Journal of Chromatography, 190 (1980) 331–337

CHROM. 12,519

CHARACTERIZATION OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC STATIONARY PHASES: THE NATURE OF SILICA GEL BONDED MATERIAL

M. VERZELE, P. MUSSCHE and P. SANDRA

State University of Ghent, Laboratory of Organic Chemistry, Krijgslaan, 271 (S.4), B-9000 Ghent (Belgium)

(Received October 11th, 1979)

SUMMARY

Alkaline hydrolysis of bonded silica gel high-performance liquid chromatographic phases, followed by trimethylsilylation with trimethylsilylimidazole leads to compounds with gas chromatographic characteristics sufficient to identify the nature of bonded chains. First results in the attempt to quantitate this approach are described.

INTRODUCTION

Recently we contributed to the analysis of trace metals in silica gel[1] and to the determination of particle size, total pore volume and mean pore size[2]. In the present paper we introduce a possible means of ascertaining the nature of side-chains bonded to silica gel. This is based on alkaline hydrolysis of the silica gel matrix, derivatization into the trimethylsilyl derivatives of the hydrolysis products and capillary gas chromatographic (GC) analysis of the resulting mixture.

Trimethylsilylation of acidified sodium silicate solutions has already been described by several authors. Lentz[3] was probably the first. His procedure is as follows: hexamethyldisilazane (HMDS; 5 ml), isopropanol (7.5 ml), concentrated HCl (3.8 ml) and water (3.1 ml) are mixed for 1 h. After cooling to 20°, two drops of acidified silicate solution (*ca.* 2.3 mg of SiO_2) are added and the mixture is stirred for 1 h. Dodecamethylpentasiloxane is added as internal standard. After four washings with 30 ml of water, the organic phase is shaken for 3–4 days with Amberlyst 15. The filtered solution is analysed by GC. Götz and Masson[4] follow practically the same procedure but with a mixture of HMDS and trimethylchlorosilane (TMCS). A summary of what has been done in the field was recently given by Garzó *et al.*[5]. In their study, an improved procedure is as follows: bis(trimethylsilyl)acetamide (BSA; 3.5 ml) acidified with gaseous HCl and HMDS (5 ml) are stirred for 20 min with acetone (10 ml). Two drops of acidified silicate (again *ca.* 2.3 mg of SiO_2) are added with stirring for 15 min at 15°. The solution is allowed to come to room temperature and kept for 3–4 h. Water is added, and dodecamethylpentasiloxane as internal standard. The organic layer is further washed three times with water. The organic

layer is analysed by capillary GC on a 16 m × 0.25 mm I.D. OV-1 column from 115° to 300° at 10°/min.

These three methods give more or less analogous profiles characterized by a relatively large number of peaks. Some of these were identified by capillary GC–mass spectrometry (MS)[6], others by comparison with reference compounds. They include the monomer [tetra(trimethylsilyloxy)silane], the dimer, trimer and tetramer, and several cyclic and branched derivatives.

EXPERIMENTAL

Analysis of wettable silica gel phases

100 mg of silica gel is stirred with 2 ml of 2 *N* KOH for 2 h at room temperature. To 25 μl of the homogenous mixture is added 75 μl of trimethylsilylimidazole (TSIM). The vigorous reaction is over after 15 min and the upper layer can be analysed directly by capillary GC at 110° on a 5 m × 0.5 mm I.D. glass capillary column statically coated[11] with SE-30.

Analysis of unwettable silica gel phases (ODS)

100 mg of the phase is suspended in 10 ml of THF and 2 ml of 2 *N* KOH is added. The solution is refluxed for 1 h. 100 μl of the organic layer and 100 μl of TSIM are mixed. The reaction is completed by heating to 80° for 30 min. The solvent and excess TSIM are removed by vacuum evaporation. The residue is dissolved in 50 μl of THF. The GC analysis is performed at 210° on a 5 m × 0.5 mm I.D. glass capillary statically coated with SE-30.

Preparation of tri(trimethylsilyloxy)octadecylsilane

Trimethoxy-octadecylsilane. 40 ml of dry methanol (freshly distilled over CaO) and 4 ml of trichloro-octadecylsilane are stirred in a two-necked flask with a reflux cooler. While stirring, Mg is added in small amounts until the vigorous reaction subsides. The mixture is refluxed for 2 h.

