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GAS CHROMATOGRAPHIC RETENTION CHARACTERISTICS OF TRIMETHYLSILYLATED SILICATE ANIONS

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SUMMARY

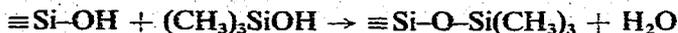
Pure volatile trimethylsilylated silicates of well-defined structures were prepared from different synthetic and natural silicates. Thin-layer chromatography followed by mass spectrometry was used for the separation and identification of the pure compounds. Eleven standard substances were chromatographed on gas chromatographic columns, having programmed temperatures, using four phases of different polarity. For the gas chromatographic characterization of the title compound, isothermic retention indices were also measured.

The retention of the trimethylsilylated silicates depended mainly on the number of trimethylsilyl groups present in the molecule. This resulted in similar retentions for molecules with rather different molecular weights and structures.

Homologue rules make possible the prediction of the identity of unknown peaks appearing in the chromatograms of natural and synthetic trimethylsilylated silicates.

INTRODUCTION

Silicate structures have been studied mainly by X-ray diffraction, but sometimes chemical methods have been used as well¹⁻³. About ten years ago, Lentz⁴ proposed the gas chromatographic (GC) analysis of the trimethylsilyl derivatives of silicate anions as a tool for the elucidation of silicate structures. A similar method was reported later by Götz and coworkers^{5,6}. According to this method, silicate minerals, which react with acids releasing silicic acids, may react in acidic medium further with mono-functional organosilicon compounds to give stable organosilyl derivatives. If the reaction partner of the silicic acid is, e.g., trimethylsilanol, formed from trimethylchlorosilane in aqueous medium, the reaction is :



These trimethylsilylated acids, designated further as TMS-SA's are soluble in common organic solvents and their volatility is high enough to make GC and mass spectrometric (MS) investigations possible.

When a silylated mineral is examined by GC after trimethylsilylation, usually the TMS derivative of the parent structure appears on the chromatogram as the main peak. In general, however, during trimethylsilylation, some side reactions occur too. These distort the GC pattern and decrease the yield of the main derivative.

Using the direct method of trimethylsilylation, Götz and Masson^{6,7} reported the conversion of the original structures into their trimethylsilyl derivatives without the formation of appreciable byproducts. In our experience, however, the suppression of the side reactions needs further investigation.

The aim of the present work was to study the GC behaviour of several TMS-SA structures obtained from synthetic and natural silicates after trimethylsilylation. Our samples were pure compounds, prepared by thin-layer chromatographic (TLC) separation of the trimethylsilylation reaction mixture. Molecular weights and stoichiometry of the compounds were established by MS and combustion analysis.

The compounds investigated are tabulated in Table I.

The short symbols in the third column of the table will be used for the designation of the samples. In these symbols $M = (\text{CH}_3)_3\text{SiO}_{0.5} = \text{TMS}$, and $Q = \text{Si}(\text{O}_{0.25})_4 = \text{skeletal SiO}_4 \text{ tetrahedron}$. Compounds marked by an asterisk in the table were produced for the first time in our laboratories.

The compound names and the structural representations indicate that linear, cyclic and polycyclic structures were investigated. For polycyclics the structures in the last column represent only examples, as several isomers are possible for each (see Table II). In the structural identification of the isomeric compounds ²⁹Si-nuclear magnetic resonance spectroscopy is a valuable tool⁸⁻¹⁰.

EXPERIMENTAL

The preparation of the TMS-SA's

TMSA-SA's were prepared by the trimethylsilylation of silicate minerals of well-defined structure, according to the direct method of Götz and Masson⁶.

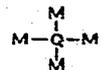
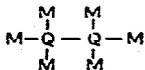
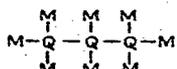
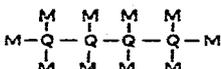
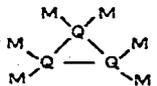
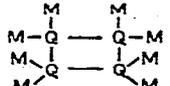
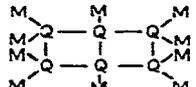
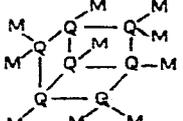
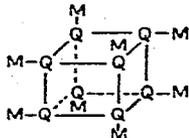
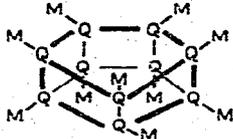
The composition of the silylation reagent—especially the amount of water—was varied slightly, in order to achieve maximal yield in the TMS-SA of the parent structure for all the silicates of different solubilities and water contents.

