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## CHARACTERIZATION OF SILICA BONDED STATIONARY PHASES

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### SUMMARY

Several different commercially available substituted silica gels were analyzed to determine the nature of their ligands. Fused alkali was used to cleave the silicon-carbon bond and the ligands released were analyzed by gas chromatography. The determinations revealed structural differences between products of the same ligand type, especially for ion exchangers. A few products did not conform with the classifications provided by the manufacturers.

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### INTRODUCTION

From the great number of stationary phases based on silica which could theoretically be used for chromatography only a few types are commercially available<sup>1</sup> (Fig. 1). First there are hydrophobic reversed-phase (RP) materials without any functional group. The ligands of all other derivatized silicas have functional groups which are fixed via an alkyl, aryl or arylalkyl spacer to the matrix. The spacer length is as a rule unknown and the structures shown are more or less based on speculations or on hints from the different manufacturers.

Strong cation exchangers (SCX) containing an aromatic sulphonic acid are widely established in ion-exchange chromatography, but alkanesulphonic acids have also been proposed for this purpose<sup>2</sup>. Quaternary ammonium groups are used as strong anion exchanger (SAX). The length of the alkyl substituents on the nitrogen is variable. Amines which are not fully alkylated act as weak anion exchangers (WAX).

For special separation purposes, ligands of the polar type are available with nitro (NO<sub>2</sub>), cyano (CN) and diol groups.

In all derivatized silicas mentioned the materials contain a relatively stable Si-C bond. Attachments via a silyl ether (Si-O-C) are more hydrolytically labile and are used only as supports for gas chromatography (GC). For completeness an example of this ligand type will also be considered, and is regarded as a RP material.

Apart from the different types of silane modifiers used for derivatization (mono-, di- or trifunctional silane), the structures of RP materials are usually known. This is not true for most of the commercially available derivatized silica gels with their different functional groups, as only a few producers are willing to give detailed

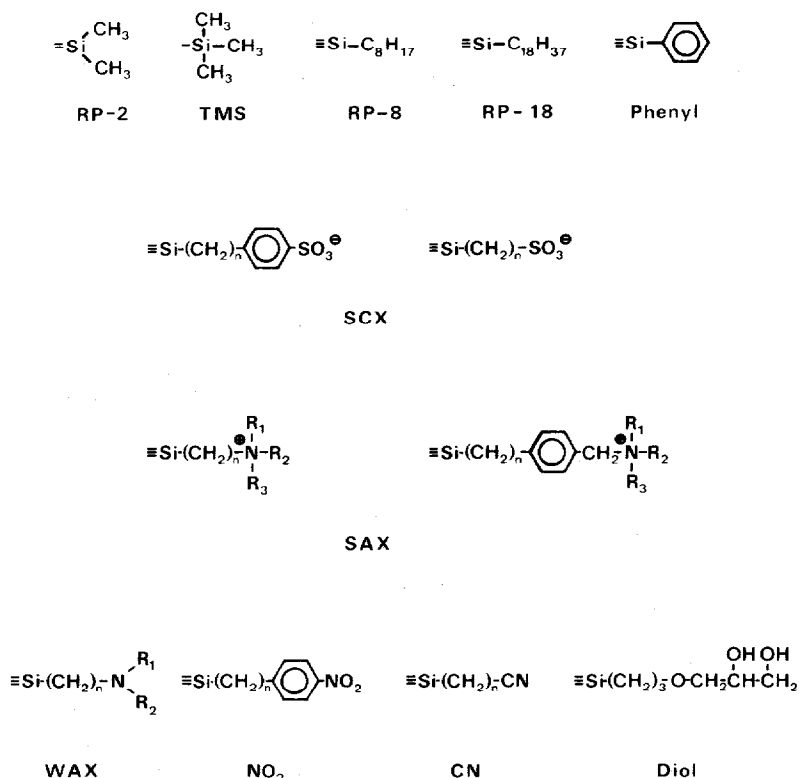


Fig. 1. Possible structures of commercially available substituted silicas.

structural information about their products. This often prevents a precise interpretation of observed separations. In spite of having the same designation, one SAX column will not be identical with that from a different manufacturer or even with a different batch from the same producer. Therefore a change of material may result in a disturbance to routine analysis.

The structure of the ligand and its degree of substitution are important factors in the separation observed. Recently we have shown that the degree of substitution differs considerably for several samples of RP-18 silicas<sup>3</sup>.

In spite of the extensive use of derivatized silicas, relatively little work has been devoted to the structural characterization of these materials<sup>3-6</sup>. Most of the published analytical procedures deal with either laboratory-prepared phases or RP types with known structural parameters. Some of the methods described can be transferred to other ligand types.

Franc and Plaček<sup>7</sup> used molten alkali for identification of organosilicon compounds. We have found this method to be suitable as a basic reaction for all important stationary phases. Fused potassium hydroxide cleaves Si-O-Si, Si-O-C and Si-C bonds<sup>8,9</sup>, and the ligand of derivatized silica is released under these conditions and can be determined by GC. When the functional groups react in an undesirable way with the alkali, a special pre- or post-treatment is necessary.

The following reactions of the different ligand types with fused KOH seem probable.

### *RP*

In the case of hydrocarbon ligands the products will be mainly alkanes and aromatic hydrocarbons, and no side reactions are expected. The appearance of the corresponding alkanol depends on the reaction conditions<sup>3</sup>. However, if the temperature of fusion is higher than 200°C pyrolytic degradation occurs<sup>10</sup> caused by the silica surface, as was shown by own model experiments with pure silica gel and *n*-octadecane. In the case of a silylether linkage, the scission with KOH should yield the corresponding alkanol or phenol<sup>8</sup>.

### *SCX*

While alkanesulphonic acids are converted into a mixture of isomeric alkenes<sup>11</sup>, aromatic acids yield phenol<sup>12</sup> and alkylphenols with hot alkali.

### *SAX*

Quaternary ammonium compounds undergo Hofmann elimination.

### *WAX*

Primary, secondary and tertiary amines are not affected under alkaline conditions.

### *NO<sub>2</sub>*

Aromatic mononitro compounds undergo a redox reaction with bases; dinitro compounds form adducts of the Meisenheimer type<sup>13</sup>. These reaction products are not suitable for direct GC analysis.

### *CN*

If polyacrylonitrile is treated with fused alkali the cyano groups are converted into carboxylates<sup>14</sup>; therefore, nitrile ligands on silica should yield the corresponding carboxylic acid after fusion and subsequent acidification.

### *Diol*

While aliphatic ether bonds are usually not cleaved by strong bases, aliphatic vicinal diol compounds presumably are oxidized under fusion conditions<sup>15</sup> yielding dicarboxylic acids and other products inconvenient to GC analysis.

## EXPERIMENTAL

### *Materials*

All chemicals and solvents used were regular products and of analytical grade. APS, CPS, MOS and ODS Hypersil were from Shandon (Runcorn, U.K.), alkylamine CPG 550 from Pierce (Rockford, IL, U.S.A.). Bond Elut PH, PSA, SAX and SCX were free test samples from Analytichem International (Harbor City, CA, U.S.A.). GC Durapak *n*-octane was from Waters (Milford, MA, U.S.A.). HPLC-Sorb SIL 60-D 10 CN, N(CH<sub>3</sub>)<sub>2</sub>, NH<sub>2</sub> and NO<sub>2</sub>, HPLC-Sorb Vydac-301 SB and 401

SA and Nucleosil 7 C<sub>6</sub>H<sub>5</sub>, C<sub>18</sub>, 10 N(CH<sub>3</sub>)<sub>2</sub>, NH<sub>2</sub>, NO<sub>2</sub>, SA and SB were from Macherey, Nagel & Co. (Düren, F.R.G.). Kieselgel 60 HPLC C<sub>8</sub>, C<sub>18</sub> and Chromosorb W AW DMCS (60–80 mesh) (1E 90019) were from Riedel de Haën (Seelze, F.R.G.). Another batch of Chromosorb (231055282) was from Fluka (Buchs, Switzerland). LiChroprep RP-8 and RP-18 were from E. Merck (Darmstadt, F.R.G.). LiChrosorb RP-2, RP-8, RP-18, CN, NH<sub>2</sub>, AXW and Diol and HPTLC Fertigplatten RP-2, RP-8 and RP-18 and Fertigplatten RP-18 were generous gifts from Dr. Becker (Merck). Partisil-10 SCX was from Whatman (Clifton, NJ, U.S.A.). The material was scraped out from a column generously supplied by P. v. Haastert (Leiden, The Netherlands). SIL-X-10 C-8, CN, NH<sub>2</sub>, NO<sub>2</sub> and SIL-X-5 C-8 were generous gifts from T. Borath (Perkin-Elmer, Überlingen, F.R.G.). SP 500 Epoxypropyl, Phenyl and RP-8 were from Serva (Heidelberg, F.R.G.). Vydac Anion Exchange was from The Separations Group (Hesperia, CA, U.S.A.) and Zorbax TMS was from Du Pont (Wilmington, DE, U.S.A.).

