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Note

Determination of ligand contents of octadecyl-modified silicas

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Hydrophobic reversed-phase octadecyl (RP_{18}) modified silica gels are well established and indispensable tools in liquid chromatography for many separation problems. Nevertheless, there still exist some difficulties in reproducing optimized separations with packing materials from different batches or different manufacturers[1–4].

One of the parameters responsible is the ligand content on the silica gel matrix. The usual method is to determine the carbon content by elemental analysis, a procedure for which the precision has been reported differently in the literature[5–7]. Moreover, this technique is not able to distinguish between the octadecyl ligand and the methyl groups of either mono- or bifunctional modifiers or end-capping trimethylsilyl groups. Infrared spectroscopy[5], thermogravimetry[8], pyrolysis–mass spectrometry[9], pyrolysis–gas chromatography (GC)[10] and GC after alkaline degradation followed by silylation[8] have also been used in attempts to determine the octadecyl ligand content. The use of ^1H nuclear magnetic resonance (NMR) spectroscopy for this purpose is under investigation in our laboratory.

In our experience, the degree of substitution of a polymeric matrix with functional groups can be measured with high accuracy if it is possible to cleave the bonds between the ligands and the support quantitatively with a suitable reagent and to analyse the fragments obtained by chromatographic methods[11].

With modified silica gel the relatively stable Si–C bond has to be cleaved. Many reagents have been reported to bring about this scission[12,13]. Concentrated sulphuric acid[14] or hot alkali[15] were used for determination of alkyl groups bound to silicon in silanes.

While testing the alkali method for its utility in cleaving modified silica gels, we recognized that the material was not wetted by the molten potassium hydroxide and therefore the cleavage yields were low. Addition of triethyleneglycol dimethyl ether (triglyme) as a suspending medium gave a 5000-fold increase in cleavage products, presumably owing to better contact between the reactants.

A model compound, tris(trimethylsilyloxy)octadecylsilane, was synthesized and treated in the same manner in order to control the cleavage rate with regard to quantitative scission.

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EXPERIMENTAL

Materials

n-Heptadecane and *n*-octadecane were purchased from EGA Chemie (Steinheim, G.F.R.) and hydrochloric acid, *n*-hexane, chlorotrimethylsilane, potassium hydroxide, dichloromethane, octadecanol-1 and triethyleneglycol dimethyl ether from E. Merck (Darmstadt, G.F.R.). Trichlorooctadecylsilane was obtained from Aldrich (Milwaukee, WI, U.S.A.).

The reversed-phase materials were Kieselgel 60 C_{18}-reversed phase (Riedel, Hannover, G.F.R.), Spherisorb S 5 ODS C_{18} (Phase Separations, Queensferry, Great Britain), Polygosil 60-5 C_{18} (Macherey, Nagel & Co., Düren, G.F.R.), HPLC-Sorb Vydac 201 RP (Separations Group), Sep-Pak C_{18} Cartridges (Waters Assoc., Milford, MA, U.S.A.) and LiChrosorb RP-18 and LiChroprep RP-18 (Merck) of partly different batches and particle diameters.

LiChrosorb batches VV 1106, VV 2249 and VV 1827 were generous gifts from Dr. Becker (Merck), HPTLC-Fertigplatten RP-18 were test samples from Merck and three batches of ODS-SIL-X-10 and ODS-SIL-X-5, respectively, were generous gifts from Dr. Borath (Perkin-Elmer, Überlingen, G.F.R.), which are gratefully acknowledged.

Analysis

For analysis of the cleavage products, a 15 m × 0.242 mm I.D. fused-silica capillary column with chemically bonded non-polar DB-1-15N (J. & W. Scientific) as the stationary phase was used with a Sigma 1 gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.).

The oven temperature was held at 150°C for 1 min and then increased at 10°C/min to 250°C while the helium flow-rate was kept at 2 ml/min. For quantification the internal standard method was used. Peak areas were determined by a connected data system.

Elemental analysis was carried out by the Mikroanalytisches Laboratorium Beller (Göttingen, G.F.R.).

Cleavage procedure

To 10 mg of the substitued silica gel were added 100 mg (1.78 mmol) of dry, solid potassium hydroxide in a small glass reaction tube (110 mm × 5 mm I.D.). The tube was dried over phosphorus pentoxide overnight.

A volume of 200 μl of triethyleneglycol dimethyl ether was added as suspending agent and the tube was placed in a silicone oil bath at 216°C for 2 h. After 30 sec, 100 μl water were added, followed by 1 μl (3.23 μmol) of *n*-heptadecane in 100 μl of *n*-hexane as internal standard and 140 μl of 37% hydrochloric acid for neutralization. Centrifugation gave a clear hexane phase for GC analysis. For quantification a standard was used containing 500 μmol of *n*-octadecane, 100 μmol of octadecanol-1 and 323 μmol of *n*-heptadecane in 10 ml of *n*-hexane.

