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IMMOBILIZATION OF STATIONARY LIQUIDS IN REVERSED- AND NORMAL-PHASE LIQUID CHROMATOGRAPHY

PRODUCTION AND TESTING OF MATERIALS FOR BONDED-PHASE CHROMATOGRAPHY

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SUMMARY

New types of silanization reagents for small-particle silica packing materials and a solventless vacuum technique for carrying out the reaction were tested with the aim of conveniently achieving a more complete reaction of the silanol groups. Materials for bonded-phase chromatography with better quality and reproducibility were obtained.

In a second series of experiments we attempted to fix monomeric and oligomeric siloxanes and also certain unsaturated hydrocarbons on either unsilanized or presilanized materials by cross-linking reactions with γ-radiation or peroxides. With the presilanized materials of the Si–O–Si$(CH_3)_3$ type we obtained better surface deactivation and fixation of the siloxane oligomers on the surface alkylsilyl groups by the cross-linking reaction.

All silicas should be examined for particle size and structure before and after chemical treatment and analysed for carbon content in bulk and in the surface layer, for permeability and for tailing behaviour after packing of a column. Surface area determinations are also advisable. Chromatographic measurements for efficiency and polarity (selectivity) gave information about the practical value of these materials.

INTRODUCTION

Stationary liquids can be immobilized on the surfaces of the usual small (3–10 μm) diameter particles of various silica materials against shear-off or dissolution by the mobile phase either by adsorption (equilibration between the stationary and mobile phases) or, more reliably, by chemical bonding to the silicas. The materials often used for bonded-phase chromatography should be stable in either isocratic and/or gradient elution with hydrophobic and hydrophilic (aqueous) mobile phases. The latter may show varying chemical agressivity, not only depending on the pH, but also due to the additives or modifiers (including salts) contained in the mobile phase. Today, the anchoring of long-chain alkyl groups to silica surfaces is preferably achieved by a silanization reaction with the silanol groups, which are located in

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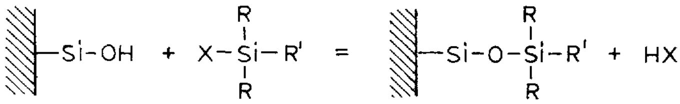
variable concentrations on the surfaces of the common spherical and non-spherical silica particles with suitable diameter, pore size and surface area, for example,



$$-Si-OH + X-\underset{R}{\overset{R}{Si}}-R' = -Si-O-\underset{R}{\overset{R}{Si}}-R' + HX$$

The Si–O–Si–C bonds formed by this reaction are more stable against agressive mobile phases than other types of bonds, *e.g.*, Si–O–C bonds. The type of layer (thickness, homogeneity, molecular geometry, polarity, etc.) of the organic material generated on silica surfaces depends on: the concentration of silanol groups on the surface, the percentage of these silanol groups actually capable of undergoing the silanization reaction, the chemical properties of the molecules to be bonded (chain length of alkyl groups and reactivity and functionality at the silicon atom in the silanization reagent) and the method of carrying out the reaction.

The products obtained by silanization or any other reaction which leads to chemical bonding to the surfaces can be characterized by a determination of the carbon content (elemental analysis) of the bulk phase or, preferably, of the generated layer on the particles by using methods of surface analysis such as ESCA (electron spectroscopy for chemical analysis). Chromatographic measurements (retention and peak symmetry) give information about the residence time of certain judiciously selected test solutes in the stationary phase relative to that in the mobile phase (k' values). The chromatographic data also reflect the interaction mechanisms of the solutes with the surface layer (stationary phase) of the packing material, as they depend on the type of intermolecular interaction between certain test solutes and the surface, especially with its silanol groups.

Residual silanol groups are a particular problem in the separation of basic compounds that can interact by an anion-exchange process. Snyder and Kirkland[1] pointed out that surface coverages of at least 3.0–3.5 μmol/m^2 are often required to eliminate unwanted residual SiOH interactions. The contribution of silanol groups to intermolecular interaction will change the selectivity of the stationary phase considerably, especially for solutes of higher polarity, but this can be diminished or avoided by a more complete silanization reaction or by perfect coverage by the chemically bonded alkyl groups. Well silanized silicas will give rise to "clean" types of intermolecular interaction, although mixed retention mechanisms may be very useful in practice to achieve the necessary characteristic selectivities for a special application. Unger *et al.*[2] calculated that fully hydrolysed silica contains a concentration of 8–9 μmol/m^2 of silanol groups. Because of steric considerations, at best a maximum of about 4.5 μmol could be reacted with phenyltrichlorosilane, the remainder of the silanol groups being shielded by the non-polar rest of the reacted groups. Independent of the chain length of the bonded alkyl group, the surface coverage, α_{exp}, is usually found to be in the range 3.5–4.1 μmol/m^2 (ref. 1). We were greatly interested to see whether α_{exp} can be increased either by a more reactive silanization reagent or by improved access of the reagent to the surface inside the pores by the application of a solventless vacuum technique.