### Analysis

*RP-8, RP-18, Phenyl, SCX, SAX (aromatic), NO<sub>2</sub>, CN, Diol 1.* Ligand analysis was performed with a Sigma 1 gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.) equipped with a 15 m × 0.242 mm I.D. fused-silica capillary column with chemically bonded non-polar stationary phase (DB-1-15N, J & W Scientific). A flame ionization detector was used and helium was the carrier gas at 1.2 ml/min. A temperature program from 50 to 300°C at 20°C/min was used in most cases for checking the whole retention area, but for routine analysis optimized conditions for faster analysis are recommended.

*SAX, WAX, Diol 2.* For GC of amines the stationary phase consisted of 10% octadecylamine on Chromosorb W AW DMCS (80–100 mesh) in a 2.5 m × 3 mm packed glass column. The analyzer was a Shimadzu GC 3 BF with flame ionization detector. The oven temperature was held at 60°C or 80°C and the carrier gas was helium at 40 ml/min.

*RP-2/TMS, SAX (aliphatic spacer).* For identification of volatile compounds, a F 22 gas chromatograph (Perkin-Elmer) with headspace equipment HS-6 and a flame ionization detector was used. Analysis was performed at room temperature with helium as carrier gas (2 ml/min) on a 25-m OV-101 capillary column.

### Cleavage procedures

The weight of silica given in the following paragraphs was calculated for materials with around 350 m<sup>2</sup>/g and high ligand loading.

For RP silicas which are poorly wetted by molten alkali the addition of triethylene glycol dimethyl ether (triglyme) is recommended. During fusion some degradation products are formed showing a characteristic GC pattern. In some cases this can disturb the analysis, especially if unknown structures are to be analyzed.

*RP-2/TMS.* Ten mg sample and 100 mg dry solid KOH were sealed in a special headspace vial and heated at 200°C for 15 min. The vial was allowed to cool and analyzed for methane with the headspace technique.

*RP-8, Phenyl, Octylsilyl ether.* Ten mg sample, 100 mg dry solid KOH and 100 μl triglyme were sealed in a glass reaction tube (110 × 5 mm I.D.) and heated for 1 h at 200°C in a silicon oil-bath. After cooling, the bottom of the tube was placed

in an ice-bath while heating the top until all condensed droplets had disappeared. The tube was opened and 100  $\mu$ l *n*-pentane were added.

*RP-18*. The sample was treated as with *RP-8*, but could be heated unsealed.

*SCX*. Ten mg sample and 100  $\mu$ l hydroiodic acid (57%) were sealed in a glass reaction tube and heated for 2 h at 200°C. After cooling, 100  $\mu$ l *n*-pentane and 1 ml water were added and the mixture was analyzed for benzene by GC. The acid/pentane was evaporated and the remaining silica was treated with fused KOH as described for *RP-8*.

*SAX, WAX*. Ten mg sample and 100 mg dry solid KOH were sealed in a glass reaction tube (110  $\times$  5 mm I.D.) and heated for 1 h at 200°C in a silicon oil-bath. After cooling, the tube was placed in an ice-bath, heating the top until all condensed droplets had disappeared. The tube was opened and 100  $\mu$ l diethyl ether were added. The ether extract was analyzed on the special stationary phase for amines. If information about the fourth amine ligand from aliphatic *SAX* samples is desired, the procedure of *RP-2* (headspace) is necessary in a second run or the whole analysis has to be performed with a headspace analyzer equipped with the special stationary phase for amines. Aromatic *SAX* types were analyzed on the capillary column because of their very long retention times on the octadecyl amine phase.

*NO<sub>2</sub>*. Ten mg sample, 100  $\mu$ l hydrazine hydrate (80%) and about 10  $\mu$ l Raney nickel suspension in ethanol (W2) were heated at 100°C in a glass reaction tube until gas evolution had stopped. The hydrazine was evaporated, the nickel partly removed with a magnet and the remaining silica was treated as described for *SAX* but the ether layer was pipetted off and 10  $\mu$ l trifluoroacetic anhydride were added for derivatization. A GC analysis was performed immediately.

*CN*. The sample was treated as described for *SAX*; it could be heated unsealed and was acidified in an ice-bath with hydrochloric acid prior to the addition of diethyl ether.

*Diol*. Ten mg sample and 100  $\mu$ l boron tribromide in *n*-pentane (1 *M*) were held in a glass reaction tube for 5 min. The supernatant layer was pipetted off, hydrolyzed with water and analyzed by GC for brominated glycerol species (*Diol 1*). The remaining silica was warmed to dryness and treated with KOH as described for *SAX*. It was neutralized with hydrochloric acid in an ice-bath prior to solvent addition and analyzed for *n*-propanol (*Diol 2*).

## RESULTS

### *RP-2/TMS*

All samples tested yielded methane (Table I, Fig. 2). It is obviously impossible to distinguish between *RP-2*, TMS from endcapping and the methyl groups introduced from using a mono- or dimethylsilane for derivatization. The use of triglyme is not recommended as undesirable signals in GC are produced.

### *RP-8*

Nearly all *RP-8* samples were substituted with *n*-octane (Table II, Fig. 3) with two remarkable exceptions. The Riedel Kieselgel C<sub>8</sub> was substituted mainly with 2,2,4-trimethylpentane and 2,2-dimethylhexane and traces of isomeric  $\alpha$ -tanenes and one octene (Fig. 4). Benzene and tetrahydrofuran seem to be residues from the washing procedures used during manufacture.

TABLE I  
LIGAND TYPES OF DIFFERENT RP-2/TMS SILICAS  
GC determination as methane after fusion with KOH at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion product	Ligand structure
Chromosorb W AW DMCS (Kieselguhr)	1E 90019	150-180			
Chromosorb W AW DMCS (Kieselguhr)	231055282	150-180	$=\text{Si}(\text{CH}_3)_2$		$=\text{Si}-\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$
HPTLC Fertigplatten RP-2	Hp/Sch 451	5			
LiChrosorb RP-2	VV 1593	10		Methane	
Zorbax TMS	-	7			
All products with encapped silanol groups and products derivatized with mono- or dimethylsilanes	-	-	$\text{Si}(\text{CH}_3)_3$		$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$

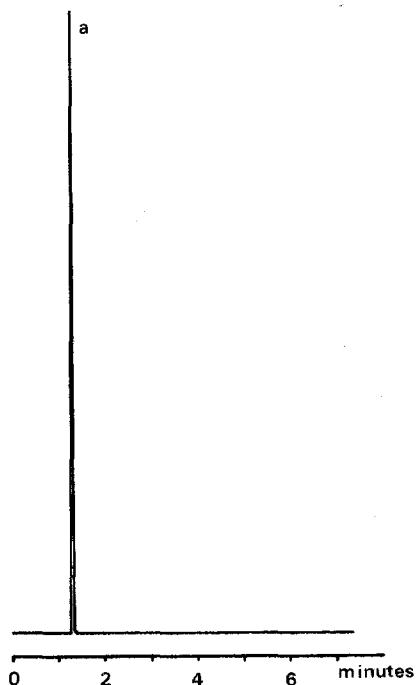


Fig. 2. Gas chromatogram of alkali fusion product from RP-2/TMS silica (15 min, 200°C). Peak: a = methane.

The MOS Hypersil which was characterized as a "dimethyloctyl" derivative yielded four unidentified signals, one of them having a molecular weight of 358 (Fig. 5).

The Serva SP 500 RP-8 which was advertised as a "Si-C bound polyhydroxyl derivative of silica with ether bound ligand" seemed to be an unmodified RP-8 material; no cleavage products resulting from ether bonds could be found. A test for ether bonds was performed with  $\text{BBr}_3$  and would have produced the corresponding bromide and alkanol.

In the case of the Si-O-C bound Durapak *n*-octanol was produced.

The formation of small amounts of the corresponding alkanol from Si-C bound RP-8 could be detected. The appearance of methane is an indicator of end-capping procedures but is also produced if mono- or dimethylsilanes were used.

#### *RP-18*

All samples tested yielded *n*-octadecane and small amounts of *n*-octadecanol. In most cases methane was also observed (Table III, Fig. 6).

#### *Phenyl*

Alkali fusion of phenyl-substituted silicas yielded benzene. The Nucleosil sample which was labelled " $\text{C}_6\text{H}_5$ " produced however propylbenzene (Table IV, Fig. 7). The SP 500 sample was identified as containing a silicon-aryl bond and no ether linkage.

