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GEL PERMEATION CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF TRIMETHYLSILYL DERIVATIVES OF SILICATE ANIONS

TSUGIO SHIMONO, HIROFUMI TAKAGI, TOSHIYUKI ISOBE and TOSHIKAZU TARUTANI*

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812 (Japan)

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SUMMARY

Low-molecular-weight trimethylsilyl (TMS) derivatives of silicate anions were prepared by the trimethylsilylation of olivine, laumontite, tetraalkylammonium silicates (TAAS) that were obtained by reaction of anhydrous silica with tetraalkylammonium hydroxides, and silicon oxychlorides (SOC) that were obtained by partial hydrolysis of tetrachlorosilane. Gel permeation chromatography was used for the separation of a mixture of the TMS derivatives. The identification of the TMS derivatives was performed by elemental analyses, gas chromatography and combined gas chromatography–mass spectrometry. $[(CH_3)_3Si]_4[SiO_4]$ was isolated from the TMS product of olivine and $[(CH_3)_3Si]_8[Si_4O_{12}]$ was isolated from that of laumontite. $[(CH_3)_3Si]_8[Si_8O_{20}]$ and $[(CH_3)_3Si]_{10}[Si_8O_{21}]$ were isolated from the TMS products of TAAS, and $[(CH_3)_3Si]_6[Si_2O_7]$, $[(CH_3)_3Si]_6[Si_3O_9]$, $[(CH_3)_3Si]_8[Si_3O_{10}]$ and $[(CH_3)_3Si]_{10}[Si_4O_{13}]$ were isolated from those of SOC. Further, the groups of $[(CH_3)_3Si]_{10}[Si_4O_{13}]$ and $[(CH_3)_3Si]_{10}[Si_5O_{15}]$, and $[(CH_3)_3Si]_{12}[Si_5O_{16}]$ and $[(CH_3)_3Si]_{12}[Si_6O_{18}]$, were separated from those of SOC. The effect of contact time with the ion-exchange resin and reaction temperature for complete trimethylsilylation of SOC were examined.

INTRODUCTION

Trimethylsilylation has been used for the elucidation of the anionic composition of silicate minerals[1–4], silicate glasses[5,6] and silicic acid solutions[1,7–9] since Lentz[1] proposed the technique in 1964. However, the quantitative analysis of trimethylsilyl (TMS) derivatives of silicate anions is difficult because of the difficulty of isolating TMS derivatives as standard substances.

In a previous paper[10], the separation of TMS derivatives obtained by the trimethylsilylation of hemimorphite and sodium silicate solution by gel permeation chromatography (GPC) was reported. GPC is useful for the isolation of TMS derivatives as standard substances. However, because of the limitation of the separation efficiency of GPC, it is necessary to optimize the synthesis of TMS derivatives.

Several TMS derivatives have been synthesized by the trimethylsilylation of silicate minerals. Hoebbel and co-workers[11-13] synthesized several TMS derivatives of ring- and cage-types substances by the trimethylsilylation of tetraalkylammonium silicates (TAAS), which were obtained by reaction of anhydrous silica with tetraalkyl-ammonium hydroxides. Shumb and Stevens[14] reported the synthesis of a series of silicon oxychlorides (SOC) by the partial hydrolysis of tetrachlorosilane.

This paper describes the synthesis of TMS derivatives of silicate anions by the trimethylsilylation of olivine, laumontite, TAAS and SOC, the separation of TMS derivatives by GPC, and their identification by elemental analyses, gas chromatography (GC) and combined gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Preparation of tetraalkylammonium silicates

Anhydrous silica (Mallinckrodt, St. Louis, MO, U.S.A.) was added to 25 ml of 10% tetramethylammonium or 10% tetraethylammonium hydroxide solution to give a molar ratio of $[(CH_3)_4N]OH$ or $[(C_2H_5)_4N]OH$ to SiO_2 of 1:1. The mixture was stirred for 20 h at 20°C and filtered to remove unreacted anhydrous silica. The filtrate was concentrated in a desiccator with concentrated sulphuric acid.

Preparation of silicon oxychlorides

Diethyl ether (278 ml) and tetrachlorosilane (150 ml) were poured into a 1-1 three-necked round-bottomed flask. The ethereal solution of tetrachlorosilane was immersed in a Dewar vessel containing solid carbon dioxide–acetone refrigerant and stirred for 20 min. Subsequently, with vigorous stirring, water (9.6 ml) was added dropwise over a 2-h period. The mixture was then stirred for 1 h and allowed to stand in the Dewar vessel for 2 h. The mixture was removed from the refrigerant and allowed to stand in air overnight, sealing the flask with rubber stoppers. After filtration, diethyl ether was removed by distillation, and from the residue a series of silicon oxychlorides was fractionated by distillation under reduced pressure of *ca.* 15 mmHg.

Trimethylsilylation

Olivine was trimethylsilylated according to the Lentz method[1] and laumontite, TAAS and SOC according to the direct method of Götz and Masson[2].

Olivine (0.5 g) was added to a mixture of ice (5 g), concentrated hydrochloric acid (15 ml), isopropanol (15 ml) and hexamethyldisiloxane (HMDS, 10 ml), which had been stirred for 1 h at 28°C. The mixture was then stirred for 25 h and filtered. The siloxane layer was separated and washed with water.