The solution is filtered on a glass filter to remove excess Mg and $MgCl_2$, and is then extracted with isooctane–ethyl acetate–water (1:1:1). The organic layer is isolated and the solvent removed on a rotavapor. Analysis with capillary GC shows a nearly pure product. (Nuclear magnetic resonance : δ : 3.6 = CH_3O–Si / δ : 1.25 = –CH_2– / δ : 0.9 = Si–CH_2–CH_2 / δ : —0.5 = Si–CH_2–; MS : $M^{+\cdot}$ m/z = 374, peak m/z = 342 loss of methanol).

Tri(trimethylsilyloxy)octadecylsilane. 100 mg of trimethoxyoctadecylsilane is dissolved in 10 ml of tetrahydrofuran (THF) and 10 ml of 2 *N* KOH. The solution is refluxed for 2 h. The organic layer is isolated and treated with 1 ml of TSIM, the solution is refluxed for 1 h.

The reaction mixture is evaporated on a rotavapor and the residue is shaken with isooctane. Tri(trimethylsilyloxy)octadecylsilane and other products dissolve. A more polar solvent dissolves the residual precipitate but this does not contain the desired compound.

Purification. Preparative GC is carried out on a OV-1 glass capillary column, 50 m × 1 mm I.D., at 240° on a Varian 1400 microcatharometer gas chromatograph. 10 μl of the sample containing *ca.* 3 mg of product is injected repeatedly. Only 10% of the injected material can be collected, the rest is not chromatographed.

RESULTS AND DISCUSSION

Conceivably silica gel and derivatised silica gels could be analysed in the same way after alkaline hydrolysis. Considerable experimentation in our laboratory led to the conclusion that hydrolysis of 100 mg of silica gel or derivatised phase (except the important octadecyl silica gel phases) in 2 ml of 2 *N* KOH is complete after 2 h at room temperature. For trimethylsilylation, the following procedure, although much simpler, gives largely the same results as the first two described above.

TMCS (5 ml) and isopropanol (7.5 ml) are mixed for 15 min at room temperature. 100 μl of the hydrolysate (*ca.* 10 mg of SiO_2) is added. After 2 h stirring, this mixture is washed twice with 10 ml of water and the upper organic layer is evaporated under a nitrogen stream. The residue is dissolved in 100 μl of ethyl acetate and analysed by capillary GC. Chromatograms for silica gel (A) and for phenylsilica gel (B) (8% phenyl) are shown in Fig. 1. Most of the early peaks could