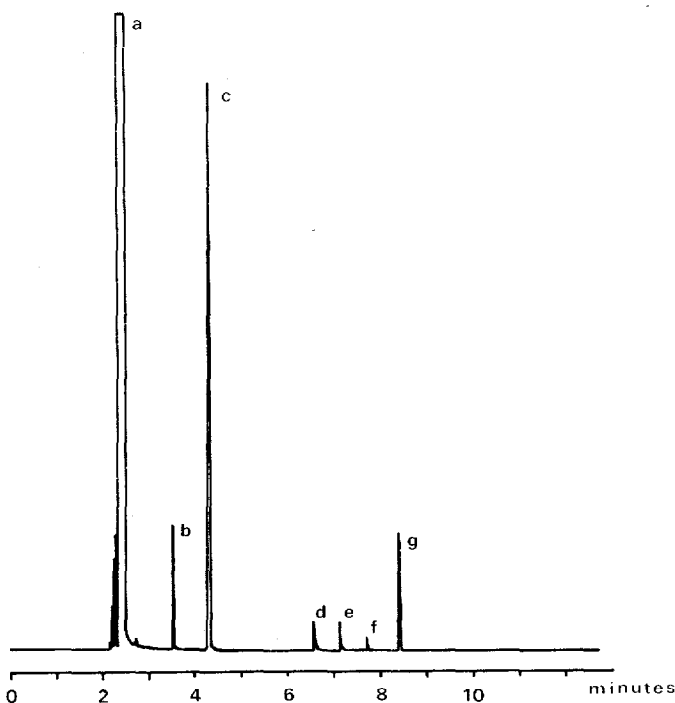


Fig. 3. Typical gas chromatogram of alkali fusion products from RP-8 silicas (1 h, 200°C, triglyme suspension). Peaks: a = *n*-pentane (solvent); b, d, f = triglyme degradation products; c = *n*-octane; e = *n*-octanol; g = triglyme.

### SCX

Alkali fusion of SCX silicas in no case resulted in alkenes or phenols. The ether extract after fusion was UV active and showed several spots on a thin-layer chromatogram, but with GC only aromatic hydrocarbons from incomplete sulphonation were detectable. It is obvious that all samples tested were of the aromatic type.

When aromatic sulphonic acids are treated with mineral acids at elevated temperatures a desulphonation process occurs<sup>16</sup> resulting in the corresponding hydrocarbon compound. Treating SCX silica in this manner, all silicon-aryl bonds are cleaved too<sup>9</sup>, so that it becomes necessary to analyze an ether extract of the desulphonation mixture for benzene, xylenes and other silicon-aryl bound compounds. A subsequent alkali fusion yielded the corresponding aromatic hydrocarbons for analysis.

This procedure is not capable of distinguishing between sulphonic acid-substituted aromatic molecules and their pure hydrocarbon parent compounds which would arise from incomplete sulphonation. The latter are distinguishable by direct fusion with KOH.

The analysis of four strong cation exchangers showed the products to be quite different. While all samples exhibited the coarse structure of an aromatic sulphonic acid, the materials were different in their spacer moiety (Table V, Fig. 8). All samples had impurities of alkylbenzenes, xylenes or benzene up to 50% which appeared partly after the desulphonation step, indicating silicon-aryl bonds.



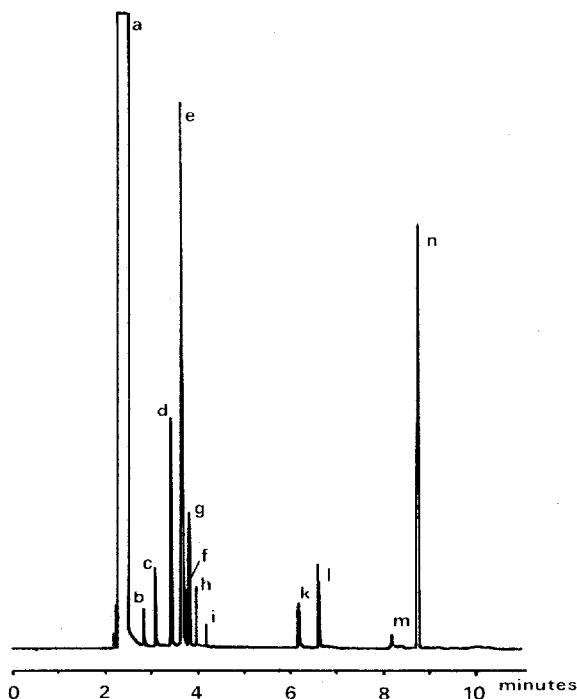


Fig. 4. Gas chromatogram of alkali fusion products from Riedel de Haën  $C_8$  silica (1 h, 200°C, triglyme suspension). Peaks: a = *n*-pentane (solvent); b = benzene; c = tetrahydrofurane; d, l, m = triglyme degradation products; e = 2,2,4-trimethylpentane; f = 2,2,4-trimethyl-1-pentene; g = 2,2-dimethylhexane; h = 2,2,3-trimethylpentane; i = 2,3,4-trimethylpentane; k = alkanol?; n = triglyme.

Partisil SCX had no aliphatic spacer as the manufacturer's literature suggested<sup>17</sup>. Incomplete sulphonation could be found in the case of Vydac SA silica. Fusion with KOH without prior desulphonation yielded ethylbenzene and *o*-xylene.

### SAX

The analysis of SAX samples showed much more variability than had been observed for other silica derivatives (Table VI). Both aromatic and aliphatic ligands were found. The aromatic species were of the benzylamine type with different spacer lengths and different alkyl groups on the quaternary nitrogen. The spacers were of the same length as in the corresponding SCX silicas from the same manufacturer.

Besides detailed structural information, the fusion products allowed conclusions to be drawn about the process of manufacture of these products (Scheme 1). The two Vydac SAX materials yielded, besides relatively small amounts of benzene, triethylamine and methylstyrene, mainly ethylbenzene and *N,N*-diethyl-4-ethylbenzylamine which were identified by gas chromatography-mass spectrometry (GC-MS) (Fig. 9) (mass spectra did not distinguish between *o*, *m* and *p* isomers). From these results we propose the following interpretation of the fusion products.

The basic compound used for derivatization of the silica surface was a phenethylsilane, as this structure was also found in SCX silicas from the same producer. The resulting phenethyl silica could have been methylated to mainly 4-methylphen-

TABLE II  
LIGAND TYPES OF DIFFERENT RP-8 SILICAS

GC determination as alkane/alkanol after fusion with KOH in triglyme suspension at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion products	Ligand structure
HPTLC Fertigplatten RP-8	Hp/Sch 451	5	$\equiv\text{Si}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
Kieselgel 60 HPLC C <sub>8</sub>	8E 20586	10	C <sub>8</sub>	Methane, benzene, tetrahydrofuran, 2,2,4-trimethylpentane, 2,2-dimethylhexane, traces of other octanes and one octene	$\begin{array}{c} \text{CH}_3 \\   \\ \equiv\text{Si}-\text{CH}_2-\text{CH}(\text{CH}_2)_4-\text{C}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\   \\ \equiv\text{Si}(\text{CH}_2)_4-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
LiChroprep RP-8	8561951	25-40	$\equiv\text{Si}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
LiChroprep RP-8	8597034	25-40	$\equiv\text{Si}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
LiChrosorb RP-8	VV 1137	10	$\equiv\text{Si}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
LiChrosorb RP-8	VV 2159	10	$\equiv\text{Si}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
MOS Hypersil C8	12/772	5	Dimethyloctyl	Methane, four unidentified peaks	$\equiv\text{Si}-?$
SIL-X-10 C-8	829081	5	C <sub>8</sub>	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
SIL-X-10 C-8	820011	10	C <sub>8</sub>	Methane (traces), <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}(\text{CH}_2)_7\text{CH}_3$
SP 500 RP-8	22050	100-200	See text	Methane, <i>n</i> -octane, <i>n</i> -octanol	$\equiv\text{Si}-\text{O}-(\text{CH}_2)_7\text{CH}_3$
GC Durapak <i>n</i> -octane	263	?	$\equiv\text{Si}-\text{O}-\text{C}_8\text{H}_{17}$	Methane, <i>n</i> -octanol	$\equiv\text{Si}-\text{O}-(\text{CH}_2)_7\text{CH}_3$

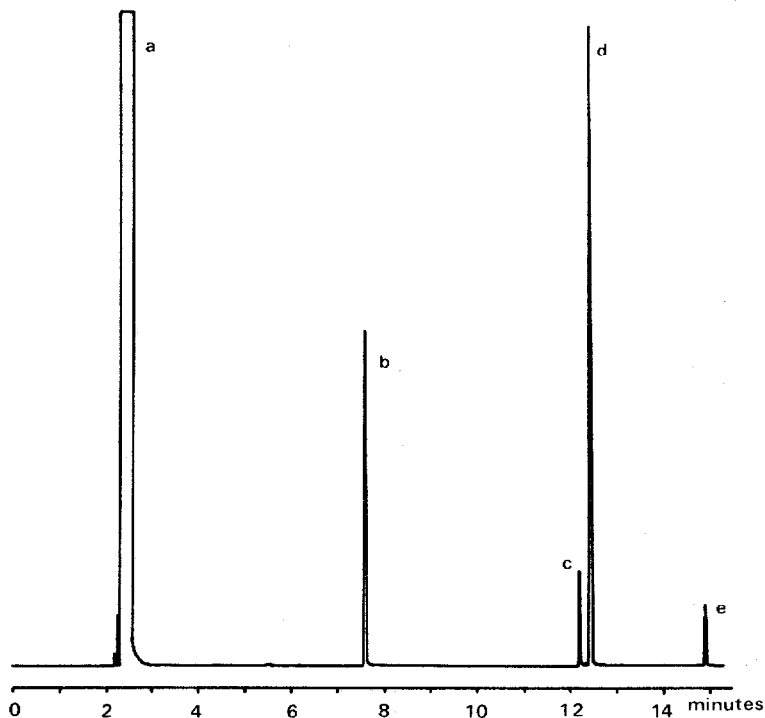


Fig. 5. Gas chromatogram of alkali fusion products from Shandon MOS Hypersil (RP-8) (1 h, 200°C). Peaks: a = *n*-pentane (solvent); b, c, e = unidentified; d = unidentified with molecular weight of 358.