Laumontite (0.5 g), TAAS (0.5 g) and SOC (0.5 ml) were added to a mixture of HMDS (18 ml), trimethylchlorosilane (4 ml), isopropanol (2 ml) and water (0.4 ml), which had been stirred for 30 min at 20°C. The mixture was then stirred for 1 h and filtered. The siloxane layer was separated and washed with water.

In order to promote the complete trimethylsilylation of partially trimethyl-silylated derivatives of silicate minerals and TAAS, the siloxane layer was contacted with Amberlyst 15 cation-exchange resin (2 g) at 20°C. With SOC, the siloxane layer was contacted with a mixture of 2 g each of Amberlyst 15 and A-26 anion-exchange resins at 20°C or with Amberlyst 15 (2 g) at 120°C. The reaction products were

concentrated at 130°C and analysed by GC. The separation of TMS derivatives was effected by GPC.

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% OV-1 silicone on Chromosorb W AW DMCS (60–80 mesh). Helium was used as the carrier gas. Samples (1–2 μl) were injected and the oven was programmed from 100 to 300°C at 5°C/min.

Gel permeation chromatography

The details of the GPC separation of TMS derivatives of silicate anions were reported in a previous paper[10]. The conditions were as follows: gel, Bio-Beads S-X1; eluent, isopropanol–chloroform (2:3); column, 90 × 1.5 cm I.D. and 45 × 1.5 cm I.D., connected in series with a PTFE tube; fraction volume, 1 ml.

The silicon in the TMS derivatives in the fractions was determined by atomic-absorption spectrometry, using a Nippon Jarrell Ash AA-781 atomic-absorption and flame-emission spectrometer. An acetylene–nitrous oxide flame and a wavelength of 251.6 nm were used.

Combined gas chromatography–mass spectrometry

A Shimadzu–LKB gas chromatograph–mass spectrometer was used. The ionization energy was 70 eV, the ion source block was maintained at 330°C and the
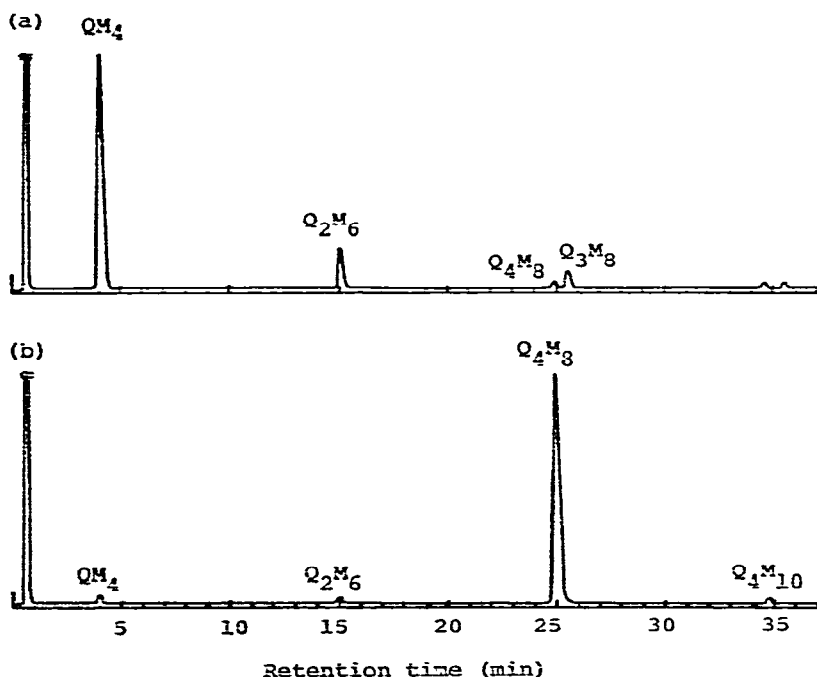

Fig. 1. Gas chromatograms of (a) TMS-olivine and (b) TMS-laumontite.

molecular separator at 310°C. The GC column was 2.0 m × 3.0 mm I.D. coiled glass tube packed with 1% OV-1 on Uniport HP. The carrier gas was helium at a flow-rate of 30 ml/min.

RESULTS AND DISCUSSION

Examples of the structures and abbreviations for the TMS derivatives of silicate anions have been proposed by Garzó and Hoebbel[15]. One tetrahedron corresponding to one SiO_2 unit in a condensed silicate system is designated as Q and the $(CH_3)_3SiO_{1/2}$ atomic group resulting from the silylation is designated as M. Therefore, the TMS derivative of the disilicate $[(CH_3)_3Si]_6 [Si_2O_7]$ is Q_2M_6.