Synthesis of model compound, tris(trimethylsilyloxy)octadecylsilane

Trichlorooctadecylsilane (100 mmol) and chlorotrimethylsilane (500 mmol) were dissolved in 100 ml of dichloromethane. While refluxing, 50 ml of 50% potassi-

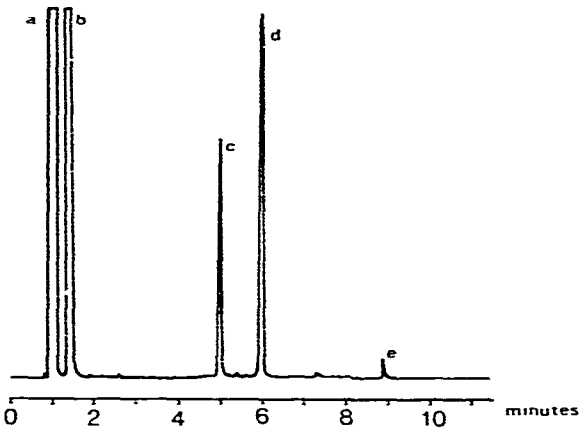
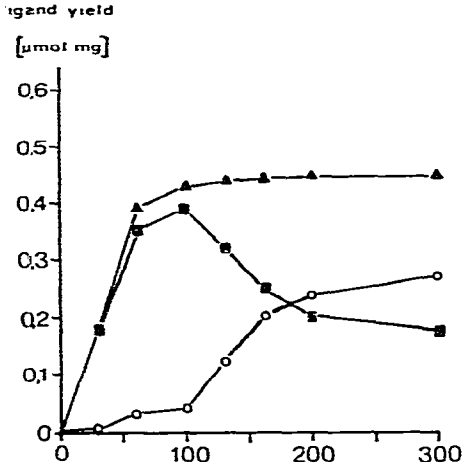


Fig. 1. Gas chromatogram of cleavage products from RP_{18}-modified silica gel and tris(trimethylsilyloxy)octadecylsilane, using fused KOH (2 h, 216°C) in a high-boiling ether suspension. Peaks: a = *n*-hexane; b = triethyleneglycol dimethyl ether; c = *n*-heptadecane (internal standard); d = *n*-octadecane; e = octadecanol-1.

um hydroxide solution were added dropwise. The end of the reaction was determined by GC analysis. The organic layer was separated and dried over sodium sulphate; the product was purified by high-vacuum distillation. ^1H NMR and mass spectrometry were used for identification. The compound has already been synthesized by a different procedure[8].

RESULTS

The cleavage products from RP_{18}-modified silica gel and fused alkali were mainly *n*-octadecane (96%) and small amounts of octadecanol-1 (4%) (Fig. 1). By



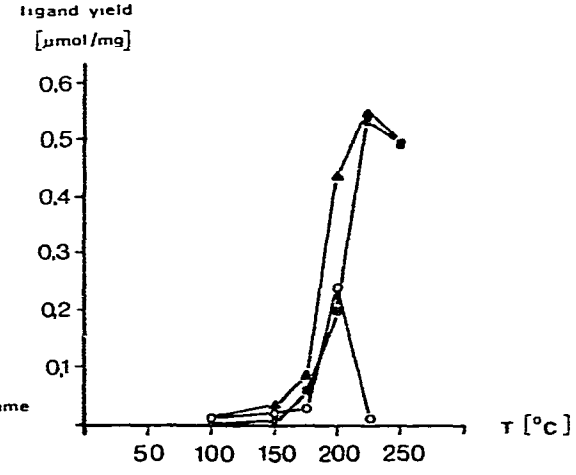


Fig. 2. Ligand yield as a function of the amount of suspending ether; 10 mg of RP_{18}-modified silica gel treated with fused alkali (2 h, 216°C). ■ = *n*-Octadecane; ○ = octadecanol-1; ▲ = sum.

Fig. 3. Ligand yield as a function of temperature; 10 mg of RP_{18}-modified silica gel, 100 mg of KOH, 200 µl of solvent, 2 h. ■ = *n*-Octadecane; ○ = octadecanol-1; ▲ = sum.

changing either the concentration of the suspending ether or the reaction temperature this ratio could be changed considerably (Figs. 2 and 3).

It could be shown, as expected, that the materials examined contained different amounts of the octadecyl ligand and that there were no signs of branched isomers or other alkanes resulting from possibly impure modifying silane reagent. Recombination products and alkenes, as have been reported for methyl group scission[12], compounds such as hexatriacontane or *n*-octadecene-1, were not detected.

The chromatogram obtained after cleavage of the model compound was identical with those obtained from the silica gels, indicating that this compound simulates the surrounding field at the Si–C bond fairly well. Nevertheless, the cleavage of a mixture of the model compound and pure silica gel, which was similar to regular RP_{18} material with respect to the number of cleavable Si–C and Si–O bonds, gave a product yield of only about 67%.