Detailed descriptions of the preparation of M_4Q , M_6Q_2 , M_8Q_3 , $M_{10}Q_4$, M_6Q_3 and M_8Q_4 (refs. 4, 6, 14), as well as of $M_{10}Q_7$ (ref. 11), M_8Q_8 (ref. 12), and $M_{10}Q_{10}$ (ref. 13) have already been given.

$M_{10}Q_6$ was prepared from tetraethylammonium silicate, $1.0 \text{ N}(\text{C}_2\text{H}_5)_4\text{OH} \cdot 1.0 \text{ SiO}_2 \cdot 10 \text{ H}_2\text{O}$. Hexamethyldisiloxane (30 ml), trimethylsilyl chloride (15 ml) and isopropanol (3 ml) were stirred together at 17°. Finely ground silicate (2.5 g) was added in portions and the mixture was shaken for 30 min. The siloxane layer was washed several times with water and dried. Amberlite 15 ion-exchange resin was added to the product, and the mixture was stirred for two days at ambient temperature. After filtration, hexamethyldisiloxane was removed by distillation at 130°. Two $M_{10}Q_6$ isomers were prepared from the end-product by TLC separation¹⁴.

For the trimethylsilylation of diopase the finely ground silicate (1 g) was

TABLE I
COMPOUNDS INVESTIGATED

<i>Trimethylsilylated silicic acid TMS-SA</i>	<i>Formula</i>	<i>Short symbol</i>	<i>Structural representation</i>
TMS Mono-SA	$[(CH_3)_3Si]_4[SiO_4]$	M_4Q	
TMS Di-SA	$[(CH_3)_3Si]_6[Si_2O_7]$	M_6Q_2	
TMS Tri-SA	$[(CH_3)_3Si]_8[Si_3O_{10}]$	M_8Q_3	
TMS Tetra-SA	$[(CH_3)_3Si]_{10}[Si_4O_{13}]$	$M_{10}Q_4$	
TMS Cyclotri-SA	$[(CH_3)_3Si]_6[Si_3O_9]$	M_6Q_3	
TMS Cyclotetra-SA	$[(CH_3)_3Si]_8[Si_4O_{12}]$	M_8Q_4	
TMS Bicyclohexa-SA*	$[(CH_3)_3Si]_{10}[Si_6O_{17}]$	$M_{10}Q_6$	
TMS Tricyclohepta-SA*	$[(CH_3)_3Si]_{10}[Si_7O_{19}]$	$M_{10}Q_7$	
TMS Hexacycloocta-SA*	$[(CH_3)_3Si]_8[Si_8O_{20}]$	M_8Q_8	
TMS Heptacyclodeca-SA*	$[(CH_3)_3Si]_{10}[Si_{10}O_{25}]$	$M_{10}Q_{10}$	

* Produced in the Zentralinstitut für anorganische Chemie, Berlin-Adlershof, G.D.R.

added to the stirred mixture of hexamethyldisiloxane (18 ml), trimethylsilyl chloride (4 ml), isopropanol (2 ml) and water (0.4 ml). The mixture was then shaken at 24° for 50 min. After this the procedure given for tetraethylammonium silicate was followed.

TABLE II
NUMBERS OF POSSIBLE AND INVESTIGATED ISOMERS

<i>Polycyclic isomers</i>	<i>Number of possible isomers</i>	<i>Number of isomers investigated</i>
M ₁₃ Q ₇	10	1
M ₁₃ Q ₆	8	2
M ₈ Q ₅	2	1
M ₁₃ Q ₁₀	2	1

Gas chromatography

The analyses were performed on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. The columns were as follows.

(1) 1.5 m × 2.7 mm stainless steel; 1% OV-1 on Chromosorb G AW DMCS-treated, 80–100 mesh.

