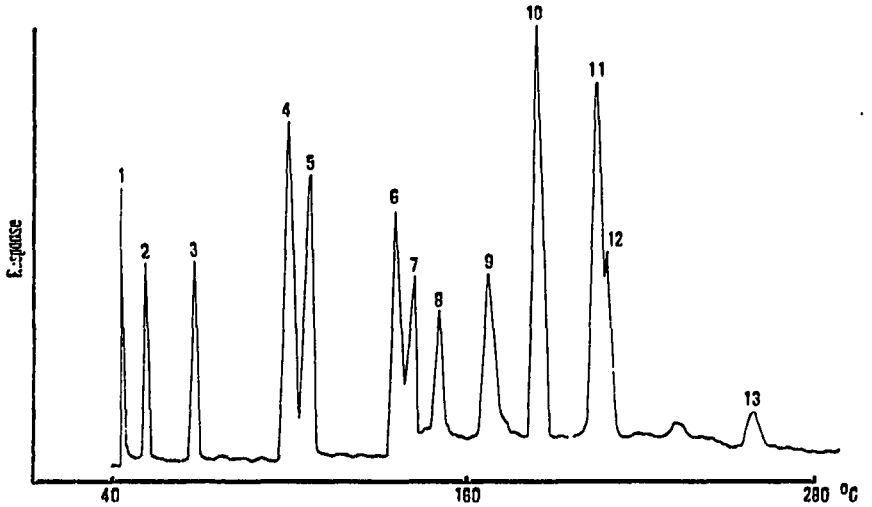

Fig. 2. Chromatogram of acetone and ethanol (1), benzene (2), octene-1 (3), aminoethanol (4), 2-octanone (5), 3-(chloromethyl)-heptane (6), benzyl chloride (7), aniline (8), tri-*n*-butylamine (9), octanoic acid (10), tri-*n*-butyl phosphate (11), bromonaphthalene (12) and *n*-octadecane (13). Column: 13.2 wt. % $(C_{18}H_{37}SiO_{3/2})_n$ on 60/80 Chromosorb G, 50 cm × 4 mm I.D. glass (Perkin-Elmer model 800). Initial temperature: 40°, 10°/min. N_2 flow rate: 40 ml/min.

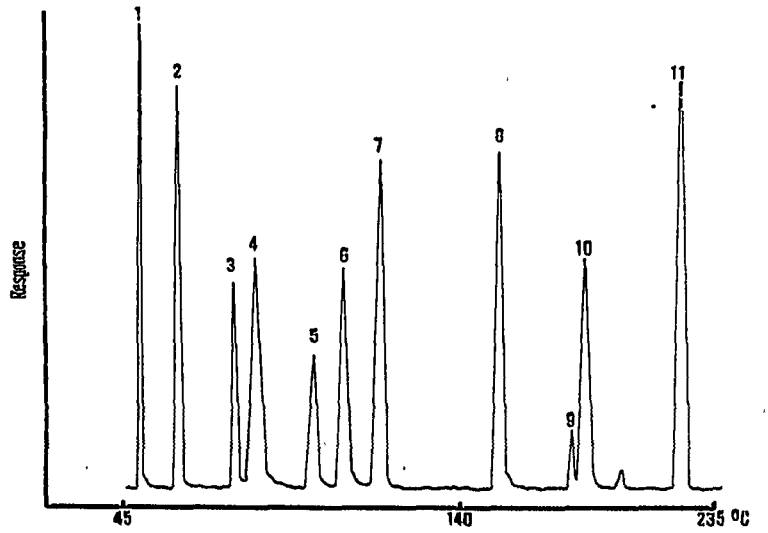

Fig. 3. Chromatogram of acetone (1), octene-1 (2), *n*-hexyl alcohol (3), di-*n*-butylamine (4), phenol (5), tri-*n*-butylamine (6), nitrobenzene (7), dodecyl alcohol (8), *n*-octadecane (9), tri-*n*-butyl phosphate (10) and 1-chloro-octadecane (11). Column: 16.3 wt. % $(C_6H_5(CH_3)SiO)_n$ on 60/80 Chromosorb G, 50 cm × 4 mm I.D. glass (Perkin-Elmer model 800). Initial temperature: 45°, 10°/min. N_2 flow rate: 25 ml/min.

cause column bleed, and the polarity of the liquid phase will determine relative retention times.

With selected materials, further testing was done to determine:

(a) Thermal stability: Plot of log (column bleed) *vs.* $1/T$ and comparison with the behavior of a corresponding commercial silicone (Fig. 6).

(b) GLC column efficiency: Van Deemter plot, compared with the commercial silicone (Fig. 5).

(c) Effect of heat on polymer structure: Extraction of material after a 220° overnight heat treatment in a gas chromatograph.