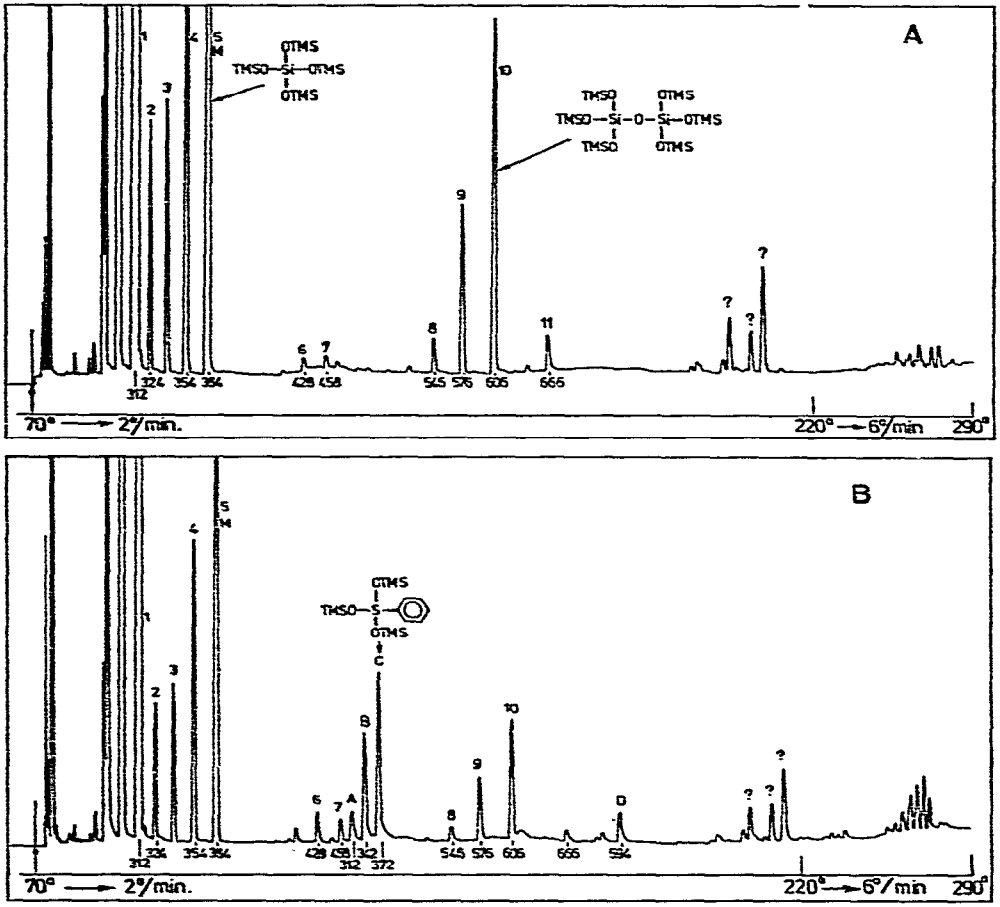

Fig. 1. Varian 2100 GC, 5 m × 0.5 mm glass capillary SE-30 column. Trimethylsilylated alkaline hydrolysis products of silica gel (A) and of phenylsilica gel (B). Peak identification in Table I. Molecular weights are CI–MS deduced mass values. M stands for monomer, or tetra(trimethylsilyloxy)silane.

be identified by capillary GC–MS in the electron impact (EI) and chemical ionization (CI) modes, and the results are presented in Table I. As indicated, the use of isopropanol introduces isopropyloxy groups in many compounds and thus needlessly complicates the chromatograms. The presence of these isopropyloxy groups was also mentioned by Addison[7].

TABLE I

IDENTIFICATION OF THE PEAKS IN FIGS. 1A AND 1B

Peak number	*m/z value*	*Assigned structure*
1	312	Tri(trimethylsilyloxy)hydroxysilane
2	324	Di(isopropyloxy) di(trimethylsilyloxy) silane
3	?	?
4	354	Isopropyloxy-tri (trimethylsilyloxy) silane
5	384	Tetra(trimethylsilyloxy) silane
6	428	?
7	458	?
8	546	Di(isopropyloxy) tetra(trimethylsilyloxy) disiloxane
9	576	Isopropyloxy-penta(trimethylsilyloxy) disiloxane
10	606	Hexa(trimethylsilyloxy) disiloxane
11	666	Hexa(trimethylsilyloxy) cyclotrisiloxane
A	312	Di(isopropyloxy) trimethylsilyloxyphenylsilane
B	342	(Isopropyloxy) di(trimethylsilyloxy) phenylsilane
C	372	Tri(trimethylsilyloxy) phenylsilane
D	594	Penta(trimethylsilyloxy) phenyldisiloxane

Surprisingly, some compounds with a free silanol function could be chromatographed normally. This was also found repeatedly later with other derivatized mixtures. The peaks with very high molecular weight could not be analysed on our instrument (Finnigan 3200 quadrupole MS). The silylated trimer already has mol. wt. of 828! Some of the peaks (A, B, C and D) do contain phenyl and the approach therefore looks promising.

There are too many peaks, however, and under slightly different conditions, the number of peaks can be much larger. This is the case when using only 10 μl of hydrolysate instead of 100 μl in the derivatization step.

The unknown peaks with mol. wt. 428 and 458 are also often larger. Changing the concentration of silica gel in the hydrolysis step does not have much effect.

We developed the following procedure leading practically exclusively to the monomer or tetra(trimethylsilyloxy)silane when working with silica gel. To 25 μl of the hydrolysate of 100 mg of silica gel in 2 ml of 2 *N* KOH is added 75 μl of TSIM. The vigorous reaction leads quickly to two liquid layers. The upper layer is analysed as such by capillary GC.