The TMS products of olivine and laumontite are abbreviated to TMS-olivine and TMS-laumontite, respectively. The gas chromatograms and the gel chromatograms of TMS-olivine and TMS-laumontite are shown in Figs. 1 and 2, respectively. By the collection of peak portions in the gel chromatograms, QM_4 was isolated from TMS-olivine and Q_4M_8 from TMS-laumontite.
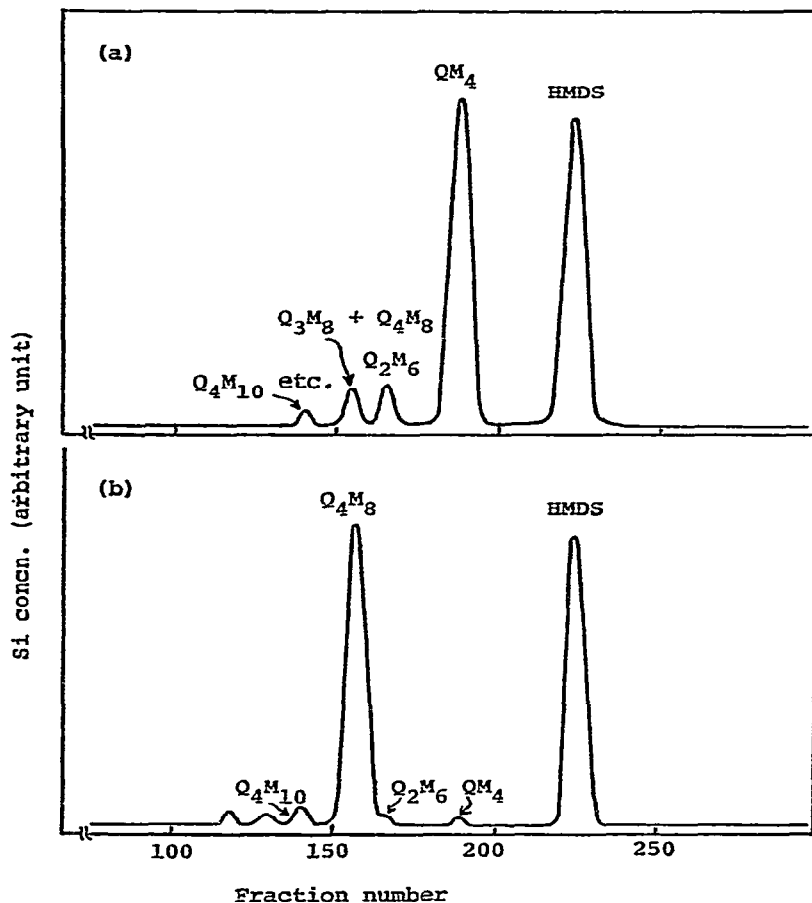

Fig. 2. Gel chromatograms of (a) TMS-olivine and (b) TMS-laumontite. Two 90 × 1.5 cm I.D. columns; total bed volume, *ca.* 318 cm³.

The TMS products of tetramethyl- and tetraethylammonium silicates are abbreviated to TMS-TMAS and TMS-TEAS, respectively. Their gas chromatograms are shown in Fig. 3. Both TMS-TMAS and TMS-TEAS contained Q_8M_8 as the main product, and Q_6M_{10}, Q_8M_{10} and Q_9M_{10} were also present. Garzó and Hoebbel[15] reported the formation of the Q_6M_{10} isomers by the trimethylsilylation of TEAS. Although their peaks were observed in the gas chromatogram of TMS-TEAS, the yields were very low. The gel chromatograms of TMS-TMAS and TMS-TEAS are shown in Fig. 4. By the collection of peak portions in the gel chromatograms, Q_8M_8 and Q_8M_{10} were isolated.
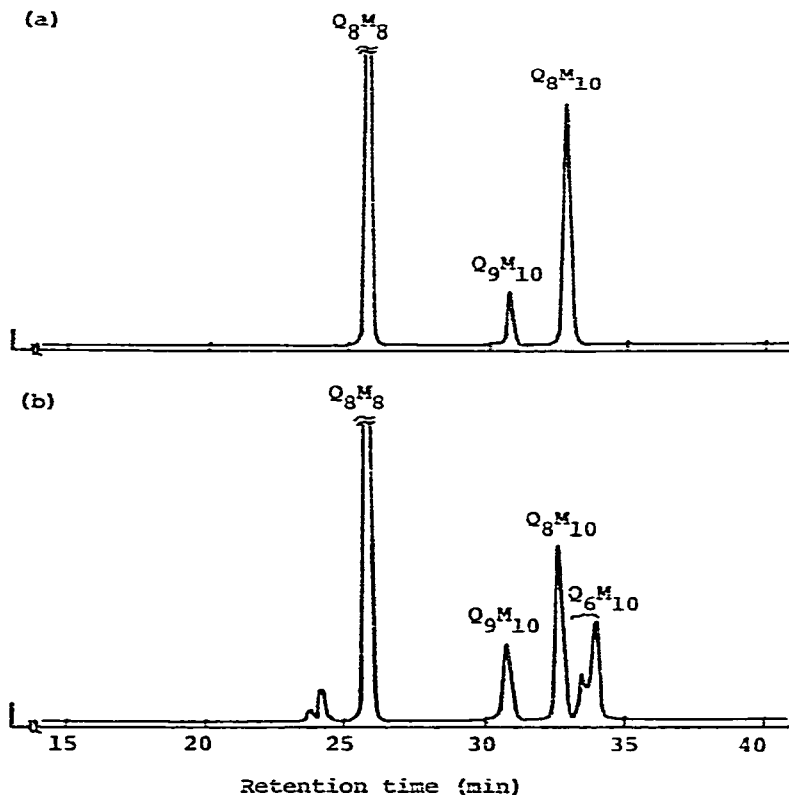

Fig. 3. Gas chromatograms of (a) TMS-TMAS and (b) TMS-TEAS.