RESULTS AND DISCUSSION

The extraction method used to distinguish surface-bonded from non-surface-bonded polymer coatings hinges on the premise that solvents, which vary as widely as possible in properties, would extract different amounts (or all) of non-bonded materials. If the extraction is carried almost to exhaustion and all solvents extract similar percentages of material, the unextracted material is most likely chemically bonded to the solid surface. Table I shows typical examples of extraction.

TABLE I

TYPICAL EXAMPLES OF EXTRACTION

A = 13.2% $C_{18}H_{37}SiCl_3$, B = 14.9% $C_6H_5(CH_3)SiCl_2$, on Chromosorb G, 60/80 mesh, H_2O and DMCS treated; C = 5.7% $(C_6H_5)_2SiCl_2$, D = 6.1% $C_6H_5(CH_3)SiCl_2$, on Chromosorb G, 60/80 mesh, HCl refluxed and DMCS treated. Extract for 15 h in Goldfisch apparatus.

Solvent	*Extraction (% of theoretical)*			
	A	*B*	*C*	*D*
Benzene	11	35	30	5
Hexane	10	34	27	2
Ethanol–chloroform (1:1)	9	31	27	5
Methylene chloride	9	33	28	2
Ether	6	34	28	4
Methanol	6	34	29	3

A comparison of extraction values from several experiments indicates that the values determined under anhydrous conditions were the same as those determined in the presence of water. The bonding between liquid and solid phases is therefore assumed hydrolytically stable at room temperature. Throughout this paper, the percentage of extractable material was used as the only standard to optimize the described multistage process.

Effects of surface treatment

The absence of any surface and initial (DMCS) treatment resulted in 100% extractability of various liquid phases (mainly from $C_{18}H_{37}SiCl_3$ and $C_6H_5(CH_3)SiCl_2$). This was done on Chromosorb G "acid-washed" (a Johns-Manville product from diatomaceous earth), Porasil (silica beads from Pechiney-Saint-Gobain, France), glass beads, untreated (Corning No. 0202 for GLC, 120/140 mesh), Microbeads No. 456 (Jackson, Miss.), and other silicious materials.

TABLE II

TYPICAL EFFECTS OF SURFACE TREATMENTS

All reactions include a DMCS initial treatment, except where indicated.

Support	*Liquid phase monomer*	*% load*	*Treatment*		*Extraction (% of theoretical)*
Chromosorb G, 60/80 "acid-washed"	$C_{18}H_{37}SiCl_3$	13.2	none		76
		13.2	1	H_2O	11
		13.2	2	HCl	16
		13.2	6,2	Heat, HCl	11
		13.2	6	Heat	68
		13.2	3	Conc. HCl, reflux	<1
		13.2	4	2 *N* NaOH	46
Chromosorb G, 60/80 "acid-washed"	$C_6H_5(CH_3)SiCl_2$	14.9	none		24
		14.9	1	H_2O	35
		14.9	2	HCl	80
		14.9	6,2	Heat, HCl	71
		14.9	6	Heat	76
		14.9	3	Conc. HCl, reflux	2
		16.3	4	6 *N* NaOH	6
Chromosorb G, 60/80, "acid-washed"	$(C_6H_5)_2SiCl_2$	5.7	3	Conc. HCl, reflux	30
		6.7	3,5	Conc. HCl, reflux, KOH, no initial reaction	9
		6.7	3,5a	Conc. HCl, reflux, KOH, no initial reaction	7
		6.7	3,5a	As above plus reflux for 2 h with monomer	12
Chromosorb G, 60/80, "acid-washed"	$C_{18}H_{37}SiCl_3$ + $C_6H_5(CH_3)SiCl_2$	6.5	1	H_2O	21
		8.3	3	Conc. HCl, reflux	2
Chromosorb G, 60/80 "acid-washed"	$C_{18}H_{37}SiCl_3$ + $C_6H_5SiCl_3$	3.3	1	H_2O	8
		4.3	3	Conc. HCl, reflux	1
Porasil type C, 100/150	$C_6H_5(CH_3)SiCl_2$	1.3	3	Conc. HCl, reflux	100
Porasil type D, 100/150	$C_6H_5(CH_3)SiCl_2$	1.5	4	NaOH calc. amount, reflux for 1 h	67
Porasil type D, 100/150	$C_{18}H_{37}SiCl_3$	2.4	3	Conc. HCl, reflux	8
Microbeads No. 456	$C_6H_5(CH_3)SiCl_2$	0.13	3	Conc. HCl, reflux for 18 h	100
	$C_6H_5(CH_3)SiCl_2$	0.26	4	6 *N* NaOH, reflux for 15 min	71
		0.29	4	6 *N* NaOH reflux for 6 h	20
	$C_6H_5(CH_3)SiCl_2$	0.26		18% HNO_3, 50°, 35 h	100
Corning glass beads No. 0202, 120/140	$C_{18}H_{37}SiCl_3$	0.9	3	Conc. HCl, reflux.	1
	$C_6H_5(CH_3)SiCl_2$	1.1	3	Conc. HCl, reflux	17
		1.3	3,5	Conc. HCl, reflux, no initial treatment	20
		1.3	4	0.5 *N* NaOH	2
Silica gel, Davidson 08, 60/80	$C_{18}H_{37}SiCl_3$	13.2	3	Conc. HCl, reflux	4
	$C_6H_5(CH_3)SiCl_2$	13.5	3	Conc. HCl, reflux	18
		13.5	3,5	Conc. HCl, reflux, KOH, no initial treatment	9
Chromosorb W, 60/80, "acid-washed"	$C_6H_5(CH_3)SiCl_2$	9.4	3	Conc. HCl, reflux	4

