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GEL PERMEATION CHROMATOGRAPHIC SEPARATION OF LOW-MOLECULAR-WEIGHT TRIMETHYLSILYLATED SILICIC ACIDS WITH ISOPROPANOL–CHLOROFORM MIXTURES

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SUMMARY

The separation of trimethylsilyl derivatives of silicic acids was examined with gel permeation chromatography, using the three kinds of gel, Sephadex LH-20 and LH-60, and Bio-Beads S-Xl. The eluents used were isopropanol for Sephadex LH-20 and LH-60, and isopropanol–chloroform mixtures for Bio-Beads S-Xl. The silicon in the trimethylsilyl derivatives in the fractions was analyzed by atomic absorption spectrometry. Bio-Beads S-Xl gave the best separation. Hexamethyldisiloxane and low-molecular-weight trimethylsilyl derivatives, *i.e.* $[(CH_3)_3Si]_4[SiO_4]$, $[(CH_3)_3Si]_6[Si_2O_7]$, and a group of $[(CH_3)_3Si]_8[Si_3O_{10}]$ and $[(CH_3)_3Si]_8[Si_4O_{12}]$ could be isolated and there is a possibility that larger derivatives could be separated. For the separation by gel permeation chromatography, partition effect as well as molecular sieve effect may be expected.

INTRODUCTION

Lentz[1] described a chemical technique for the study of mineral silicate structures based on trimethylsilylation of silicic acids liberated from minerals by acid leaching. Many workers[2–9] have applied this technique to the study of silicate structures. Separation of trimethylsilyl (TMS) derivatives has usually been achieved by gas–liquid chromatography (GLC) and thin-layer chromatography (TLC)[10].

Gel permeation chromatography (GPC) is a method for separating solute molecules according to their size. It can be used for the separation of the components of a mixture of TMS derivatives and their isolation in large amounts.

This paper describes the GPC separation of crude products obtained by trimethylsilylation of hemimorphite and sodium silicate solution. As TMS derivatives are soluble only in organic solvents, GPC was performed in an organic solvent system.

EXPERIMENTAL

Trimethylsilylation

The silicate samples used in this study were hemimorphite, $Zn_4(Si_2O_7)$

$(OH)_2 \cdot H_2O$, and sodium silicate solution prepared from water glass (*ca.* 1 *M*, Na_2O: $SiO_2 = 1:1$). TMS derivatives were prepared by the method of Lentz. Silicate sample was added to the reaction mixture of 20 g of ice, 60 ml of isopropanol (iso-PrOH), 60 ml of conc. HCl and 40 ml of hexamethyldisiloxane (HMDS), which had been stirred for 1 h at 28°. The amount of sample added was 2.5 g of powdered hemimorphite or 10 ml of sodium silicate solution. The mixture was then stirred for 2 h and filtered. The siloxane layer was separated and washed with water. It was then mixed with 2 g of Amberlyst 15 ion-exchange resin and stirred for 2 h at room temperature. The mixture was filtered and the filtrate was concentrated by distillation at 120–130°. The products were named TMS-hemimorphite and TMS-W.G., respectively, and were analyzed by GPC and GLC.

Gel permeation chromatography

TMS derivatives are soluble only in organic solvents. Therefore, the gels used for organic solvents. Sephadex LH-20 (25–100 μm) and LH-60 (40–120 μm) (Pharmacia, Uppsala, Sweden), and Bio-Beads S-Xl (200–400 mesh, Bio-Rad Labs., Richmond, Calif., U.S.A.) were examined. The eluent used with Sephadex LH-20 and LH-60 was iso-PrOH, and with Bio-Beads S-Xl it was iso-PrOH–chloroform.

The gel was suspended in the solvent to be used as the eluent and allowed to swell for 5 h. The column, 90 × 1.5 cm I.D. glass tube with a porous teflon disc at the bottom, was wet-packed with gel to a total bed volume of *ca.* 160 ml. The sample (1–2 ml), which was diluted with eluent, was placed on the top of the column and the eluent was applied. Using an automatic fraction collector, the effluent was collected in fractions of 1 ml.