As expected, the analysis of several commercially available reversed-phase materials showed great differences in their ligand contents (Table I). Relative root-mean square deviations were determined to be better than 3%, with two exceptions. For three samples the carbon content was also determined. In all instances the carbon percentages calculated from our data were lower than those obtained from elemental analysis. The difference may be explained by the presence of methyl groups* from

TABLE I

LIGAND CONTENTS OF DIFFERENT RP_{18}-MODIFIED SILICA GELS

GC determination as *n*-octadecane and octadecanol-1 from KOH fusion of octadecyl-modified silica gels in a high-boiling ether suspension (216°C, 2 h). Data are mean values from ten determinations per batch.

Name	*Batch No.*	*Particle diameter (μm)*	*Ligand content (μmol/mg)*	*Carbon content (%, w/w)*
LiChrosorb RP-18	VV 2053	5	0.67 ± 0.020	–
LiChrosorb RP-18	VV 1187	5	0.74 ± 0.018	–
LiChrosorb RP-18	091839*	5	0.60	–
ODS-SIL-X-5	–**	5	0.48 ± 0.017	–
Spherisorb S5 ODS C_{18}	18/157	5	0.22 ± 0.005	6.72
Polygosil 60-5 C_{18}	810606*	5	0.26	–
HPTLC-Fertigplatten	–**	5	0.66 ± 0.074	–
LiChrosorb RP-18	VV 1220	7	0.78 ± 0.015	–
LiChrosorb RP-18	VV 1106	10	0.80 ± 0.023	21.24
LiChrosorb RP-18	VV 1827	10	0.67 ± 0.019	–
LiChrosorb RP-18	VV 2249	10	0.68 ± 0.013	–
Kieselgel 60 C_{18}RP	7R20459	10	0.58 ± 0.014	–
ODS-SIL-X-10	1**	10	0.47 ± 0.012	–
ODS-SIL-X-10	2**	10	0.54 ± 0.014	13.89
LiChroprep RP-18	8572024	25–40	0.59 ± 0.015	–
Vydac 201 RP	–**	30–44	0.03 ± 0.001	–
Sep-Pak	–**	?	0.16 ± 0.004	–

* Material was scraped out from the bottom of a used HPLC column: the column number is given; only one sample was analysed.

** No batch number available.

* The methyl groups are cleaved by the potassium hydroxide fusion also, but the methane released could not be measured under the experimental and GC conditions described here.

end-capping and from mono- or bifunctional silane modifiers, respectively, but incomplete cleavage must, of course, also be taken into consideration.

CONCLUSIONS

The method described is able to give information about the ligand types and the relative ligand contents of modified silica gels. Other ligand types can also be analysed, provided that the physical properties of the released compounds, such as boiling points, and the chemical behaviour in fused alkali are taken into consideration.

By measuring the release of methane it should also be possible to distinguish between ligand and methyl groups and to determine the degree of capping.

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REFERENCES

1 B. S. Das and G. H. Thomas, *Anal. Chem.*, 50 (1978) 967.
2 K. Ogan, E. Katz and W. Slawin, *Anal. Chem.*, 51 (1979) 1315.
3 A. L. Colmsjö and J. C. Mac Donald, *Chromatographia*, 13 (1980) 350.
4 C. Hansson, G. Agrup, H. Rorsman, A.-M. Rosengren, E. Rosengren and L.-E. Edholm, *J. Chromatogr.*, 162 (1979) 7.
5 J. L. M. van de Venne, J. P. M. Rindt, G. J. M. M. Coenen and C. A. M. G. Cramers, *Chromatographia*, 13 (1980) 11.
6 K. Karch, I. Sebestian and I. Halász, *J. Chromatogr.*, 122 (1976) 3.
7 G. E. Berendsen and L. de Galan, *J. Liquid Chromatogr.*, 1 (1978) 561.
8 M. Verzele, P. Mussche and P. Sandra, *J. Chromatogr.*, 190 (1980) 331.
9 G. E. Berendsen, *Thesis*, Delft University, 1980.
10 L. Hansson and L. Trojer, *J. Chromatogr.*, 207 (1981) 1.
11 H.-G. Genieser, D. Gabel and B. Jastorff, *J. Chromatogr.*, 215 (1981) 235.
12 V. Chvalovsky, in E. I. Becker and M. Tsutsui (Editors), *Organometallic Reactions*, Vol. 3, Wiley-Interscience, New York, 1972, p. 191.
13 C. Eaborn and R. W. Bott, in A. G. Mac Diarmid (Editor), *The Bond to Carbon*, Vol. 1/1, Marcel Dekker, New York, 1968, p. 359.
14 J. Franc and J. Dvořáček, *J. Chromatogr.*, 14 (1964) 340.
15 R. H. Krieble and J. R. Elliott, *J. Amer. Chem. Soc.*, 68 (1946) 2291.