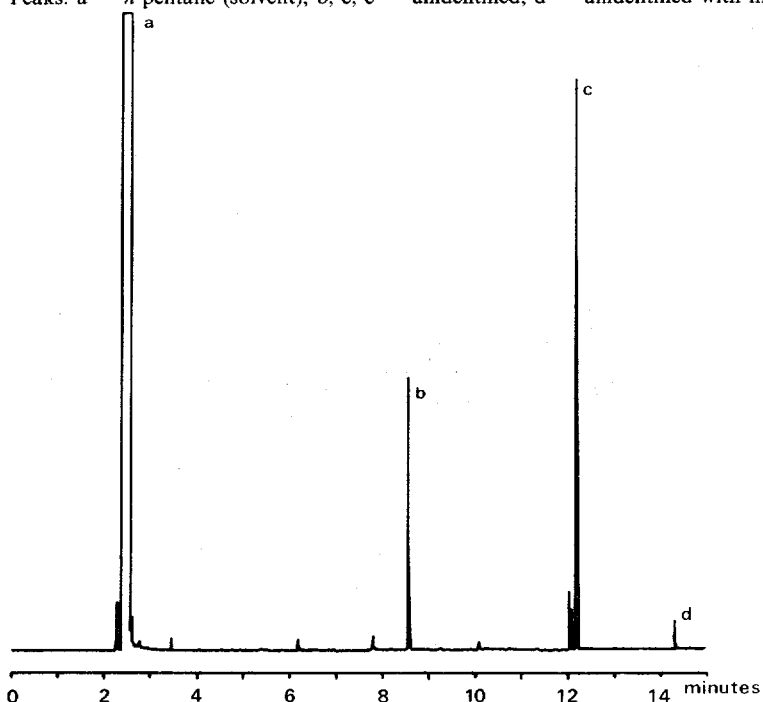


Fig. 6. Gas chromatogram of alkali fusion products from RP-18 silicas (1 h, 200°C, triglyme suspension). Peaks: a = *n*-pentane (solvent); b = triglyme; c = *n*-octadecane; d = *n*-octadecanol.

TABLE III  
LIGAND TYPES OF DIFFERENT RP-18 SILICAS

GC determination as alkane/alkanol after fusion with KOH in triglyme suspension at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion products	Ligand structure
Fertigplatten RP-18	2502566	5			
HP/TLC Fertigplatten RP-18	HP/Sch 451	5			
Kieselgel 60 C <sub>18</sub> RP	7R20459	10			
Kieselgel 60 C <sub>18</sub> RP	Ch-B2174	10			
LiChroprep RP-18	8572024	25-40			
LiChrosorb RP-18	VV 2053	5			
LiChrosorb RP-18	VV 1187	5			
LiChrosorb RP-18	VV 1220	7			
LiChrosorb RP-18	VV 1106	10			
LiChrosorb RP-18	VV 1827	10			
LiChrosorb RP-18	VV 2249	10			
Nucleosil 7 C <sub>18</sub>	3022	7			
ODS Hypersil	11/1067	5			
ODS SIL-X-10	—	10			
ODS SIL-X-5	—	5			
Sep-Pak	—	50-100			
Spherisorb S5 ODS C <sub>18</sub>	18/157	5			
Vydac 201 RP (glass beads)	—	30-44			



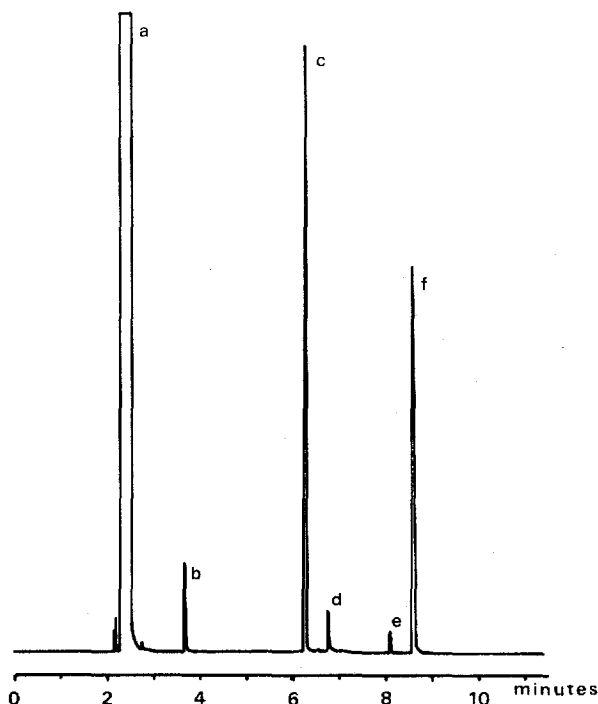


Fig. 7. Gas chromatogram of alkali fusion products from Nucleosil  $C_6H_5$  silica (1 h,  $200^\circ C$ , triglyme suspension). Peaks: a = *n*-pentane (solvent); b, d, e = triglyme degradation products; c = *n*-propylbenzene; f = triglyme.

ethyl silica under Friedel-Crafts conditions. The reaction was incomplete and a relatively large amount of unchanged phenethyl groups remained. This reaction step could have been followed by halogenation of the newly introduced methyl group, but the ethyl spacer chain was partly halogenated as well. Subsequently the silica could have been treated with triethylamine to obtain quaternary ammonium groups. The products of fusion with KOH, methylstyrene and triethylamine, show that a few quaternary ammonium groups had been fixed to the ethyl spacer, for these are typical elimination products of quaternary amines. Benzene seems to be an impurity in the gel arising from washing procedures used during manufacture.



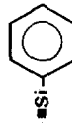
In the case of Nucleosil we found the same basic structural elements, but a propyl spacer was used and the other three substituents on nitrogen were methyl groups. The amount of propylbenzene was very high (Fig. 10). The presumed manufacturing process for this material could have been the same as used for Vydac samples, but some more fragments were detected providing evidence for Scheme 2. The benzene impurity present in the gel presumably underwent the same reactions since traces of toluene and *N,N*-dimethyl-4-toluidine were found. *N,N*-Dimethyl-2-methyl-4-propylbenzylamine seems to be a fusion product from a rearrangement of the Sommelet-Hauser type<sup>18</sup>.

Bond Elut SAX was a representative of the aliphatic trialkylammonium type with the same substituents on nitrogen as found for WAX tertiary amines, but the amounts of propene and trimethylamine were much higher. Peaks, especially of *n*-

TABLE IV

## LIGAND TYPES OF DIFFERENT PHENYL SILICAS

GC determination as benzene/alkylbenzene after fusion with KOH in triglyme suspension at 200°C.