The silicon in the TMS derivatives in the fractions was analyzed by atomic absorption spectrometry (AAS), using a Nippon Jarrell Ash AA-781 Atomic Absorption & Flame Emission Spectrometer. The conditions were as follows: C_2H_2-rich N_2O flame, wavelength 251.6 nm.

Gas chromatography

A Yanaco G 180 gas chromatograph equipped with a flame ionization detector was used. The column was 3.0 m × 3.0 mm I.D. glass tube packed with 2% Silicone OV-1 on Chromosorb W AW DMCS-treated, 60–80 mesh. Helium was used as carrier gas. Samples (1–2 μl) were injected and the oven was programmed from 100 to 300° at 5° /min.

RESULTS AND DISCUSSION

TMS derivatives of the following anions, monomer SiO_4^{4-}, dimer $Si_2O_7^{6-}$, trimeric chain $Si_3O_{10}^{8-}$ and tetrameric ring $Si_4O_{12}^{8-}$ are abbreviated Si_1, Si_2, Si_3 chain and Si_4 ring, respectively.

Sephadex LH-20 and LH-60 swell in iso-PrOH, but Bio-Beads S-Xl does not swell in iso-PrOH, only in relatively non-polar solvents such as benzene, heptane, cyclohexane and chloroform. Benzene, heptane and cyclohexane were not satisfactory eluents because they interfere with the determination of silicon because of a very strong absorption at 251.6 nm in AAS. The equivalent absorption by

$CHCl_3$ can be regarded as a background when chloroform–iso-PrOH mixtures are used.

In Table I, the variation of the swelling volume of the gel with different proportions of iso-PrOH and chloroform is shown for Bio-Beads S-Xl and Sephadex LH-20. At iso-PrOH: chloroform ratios of 5:0 (v/v) and 4:1, Bio-Beads S-Xl swelled very little. At 3:2, the apparent swelling volume of Bio-Beads S-Xl was greater than that at 2:3 because the gel bed was fluffy, but it seemed that the swelling was inadequate. For Bio-Beads S-Xl, the swelling volume, *i.e.* the pore size, became progressively larger with increasing proportion of chloroform compared with Sephadex LH-20, the swelling volume of which did not vary so much.

TABLE I

VARIATIONS OF THE SWELLING VOLUME OF GELS WITH CHANGING PROPORTIONS OF iso-PrOH AND CHLOROFORM FOR BIO-BEADS S-X1 AND SEPHADEX LH-20

iso-PrOH–$CHCl_3$	*Swelling volume (ml/g)*	
	Bio-Beads S-X1	*Sephadex LH-20*
5:0	—	3.7
4:1	—	4.6
3:2	(4.0)	4.8
2.5:2.5	3.7	5.0
2:3	4.4	5.0
1:4	6.8	5.2
0:5	8.3	4.5

Effect of solvent composition on the chromatograms of TMS-W.G. using the Bio-Beads S-Xl column is shown in Fig. 1. Each peak was named D_1, D_2, . . . in the order of molecular size, from a small one to a larger one. The elution volumes of TMS derivatives shift to right with increasing proportion of chloroform. At iso-PrOH:$CHCl_3$ ratios of 2:3 and 1:4, the separation efficiency is better than that using chloroform alone. The partition effect may operate in addition to the molecular sieve effect (see later). If the separation efficiency is compared at ratios 2:3 and 1:4, it is found that the former ratio is better in the low-molecular-weight region, but the latter is better in the high-molecular-weight region. Therefore, the mixing ratios of 2:3, in the low-molecular-weight region, and 1:4, in the high-molecular-weight region, are adequate for the separation. In our later investigations, the 2:3 mixture was used as eluent for Bio-Beads S-Xl.