(2) The same as (1); stationary phase, 3% OV-17.

(3) The same as (1); stationary phase, 3% QF-1.

(4) 20 m × 0.2 mm glass capillary column, coated with APL¹⁵.

Isothermic column temperatures are given in Table III. Conditions of the temperature programme were as follows: initial temperature, 70°; final temperature, 300°; programme rate, 10°/min.

TABLE III
DIMETHYLSILOXANE NUMBERS (DN) OF TRIMETHYLSILYLATED SILICIC ACIDS

<i>Short symbol</i>	<i>MW</i>	<i>APL</i> (<i>glass capillary</i>)		<i>OV-1</i> (<i>packed column</i>)		<i>OV-17</i> (<i>packed column</i>)	
		<i>Temp.</i> (°C)	<i>DN</i>	<i>Temp.</i> (°C)	<i>DN</i>	<i>Temp.</i> (°C)	<i>DN</i>
M ₄ Q	384	80	511.5	80	515.5	80	515
M ₆ Q ₂	606	140	796.5	140	797	140	792.5
M ₆ Q ₃	666	160	855.5	170	854	160	902
M ₆ Q ₄	888	200	1121.5	200	1117	200	1150
M ₈ Q ₃	828	210	1172	210	1138.5	210	1165.5
M ₆ Q ₈	1128	200	1170.5	200	1158.5		
				240	1141	240	1318
M ₁₀ Q ₇	1230	210	1413	240	1390.5	240	1522.5
M ₁₀ Q ₁₀	1410	210	1447	240	1399	240	1599.5
M ₁₀ Q ₆ (1)	1170	210	1446	240	1428.5	240	1549.5
M ₁₀ Q ₆ (2)	1170	210	1470	240	1445	240	1561
M ₁₀ Q ₄	1050	210	—	240	1456.5	240	1574

For the packed columns, nitrogen (20 ml/min), and for the capillary column hydrogen (2 ml/min), were used as carrier gas. Sample amounts: 10⁻⁵ g per component (packed columns) and 10⁻⁷ g per component (capillary column). The samples were diluted with *n*-heptane.

Retention indices were measured by the simultaneous injection of the sample compound, two suitable dimethylsiloxane chain oligomers — [(CH₃)₃SiO_{0.5}]₂ [(CH₃)₂SiO]_{*n*}— and methane¹⁶.

Retention times were measured by the timer unit of a Perkin-Elmer D-24 electronic integrator. Data were recorded with a resolution of 0.01 min by a Kienzle printer.

The precision of our retention indices was ± 2 DN units as calculated from three subsequent determinations.

RESULTS AND DISCUSSION

For the GC characterization of the title compounds isothermic retention indices were measured on various stationary phases. According to our earlier proposal¹⁶, the homologous series of dimethylsiloxane oligomers were used as secondary standards for the retention index determinations of these organosilicon compounds. The resulting retention value is called the dimethylsiloxane number, abbreviated as DN and defined as:

$$DN_x = \left[\frac{\log t'_x - \log t'_{D_m}}{\log t'_{D_{m+1}} - \log t'_{D_m}} + m \right] \cdot 100$$

t'_x , t'_{D_m} , $t'_{D_{m+1}}$ are the adjusted retention times for the sample and two subsequent dimethylsiloxane cycles, respectively.

The DN values for hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane are by definition 300 and 400, respectively. DN values can easily be converted to Kováts retention indices. For an example, DN values for M_4Q at 80° on APL and SE-30 are 511.5 and 515.5, respectively. The corresponding RI values in the Kováts system are 1017 and 1203, respectively.

DN values of the eleven TMS-SA's investigated, are shown in Table III. The three stationary phases were so chosen that they represented both polar and non-polar and, at the same time, both siloxane and non-siloxane phases.

The DN values on all the three phases reflect an interesting phenomenon: the DN values of the TMS-SA's investigated—regardless of M_4Q —form three well-separated groups. In the first group, *e.g.* on APL, DN values ranged from 800 to 900, in the second group from 1100 to 1200, and in the third from 1400 to 1500. In this way compounds of considerably different molecular weights and structures showed similar GC retentions. Let us look, *e.g.*, at OV-17 values of $M_{10}Q_{10}$ and $M_{10}O_4$. DN values are similar, whereas the molecular weights are considerably different; moreover, $M_{10}Q_4$ is a chain molecule and $M_{10}Q_{10}$ has a polycyclic cage structure.