The following trends could be observed (predominantly on Chromosorb): Treatment No. 1 (with water) gave a small amount of improvement, dependent on the liquid phase used. Generally, $C_{18}H_{37}SiCl_3$ gave the best results. The improvement was considerable when followed by a DMCS treatment. Treatment No. 2 (with calculated HCl) performed slightly better than No. 1. Treatment No. 3 (reflux with conc. HCl) in combination with the DMCS treatment led to practically complete bonding (extractibility $\approx 1\%$) with several monomers and is considered the shortest and best method for coating a Chromosorb. Treatment No. 4 gave good results for Chromosorb; it also performed with limited success for Porasil. Treatment No. 5 gave complete bonding for Chromosorb, but involves considerably more effort than No. 3.

Other treatments included HNO_3 treatment for glass, sodium methoxide treatment for Chromosorb, etc. Table II shows typical examples of the effect of surface treatments on Chromosorb and the application to other support materials.

Effect of initial reaction

In Table III, typical runs are compared on the basis of their initial silylation reaction. Previous experience indicated that small chlorosilanes with high reactivity are essential for good results. Initial reaction with DMCS or MTCS gave best results. No larger difference is found between DMCS and MTCS on Chromosorb G; however, DMCS is clearly the reagent of choice on Chromosorb W. Limited success was obtained with chloromethylmethyldichlorosilane and dichloromethylmethyldichlorosilane.

TABLE III

EFFECTS OF INITIAL REACTION

A = reactions on Chromosorb G, 60/80, refluxed with conc. HCl; B = reactions on Chromosorb W, 60/80, refluxed with conc. HCl.

	Liquid phase from	*% load*	*Initial reaction*[a]	*Extraction (% of theoretical)*
(A)	$C_6H_5(CH_3)SiCl_2$	14.9	DMCS	2
		14.9	MTCS	3
		6.1	DMCS	5
		6.1	MTCS	2
	p-$ClC_6H_4SiCl_3$	3.1	DMCS	4
		3.1	MTCS	2
	$C_6H_5SiCl_3$	3.2	DMCS	4
		3.2	MTCS	3
		6.2	DMCS	2
		6.2	MTCS	1
(B)	$C_{18}H_{37}SiCl_3$	6.6	DMCS	5
		6.6	MTCS	13
	$C_6H_5SiCl_3$	6.2	DMCS	3
		6.2	MTCS	33

[a] DMCS = dimethyldichlorosilane; MTCS = methyltrichlorosilane.

Effect of monomer structure

In Table IV, various monomers are compared. Generally, the results appear to relate to the rate of hydrolysis of these compounds[6]; *i.e.* the most easily hydrolyzed

monomers would tend to yield the highest amount of bonding to the surface. Much more work would be needed, however, to reach more than a perfunctory conclusion. A thorough investigation would have to include kinetic studies on the rate of polymerization *vs.* surface bonding, on the water and HCl concentrations, etc.

For a comparison of monomer structure effects, data from the best surface treatment (No. 3) cannot be used, since the extraction values are too low to show meaningful differences.

TABLE IV

EFFECT OF MONOMER STRUCTURE

All phases on Chromosorb G, 60/80 mesh, surface treatment with water, subsequent DMCS treatment.