The gel chromatograms of TMS-W.G. obtained by three kinds of gel are shown in Fig. 2. TMS derivatives were separated into only two peaks with Sephadex LH-60, possibly because the pore size was too great. With Sephadex LH-20, though the peaks of HMDS and D_1 were almost separated, the peak of D_2 was appeared as a shoulder, and D_3 and higher derivatives were eluted as one peak. On the other hand, with Bio-Beads S-Xl, the peaks of HMDS, D_1, D_2 and D_3 were almost entirely separated. As mentioned above, Bio-Beads S-Xl gave the best separation of the three gels investigated.

The gel chromatograms of TMS-hemimorphite and TMS-W.G. are shown in Fig. 3. The dotted and the continuous lines show the chromatograms obtained using

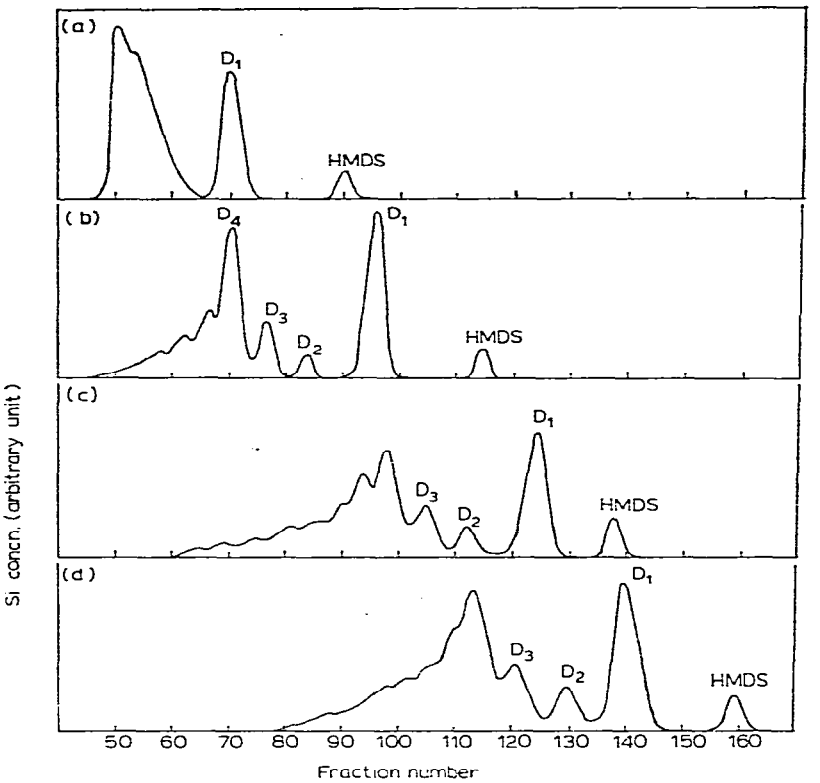

Fig. 1. Effect of solvent composition on the separation efficiency. Gel, Bio-Beads S-X1; sample, TMS-W.G.; column, 90 × 1.5 cm I.D.; fraction volume, 1 ml. Eluents: a, iso-PrOH–$CHCl_3$ (3:2); b, iso-PrOH–$CHCl_3$ (2:3); c, iso-PrOH–$CHCl_3$ (1:4); d, $CHCl_3$.

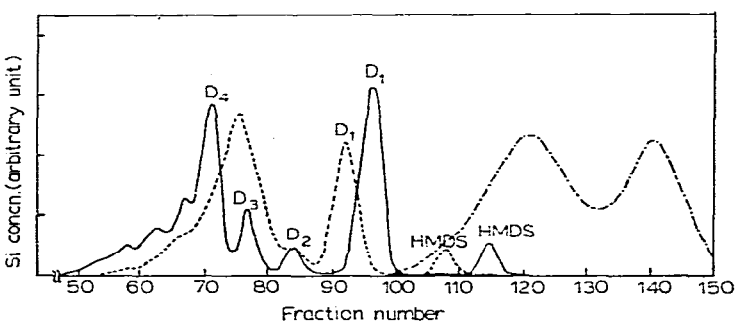

Fig. 2. Gel chromatograms of TMS-W.G. with three kinds of gel. - - - - -, Sephadex LH-20; — · — · — ·, Sephadex LH-60; ———, Bio-Beads S-X1. Column, 90 × 1.5 cm I.D.; fraction volume, 1 ml; eluents, iso-PrOH for Sephadex LH-20 and LH-60, and iso-PrOH–$CHCl_3$ (2:3) for Bio-Beads S-X1.