<i>Sample</i>	<i>Batch No.</i>	<i>Particle size (<math>\mu\text{m}</math>)</i>	<i>Manufacturer's structural hint</i>	<i>KOH fusion products</i>	<i>Ligand structure</i>
Bond Elut PH	—	?	Phenyl groups	Methane, benzene	
Nucleosil 7 C <sub>6</sub> H <sub>5</sub>	1121	7	C <sub>6</sub> H <sub>5</sub>	Methane, propylbenzene	
SP 500 Phenyl	02040	100-200	See text	Methane, benzene	

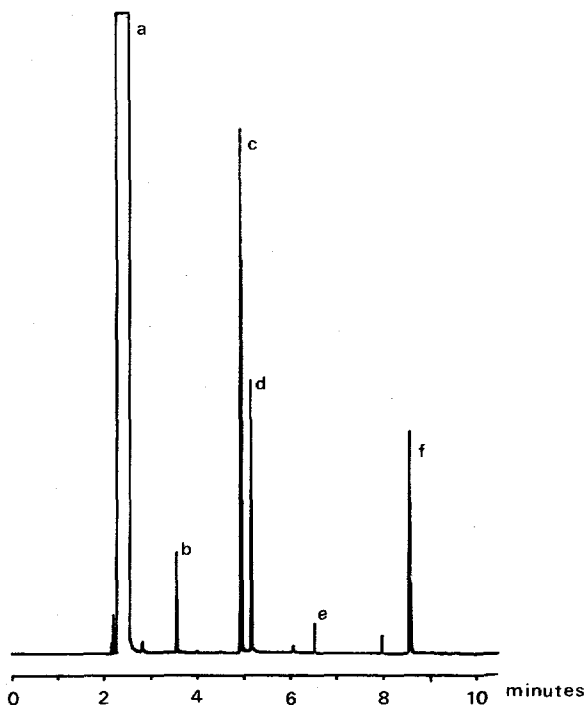


Fig. 8. Gas chromatogram of alkali fusion products from Vydac 401 SA silica (1 h, 200°C, triglyme suspension after desulphonation with hydroiodic acid). Peaks: a = *n*-pentane (solvent); b, e = triglyme degradation products; c = ethylbenzene; d = *o*-xylene; f = triglyme.

propanol, resulting from a side reaction during manufacture were also present as described for WAX (LiChrosorb AXW).

### WAX

The WAX silicas tested gave very uniform results (Table VII). Tertiary amino ligands yielded an interesting GC pattern which is explained by the example of LiChrosorb AXW (Fig. 11). Propene is a Hofmann elimination product of a quaternary amine and represents with high probability the spacer; trimethylamine is the other product of this reaction. Both compounds appear only in traces but prove the presence of some charged nitrogen atoms on the matrix. *N,N*-Dimethyl-*n*-propylamine as a major fusion product is an indicator for the main structure of this silica. The relative large amount of *N*-methyl-di-*n*-propylamine is an evidence for crosslinking between silanol groups and probably a product of drastic methylation, as shown by own experiments with propylamine and methyl iodide. Originally this silica must have carried free aminopropyl groups. During drastic methylation not only the dimethyl and traces of the trimethyl species were formed but also replacement of the  $\text{NH}_2$  function by halogen occurred in a reversal of the alkylation<sup>19</sup>. The resulting propyl halogenide partly alkylated a neighbouring aminopropyl group and subsequent methylation took place, but some halogenides were hydrolyzed to propanol groups and others remained unchanged. (Treatment of AXW samples with diethyl-

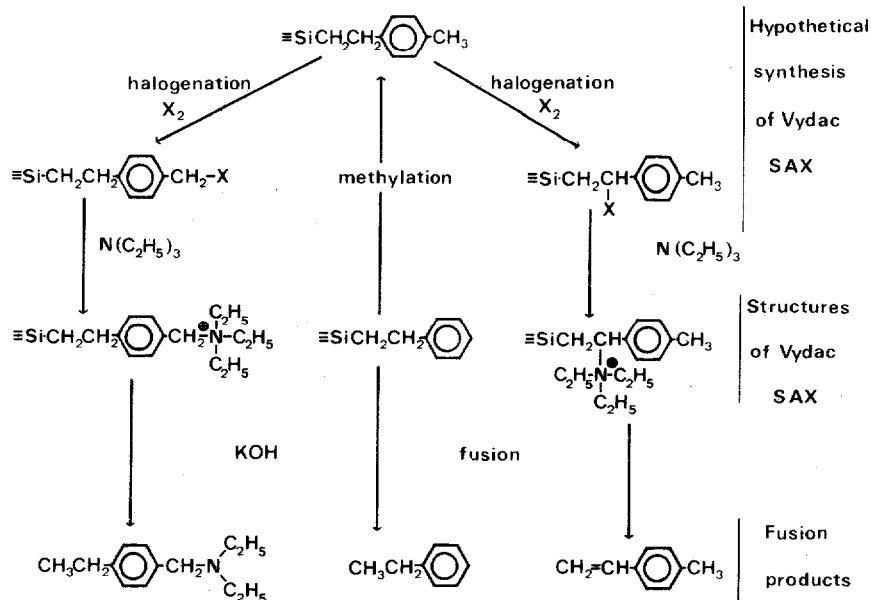
TABLE V

## LIGAND TYPES OF DIFFERENT SCX SILICAS

GC determination as benzene/alkylbenzenes after desulphonation with hydroiodic acid and subsequent fusion with KOH in triglyme suspension at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	Desulphonation product	KOH fusion product	Ligand structure
Bond Elut SCX	—	?	Benzenesulphonic acid	—	Ethylbenzene, <i>o</i> -xylene	$\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{SO}_3^\ominus$ $\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_3(\text{SO}_3^\ominus)\text{CH}_3$
Nucleosil 10 SA	7041	10	$\text{SO}_3\text{H}$	Benzene (traces)	Methane, <i>n</i> -propylbenzene	$\equiv\text{Si}(\text{CH}_2)_3\text{C}_6\text{H}_4\text{SO}_3^\ominus$
HPLC-Sorb Vydac 401 SA (glass beads)	17	30-44	—	—	Methane, ethylbenzene, <i>o</i> -xylene	$\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{SO}_3^\ominus$ $\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_3(\text{SO}_3^\ominus)\text{CH}_3$
Partisil PXS 10/25 SCX	1E3077 (column no.)	10	$\equiv\text{Si}(\text{CH}_2)_x\text{C}_6\text{H}_4\text{SO}_3\text{H}$	Benzene	Methane (traces), benzene (traces), toluene (traces)	$\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{SO}_3^\ominus$ $\equiv\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_3(\text{SO}_3^\ominus)\text{CH}_3$





Scheme 1. Hypothetical synthesis of Vydac SAX silica, based on the products of its fusion with KOH.

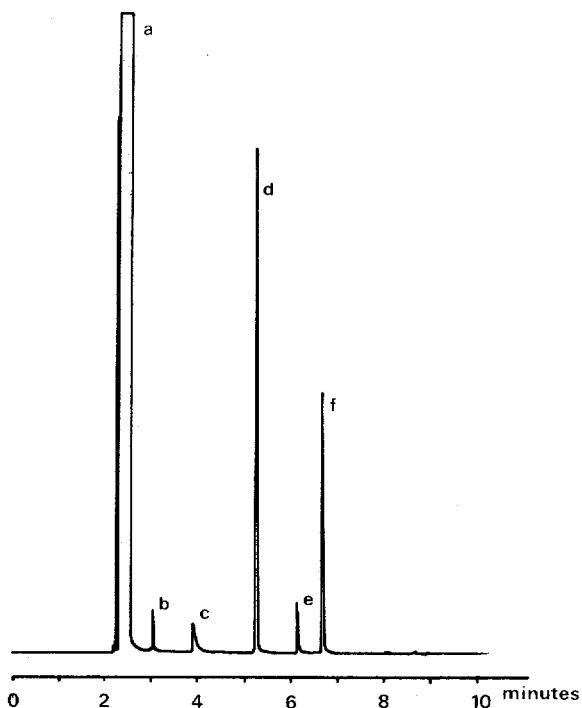
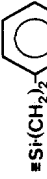
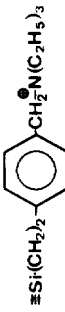

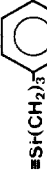
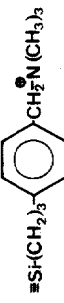
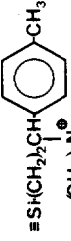



Fig. 9. Gas chromatogram of alkali fusion products from Vydac SAX silica (1 h, 200°C). Peaks: a = diethyl ether (solvent); b = benzene; c = triethylamine; d = ethylbenzene; e = 4-methylstyrene; f = N,N-diethyl-4-ethylbenzylamine.