It is evident from Table III that retention characteristics depend mainly on the number of M groups located on the surface of a molecule while the size and the structure of the molecular skeleton have only minor effects.

Data from the literature and our experience show that there exists no other class of compounds whose GC retention is so much determined by the surface atoms of the molecules, and where molecular weight and structure of the molecular skeleton play an almost negligible role. The considerable shielding effect of the voluminous TMS (M) groups may be considered as a possible explanation for this unexpected phenomenon.

In Fig. 1, temperature-programmed chromatograms of the mixture of the eleven sample molecules are demonstrated in the form of bar graphs on four stationary

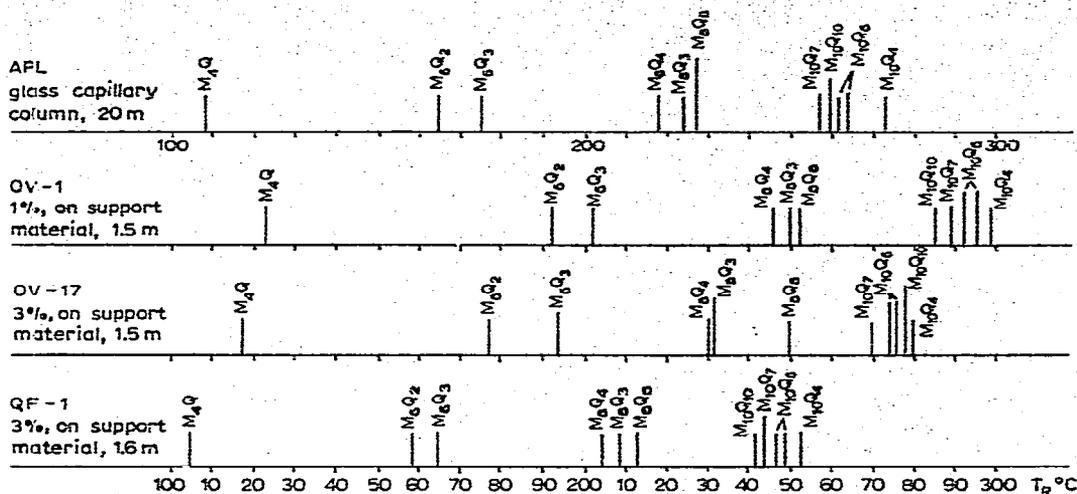


Fig. 1. Bar graphs of the chromatograms of mixed test substances.

phases. Complete separation was achieved only on the 20-m glass capillary column. Here, too, the elution pattern grouped according to the number of M groups in the molecule is evident.

Based on the well-known GC homologue rules, the temperature-programmed chromatograms make possible the prediction of the retention temperatures of some TMS-SA molecules not so far studied, e.g. $M_{10}Q_5$, $M_{12}Q_6$, $M_{12}Q_5$, M_6Q_6 .

From observed values for M_8Q_3 and $M_{10}Q_4$ as well as for M_6Q_3 and M_8Q_4 it follows that the enlargement of both cyclic and chain molecules with an M_2Q atomic group results in a retention temperature increment of about 44° on all phases investigated. Similarly, retention temperature values for M_8Q_8 and $M_{10}Q_{10}$ show that a retention temperature increment of approximately 30° is caused by the M_2Q_2 atomic group.

The retention values for some further polycyclics, such as M_8Q_6 , $M_{12}Q_7$, can also be estimated from the grouped elution pattern according to the number of M groups.

In conclusion it may be stated that the relationships found between GC retention and molecular structure form a basis for the more or less correct chemical and structural identification of unknown peaks appearing in the chromatograms of TMS-SA reaction mixtures.