a single column and two columns connected in series, respectively. As shown in Fig. 3a, five peaks (from HMDS to D_4) were almost completely separated in the chromatogram of TMS-hemimorphite using the double column. In the chromatogram of TMS-W.G. shown in Fig. 3b, several peaks of TMS derivatives larger than D_4

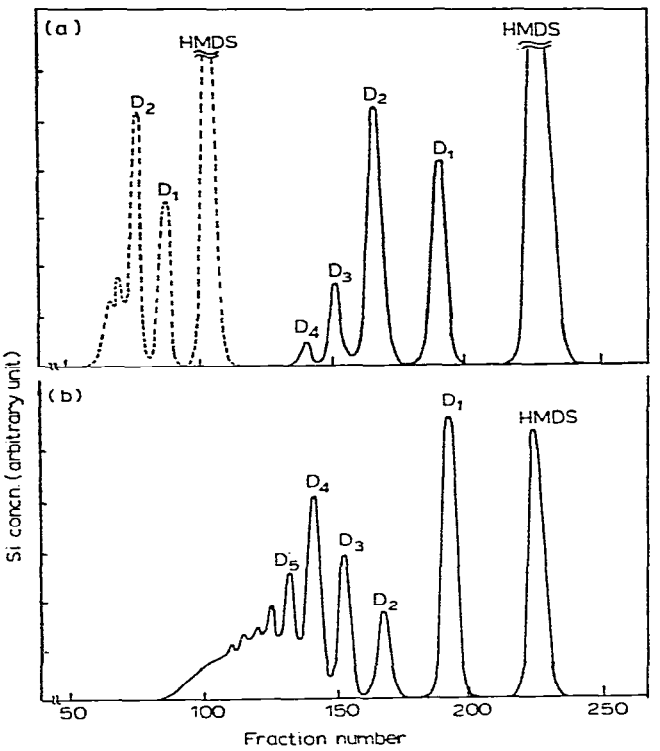

Fig. 3. Gel chromatograms of (a) TMS-hemimorphite and (b) TMS-W.G. Gel, Bio-Beads S-X1; eluent, iso-PrOH–$CHCl_3$ (2:3); column: ----, 90 × 1.5 cm I.D.; ———, (90 × 1.5 cm I.D.) × 2; one fraction, 1 ml. Flow-rate, single column 0.53 ml/min, two columns 0.12 ml/min.

were obtained. Separation of larger TMS derivatives may be possible by changing the experimental conditions.

The TMS derivatives that appeared as peaks in the gel chromatogram of TMS-hemimorphite were isolated, and identified by GLC and elemental analysis. The results are shown in Fig. 4 and Table II. The peaks D_1, D_2 and D_3 were assigned to Si_1, Si_2 and a group of Si_3 chain and Si_4 ring, respectively. The D_4 portion has not yet been identified.

It is generally supposed that the major separation mechanism in GPC is the molecular sieve effect. However, in this study, the partition effect as well as molecular sieve effect may be operative, because Bio-Beads S-Xl has an affinity for non-polar solvents, and the eluent is a mixture of iso-PrOH and $CHCl_3$. The difference in polarity means that Bio-Beads S-Xl has a greater affinity for $CHCl_3$ than for iso-PrOH. Therefore, it is to be expected that the solvent composition inside the gel may be different from that outside the gel. The gel and the solvent mixture were shaken together for 10 h, and the composition of iso-PrOH and chloroform in the external solvent before and after shaking was analyzed by GLC. The results for Bio-Beads S-Xl and Sephadex LH-20 are shown in Fig. 5. D_c (before) and D_c (after) are the proportion of chloroform before and after shaking with gel, respectively. The abscissa is the composition of the initial solvent mixture and the ordinate is the