Monomer	*% load*	*Extraction (% of theoretical)*
$C_{18}H_{37}SiCl_3$	13.2	11
$C_6H_5(CH_3)SiCl_2$	14.9	35
$C_6H_5SiCl_3$	11.6	30
p-$ClC_6H_4SiCl_3$	32.7	10

Effect of loading

The percent loading is an important factor in the bonding efficiency and the projected application of these materials. Table V shows a comparison of different loadings. Why loading influences the amount of surface-bonded material, is open to speculation. Perhaps the thickness of the silicone monomer film at low loadings can become a limiting factor for the efficient formation of siloxane chains or networks. As can be estimated, the thickness of most silicone coatings on Chromosorb described in this paper is in the order of 1 μ. Nothing is known about the average "molecular weight" of the siloxane polymers formed in our experiments; however, even the aromatic chain type of molecules should attain a molecular weight higher than 10^4. Conceivably, film thickness could become a determining factor by limiting the attainable molecular weight and thereby reducing the percentage of siloxane molecules bonded to the surface. The amount of loading also influences the local water and hydrogen chloride concentrations of the liquid–solid interface and in the polymerizing monomer film.

Diatomaceous earth particles (*e.g.* the Chromosorbs) have an almost infinite variety of shapes and surface structures[3]. Little is known about the way in which these surfaces are covered by silicones[7]. In Table V, the differences between Chromosorbs G and W become quite evident. Furthermore, one could imagine a preferential steric arrangement of monomers on the solid surface, *e.g.* $C_{18}H_{37}SiCl_3$ being primarily adsorbed via the $-SiCl_3$ portion of the molecule. All these effects could significantly influence the final product.

Empirically, the obtainable range of loading is wide enough to accommodate most GLC demands and can most probably be further extended below 3 % by better methods of surface treatment. On the high side, the range is limited by the effect of particles sticking together in the fluidized bed polymerization. This effect becomes noticeable above 25 % loading on Chromosorb G.

TABLE V

EFFECTS OF LOADING

(A) on Chromosorb G, 60/80 mesh; (B) on Chromosorb W, 60/80 mesh. Both are refluxed with conc. HCl, initial reaction with DMCS.

	Monomer	*% load*	*Extraction (% of theoretical)*
(A)	$C_6H_5(CH_3)SiCl_2$	3.2	30
		6.1	5
		7.3	1
		14.9	2
	$C_6H_5SiCl_3$	3.2	4
		6.2	2
	p-$ClC_6H_4SiCl_3$	3.1	4
		6.1	1
	$(C_6H_5)_2SiCl_2$	1.2	20
		5.7	30
	$C_{18}H_{37}SiCl_3$	3.9	14
	$C_{18}H_{37}SiCl_3$ + $C_6H_5SiCl_3$	6.5 8.4	1
	$C_{18}H_{37}SiCl_3$ + $C_6H_5SiCl_3$	3.3 4.3	1
	$C_6H_5(CH_3)SiCl_2$ + $C_6H_5SiCl_3$	4.5 6.6	2
	$C_6H_5(CH_3)SiCl_2$ + $C_6H_5SiCl_3$	7.4 5.7	1
(B)	$C_{18}H_{37}SiCl_3$	6.6	5
		12.4	11
		17.5	43
	$C_6H_5(CH_3)SiCl_2$	9.4	4
		13.5	11
	$C_6H_5SiCl_3$	4.2	3
		6.2	3
		11.6	3

Effect of water supply and temperature on the polymerization

Generally, a low content of water in the carrier gas will result in a better material. In a typical case (20 g Chromosorb G, 60/80 mesh, water treated, DMCS–$C_{18}H_{37}SiCl_3$, 14% loading, room temperature) the extraction value varied between 4.9% (0.46 ml H_2O/day), and 12.3% (3.0 ml H_2O/day).

Polymerization at elevated temperatures can be used advantageously to decrease the time necessary for complete polymerization and obtain materials with low extraction values.

As in the discussion on the effects of % loading, the physicochemical reasons for the influence of temperature and water content of the carrier gas on the extractions

characteristic of the final product are open to speculation. For practical purposes, an optimization of the process should be carried out for a specific desired material.

Preparation of mixed phases

The demands of gas chromatographers for liquid phases of different "polarities" are as varied as their fields of pursuit. It is often possible to predict the degree of separation of two compounds by GLC from a knowledge of the liquid phase[8]; for instance, from the phenyl/methyl group ratio in the commercial OV series of polysiloxanes[9].

Table VI shows the characteristics of typical "mixed" phases. Using the described methodology, it is very easy to obtain any desired final composition by simply applying the monomers in appropriate ratios. The process would need some modification, however, if highly volatile monomers (*e.g.* $(CH_3)_2SiCl_2$) were included.

TABLE VI

TYPICAL MIXED PHASES

All on Chromosorb G, 60/80 mesh, refluxed with conc. HCl, subsequent DMCS treatment. Other suitable monomers, which have been polymerized with various degrees of success, include α-chloroethyltrichlorosilane, 1,2-dichloroethyltrichlorosilane, phenylvinyldichlorosilane, vinyltrichlorosilane and dichlorophenyltrichlorosilane.