By the partial hydrolysis of tetrachlorosilane, the homologous series of silicon oxychlorides, $Si_nO_{n-1}Cl_{2n+2}$, were prepared. The results of the fractional distillation of silicon oxychlorides under reduced pressure (ca. 15 mmHg) are given in Table I.

With silicate minerals and TAAS, the partially trimethylsilylated derivatives were completely trimethylsilylated in contact with Amberlyst 15 at room temperature. However, with silicon oxychlorides, the trimethylsilylation was not promoted effectively in contact with Amberlyst 15 at room temperature but was promoted in contact with a mixture of Amberlyst 15 and A-26 at room temperature or by refluxing with Amberlyst 15, as discussed later.
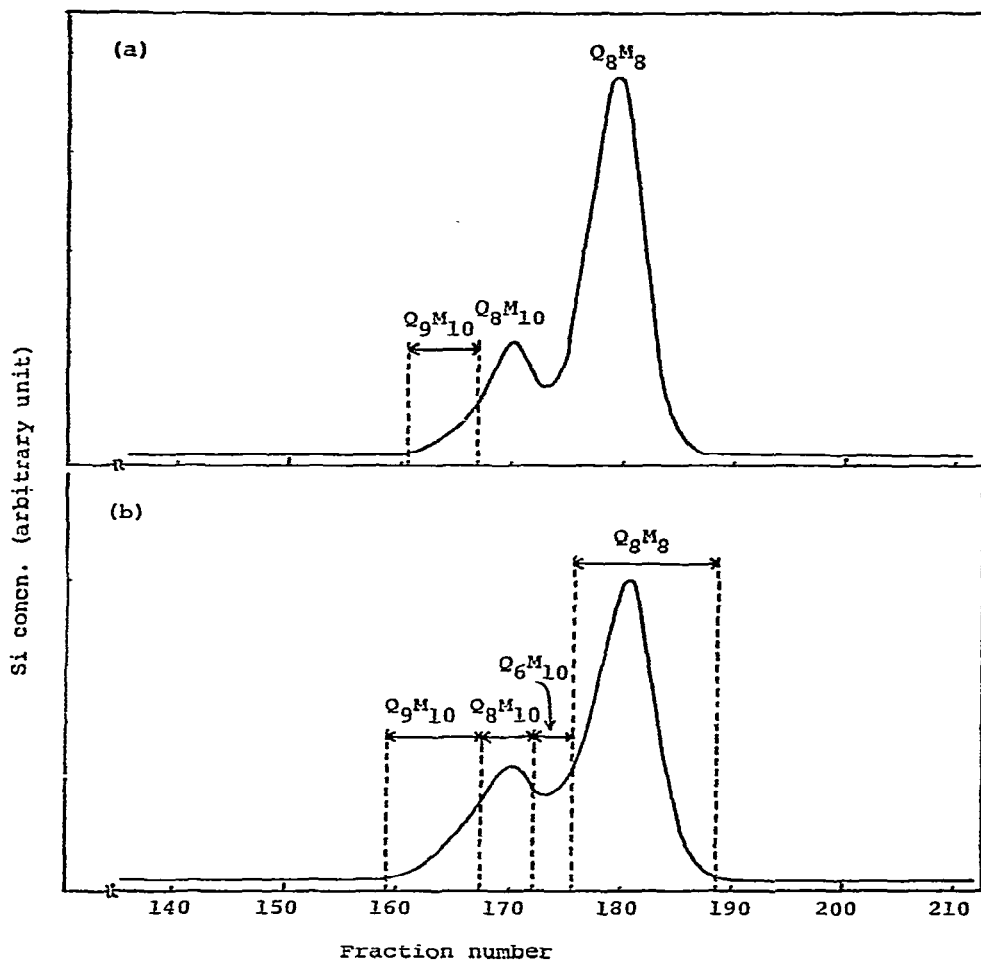
Fig. 4. Gel chromatograms of (a) TMS-TMAS and (b) TMS-TEAS. Two 90×1.5 cm I.D. columns plus one 45×1.5 cm I.D. column; total bed volume, *ca*. 397 cm^3.

The TMS products of silicon oxychlorides are abbreviated to TMS-SOC. Their gas chromatograms are shown in Fig. 5. The promotion of the trimethylsilylation for the partially trimethylsilylated derivatives in TMS-SOC was accomplished by contacting with the mixed resin at 20°C. The SOC distilled at 45°C contained mainly

TABLE I

RESULTS OF SEPARATION OF SILICON OXYCHLORIDES

Boiling point at ca. 15 mmHg (°C)	Yield (ml)	Compound (reported[14])
45	28.5	Si_2OCl_6
85	9.5	$Si_3O_2Cl_8$
121.5	7.0	$Si_4O_3Cl_{10}$
143.5	6.5	$Si_5O_4Cl_{12}$
160	4.5 ⎱	$Si_6O_5Cl_{14}$
170	4.0 ⎰	