TABLE VI

## LIGAND TYPES OF DIFFERENT SAX SILICAS

GC determination as alkene and amine after fusion with KOH at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion products	Ligand structure
Bond Elut SAX	—	?	Quaternary amines	Propene, trimethylamine, N,N-dimethyl- <i>n</i> -propylamine, <i>n</i> -propanol, N-methyl- <i>n</i> -propylamine	$\equiv\text{Si}(\text{CH}_2)_5\text{N}(\text{CH}_3)_3$ $\equiv\text{Si}(\text{CH}_2)_5\text{N}(\text{CH}_3)_2$ $\equiv\text{Si}(\text{CH}_2)_5\text{N}(\text{CH}_2)_3\text{Si}=\text{CH}_3$ $\equiv\text{Si}(\text{CH}_2)_3\text{N}(\text{Hal})(\text{OH})$
HPLC-Sorb Vydac 301 SB (glass beads)	27	30-44	—	Methane, benzene, triethylamine, ethylbenzene, 4-methylstyrene, N,N-diethyl-4-ethylbenzylamine	  
Vydac Anion Exchange (glass beads)	135	10	—		
Nucleosil 10 SB	7041	10	$^+\text{N}(\text{CH}_3)_3\text{Cl}^-$	Methane, trimethylamine, benzene, toluene, <i>n</i> -propylbenzene, 4-methyl- <i>n</i> -propylbenzene, isomeric methyl- <i>n</i> -propenylbenzenes, N,N-dimethyl-4-toluidine, N,N-dimethyl-4- <i>n</i> -propylbenzylamine and isomer, N,N-dimethyl-2-methyl-4- <i>n</i> -propylbenzylamine; 4,4'-di- <i>n</i> -propyldiphenylmethane	   

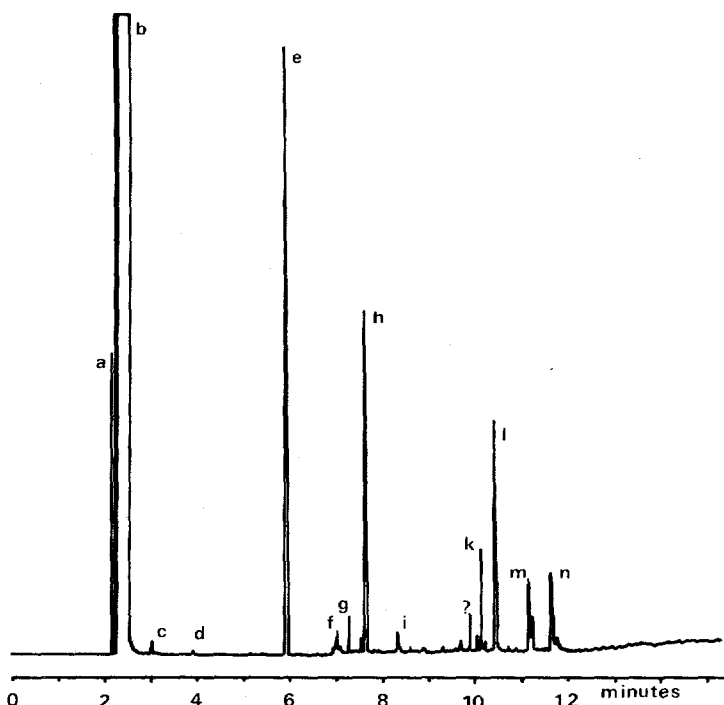


Fig. 10. Gas chromatogram of alkali fusion products from Nucleosil SAX silica (1 h, 200°C). Peaks: a = trimethylamine; b = diethyl ether (solvent); c = benzene; d = toluene; e = *n*-propylbenzene; f = 4-methyl-*n*-propylbenzene; g, h = isomeric methyl-*n*-propenylbenzenes; i = N,N-dimethyl-4-toluidine; k = 4-methyl- $\alpha$ -N,N-dimethylaminopropylbenzene?; l = N,N-dimethyl-4-*n*-propylbenzylamine; m = N,N-dimethyl-2-methyl-4-*n*-propylbenzylamine; n = 4,4'-di-*n*-propyldiphenylmethane.

amine and subsequent fusion with KOH yielded N,N-diethyl-*n*-propylamine in addition to the known GC pattern and proved the presence of free propyl halogenide.) The halogenide and its corresponding product from hydrolysis both yield *n*-propanol under fusion conditions.

HPLC-Sorb and Nucleosil showed identical signals; the products of the side reaction described were present only in traces.

N-Propylethylenediamine was the major product from fusion of Bond Elut PSA and combined a primary with a secondary amine.

The analytical results of NH<sub>2</sub> silicas were as expected. All samples were substituted with an aminopropyl group and some showed methane, probably due to the use of a mono- or dimethylsilane used for derivatization and not from endcapping which would be inappropriate for NH<sub>2</sub> silicas. LiChrosorb NH<sub>2</sub> contained an unknown impurity (Fig. 12).

In testing suitable stationary GC phases for the analysis of lower amines we found that 10% octadecylamine on a silanized support had superior properties, all three types of lower amines being separated without tailing effects.

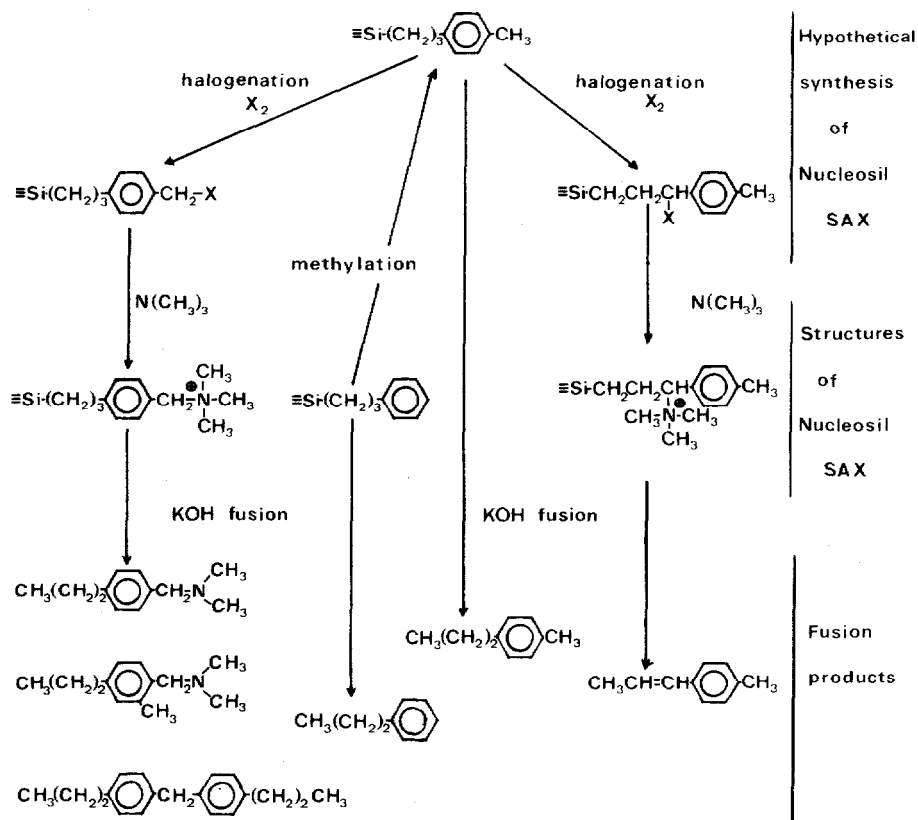
## NO<sub>2</sub>

Our tests with potassium hydroxide fusion produced dark brown mixtures with several spots upon thin-layer chromatography (TLC) but no signals were observed

TABLE VII  
LIGAND TYPES OF DIFFERENT WAX SILICAS

GC determination as amines after fusion with KOH at 200°C.

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion products	Ligand structure
Bond Elut PSA	—	?	Primary, secondary amines	<i>n</i> -Propylamine, <i>N</i> , <i>n</i> -propylethylenediamine, di- <i>n</i> -propylamine, unidentified amine with high molecular weight	$\blacksquare\text{Si}(\text{CH}_2)_5\text{NHCH}_2\text{CH}_2\text{NH}_2$ $\blacksquare\text{Si}(\text{CH}_2)_5\text{NH}_2$ $\equiv\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{CH}_3$
HPLC-Sorb SIL 60-D 10 $\text{N}(\text{CH}_3)_2$	—	10	$-\text{N}(\text{CH}_3)_2$	Methane, propene(traces), trimethylamine(traces), <i>N</i> , <i>N</i> -dimethyl- <i>n</i> -propylamine, <i>n</i> -propanol, <i>N</i> -methyl-di- <i>n</i> -propylamine	$\blacksquare\text{Si}(\text{CH}_2)_5\text{N}(\text{CH}_3)_2$ $\blacksquare\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{Si}\blacksquare$ $\text{CH}_3$
LiChrosorb AXW (non-commercial research sample)	KE 51083	10	—	Propene(traces), trimethylamine(traces), <i>N</i> , <i>N</i> -dimethyl- <i>n</i> -propylamine, <i>n</i> -propanol, <i>N</i> -methyl-di- <i>n</i> -propylamine	$\blacksquare\text{Si}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{OH}$
Nucleosil 10 $\text{N}(\text{CH}_3)_2$	7021	10	$-\text{N}(\text{CH}_3)_2$	Methane, propene(traces), trimethylamine(traces), <i>N</i> , <i>N</i> -dimethyl- <i>n</i> -propylamine, <i>n</i> -propanol, <i>N</i> -methyl-di- <i>n</i> -propylamine	
Alkylamine CPG 550	D07-10	177-840	Alkylamine	Methane, <i>n</i> -propylamine	$\blacksquare\text{Si}(\text{CH}_2)_3\text{NH}_2$
HPLC-Sorb SIL 60-D 10 $\text{NH}_2$	6061	10	$\text{NH}_2$	<i>n</i> -Propylamine	
APS Hypersil LiChrosorb $\text{NH}_2$	— VV 1818	5 10	<i>n</i> -Propylamine <i>n</i> -Propylamine	Methane, <i>n</i> -propylamine Methane(traces), <i>n</i> -propylamine, unidentified impurity	
Nucleosil 10 $\text{NH}_2$ SIL-X-10 $\text{NH}_2$	7041 822041	10 10	$\text{NH}_2$ $\text{NH}_2$	Methane(traces), <i>n</i> -propylamine <i>n</i> -Propylamine	



Scheme 2. Hypothetical synthesis of Nucleosil SAX silica, based on the products of its fusion with KOH.

in GC. We tried some reductive pretreatments and found the hydrazine/Raney nickel method to be suitable for the reduction of aromatic nitro groups in NO<sub>2</sub> silicas to amino groups. A subsequent alkali fusion yielded the corresponding aromatic amine. Although a direct observation of this compound type is possible, a derivatization with trifluoroacetic anhydride was performed for GC analysis. All samples tested were substituted with *p*-nitrobenzyl groups (Table VIII, Fig. 13). The *o*-isomer was completely absent, probably due to steric hindrance.