Monomer I	*% load*	*Monomer II*	*% load*	*Extraction (% of theoretical)*
$C_{18}H_{37}SiCl_3$	6.5	$C_6H_5(CH_3)SiCl_2$	8.3	2
$C_{18}H_{37}SiCl_3$	6.5	$C_6H_5SiCl_3$	8.4	1
$C_{18}H_{37}SiCl_3$	3.3	$C_6H_5SiCl_3$	4.3	1
$C_6H_5(CH_3)SiCl_2$	4.5	$C_6H_5SiCl_3$	6.6	2
$C_6H_5(CH_3)SiCl_2$	7.4	$C_6H_5SiCl_3$	5.7	1
p-$ClC_6H_4SiCl_3$	5.7	$C_6H_5SiCl_3$	5.8	1
$C_{18}H_{37}SiCl_3$	4.8	$C_6H_5SiCl_3$	1.2	6

Gas–liquid chromatography

Test mixtures. All materials with low extraction values were tested to their ability to chromatograph a variety of typical "problem compounds" (acids, alcohols, amines, etc.) as well as a number of other organic substances. Figs. 2 and 3 present examples on Chromosorbs and Fig. 4 on Porasil. The GLC performance was generally similar to that obtained from corresponding commercial liquid phases. After appropriate column conditioning, the bleed rate of surface-bonded materials was extremely low.

Resolution. Van Deemter plots[10] were determined and compared for two model systems, *viz.* (1) $(C_{18}H_{37}SiO_{3/2})_n$, 14% loading on Chromosorb G, 80/100 mesh. This phase was synthesized on water-treated "acid-washed" Chromosorb G from DMCS–$C_{18}H_{37}SiCl_3$. For comparison, a similar liquid phase was purchased (Silicone E 301) and applied to "High Performance" Chromosorb G by the common rotary evaporation technique. Both materials gave very similar Van Deemter graphs, as shown in Fig. 5. The minimum represents a HETP of about 0.4 mm (*ca.* 2 particle diameters).

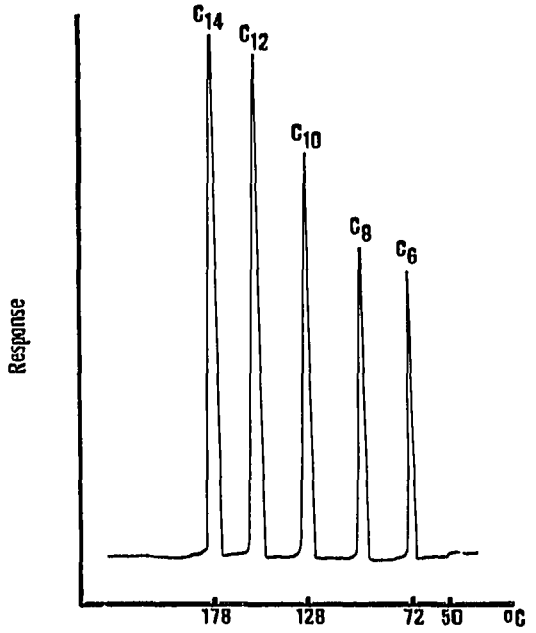

Fig. 4. Chromatogram of C_6 through C_{14} even-numbered hydrocarbons (0.4 μl). Column: 2.4 wt. % $(C_{18}H_{37}SiO_{3/2})_n$ on 100/150 type D Porasil, 50 cm × 4 mm I.D. glass (Perkin-Elmer model 800). N_2 flow rate: 65 ml/min. Initial temperature: 50°, 16°/min.

