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Note

Structural investigations on reversed-phase silicas

II. Evidence for endcapping trimethylsilyl groups

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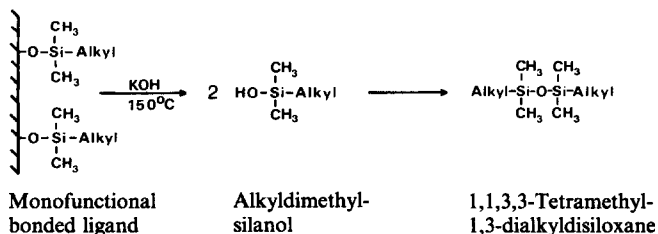
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Reversed-phase (RP) silicas are extremely useful in solving many separation problems in modern liquid chromatography. Nevertheless there are still problems with the reproducibility of chromatographic results obtained with these materials. One important obstacle to the improvement of RP silicas, with respect to constant properties and quality, might be the lack of reliable analytical methods giving detailed information about the silica matrix itself and about the ligands attached to the surface.

In our studies we focus on the analysis of ligands. Items of interest are the structure of the ligand and its purity, its degree of substitution and its distribution on the surface as mono-, di- and trifunctional bonded alkyl groups, and mono- and polymeric substitution. Other important parameters are the proportion of unchanged silanol groups and the degree of endcapping.

For elemental analysis offers only poor information about these structural parameters, several authors have contributed to an improved characterization of RP silicas¹⁻¹⁶. With special respect to endcapping trimethylsilyl (TMS) groups, methods using pyrolysis^{4,9,12,14}, thermogravimetry², ¹³C and ²⁹Si NMR measurements^{3,8,10} and hydrofluoric acid digestion¹⁶ as well as chromatographic tests⁵ have already been published.

We found the alkali fusion reaction to be a simple and valuable tool for the ligand analysis of silica-bonded stationary phases^{7,11}. RP silicas with monofunctional ligands yielded alkyldimethylsilanol and its dimer, 1,1,3,3-tetramethyl-1,3-dialkyldisiloxane during alkali fusion¹⁵.



For the TMS group, which is the most simple monofunctional ligand, we expected to find trimethylsilanol and hexamethyldisiloxane by gas chromatographic (GC) analysis of alkali fusion products from endcapped RP silicas.

EXPERIMENTAL

To 20 mg of the derivatized silica in a glass reaction tube (110 mm \times 5 mm I.D.), 200 mg of dry powdered potassium hydroxide and 100 μ l of triethylene glycol dimethyl ether (triglyme) were added. The tube was heated to 150°C for 30 min in an oil bath and two 100- μ l lots of diethyl ether were added subsequently. Analysis of the ether extract was performed with a 437 S gas chromatograph (Packard Instruments, Delft) equipped with a non-polar 50-m OV-1 fused-silica capillary column (Orion, Espoo, Finland) and a flame ionization detector. The oven temperature was set to 33°C isothermally and the carrier gas flow-rate was 2 ml/min. After analysis, the oven temperature was set to 280°C to remove the reaction products of the main ligand from the column.

Structural characterization of organosilicon compounds was achieved by GC-mass spectrometry.

Unreliable results are possible when the glass surface of the reaction tube is silanized in order to promote antiwetting properties.

RESULTS

Laboratory-made TMS silica was fused with potassium hydroxide in triglyme suspension at 150°C for 30 min. The ether extract of the reaction products was analysed for trimethylsilanol and its condensation product hexamethyldisiloxane. Both components were found in the chromatogram (Fig. 1), but the silanol peak rapidly

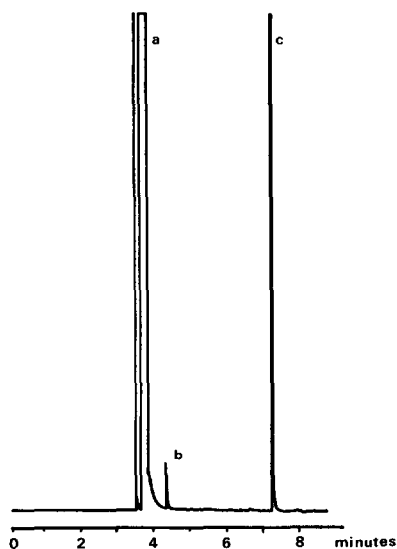


Fig. 1. Gas chromatogram of alkali fusion products from endcapped RP silicas (0.5 h, 150°C, triglyme suspension). Peaks: a = diethyl ether (solvent); b = trimethylsilanol; c = hexamethyldisiloxane.