Si_2OCl_6 and some $Si_3O_2Cl_8$. Q_4M_8 and Q_4M_{10} may be suggested to be formed by the condensation of $Si_2O_7{}^{6-}$ during the trimethylsilylation. The SOC distilled at 85°C was almost entirely $Si_3O_2Cl_8$. Q_3M_6 may be also suggested to be formed by an intramolecular condensation of $Si_3O_{10}{}^{8-}$ during the trimethylsilylation. The SOC distilled at 121.5°C mainly contained $Si_4O_3Cl_{10}$ and $Si_3O_2Cl_8$. Q_4M_8 may be presumed to be formed by an intramolecular condensation of $Si_4O_{13}{}^{10-}$. TMS-SOC from SOC distilled at 143.5°C contained unknown derivatives, A, B and C, shown in Fig. 5d, as well as Q_4M_8 and Q_4M_{10}. The proportion of A, B and C increased in TMS-SOC from SOC distilled at 160°C. It is considered that these derivatives were probably derived from $Si_5O_4Cl_{12}$ or $Si_6O_5Cl_{14}$. Although TMS-SOC from SOC distilled at 170°C reacted with the mixed resin, partially trimethylsilylated derivatives were not easily eliminated. It was observed that a longer time is necessary to promote the complete trimethylsilylation of the partially trimethylsilylated derivatives of higher molecular weight.
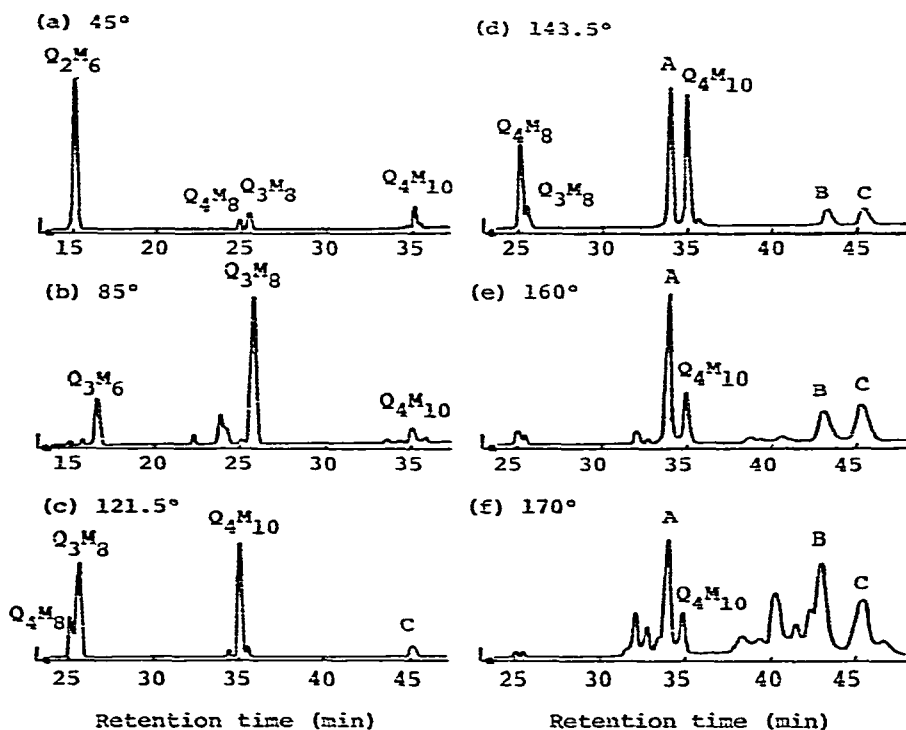

Fig. 5. Gas chromatograms of TMS-SOC (temperatures indicated are boiling points of SOC at *ca.* 15 mmHg).

The gel chromatograms of each TMS-SOC are shown in Fig. 6. By the collection of the peak portions in the gel chromatograms, Q_2M_6, Q_3M_6, Q_3M_8 and Q_4M_{10} were isolated. By the GPC separation of TMS-SOC from SOC distilled at 160°C, Q_4M_{10} and A, and B and C were separated as a group.

As a result, eight TMS derivatives, QM_4, Q_2M_6, Q_3M_6, Q_3M_8, Q_4M_8, Q_4M_{10}, Q_8M_8 and Q_8M_{10}, were isolated by GPC. The results of their elemental analyses are
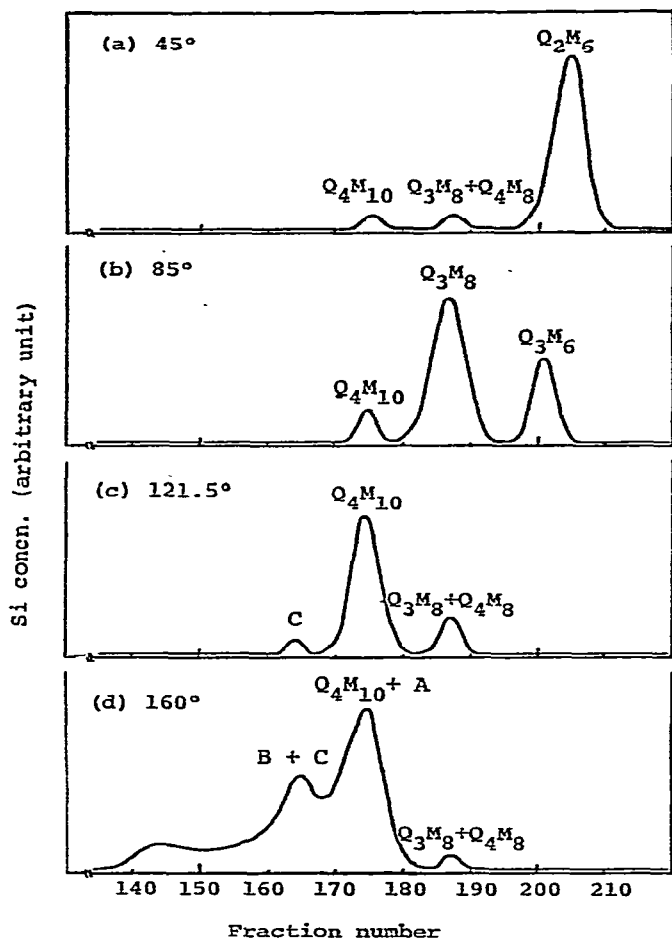
Fig. 6. Gel chromatograms of TMS-SOC (temperatures indicated are boiling points of SOC at *ca.* 15 mmHg). Two 90 × 1.5 cm I.D. columns plus one 45 × 1.5 cm I.D. column.