### CN

All silicas examined were from the cyanopropyl type and yielded *n*-butyric acid after fusion and subsequent acidification (Table IX, Fig. 14).

### Diol

Upon alkali fusion of Diol silicas no GC signals from an ether extract were obtained. We tried cleavage of the ether bond with boron tribromide and a subsequent fusion with KOH. The treatment with BBr<sub>3</sub> should yield brominated glycerol species<sup>20</sup> and the fusion should release the spacer as alkanol. Diol silicas yielded only traces of isomeric dibromopropanols and tribromopropane after BBr<sub>3</sub> treatment; however, *n*-propanol was identified after fusion and subsequent neutralization (Table X, Fig. 15).

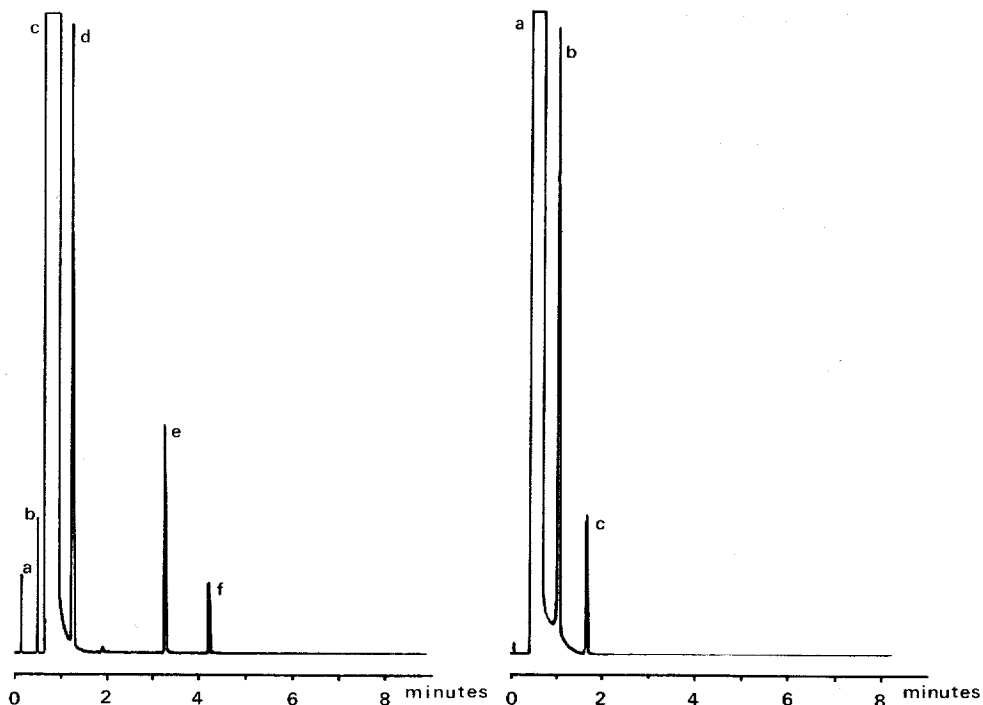


Fig. 11. Gas chromatogram of alkali fusion products from LiChrosorb AXW silica (1 h, 200°C). Peaks: a = propene; b = trimethylamine; c = diethyl ether (solvent); d = N,N-dimethyl-*n*-propylamine; e = *n*-propanol; f = N-methyl-di-*n*-propylamine.

Fig. 12. Gas chromatogram of alkali fusion products from LiChrosorb NH<sub>2</sub> silica (1 h, 200°C). Peaks: a = diethyl ether (solvent); b = *n*-propylamine; c = unknown impurity.

## CONCLUSIONS

The examination of stationary phases showed that besides the well known main structures a broad variation of substructures exists, especially in the case of ion exchangers.

The user of CN, NH<sub>2</sub>, Diol and the RP phases can be relatively sure about the structure of the stationary phase, but some RP phases are classified incorrectly. This does not necessarily present a disadvantage for chromatographic applications. The Riedel C<sub>8</sub> silica, for example, with branched alkyl chains, was superior in chromatographic properties to other RP-8 phases. However, the fact that the manufacturer's structural classification does not always reflect the real structure of the ligand is not acceptable for scientific work.

Stationary phases such as SCX and SAX which are products of further reaction steps after binding of the ligand to silica often contain the parent hydrocarbon in amounts that are not negligible for chromatographic purposes, as they affect separations by hydrophobic interactions<sup>17,21</sup>. Hydrophobic interaction, however, is also possible with the hydrocarbon skeleton of the ion exchanger. It would be interesting to correlate systematically different ligand structures with their chromatographic behaviour as was done for RP phases by several workers<sup>22-26</sup>. Thereby one could estimate the contribution of, e.g., a spacer in ion exchangers to the hydrophobic interactions in the ion-exchange process.

In this study we found that the silicas tested seemed to be very different in their degree of substitution; the precise determination of the latter seems therefore to be called for.

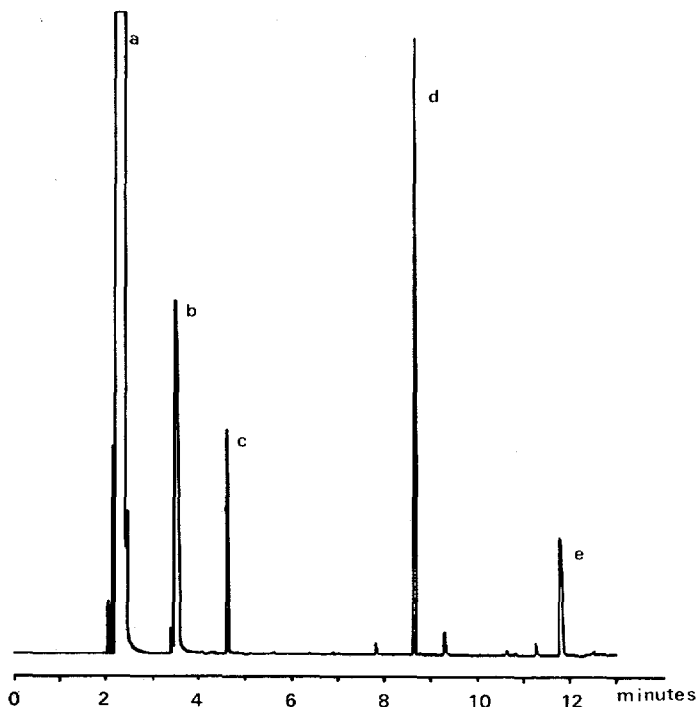


Fig. 13. Gas chromatogram of alkali fusion products from reduced Nucleosil NO<sub>2</sub> silica (1 h, 200°C after reduction with Raney nickel/hydrazine). Peaks: a = diethyl ether (solvent); b, c = signals from trifluoroacetic anhydride; d = *p*-toluidine (trifluoroacetyl derivative); e = unknown.

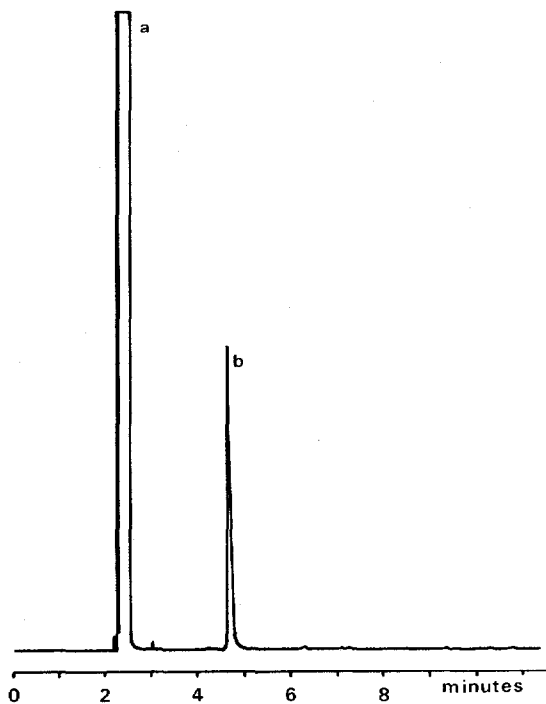


Fig. 14. Gas chromatogram of alkali fusion products from CN silicas after acidification (1 h, 200°C). Peaks: a = diethyl ether (solvent); b = *n*-butyric acid.

