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## GAS CHROMATOGRAPHY OF TRIMETHYLSILYLATED SILICATE ANIONS

### SEPARATION WITH GLASS CAPILLARY COLUMNS AND NEW ASPECTS IN DERIVATIZATION

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#### SUMMARY

The advantages of capillary-column gas chromatography (GC) in the analysis of trimethylsilylated silicate systems are demonstrated and separation parameters and measurement and calculation methods for the qualitative and quantitative analysis of different silicic acid solutions are outlined.

The problems of the trimethylsilylation procedures are discussed. Results obtained by GC after derivatization with bistrimethylsilylacetamide (BSA) as the trimethylsilylating agent indicate that both the unwanted condensation and hydrolysis during silylation are suppressed if the proton-trimethylsilyl exchange is accelerated, e.g., by a powerful trimethylsilyl donor such as BSA, and if the pH of the silylation reaction mixture is controlled.

Chromatograms of some silicic acid samples are compared with those of identical samples silylated according to Lentz and Götz-Masson, respectively. Comparison of both the qualitative and quantitative results indicates that the compositions of the original silicic acid solutions are best reflected in the chromatograms after silylation with BSA. The effect of the after-treatment of the silylated silicic acid solution with Amberlyst 15 cation-exchange resin is discussed separately.

## INTRODUCTION

Investigations on the gas chromatography (GC) of several trimethylsilylated (TMS) inorganic anions have been reported since 1964<sup>1-3</sup>. Among the different types of anions investigated, silicate anions seem to be of the greatest importance. The main reasons for this are the following. Low-molecular-weight (MW) silicates are important constituents of several minerals and industrial products. The reactions of these low MW silicates determine at the same time several industrial processes. The anionic constitutions of these silicate materials, the structures (stoichiometric and isomeric) and even the reactions going on in the industrial processes have scarcely been known, as apart from trimethylsilylation followed by GC only few methods give reliable information to the problems outlined.

The anionic composition of alkali silicate solutions<sup>1,4,5</sup>, silicate glasses<sup>6-8</sup>, metallurgical slags<sup>9</sup> and products of cement hydration<sup>10-13</sup> have so far been investigated by means of GC.

Detailed parameters for the GC measurements were first published by Wu *et al.*<sup>15</sup>. Using a packed column and a multi-level temperature programme, the trimeric chain silicate was eluted at 286° (23 min). In 1977, Dent Glasser *et al.*<sup>5</sup> published measurements using similar GC parameters and reported on the elution of hexameric and octameric species. Taking into account our earlier experiments<sup>14</sup>, the elution of these molecules is rather unlikely under the given operating conditions.

In 1974, Wu *et al.*<sup>9</sup> published chromatograms for metallurgical slag samples, obtained with the same column as earlier<sup>15</sup> but applying a more sophisticated temperature programme. The elution of all main components up to the tetrameric chain was achieved within 44 min (ref. 9).

In a previous paper<sup>14</sup> we reported some experiences gained by glass capillary separations of different trimethylsilylated silicate systems. Ten major peaks in these TMS-silicate systems were identified. They consist of the TMS-monosilicate, the trimethylsilylated dimeric, trimeric and tetrameric chains, tri- and tetracyclic compounds and four types of polycycles.

We also reported<sup>14</sup> a unique retention characteristic of this group of compounds.

Up to now, two methods have been used for the silylation of different silicate systems. The method proposed by Lentz<sup>1</sup> in 1964 proved to be more advantageous for silicate solutions than the direct method proposed by Götz and Masson<sup>16</sup> in 1970 (pointed out by Dent Glasser *et al.*<sup>5</sup> in 1977). For solid silicates, however, the later method was found better by the same group<sup>4,5</sup>. Essential features of the two methods are demonstrated in Table I.

The two methods have several common characteristics:

- (i) protonated silicate anions in strongly acidic aqueous solution are silylated in the interface layer of two immiscible liquid phases;
- (ii) the solvent is hexamethyldisiloxane (HMDS) + isopropanol;
- (iii) a large excess of silylating agent is applied; most of it is used for the silylation of water and isopropanol;
- (iv) the true silylating agent in both methods is probably trimethylchlorosilane (TMCS), which is produced in the Lentz method by hydrochloric acid cleavage from HMDS;

TABLE I  
COMPARISON OF SILYLATION METHODS

Parameter	Lentz <sup>1</sup> method	Götz and Masson <sup>16</sup> method	
Silylating mixture	Solvent	Part of 5 ml of HMDS* + 7.5 ml of isopropanol	9 ml of HMDS + 1 ml of isopropanol
	Etching agent	Part of 3.8 ml of conc. HCl + 3.1 ml of water	0.2 ml of water + HCl generated from 2 ml of TMCS**
	Silylating agent	Part of 5 ml of HMDS + part of 7.5 ml of HCl + Amberlyst 15	2 ml of TMCS + Amberlyst 15
Time of reaction	15 h	13 h	
Amount of sample	0.1 g of silicate	0.1 g of silicate	

\* HMDS = hexamethyldisiloxane.