Other derivatization reactions of the silanol groups (tritium exchange; methane, hydrogen or ethane release after hydrolysis of suitable reagents by Si–OH groups and volumetric measurement of the gases) could give more and maybe better information about the reactive OH groups and help to explore the maximum percentage of groups that can undergo reaction in comparison with the common silanization reactions. The above-mentioned determination of the carbon content in bulk or in the layer gives reliable information about the percentage of reacted silanol groups only if the formation of carbon-containing insoluble high-molecular-weight materials that are not bonded to the surface via silanol groups can be excluded.

The immobilization of various kinds of monomers and oligomers (alkylsilanes, hydrocarbons, etc.) could possibly also be achieved by other reactions of chemical bonding to the surface, such as PSD (polysiloxane degradation)[3,4] and/or by cross-linking (γ-radiation, ^{60}Co source) or thermal peroxide degradation[5–7,12] of the deposited layers of the stationary liquid. Similar methods have been used successfully for glass and fused-silica column manufacture in gas chromatography (GC). However, it is important to generate coatings of variable layer thickness that are also of good homogeneity. If the coatings are too thick, they will, of course, retard the mass transfer between stationary and mobile phase and will decrease the separating efficiency. Support materials obtained by these techniques should give the same if not superior chromatographic performance with respect to separation efficiency, selectivity for hydrocarbon type and polar test solutes and tailing behaviour.

For isocratic chromatographic testing a mixture of ethylbenzene, butylbenzene, hexylbenzene, acetophenone and benzophenone, benzyl benzoate and 2-*n*-octylpyridine was used (for further testing, see refs. 8 and 9).

The aromatic hydrocarbons were to serve the purpose of testing for lipophilic selectivity and the ketones, ester and pyridine derivatives for dipole–dipole and hydrogen-bonding types of interactions with the surface layer or incompletely coated regions of the support surface and, especially, the silanol groups.

TABLE I

CARBON CONTENTS OF SILANIZED SILICAS

Silica material	*Silylation reagent*	*C (%)*	α_{exp}*	*ESCA results*		
				Si (%)	*C (%)*	*O (%)*
Nucleosil 100-5	Octadecyltrichlorosilane	20.7	4.4			
LiChrosorb Si-100-5	Octadecyltrichlorosilane	18.3	3.7			
LiChrosorb Si-100-5	Octadecyltriethoxysilane	14.7	3.0			
Nucleosil 100-5	Octadecyldimethylsilyl enolate**	20.6	3.9	20.9	43.2	35.9
Nucleosil 100-5	Trimethylsilyl enolate**	6.2	6.6			
Nucleosil 100-5	Allyldimethylsilyl enolate**	8.6	5.6			
Nucleosil 5-C_{18}	?	15.6	–	23.6	33.3	43.1
Nucleosil 100-5	–	–	–	32.0	1.3	66.7

* $\alpha_{exp}\ (\mu mol/m^2) = \dfrac{\%C \cdot 10^6}{(1200 N_C - \%C \cdot MW)\ A}$, where %C = carbon content; MW = molecular weight of silane ligand; N_C = number of C atoms in silane ligand; A = area of silica per gram (assumed values), LiChrosorb Si-100-5 = 280 m^2/g, Nucleosil 100-5 = 300 m^2/g.

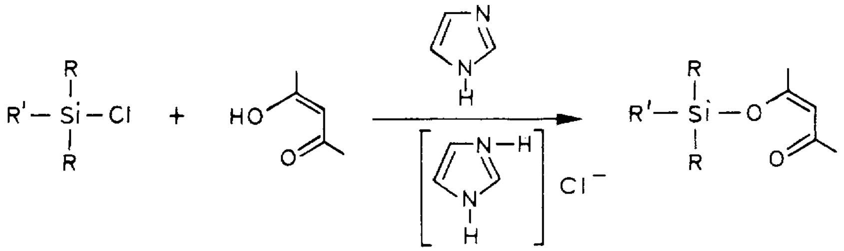
** Enolate = enolate of pentane-2,4-dione.

Table I lists various bonded phases obtained with different silicas and different silanization reagents.

EXPERIMENTAL

Preparation of reversed-phase materials

By the reaction of the silicas with alkylsilanes. To remove physically adsorbed surface water from the porous silica it was heated under vacuum (2 × 10^{-6} mbar) to 200°C for 24 h and then stored under argon. The alkyl silyl enol ethers of pentane-2,4-dione were prepared under inert conditions from alkylchlorosilane and pentane-2,4-dione in the presence of imidazole by using dry tetrahydrofuran as solvent after distillation in a yield of about 90% according to the following reaction scheme:[10,11]



$R = CH_3$, $R' = CH_3$, $CH_2CH{=}CH_2$, $n\text{-}C_{18}H_{37}$

The products were characterized by the usual methods. Further details of the reaction and physical data of the compounds obtained will be published elsewhere.