Similar results were obtained for chloropropylsilica gel, phenylsilica gel, cyanopropylsilica gel, nitrophenylsilica gel and aminopropylsilica gel. Strongly silylated (deactivated) and octadecylsilica gel phases are not wetted by 2 *N* KOH. Adding THF and refluxing solves this problem. Without THF the waxy octadecylsilicic acid or other intermediates are insoluble in the system and the trimethylsilylation is erratic. With diolsilica gel and some anion-exchanging silica gels, multiple peak GC patterns were obtained.

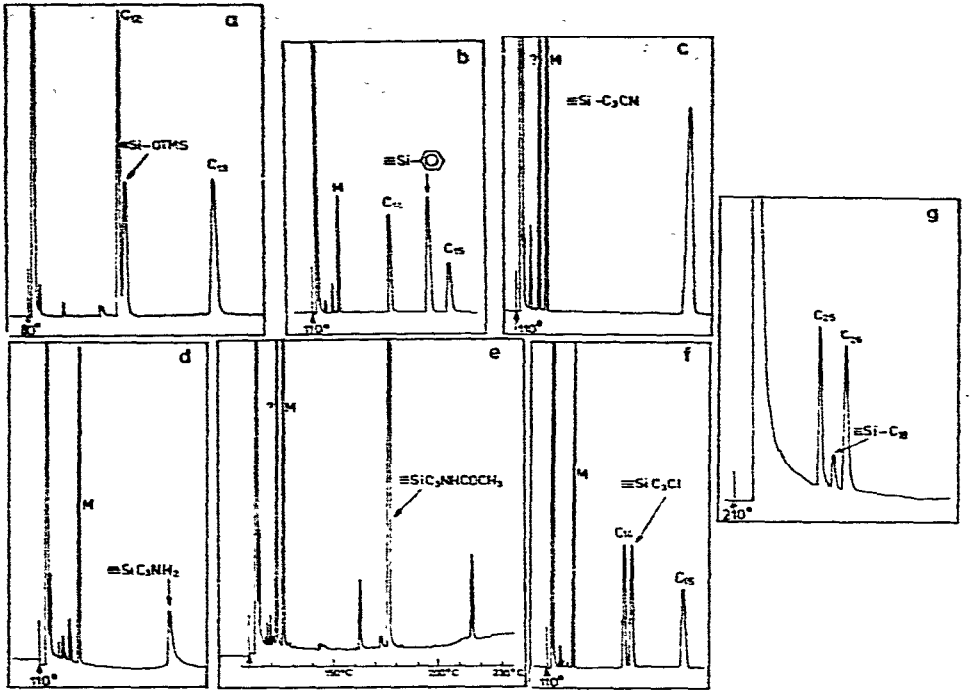

Fig. 2. Experimental details as for Fig. 1. All traces are isothermal, except (e), which is programmed as shown.

Chromatograms for most of the bonded silica gel phases mentioned above are reproduced in Fig. 2. The important peaks were again identified by capillary GC–MS analysis in the CI and EI modes. The results are listed in Table II.

Most results were as expected. The amino function in aminopropylsilica gel is not trimethylsilylated. In chloropropylsilica gel, the halogen is hydrolysed and then substituted by a trimethylsilyloxy group.

TABLE II

IDENTIFICATION OF PEAKS IN FIG. 2a–g

Fig.	*Peak*	*m/z value*	*Assigned structure*
2a	1	384	Tetra(trimethylsilyloxy) silane
2b	1	384	Tetra(trimethylsilyloxy) silane
	2	372	Tri(trimethylsilyloxy) phenylsilane
2c	1	384	Tetra(trimethylsilyloxy) silane
	2	363	(3-Cyanopropyl) tri(trimethylsilyloxy) silane
2d	1	384	Tetra(trimethylsilyloxy) silane
	2	353	(3-Aminopropyl) tri(trimethylsilyloxy) silane
2e	1	384	Tetra(trimethylsilyloxy) silane
	2	395	(N-Acetyl-3-aminopropyl) tri(trimethylsilyloxy) silane
2f	1	384	Tetra(trimethylsilyloxy) silane
	2	426	Tri(trimethylsilyloxy)-3-(trimethylsilyloxypropyl) silane ($\equiv Si{-}O)_3{-}Si{-}C_3OSi\equiv$
2g	1	548	Tri(trimethylsilyloxy) octadecylsilane

Characterization of the silica gel phases can thus be achieved through the Kováts indices for those peaks which are specific for the different phases (Table III; in this table the three remaining valencies on silicon are occupied by trimethylsilyloxy groups).