\*\* TMCS = trimethylchlorosilane.

(v) overnight treatment with a cation-exchange resin completes the silylation reaction;

(vi) both methods employ millilitre volumes of reagents and gram amounts of the silicates.

In this work, only silicic acid (SA) solutions were investigated. Optimal conditions and methods for qualitative and quantitative analysis are presented and a new silylating method, employing bistrimethylsilylacetamide (BSA), is proposed. The results obtained are compared with those of the Götz and Masson and Lentz methods.

## EXPERIMENTAL

### Gas chromatography

A Hewlett-Packard Model 5830A microprocessor-controlled instrument with a flame-ionization detector (FID) was used. The column, a 16 m × 0.25 mm soft glass capillary, was coated without any pre-treatment with OV-1 silicone liquid phase (phase ratio *ca.* 600) and conditioned for several days at 240°. The column technology has been described earlier<sup>17</sup>. Detailed separation and detector parameters are given in the legend of Fig. 1.

For quantitative evaluation of the chromatograms, both the "Internal Standard" and the "Area %" automatic programmes of the microprocessor-controlled integrator of the instrument were used. The printout in the first method was a list of the relative amounts (expressed in SiO<sub>2</sub> amounts) of the eight main components, with known elemental compositions and known response factors, related to the total amount of the SA mixture (also expressed in SiO<sub>2</sub> amounts) consumed during the trimethylsilylation reaction. Consequently, the figures in the printout represent percentage SiO<sub>2</sub> values occurring as QM<sub>4</sub>, Q<sub>2</sub>M<sub>6</sub>, etc., on the chromatograms.

The "Area %" printout was used for calculating the approximate cumulative amounts of minor by-products appearing on the chromatograms. These values are also expressed in terms of SiO<sub>2</sub> percentages of the total trimethylsilylated SA sample.

Mono-, di- and trisilicic acid solutions (0.5 M) were obtained by the acidic hydrolysis (0.01 N hydrochloric acid, -2°) of tetramethoxysilane, hexamethoxydisiloxane and octamethoxytrisiloxane, respectively. The SA stock solutions were stored at -2° and samples were taken for silylation at stated intervals<sup>18</sup>.

*Silylation of SA solutions according to Lentz*<sup>1</sup>

HDMS (5 ml), isopropanol (7.5 ml), concentrated hydrochloric acid (3.8 ml) and water (3.1 ml) were stirred together for 1 h at ambient temperature. The mixture was cooled to 2° and 2 drops of 0.5 M SA solution (2.27 mg of SiO<sub>2</sub>) were added, while stirring vigorously. Stirring was continued, without cooling, for a further 1 h. A weighed amount of dodecamethylpentasiloxane (M<sub>2</sub>D<sub>3</sub>) as internal standard was then added and the mixture was washed four times by adding 30-ml portions of water followed by shaking and separation of the phases. Then the organic phase was shaken for 3–4 days in the presence of Amberlyst 15 ion-exchange resin. After filtration, 1–5- $\mu$ l volumes were injected.

*Silylation of SA solutions according to Götz and Masson*<sup>16</sup>

HMDS (9 ml), isopropanol (1 ml) and TMCS (2 ml) were stirred together for 10 min at ambient temperature. Then 0.2 ml of water was added and the mixture stirred again for 2 min. After adding 3 drops of 0.5 M SA solution (SA content equivalent to 3.42 mg of SiO<sub>2</sub>) the mixture was stirred vigorously for a further 20 min. A weighed amount of M<sub>2</sub>D<sub>3</sub> as internal standard was then added in the form of a stock solution and the mixture was washed four times with water by shaking and separation of the phases. Then the organic phase was shaken for 3–4 days in the presence of Amberlyst 15 ion-exchange resin. Volumes of 1–5  $\mu$ l were injected after filtration.