The silanization reactions were performed in the absence of gases and solvents with an excess of silanes in a specially designed vacuum apparatus (Fig. 1). At temperatures ranging from 25 to 80°C and 2 × 10^{-6} mbar the acetylacetone released could easily be removed from the reaction mixture continuously, thus yielding the best possible conversion. The reaction was complete after 3–4 h. The silica was filtered from the liquid (excess of reagent) and washed in succession with 200-ml portions of dry toluene, dichloromethane, methanol, methanol–water (1:1) and pure methanol. After drying at 80°C under vacuum, the reversed-phase materials were submitted to further investigation. Comparable silicas have been prepared with octadecyltrichloro- and triethoxysilane in the same way.

By cross-linking of polysiloxanes, induced by (a) peroxides, (b) γ-radiation and (c) thermal decomposition. A 3–5-g amount of silica was suspended in a solution of dissolved polysiloxanes [10–40% (w/w) with respect to the amount of silica] with the help of an ultrasonic bath. After removal of the solvent, the covered silica was dried at 30–80°C and 2 · 10^{-6} mbar.

(a) In peroxide reactions with polymethyloctylsiloxane, 10–80% (w/w) of dicumyl peroxide (with respect to the amount of polysiloxane) was dissolved in the suspension before drying. The solid was then placed in a glass tube and heated in a cylindrical oven at 200°C for 3 h while passing a constant stream of argon through

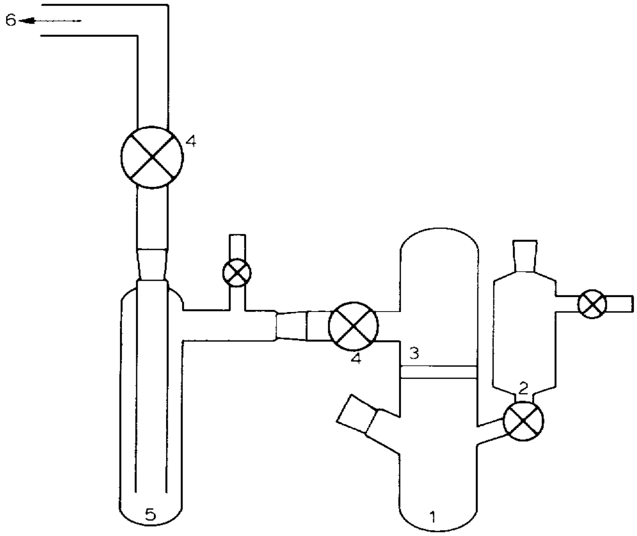


Fig. 1. Apparatus for vacuum silica silanization. 1 = Reaction vessel; 2 = dropping funnel for reagent; 3 = sintered-glass frit; 4 = Young valves; 5 = cold trap; 6 = to double stage diffusion pump.

the tube in order to exclude oxygen and to remove reaction products. The material was rinsed with a suitable solvent in order to remove unreacted polymers, then dried and tested.

(b) γ-Radiation (^{60}Co source available at the Max-Planck Institut für Strahlenchemie, Mülheim, F.R.G.; 3–40 Mrad) was applied to OV-17, polydimethylsiloxane, polymethyl-3,3,3-trifluoropropylsiloxane, polymethyloctylsiloxane and OV-17 vinyl gum as organic modifiers. All experiments were performed with dry silica in glass flasks. Work-up was carried out as in (a).

(c) Heating of silicas, coated with OV-17 and DC-200 at 350–450°C, analogous to the peroxide reactions, for 2.5 h yielded products that were treated as in (a).

Characterization

The silicas were characterized by physical, chemical and chromatographic methods.

Physical methods. Optical and scanning electron microscopy, ESCA and infrared spectroscopy in a potassium bromide matrix were used.

Chemical methods. Methyl- or ethyllithium[13], propyldiborane[14], activated (diethylboryl pivalate) triethylborane[15–17] and pure diethylboryl pivalate, as a result of their reaction with silanol groups, release gases, *e.g.*, methane, hydrogen or ethane, that are determined volumetrically and by mass spectrometry. With propyldiborane, the C=C bonds of alkenyl groups on the silica (resulting from presilanization reactions with allyldimethyl silyl enolate, for example) are hydroborated. After hydrolysis of excess of propyldiborane, the release of hydrogen can be used for the determination of the number of unsaturated groups.