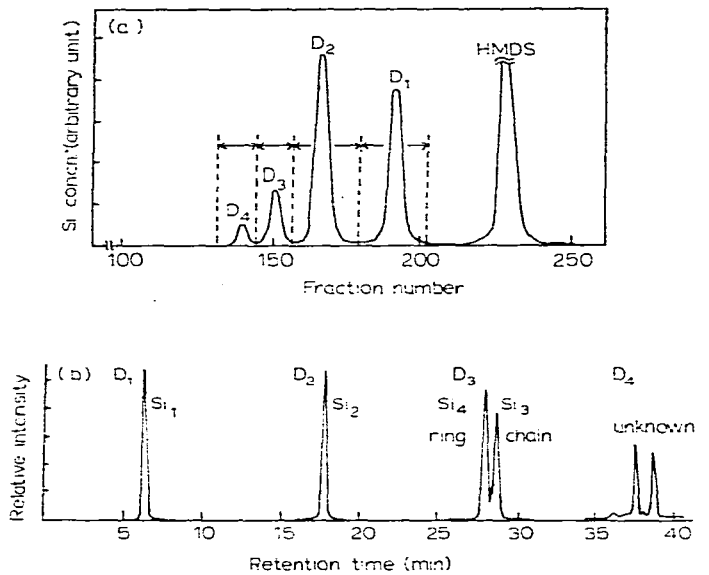

Fig. 4. (a) Isolation of TMS derivatives shown as peaks in gel chromatogram for TMS-hemimorphite and (b) gas chromatograms for each portions (D_1–D_4 in GPC).

TABLE II

ELEMENTAL ANALYSES OF TMS DERIVATIVES ISOLATED BY GPC (D_1–D_4 SHOWN IN FIG. 4)

GPC peak	*Found (%)*		*Calcd. (%)*		*Species*
	C	*H*	*C*	*H*	
D_1	37.35	9.39	37.45	9.45	Si_1
D_2	35.50	8.95	35.59	8.98	Si_2
D_3	33.25	8.30	33.43	8.43	Si_3 chain + Si_4 ring
D_4	31.37	7.59	—	—	unknown

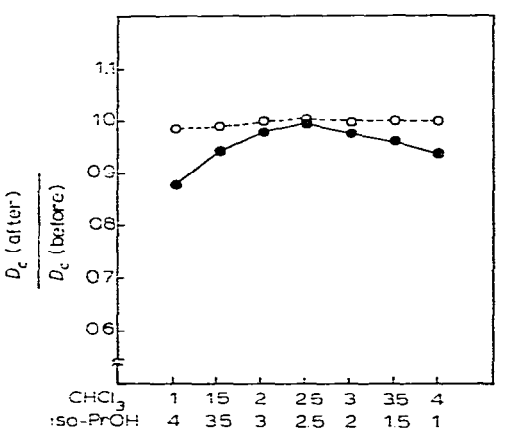

Fig. 5. Relationship between D_c (after)/D_c (before) and initial mixed solvent ratio for Bio-Beads S-X1 (●—●) and Sephadex LH-20 (○---○). Bio-Beads S-X1, 5 g; Sephadex LH-20, 5 g; volume of solvent, 50 ml.

value of D_c (after) $/D_c$ (before) ratio. For Bio-Beads S-Xl, it can be seen that chloroform is always poor in the external solvent after shaking compared with the starting mixture. In other words, Bio-Beads S-Xl takes up chloroform more easily than iso-PrOH. Therefore, there is a difference between the solvent compositions inside and outside the gel for Bio-Beads S-Xl. For Sephadex LH-20 this difference is very small, as would be expected from the fact that Sephadex LH-20, which has alkyl and hydroxyl groups, swells in both iso-PrOH and chloroform. From these results, the partition effect on the separation can be expected to be operative for Bio-Beads S-Xl but not for Sephadex LH-20.

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