TABLE II

ELEMENTAL ANALYSES OF TMS DERIVATIVES ISOLATED BY GPC

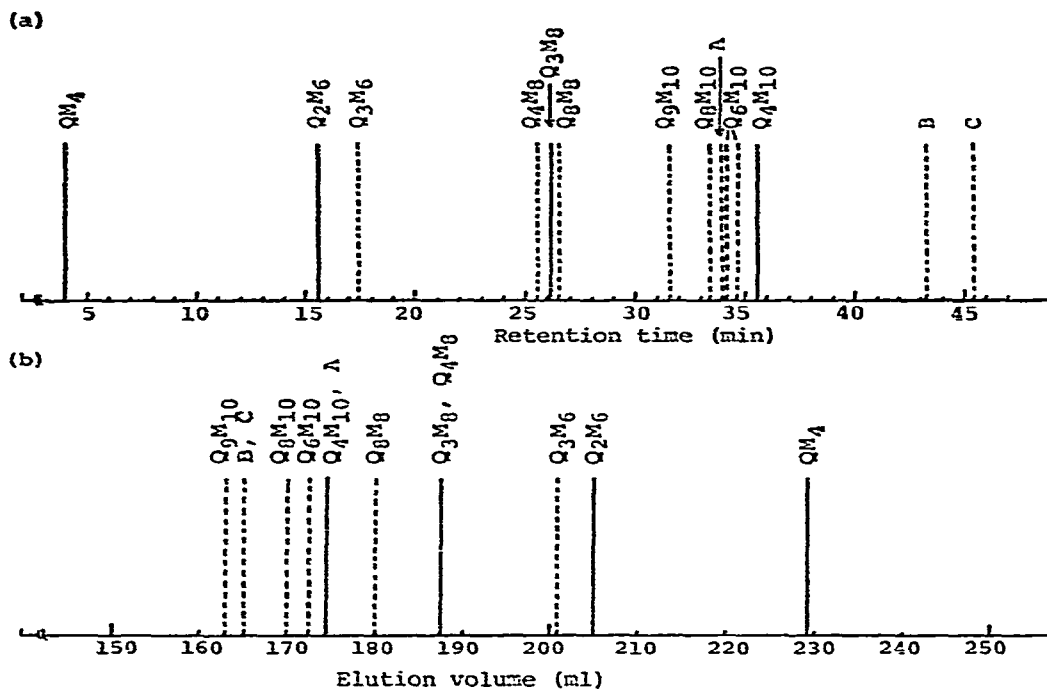| Compound	Found (%)		Calculated (%)	
	C	H	C	H
QM_4	37.35	9.39	37.45	9.45
Q_2M_6	35.50	8.95	35.59	8.98
Q_3M_6	32.25	7.96	32.29	8.17
Q_3M_8	34.98	8.69	34.73	8.76
Q_4M_8	32.18	8.05	32.39	8.17
Q_4M_{10}	33.83	8.41	34.24	8.64
Q_8M_8	25.69	6.41	25.51	6.42
Q_8M_{10}	27.67	6.84	27.89	7.02

(a)

(b)

Fig. 7. Representation of (a) the gas chromatogram and (b) the gel chromatogram of TMS derivatives.

given in Table II. Because the purity for Q_4M_{10} is about 93%, its found value is slightly different from the calculated value. Each TMS derivative was also identified by GC–MS.
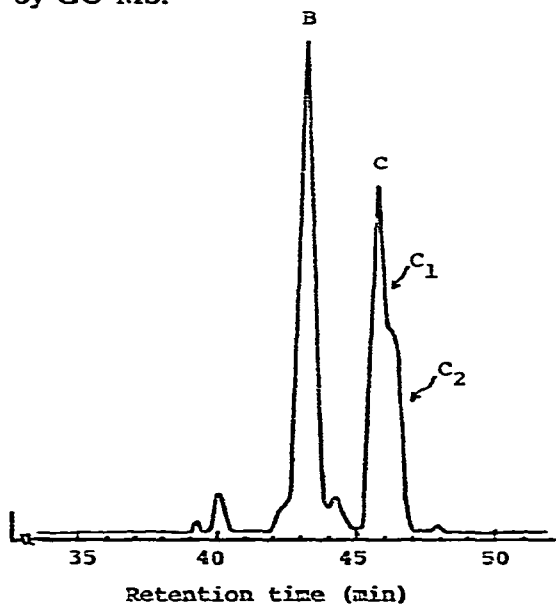

Fig. 8. Gas chromatogram of the peak portion shown as a mixture of B and C in Fig. 6d.