Chromatographic methods. With several test mixtures, isomeric alkylbenzenes and mixtures of different polarities, the most important containing acetophenone, benzophenone, ethylbenzene, benzyl benzoate, *n*-butylbenzene, 2-*n*-octylpyridine and *n*-hexylbenzene, the different phases were investigated with respect to *k'* value, plate height, peak symmetry and adsorptivity when different eluent compositions were applied.

Instrumentation

Chromatographic measurements were performed with a Varian 5010 and 5020 liquid chromatograph and a Varian UV 1 254-nm fixed-wavelength detector.

Commercially available reversed-phase materials and those developed by ourselves were packed by a viscosity–slurry method in stainless-steel columns (150 × 4.4 mm I.D.), terminated by specially modified Swagelok fittings.

Chemicals

The compounds used are listed in Table II. The trialkylchlorosilanes and octadecylmethyldichlorosilane were purified by vacuum distillation and then stored under inert conditions. All solvents were dried, distilled and stored under argon gas. Identical batches of silicas were always used for making comparisons.

TABLE II

COMPOUNDS AND MATERIALS USED

Material	*Supplier*
Trimethylchlorosilane	Wacker-Chemie, F.R.G.
Octadecyltrichlorosilane	Petrarch Systems, U.S.A.
Octadecyltriethoxysilane	Petrarch Systems
Allyldimethylchlorosilane	Petrarch Systems
Octadecyldimethylchlorosilane	Petrarch Systems
Octadecylmethyldichlorosilane	Petrarch Systems
Pentane-2,4-dione	Wacker-Chemie
Imidazole	EGA-Chemie, F.R.G.
Nucleosil 5-100	Macherey, Nagel & Co., F.R.G.
LiChrosorb Si 100 5 μm	E. Merck, F.R.G.
OV-17	Ohio Valley, U.S.A.
OV-17 vinyl gum	Ohio Valley
DC-200	Serva, F.R.G.
Polydimethylsiloxane	Petrarch Systems
Polymethyl-3,3,3-trifluoropropylsiloxane	Petrarch Systems
Polymethyloctylsiloxane	Petrarch Systems
Dicumyl peroxide	ELFA, Oxy-Chemie, Switzerland

RESULTS

Silanization reaction

The new silanization reagents can be easily prepared by starting from mono- and dichlorosilanes and pentane-2,4-dione. The silanization reaction takes place under moderate (ambient) conditions and can be completed by removal of volatile pentane-2,4-dione under vacuum. Secondary reactions can be avoided by well-de-