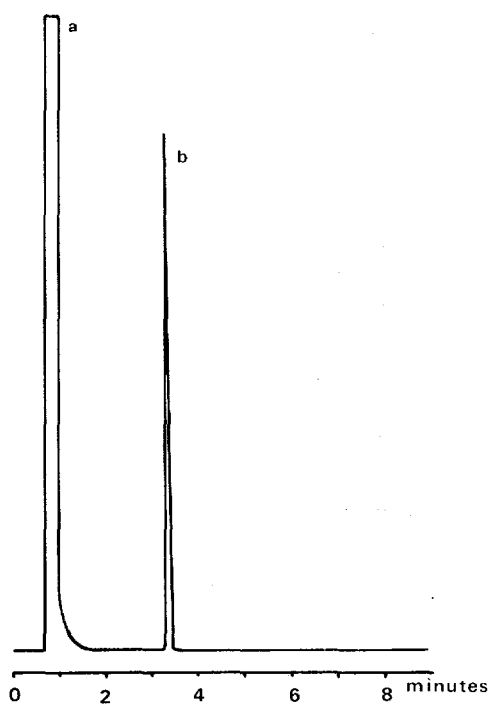


Fig. 15. Gas chromatogram of alkali fusion product from Diol silicas (1 h, 200°C) after ether cleavage with BBr<sub>3</sub>. Peaks: a = diethyl ether (solvent); b = *n*-propanol.

TABLE VIII  
LIGAND TYPES OF DIFFERENT NO<sub>2</sub> SILICAS  
GC determination as trifluoroacetyl derivatives of alkylnamines after reduction and subsequent fusion with KOH at 200°C.

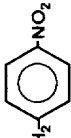
Sample	Batch No.	Particle size (μm)	Manufacturer's structural hint	KOH fusion products	Ligand structure
HPLC-Sorb SIL 60-D 10 NO <sub>2</sub>	6061	10	NO <sub>2</sub>	<i>p</i> -Toluidine	
Nucleosil 10 NO <sub>2</sub>	7041	10	NO <sub>2</sub>	Methane, <i>p</i> -toluidine	
SIL-X-10 NO <sub>2</sub>	821051	10	NO <sub>2</sub>	Methane, <i>p</i> -toluidine	

TABLE IX  
LIGAND TYPES OF DIFFERENT CN SILICAS  
GC determination as carboxylic acids after fusion with KOH at 200°C and subsequent acidification.

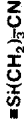
Sample	Batch No.	Particle size (μm)	Manufacturer's structural hint	KOH fusion products	Ligand structure
HPLC-Sorb SIL 60-D 10 CN	6121	10	CN	<i>n</i> -Butyric acid	
CPS Hypersil	12/774	5	Cyanopropyl group	Methane, <i>n</i> -butyric acid	
LiChrosorb CN	VV 2107	10	Cyanopropyl group	<i>n</i> -Butyric acid	
SIL-X-10 CN	821101	10	CN	<i>n</i> -Butyric acid	



TABLE X

## LIGAND TYPES OF DIFFERENT DIOL SILICAS

GC determination as *n*-propanol after ether cleavage with  $\text{BBr}_3$  and subsequent fusion with  $\text{KOH}$  at  $200^\circ\text{C}$ .

Sample	Batch No.	Particle size ( $\mu\text{m}$ )	Manufacturer's structural hint	KOH fusion products	Ligand structure
LiChrosorb Diol	VV 758	10	See Fig. 1	<i>n</i> -Propanol	$\equiv\text{Si}(\text{CH}_2)_5\text{O}-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})_2$
LiChrosorb Diol	VV 1903	10	See Fig. 1	<i>n</i> -Propanol	$\equiv\text{Si}(\text{CH}_2)_5\text{O}-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})_2$
SP 500 Epoxypropyl	22050	100-200	Epoxypropyl	Methane, <i>n</i> -propanol	$\equiv\text{Si}(\text{CH}_2)_7\text{O}-\text{CH}_2\text{CH}(\text{O})_2\text{CH}_2$

Our analytical method is based on very simple operations which can be performed in almost every laboratory. If the chemical behaviour in fused alkali is taken into consideration, many other ligand types are analyzable and laboratory-synthesized silicas can readily be controlled. The method is not capable of distinguishing between one, two or three ligands attached to silicon. Also the distinction between monomeric and polymeric substitution and between methane evolved from mono- or dimethylsilanes and from endcapping processes is not possible. For such distinctions, a Si-C cleavage must be avoided in favour of a scission of siloxane bonds<sup>4,6</sup>.

#### NOTE ADDED IN PROOF

During printer's preparation of this article, the identification of the unknown signals from MOS Hypersil RP-8 silica has been accomplished. Peaks b and d from Fig. 5 were characterized to be dimethyl-*n*-octylsilanol and 1,1,3,3-tetramethyl-1,3-*n*-octyldisiloxane. MOS Hypersil therefore is the only monosubstituted RP-8 silica. Evidently the Si-C bond in monofunctional derivatized silicas is not cleaved under the conditions described and this allows a clear identification of monofunctional substituted materials, in contrast to the statement just made above. This must be true also for TMS-groups from endcapping. The evaluation of the result described will be the subject of a forthcoming paper.

#### REFERENCES

- 1 R. E. Majors, *J. Chromatogr. Sci.*, 15 (1980) 488.
- 2 B. B. Wheals, *J. Chromatogr.*, 177 (1979) 263.
- 3 H.-G. Genieser, D. Gabel and B. Jastorff, *J. Chromatogr.*, 244 (1982) 368.
- 4 M. Verzele, P. Mussche and P. Sandra, *J. Chromatogr.*, 190 (1980) 331.
- 5 L. Hansson and L. Trojer, *J. Chromatogr.*, 207 (1981) 1.
- 6 J.-F. Erard and E. Kováts, *Anal. Chem.*, 54 (1982) 193.
- 7 J. Franc and K. Plaček, *J. Chromatogr.*, 67 (1972) 37.
- 8 V. Bažant, V. Chvalovský and J. Rathouský (Editors), *Organosilicon Compounds*, Vol. 1, Academic Press, New York, 1965, p. 40.
- 9 V. Chvalovský, in E. I. Becker and M. Tsutsui (Editors), *Organometallic Reactions*, Vol. 3, Wiley-Interscience, New York, 1972, p. 191.
- 10 K. Karch, *Ph.D. Thesis*, University of Saarbrücken, 1974, p. 13.
- 11 T. Nakagawa, K. Miyajima and T. Uno, *J. Gas Chromatogr.*, 6 (1968) 291.
- 12 M. C. Boswell and J. V. Dickson, *J. Amer. Chem. Soc.*, 40 (1918) 1786.
- 13 P. Buck, *Angew. Chem.*, 81 (1969) 136.
- 14 S. Frankoski, *Ph.D. Thesis*, University of Massachusetts, Amherst, MA, 1972, p. 68.
- 15 H. S. Fry and E. L. Schulze, *J. Amer. Chem. Soc.*, 50 (1928) 1131.
- 16 J. Franc, J. Šenkýřová, F. Mikeš and K. Plaček, *J. Chromatogr.*, 43 (1969) 1.
- 17 P. J. M. van Haastert, *J. Chromatogr.*, 210 (1981) 241.
- 18 E. H. White and D. J. Woodcock, in S. Patai (Editor), *The Chemistry of the Amino Group*, Interscience, London, 1968, p. 420.
- 19 P. A. S. Smith, *The Chemistry of Open-Chain Organic Nitrogen Compounds*, Vol. 1, W. A. Benjamin, New York, 1965, p. 25.
- 20 H.-G. Genieser, D. Gabel and B. Jastorff, *J. Chromatogr.*, 215 (1981) 235.
- 21 P. J. Twitchett, A. E. P. Gorvin and A. C. Moffat, *J. Chromatogr.*, 120 (1976) 359.
- 22 K. Karch, I. Sebastian and I. Halász, *J. Chromatogr.*, 122 (1976) 3.
- 23 H. Hemetsberger, W. Maasfeld and H. Ricken, *Chromatographia*, 9 (1976) 303.
- 24 P. Roumeliotis and K. K. Unger, *J. Chromatogr.*, 149 (1978) 211.
- 25 M. C. Hennion, C. Picard and M. Caude, *J. Chromatogr.*, 166 (1978) 21.
- 26 G. E. Berendsen, K. A. Pikaart and L. de Galan, *J. Chromatogr. Sci.*, 20 (1982) 97.