The GC retention time and the GPC elution volume of TMS derivatives the presence of which was confirmed in this work are illustrated in Fig. 7. The full lines indicate chain-type derivatives and the broken lines cyclic- and cage-type derivatives. The chain-type derivatives were eluted regularly in both GC and GPC. In GC, the peaks of the TMS derivatives are located so as to form well separated groups according to the number of trimethylsilyl groups (M number) contained in the molecule, as was also reported by Garzó and Hoebbel[15]. The M number for A is expected to be 10 and those for B and C are expected to be 12 according to the characteristic elution patterns. Considering that A, B and C may be derived from $Si_5O_4Cl_{12}$ or $Si_6O_5Cl_{14}$, it is concluded that A is either Q_5M_{10} or Q_6M_{10}, and B and C are either Q_5M_{12} or Q_6M_{12}, respectively. According to mass spectrometry, as the $[M - 15]^+$ ion for A was observed at m/e 1096, A is considered to be Q_5M_{10} (the calculated m/e value of $[M - 15]^+$ ion derived from Q_5M_{10} is 1095). Here, the $[M - 15]^+$ ion is that
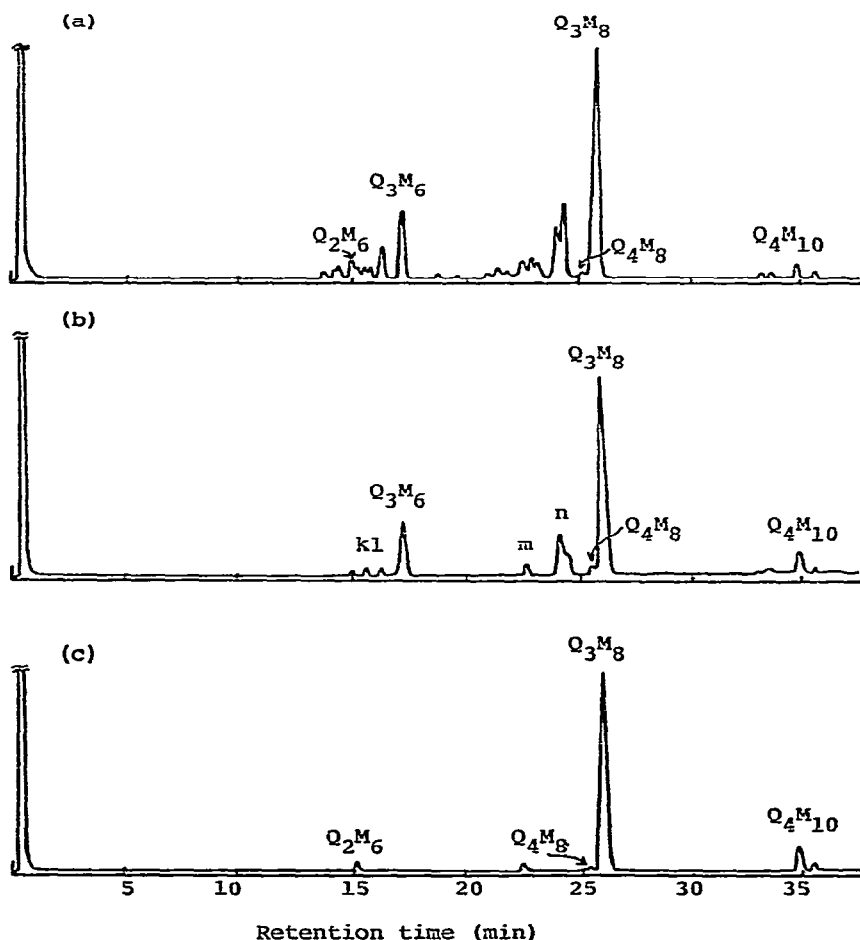

Fig. 9. Variations of peaks in gas chromatograms with time for TMS-SOC (85°C) in contact with resin. (a) Amberlyst 15 for 3 h; (b) mixed Amberlyst 15 and Amberlyst A-26 for 15 h; (c) mixed resin for 2 days.

corresponding to the loss of a methyl radical from the molecular ion and the most informative ion in the mass spectra of TMS derivatives. The gas chromatogram for a group of B and C, which was collected by GPC separation of TMS-SOC derived from SOC distilled at 160°C is shown in Fig. 8. From this chromatogram, C is expected to contain two components (C_1 and C_2 as shown in Fig. 8). The $[M - 15]^+$ ions for B, C_1 and C_2 obtained by GC–MS were observed at m/e 1318, 1258 and 1318, respectively. Therefore, C_1 is considered to be Q_5M_{12}, and B and C_2 are Q_6M_{12} (the calculated m/e values of $[M - 15]^+$ ions derived from Q_5M_{12} and Q_6M_{12} are 1257 and 1317, respectively). B and C_2 may be isomers of each other.