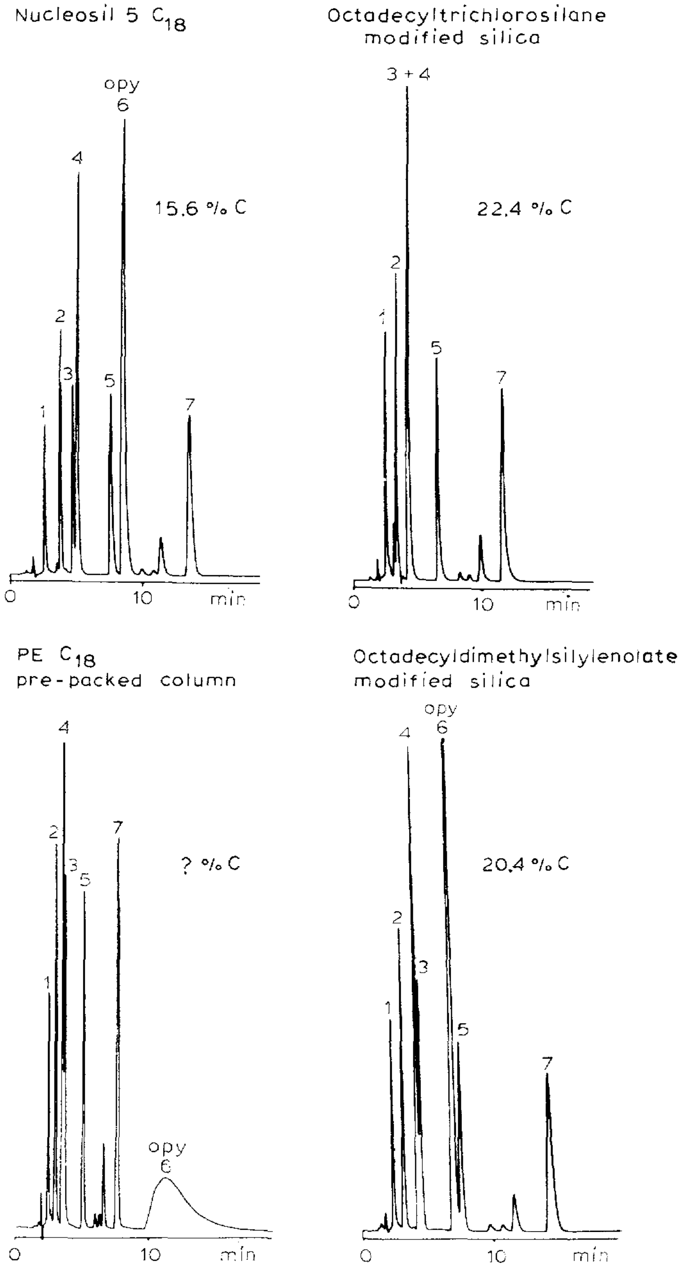


Fig. 2. Chromatographic reversed-phase test measurements of commercial materials in comparison with those obtained with enolate and trichlorosilane. Peaks: 1 = acetophenone; 2 = benzophenone; 3 = ethylbenzene; 4 = benzyl benzoate; 5 = *n*-butylbenzene; 6 = 2-*n*-octylpyridine; 7 = *n*-hexylbenzene. Columns, 150 × 4.4 mm I.D., except PE C_{18} (100 × 4.6 mm I.D.); temperature, 22°C; mobile phase, methanol–water (5:1, v/v); flow-rate, 0.8 ml/min, except PE C_{18} (0.5 ml/min); detection, UV at 254 nm.

fined dehydration of the starting silica. By degassing, improved access of the undiluted reagent to the surface inside the pores is obtained. Solvents for the silanization reagent are not used. Excess of reagents can be easily recovered and used for further silanizations.

The new silanes are free of halogens and therefore do not contaminate the bonded-phase silicas thus obtained. Polymers are either not formed or are removed by solvent rinsing. Products with hitherto unobtainable carbon content in the bulk and layer were obtained without damage to the physical structure of the spherical particles (Table I, Fig. 2).

Optimal chromatographic performance in terms of separation efficiency (plate height and peak symmetry) was obtained. The residual silanol groups were very effectively shielded, as could be concluded from the low retention of polar test solutes, such as basic 2-*n*-octylpyridine, relative to that of lipophilic compounds (alkylbenzenes). Fig. 2 shows a comparison between commercial products and silica modified by octadecyldimethylsilyl enolate according to our reaction.

Measurements for the determination of silanol groups before and after silanization were carried out with suitable reagents that can be hydrolysed (Table III). With propyldiborane, the number of silanol groups of unreacted silica, the number of silanol groups after the silanization reaction and (in the case of unsaturated groups on the surface) the number of functional unsaturations can easily be determined.

Peroxide reactions

Applying different amounts of peroxides and preliminary coatings of polysiloxane, layers of varying type and thickness were obtained (Table IV).

TABLE III

SURFACE COVERAGE OF OH GROUPS, DETERMINED BY DIFFERENT CHEMICAL METHODS

Silica material	α_{OH}*				α_{exp}
	A	*B*	*C***	*D*	
Nucleosil 5-100	8-13***	6.73 6.76	6.83 6.97	6.83	0
Nucleosil 5-C_1	–	–	1.00	–	6.59
Nucleosil 5-C_{18}	–	1.50	1.43	–	5.11
Nucleosil 5-allyl	–	–	2.23 (4.83) 2.27 (4.70)	–	5.55

* α_{OH} evaluated from volumetric measurements: A = alkyllithium (LiEt and LiMe); B = triethylborane activated by diethylboryl pivalate, Et_3B; C = propyldiborane, $Pr_4B_2H_2$; D = diethylboryl pivalate, *tert.*-butyl-C(O)OBEt$_2$. Me = methyl; Et = ethyl.

** Numbers in parentheses indicate the amount of allyl groups that are hydroborated by the reagent. The sum of the number of free OH groups after silanization and the number of allyl groups is identical with the amount of silanol groups in unsilanized silica, measured with the help of alkylboron reagents.

*** Reactions of silanol groups with alkyllithium did not lead to reproducible results. Working with an excess of alkyllithium no residual activity could be observed. Applying very large excesses of the metal compound, a limit of 22 μmol/m^2 was determined.

TABLE IV

CROSS-LINKING OF POLYMETHYLOCTYLSILOXANE, INDUCED BY THERMAL DECOMPOSITION OF DICUMYL PEROXIDE ON TRIMETHYLSILYLATED SILICA

*A**	*B***	*C (%)****	*ESCA*		
			Si (%)	*C (%)*	*O (%)*
10	20	11.2			
10	80	12.3			
30	20	20.7			
30	40	19.6			
30	80	20.6	29.6	17.2	53.2
40	40	22.8			

* A = amount of siloxane [% (m/m)] with respect to the amount of silica.