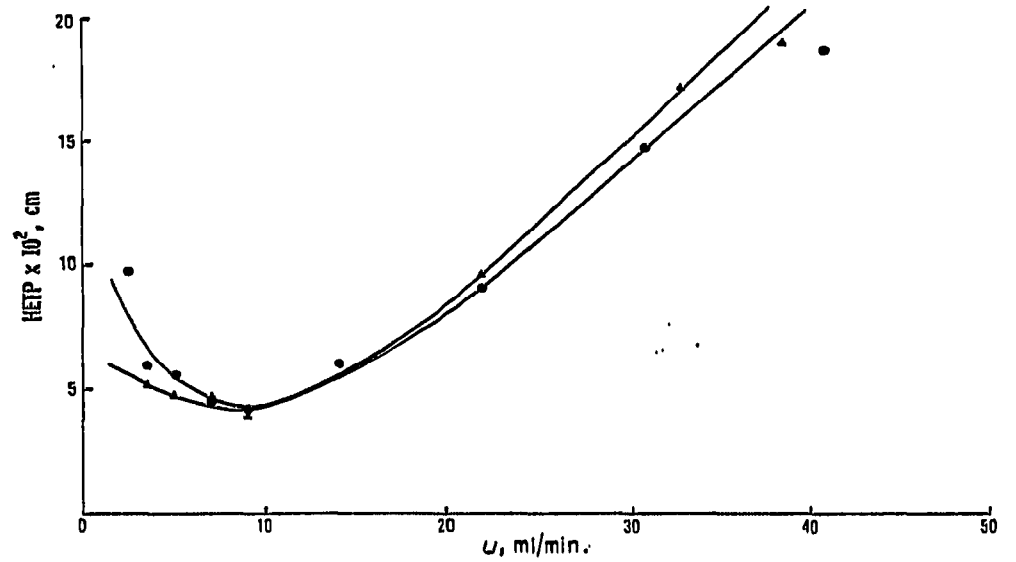

Fig. 5. GLC column efficiency (Van Deemter plot). ▲—▲, Silicone E 301; ●—●, $(C_{18}H_{37}SiO_{3/2})_n$.

(2) $[C_6H_5(CH_3)SiO]_n$, 14 % loading on Chromosorb G, 80/100 mesh. As above, this phase was both purchased (OV-17) and synthesized. Again, the GLC characteristics matched.

This behavior shows that surface-bonded liquid phases are equivalent in performance to commercially available silicones. This is surprising, since the latter can be produced under exactly controlled conditions with a relatively narrow molecular

weight range. Some of them are even further fractionated before they reach the consumer.

From the similarity of the HETP values at high flow rates (predominance of the mass transfer resistance effect), it can be assumed that the viscosities of the purchased and the synthesized materials should be in the same order of magnitude.

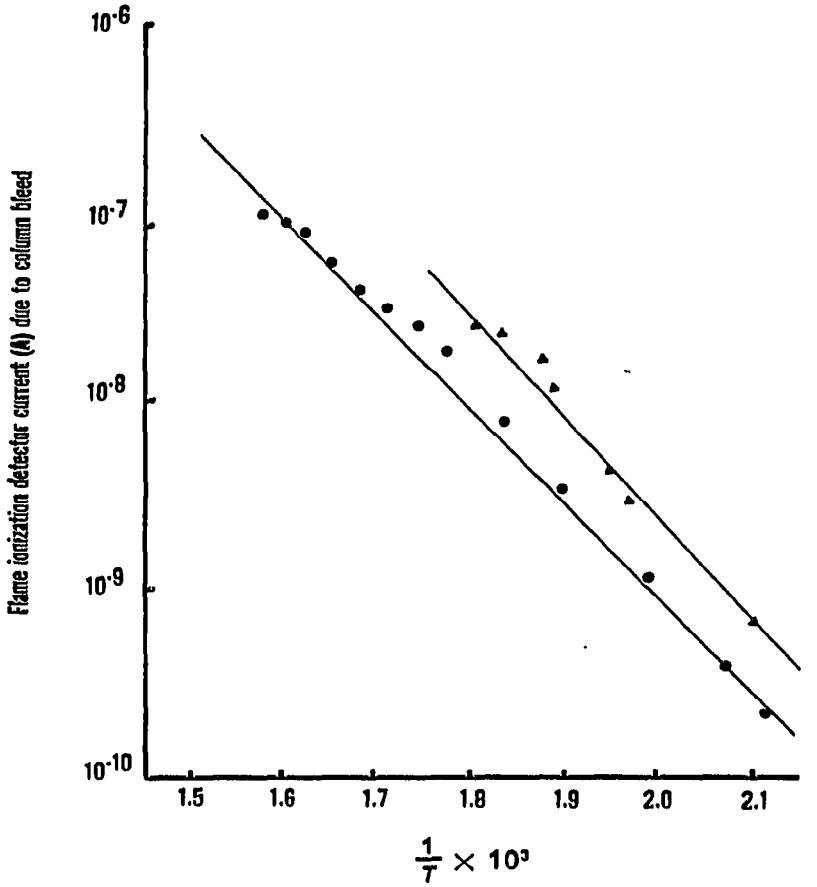

Fig. 6. Plot of log column bleed *vs.* $1/T$. ●—●, 13.2 wt. % $(C_{18}H_{37}SiO_{3/2})_n$ on 60/80 Chromosorb G; ▲—▲, 13.2 wt. % Silicone E 301 on 80/100 Chromosorb G, H.P.