With silicon oxychlorides, the trimethylsilylation of the partially trimethylsilylated derivatives was not promoted effectively in contact with Amberlyst 15 at room temperature. As the presence of partially trimethylsilylated derivatives still having Si–Cl bonds was expected, the utility of Amberlyst A-26 anion-exchange resin was examined at room temperature. Although the trimethylsilylation was scarcely
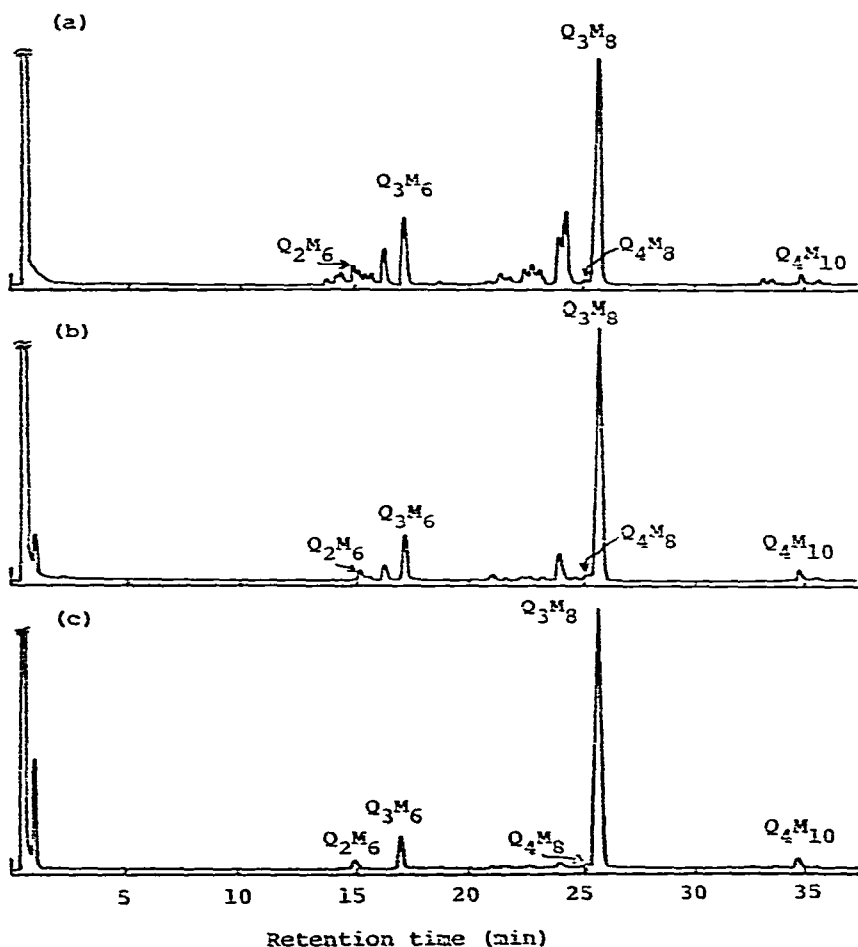

Fig. 10. Variations of peaks in gas chromatograms with refluxing time for TMS-SOC (85°C) in contact with Amberlyst 15. (a) 0 h; (b) 1 h; (c) 3 h.

promoted in contact with only Amberlyst A-26, it was promoted in contact with a mixture of Amberlyst 15 and A-26. Variations of peaks in the gas chromatograms with time for TMS-SOC (85°C) in contact with the resin are shown in Fig. 9. The peaks except for those indicated in Fig. 9a show the partially trimethylsilylated derivatives. They gradually disappeared with time and the completely trimethylsilylated derivatives, except for Q_3M_6, increased with time. Q_3M_6 gradually disappeared with time in contact with the mixed resin. This is probably due to the instability caused by a strain in the ring in Q_3M_6, as was described by Hoebbel *et al.*[9]. Therefore, the reaction time with the mixed resin was limited to 15 h for collecting Q_3M_6.

The $[M - 15]^+$ ions for the peaks labelled m and n in Fig. 9b were observed at m/e 754 and 784, respectively. The ion observed at m/e 43 in their mass spectra was regarded as $[C_3H_7]^+$. Therefore, m and n were identified as di- and mono-isopropyl-substituted trimethylsilyl derivatives of Q_3M_8, respectively. Similarly, the peaks, labelled k and l in Fig. 9b are considered to be di- and mono-isopropyl-substituted derivatives of Q_4M_6, respectively.

For the complete trimethylsilylation of the isopropyl-substituted trimethylsilyl derivatives, a long reaction time with the mixed resin at room temperature is required (Fig. 9). Therefore, the effect of heating on the complete trimethylsilylation of TMS-SOC was examined by reflux with Amberlyst 15 at *ca.* 120°C. Variations of the peaks in the gas chromatograms with refluxing time for TMS-SOC (85°C) in contact with Amberlyst 15 are shown in Fig. 10. The partially trimethylsilylated derivatives almost disappeared on refluxing for 3 h. As a result, it seems that for the complete trimethylsilylation of TMS-SOC, trimethylsilylation by refluxing with Amberlyst 15 at *ca.* 120°C is superior to that by contact with the mixed resin at room temperature.

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