** B = amount of dicumyl peroxide [% (m/m)] with respect to the amount of siloxane.

*** C (%) = carbon content from elemental analysis.

The experiments were successful only after silanization, *e.g.*, with trimethylsilyl groups. Without presilanization only broad peak shapes could be observed. High peroxide concentrations (up to 80%) were necessary for immobilization and sufficiently stable coatings.

Scanning electron microscope photographs revealed no structural defects of the spherical particles (Fig. 3). The phases obtained showed good chromatographic performance and maximum deactivation and/or shielding of the silanol groups, as can be seen from the lowest retention times of 2-*n*-octylpyridine ever observed in our experiments (Fig. 4).

γ-Radiation experiments

Only those oligomers which have been used successfully for capillary column manufacture in GC could be immobilized on silica by γ-radiation (high-molecular-weight polydimethylsiloxane and polymethyl-3,3,3-trifluoropropylsiloxane, Table V). The silica products were of medium carbon content, but gave acceptable chromatographic performance.

Siloxane monomers could not be immobilized, obviously because of too low a radical yield. Nevertheless, further experiments on oligomerizations by γ-radiation seem promising, as can be concluded from preliminary oligomerization experiments with divinylbenzene.

Commercially available bonded reversed-phase materials have also been treated by γ-radiation, but they did not exhibit any change of chromatographic performance. Chemical bonding of alkylpolysiloxanes could also be achieved by thermal decomposition (Fig. 4).

Immobilization is due only to chemical reactions and not to physical adsorption, as could be demonstrated by parallel experiments without peroxides, γ-radiation and heating, where the polysiloxanes could be completely removed by rinsing with suitable solvents.