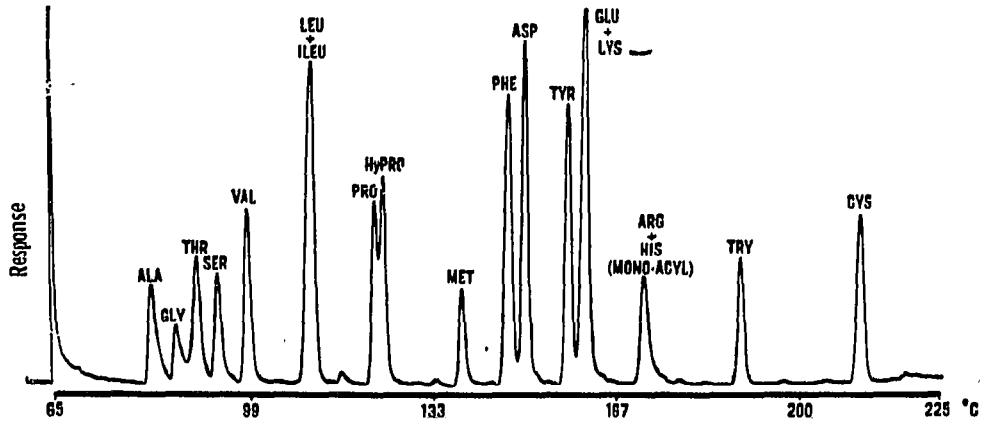

Fig. 7. Chromatogram of the N-trifluoroacetyl *n*-butyl esters of 19 amino acids. Column: 13.2 wt. % $(C_{18}H_{37}SiO_{3/2})_n$ on 60/80 Chromosorb G, 1 m × 4 mm I.D., glass (Varian Aerograph 2100). Initial temperature: 65°, 6°/min. N_2 flow rate: 45 ml/min. The injection mixture contained *ca.* 5 μg of each amino acid.

It is also likely that regular column conditioning brings about further structural alteration of the synthesized phases. In one case, the extraction value of a phenylmethylpolysiloxane decreased from the original 83 % to 34 % when the material was conditioned overnight in a gas chromatograph at 220°, a drop which could not be accounted for by column bleed alone.

Column bleed. Even after slight conditioning of the two model systems described above, the experimental column bled somewhat less than the commercial one. This behavior improved with time.

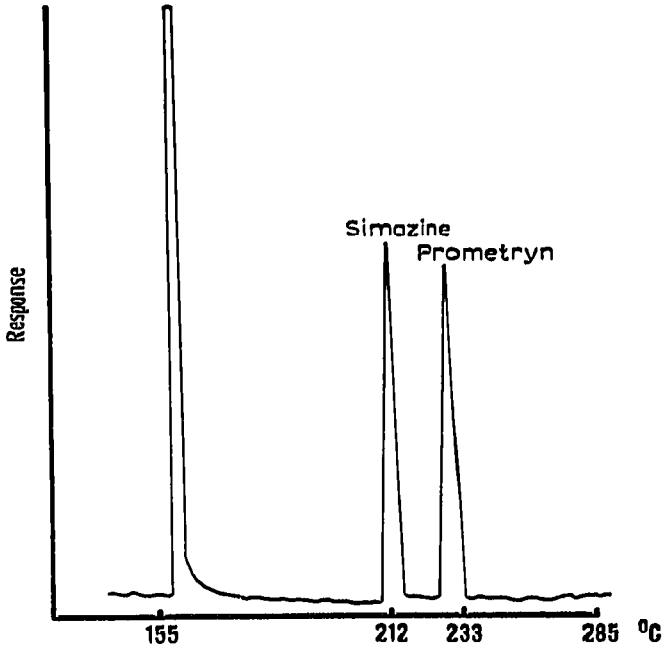

Fig. 8. Peak shapes of *s*-triazines using a column of 13.2 wt. % $(C_{18}H_{37}SiO_{3/2})_n$, on 60/80 Chromosorb G.