TABLE III

KOVÁTS INDICES FOR PEAKS SPECIFIC FOR DIFFERENT PHASES

Phase	*Temperature (°C)*	*Kováts index (SE-30)*
≡Si-OTMS (silica gel)	80	1210
≡Si-C_6H_5	110	1470
≡Si$(CH_2)_3$OTMS (for Si–C_3–Cl)	110	1416
≡Si$(CH_2)_3NH_2$	110	1400
≡Si$(CH_2)_3$CN	110	1500
≡Si$(CH_2)_{17}CH_3$	210	2560

As to the mechanism and chemistry behind these results, it is clear that the hydrolysis depolymerizes the investigated materials to the monomeric species at least partly. However, whereas dimeric and even higher silicic acids can be run through GC (in derivatized form) it is not improbable that dimers with a longish side-chain are simply not volatile and are therefore not seen. Hydrolysis of silica gel goes to completion, but the other materials are more sterically hindered.

Apparently, when a less active or different trimethylsilylation reagent than TSIM is used, the polycondensation of silicic acid and the silylation are competing. This leads to complex reaction mixtures. With TSIM the silylation is fast enough to avoid polycondensation of the silicic acid. This explanation covers the facts so far known or considered.

The next step is obviously the quantitation of these qualitative results. With different octadecylsilica gels containing 8, 13 and 17% bonded material (thermogravimetric analysis) the GC patterns followed the trend and they were moreover reproducible. To establish the response factor for octadecyltri(trimethylsilyloxy)silane this compound had to be synthesized. Following indications in the literature[8–10] and after some difficulties, this was successfully achieved by methanolysing trichlorooctadecylsilane (with Mg as HCl trapper) and subjecting the trimethoxyoctadecylsilane to the hydrolysis and TSIM derivatizing procedure described in this paper. Purification was carried out by preparative scale GC followed by reversed-phase high-performance liquid chromatography to remove OV-1 bleed. The response factor was measured in the usual way against C_{26} *n*-alkane, and turned out to be 0.64.

Application of this knowledge to the quantitations of octadecylsilica gels gave such low results (*ca.* 20% of thermogravimetric figures) that we must conclude there is something wrong with the procedure. This is under further investigation.

All phases investigated were of the trifunctional type (3-chloro- or 3-alkoxysilanes). Phases such as dimethylalkylsilylsilica gel (monomeric bonded phase?) cannot repolymerize after hydrolysis. Hydrolysis of such phases must also be possible, and this is under investigation. The qualitative results so far, however, are interesting and useful enough to warrant this first report.

ACKNOWLEDGEMENTS

We thank the Ministry of Science (Ministerie voor Wetenschapsbeleid) and the National Foundation for Scientific Research (Nationaal Fonds voor Wetenschappelijk Onderzoek) for financial help to the laboratory.

REFERENCES

1 M. Verzele, M. De Potter and J. Ghysels, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 151.
2 M. Verzele, J. Lammens and M. van Roelenbosch, *J. Chromatogr.*, 186 (1979) 435.
3 C. Lentz, *Inorg. Chem.*, 3 (1964) 574.
4 J. Götz and C. Masson, *J. Chem. Soc., A*, (1970) 2683.
5 G. Garzó, D. Hoebbel, Z. Ecsery and K. Ujszászi, *J. Chromatogr.*, 167 (1978) 321.
6 F. F. H. Wu, J. Götz, W. D. Jamieson and C. R. Masson, *J. Chromatogr.*, 48 (1970) 515.
7 J. Addison, *Analyst (London)*, 14 (1979) 766, and references therein.
8 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, Ch. 8.
9 E. Wiberg and W. Simmler, *Z. Anorg. Chem.*, 282 (1955) 330.
10 S. Fukukawa and S. Kohama, *Kagaku to Kogyo (Osaka)*, 31 (1957) 85; *C. A.*, 51 (1957) 12845.
11 J. Bouche and M. Verzele, *J. Chromatogr. Sci.*, 6 (1968) 501.