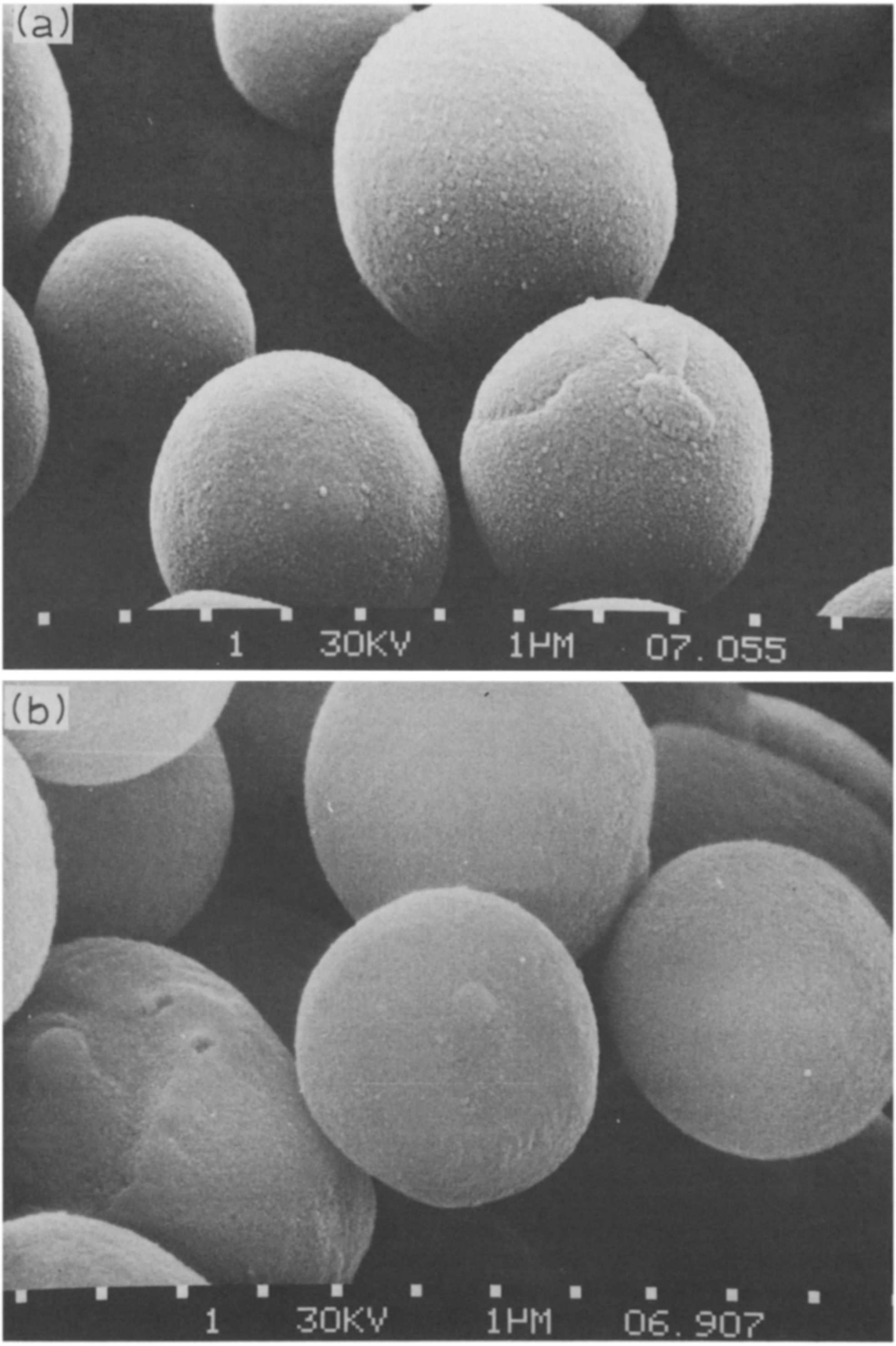


Fig. 3.

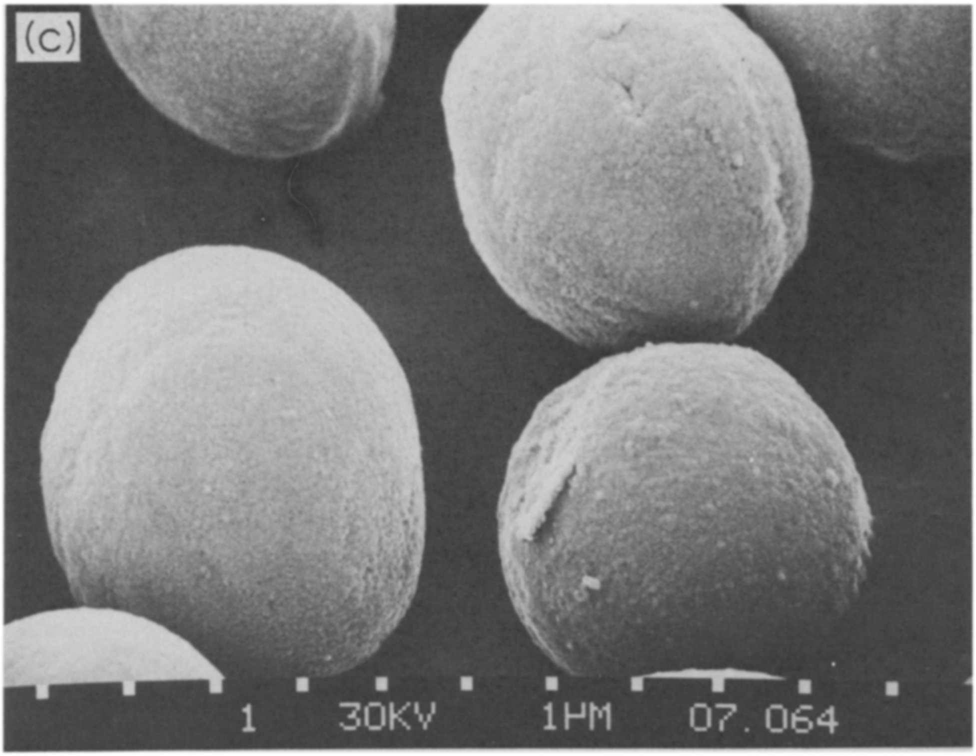


Fig. 3. Scanning electron microscope photographs. (a) Trimethylsilylated Nucleosil 100-5; (b) Nucleosil 5-C_{18}, prepared by reaction of Nucleosil 100-5 with octadecyldimethylsilyl enolate (*cf.* Table I); (c) trimethylsilylated Nucleosil 100-5 with 30% polymethyloctylsiloxane and 80% dicumyl peroxide (*cf.*, Table IV).

DISCUSSION AND CONCLUSION

Silanized silicas for bonded-phase chromatography can be produced with advantage by the chromatographer himself. Unfortunately, commercially bonded phases are synthesized by procedures and reagents unknown to the user. Especially the adsorptive properties of such materials may differ widely, depending on their origin. We propose that even the average user of such materials can perform in his own laboratory silanization reactions with silica of defined particle and pore size and, particularly, silanol group concentration on the surface in order to obtain support materials with defined and reproducible chromatographic properties. The solventless vacuum technique of silanization with various enolate-type silanization reagents presented in this paper provides excellent products. However, the silicas used as starting materials should be examined for particle and pore size, surface area and, even more important, for the silanol group concentration on the surface.