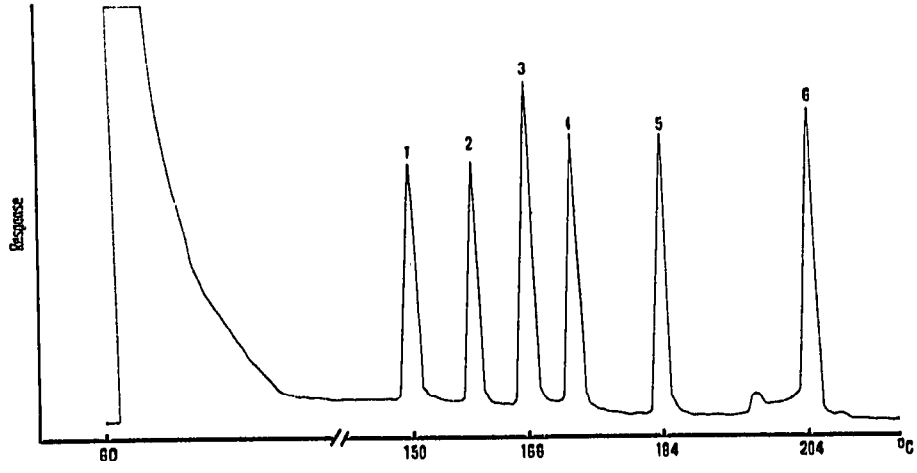

Fig. 9. Chromatogram of pesticides on a mixed liquid phase, 3.3 wt. % $(C_{18}H_{37}SiO_{3/2})_n$ and 4.3 wt. % $(C_6H_5SiO_{3/2})_n$, on 60/80 Chromosorb G, 1 m × 4 mm I.D. glass (Varian Aerograph 2100). Initial temperature: 60°, 4°/min. N_2 flow rate: 45 ml/min. The injection mixture contained *ca.* 0.5 μg of each chlorinated hydrocarbon. 1 = lindane, 2 = heptachlor, 3 = aldrin, 4 = heptachlor-epoxide, 5 = dieldrin, 6 = *p,p'-DDT*.

Plots of the log column bleed *vs.* $1/T$ (Fig. 6) displayed the same linear behavior for both types of liquid phases in the 100–350° range measured. Some differences in slope could be expected. The surface-bonded liquid phase bleeds by silicone deterioration and subsequent volatilization. The breaking of interface bonds may also play a role. The regular liquid phase would predominantly bleed through volatilization, at least in the initial stages of column life. However, the measurements made were not precise enough to allow speculation on the differences observed and their correlation to $\Delta H_{vap.}$ or E_A values.

Gas-liquid chromatography of biologically important molecules. Some of the more demanding types of chromatography were tried on experimental columns to assess their potential for practical analytical work. Out of the nineteen protein amino acid derivatives, prepared according to the method of GEHRKE *et al.*[11], only six were not resolved on a $(C_{18}H_{37}SiO_{3/2})_n$ column (Fig. 7). The same liquid phase gave sharp peaks for the *s*-triazine herbicides Prometryn and Simazine (Fig. 8).

A column made from 3.3 % $C_{18}H_{37}SiCl_3$ and 4.3 % $C_6H_5SiCl_3$ separated the chlorinated hydrocarbon insecticides lindane, heptachlor, aldrin, heptachlorepoxide, dieldrin, and *p,p'*-DDT as symmetrical peaks (Fig. 9).

The TMS derivatives of nucleic bases[12] were separated on a column made from 16.3 % $C_6H_5(CH_3)SiCl_2$ (Fig. 10).

No special effort was made to find the columns best suited for these particular types of analyses. Rather, columns that appeared promising, were tested at random with samples from Dr. CHARLES W. GEHRKE's and our own research programs.

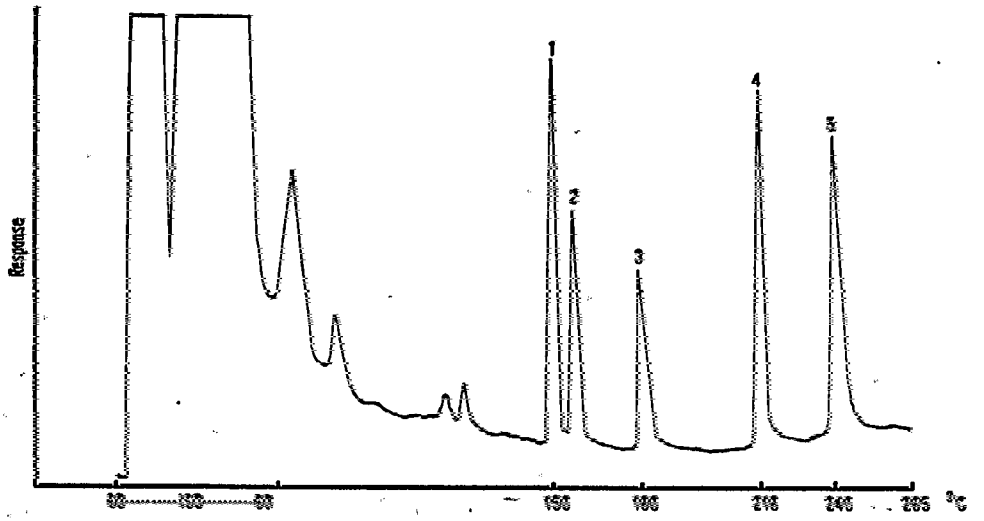

Fig. 10. Separation of TMS nucleic bases on a column of 16.3 wt. % $(C_6H_5(CH_3)SiO)_n$ on 60/80 Chromosorb G, 50 cm × 4 mm I.D. glass (Perkin-Elmer Model 800). Initial temperature: 60°, 6 min initial program delay, 8°/min. N_2 flow rate: 25 ml/min. The injected mixture contained *ca.* 4 μg of each base except adenine of which *ca.* 10 μg was present. 1 = uracil, 2 = thymine, 3 = cytosine, 4 = adenine, 5 = guanine.

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