TABLE I

ANALYSIS OF COMMERCIALY AVAILABLE RP-8 SILICAS FOR ENDCAPPING TMS GROUPS BY ALKALI FUSION AND SUBSEQUENT GC PROOF OF HEXAMETHYLDISILOXANE

<i>Sample</i>	<i>Batch No.</i>	<i>Endcapping</i>
Kieselgel 60 HPLC C ₈ (Riedel de Haen)	—	Yes
LiChrorep RP-8 (Merck)	8597034	No
LiChrosorb RP-8 (Merck)	VV 1137	No
LiChrosorb RP-8 (Merck)	VV 2159	No
MOS Hypersil C ₈ (Shandon)	12772	No
Nucleosil 10 C ₈ (Macherey & Nagel)	—	No
SIL-X5 C ₈ (Perkin-Elmer)	829081	Yes
SIL-X10 C ₈ (Perkin-Elmer)	820011	Yes

decreased during repeated injections. Methane, which is also evolved in small amounts, was not detected because of the experimental conditions. The presence of hexamethyldisiloxane caused us to check commercially available RP silicas with respect to TMS groups resulting from endcapping procedures with trimethylchlorosilane or other trimethylsilylating agents. Tables I and II show the results for several RP-8 and RP-18 materials based on GC analysis for hexamethyldisiloxane. During fusion the main ligand (RP-8/RP-18) is also cleaved, and products such as alkanes, alkanols and alkylsiloxanes as well as triglyme can be identified in temperature-programmed GC runs¹¹, so simultaneous determination of the main ligand structure is also possible.

TABLE II

ANALYSIS OF COMMERCIALY AVAILABLE RP-18 SILICAS FOR ENDCAPPING TMS GROUPS BY ALKALI FUSION AND SUBSEQUENT GC PROOF OF HEXAMETHYLDISILOXANE

<i>Sample</i>	<i>Batch No.</i>	<i>Endcapping</i>
Kieselgel 60 HPLC C ₁₈ (Riedel de Haen)	CH-B2174	Yes
LiChrorep RP-18 (Merck)	8572024	No
LiChrosorb RP-18 (Merck)	VV 1106	No
Micro-Pak MCH-10 (Varian)	—	No
Nucleosil 7 C ₁₈ (Macherey & Nagel)	3022	Yes
Nucleosil 10 C ₁₈ (Macherey & Nagel)	—	Yes
ODS Hypersil (Shandon)	11/1067	Yes
ODS SIL-X5 (Perkin-Elmer)	—	Yes
ODS SIL-X10 (Perkin-Elmer)	—	Yes
Sep-Pak C ₁₈ (Waters)	—	Yes
Spherisorb S5 ODS (Separations Group)	18/157	Yes
Co:Pell ODS (Whatman)	100727	No

DISCUSSION

The condensation of trimethylsilanol can yield not only the symmetrical hexamethyldisiloxane but also mixed siloxanes with alkylsilanols derived from the main ligand. Normally the degree of substitution of the main ligand should be considerably higher than that of the TMS group, so that mixed siloxanes would be expected to be the main TMS-containing reaction products.

However, in the case of endcapped difunctional RP-8 silica we found only traces of 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane; the main TMS-containing product was hexamethyldisiloxane.

Alkali fusion of endcapped monofunctional RP-8 material yielded only traces of 1,1,1,3,3-pentamethyl-3-octyldisiloxane; the main TMS-containing product was again hexamethyldisiloxane.

These findings may be due to a possible concentration of TMS ligands in narrow pores of the silica matrix.

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