For comparison of various silanization procedures we used commercial spherical silicas, originating from the same production lots. They were tested with several known and new reagents (alkylboranes and hydroboranes) for silanol group reaction, which give at least the same (if not considerably higher) percentages of Si–OH group

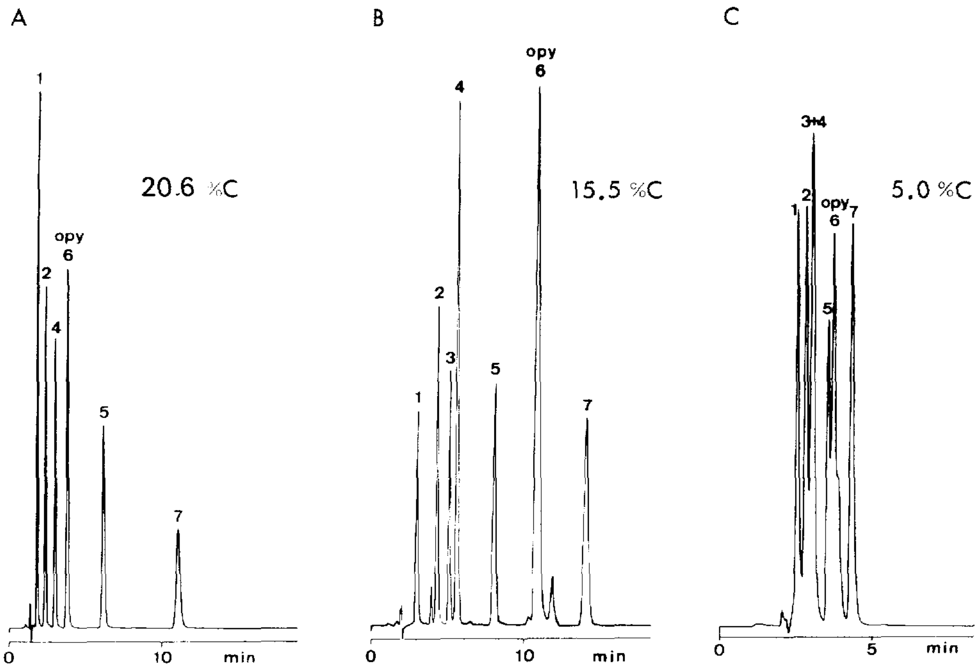


Fig. 4. Chromatographic reversed-phase test measurements with alkylpolysiloxanes on silica obtained by peroxide and thermal treatment. (A) Thermal peroxide treatment of polymethyloctylsiloxane on trimethylsilylated silica; (B) Nucleosil 5-C_{18}; (C) thermal treatment of DC 200 on silica. Peaks: 1 = acetophenone; 2 = benzophenone; 3 = ethylbenzene; 4 = benzyl benzoate; 5 = *n*-butylbenzene; 6 = 2-*n*-octylpyridine; 7 = *n*-hexylbenzene. Columns, 150 × 4.4 mm I.D.; temperature, 22°C; mobile phase, methanol–water (5:1, v/v); flow-rate, 0.8 ml/min; detection, UV at 254 nm.

TABLE V

CROSS-LINKING OF POLYMETHYL-3,3,3-TRIFLUOROPROPYLSILOXANE, INDUCED BY γ-RADIATION ON SILICA AND TRIMETHYLSILYLATED SILICA

Material	*A**	*B***	*C****	*C (%)*§
Silica	10	3	47	3.2
	20	3	94	5.8
	20	10	98.3	5.6
	40	3	94.2	9.4
	40	–	0	–
Trimethylsilylated silica	20	10	86.7	8.4 (5.8)
	40	10	80.0	10.5 (5.8)

* A = amount of siloxane [% (m/m)] with respect to the amount of silica.

** B = γ-radiation dose (Mrad).

*** C = non-extractable cross-linked siloxane [% (m/m)] with respect to the amount of siloxane.

§ C(%) = carbon content from elemental analysis. Numbers in parentheses indicate the carbon content of the silica after presilanization with trimethylsilyl groups.

reactions as the usual short- and long-chain alkylsilane derivatives for the actual surface modification. The silanization reagents successfully used by us, together with a vacuum technique without solvents and gases are free of halogenes and are highly reactive, even under moderate conditions. High carbon contents, have been obtained, together with excellent shielding of the silanol groups against interaction with polar solutes.

Our experiments on other methods of immobilization of stationary phases on silica surfaces by either chemical bonding or by intermolecular cross-linking of various types of preferably siloxane oligomers were successful and promise to yield bonded phases with good coverage of the silanol groups and variable layer thicknesses. Chemical bonding via silanol groups is not necessarily achieved thereby. With all methods of cross-linking or chemical bonding by γ-radiation, peroxide and thermal treatments of siloxanes, column materials of good if not excellent chromatographic performance could be obtained. Further experiments on this subject are in progress.

Recent experiments with silica materials, well characterized by ourselves with regard to the surface area, indicate that some of these materials leading to the results reported in Table I had a higher surface area than specified by the manufacturer. This would decrease the α-values given.

Nevertheless, the chromatographic performance of the reversed phases obtained was excellent and superior to commercially available products. Further results on this special subject matter will be published soon.

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