This informative value of GC retention may be exemplified on dioptase, which according to X-ray investigations¹⁷ is a cyclohexasilicate. Götz and Masson⁷ investigated the silylation product of dioptase with GC and published a chromatogram in which the main peak with a retention temperature of 289° was claimed to be the TMS-cyclohexa-SA. According to our results this compound should have a retention temperature of about 330° . On repeating the experiments of Götz, in the chromatogram of the silylation product of the dioptase, we found no peak with a retention temperature of 330° but two peaks appeared with retention temperatures of 291 and 293° , respectively. These retention temperatures exactly coincide with those

of the two bicyclohexa-TMS-SA isomer standard substances ($M_{10}Q_6$) which are presented in our bar graphs in Fig. 1 (OV-1 column). They also coincide with the retention temperature published by Götz. Fig. 2 shows a chromatogram of the dioptase silylation product. The third main peak is not yet identified, but it is believed to be a third isomer of $M_{10}Q_6$. This chromatogram illustrates the high resolution of the isomers on a capillary column.

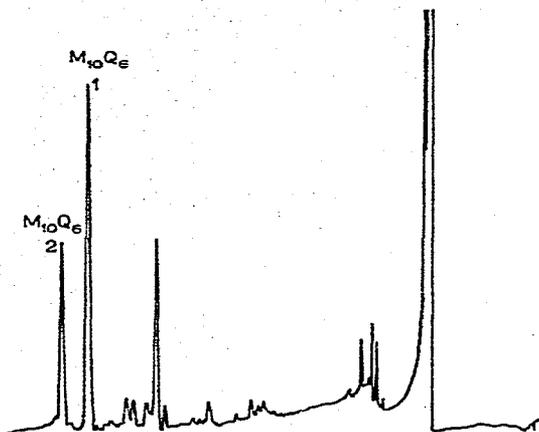


Fig. 2. Chromatogram of the dioptase silylation product. Column: 20 m glass capillary, coated with OV-101. Temperature: 245°. Carrier gas: N_2 . Inlet pressure: 0.6 atm. Split ratio: 1/50. Amplifier: 10×2 . Chart speed: 1 cm/min.

In conclusion we may state that trimethylsilylation followed by GC gives firm evidence for a new type of side reaction during trimethylsilylation: namely for the occurrence of intramolecular condensation or cyclization.

REFERENCES

- 1 E. Thilo and W. Miedreich, *Z. Anorg. Allg. Chem.*, 267 (1951) 76.
- 2 E. Thilo, W. Wieker and H. Stade, *Z. Anorg. Allg. Chem.*, 340 (1965) 261.
- 3 W. Wieker and D. Hoebbel, *Z. Anorg. Allg. Chem.*, 366 (1969) 139.
- 4 C. W. Lentz, *Inorg. Chem.*, 3 (1964) 574.
- 5 F. F. H. Wu, J. Götz, W. D. Jamieson and C. R. Masson, *J. Chromatogr.*, 48 (1970) 515.
- 6 J. Götz and C. R. Masson, *J. Chem. Soc. A*, (1970) 2683; (1971) 686.
- 7 J. Götz and C. R. Masson, *Comptes Rend. IX. Congr. Int. du Verre, Versailles, 1971*, p. 261.
- 8 D. Hoebbel, G. Garzó, H. Jancke, G. Engelhardt, P. Franke and W. Wieker, *Z. Anorg. Allg. Chem.*, in press.
- 9 G. Engelhardt, H. Jancke, M. Mägi, T. Pehk and E. Lippmaa, *J. Organometal. Chem.*, 28 (1971) 293.
- 10 H. Jancke, G. Engelhardt, M. Mägi and E. Lippmaa, *Z. Chem.*, 13 (1973) 392.
- 11 D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.*, 405 (1974) 267.
- 12 D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.*, 384 (1971) 43.
- 13 D. Hoebbel, W. Wieker, P. Francke and A. Otto, *Z. Anorg. Allg. Chem.*, in press.
- 14 D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.*, 405 (1974) 163.
- 15 G. Alexander, G. Garzó and G. Pályi, *J. Chromatogr.*, 91 (1974) 25.
- 16 G. Garzó and G. Alexander, *Chromatographia*, 4 (1971) 554.
- 17 H. G. Heide, K. Boll-Dornberger, E. Thilo and E. M. Thilo, *Acta Crystallogr.*, 8 (1953) 425.