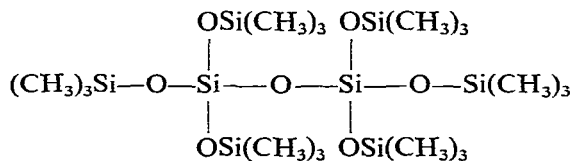
*Silylation with bistrimethylsilylacetamide (BSA)*

HMDS (5 ml), acetone (10 ml) and BSA (3.5 ml) were mixed and allowed to stand for 20 min at ambient temperature. (BSA used for this purpose was acidified with gaseous hydrogen chloride, to give a 0.075 M H<sup>+</sup> solution.) After cooling, a controlled and weighed amount of 0.5 M SA solution (*ca.* 2 drops; 2.27 mg of SiO<sub>2</sub>) was added while stirring the homogeneous mixture at 15°. Stirring was continued for 15 min, then the mixture was allowed to stand for 3–4 h at ambient temperature. Water (40 ml) was added, followed by a weighed amount (1.7–3.5 mg) of M<sub>2</sub>D<sub>3</sub> as internal standard, and mixing. After separating the phases, the organic phase was washed with three 30-ml portions of water. Volumes of 1–5  $\mu$ l were injected.

*Nomenclature*

Silicates consist of condensed SiO<sub>4</sub> tetrahedra. In addition to orthosilicate, chain, branched-chain, double-chain, cyclic and polycyclic structures and chain-cycle combinations of low, medium and high MW, sheet and cross-linked silicates of high MW are also known.

In order to silylate any low-MW silicate, it has to be dissolved by acidic water, *i.e.*, changed into the corresponding silicic acid. Therefore, it is assumed that the protonated forms of the anions are converted into the TMS compounds. For example, the empirical formula of the mineral hemimorphite is Zn<sub>4</sub>(OH)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O; *i.e.*, the mineral contains Si<sub>2</sub>O<sub>6</sub><sup>6-</sup> anions, but the acidic solution consists mainly of H<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> molecules and Zn salts. After silylation, the (TMS)<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> organosilicon compound:



has to be chromatographed. Let us further designate one tetrahedron corresponding to one  $\text{SiO}_2$  in a condensed silicate system as Q (one tetrafunctional Si atom) and the  $(\text{CH}_3)_3\text{SiO}_{1/2}$  atomic group resulting from the silylation as M (one monofunctional Si atom)<sup>14</sup>. Therefore, the trimethylsilylated hemimorphite will be designated as  $\text{Q}_2\text{M}_6$ . This formula shows that the original structure is a disilicate system with six negative charges, *i.e.*, it is a chain silicate. Similarly,  $\text{Q}_4\text{M}_8$  was originally a cyclotetrasilicate anion while, *e.g.*,  $\text{Q}_5\text{M}_8$  another, actually polycyclic structure.

Let us arbitrarily define the MW of trimethylsilylated bicyclododecasilicate ( $\text{Q}_{12}\text{M}_{12}$ ; MW = 2664) as the upper limit for low-MW silicate anions. In this case an approximate calculation of the stoichiometrically and sterically possible low-MW silicate anions (combining 1, 2, 3, . . . , 12 silicon atoms and 4, 6, 8, 10, 12 charge numbers) gives positively more than 250 species. Considering this definition, the terms "low-MW" and "gas chromatographically accessible" silicate anions coincide (*cf.*, discussion of results).

## RESULTS AND DISCUSSION

It is known from earlier experiments<sup>14</sup> that the TMS-silicate peaks are located so as to form well separated groups in the temperature-programmed chromatogram (this is also evident from the representative chromatogram shown in Fig. 1).

Retention index measurements on standard substances have shown that peaks of TMS-silicates with identical M numbers, *i.e.*, silicates with identical charge numbers form one group. As a consequence, compounds of considerably different MW (*e.g.*, 1170 and 1410) and structures (chains and mostly compact cage structures) are eluted with very similar GC retentions.

Due to the above retention characteristic of the TMS-silicic acids, columns with very high separation efficiencies are needed in order to obtain a reasonable resolution for the different compounds with identical M numbers (for  $M = 10$  compounds more than 50 species and for  $M = 12$  approximately 150 species are to be expected). As for a further advantage, when using highly efficient (preferably glass capillary) columns in silicate GC, all of the complex silicate systems contain the monomer and "oligomers", in a wide variety with respect to both structure and MW, and also polymers. Part of the "oligomers" in these systems represents transitional forms towards the polymeric structures. Therefore, the amount of the GC information is increased by increasing the MW limit of the gas chromatographically accessible compounds.

On the other hand, if the conditions are suitable, the elution time of a given compound in a capillary column is considerably shorter than in a packed column. Therefore, the use of capillary columns is clearly advantageous if the upper MW limit of the gas chromatographically accessible species has to be increased.

A typical BSA silylated silicic acid gas chromatogram, taken by glass capillary column, is shown in Fig. 1.

The column and separation parameters were designed in advance so as to give a relatively short analysis time (19 min), and proper separation of all the important low-MW SA components (*i.e.*, those with MW up to 2664) could be achieved simultaneously. This can be regarded as a considerable progress compared with the best results obtained with packed columns by Masson *et al.*<sup>9</sup>.

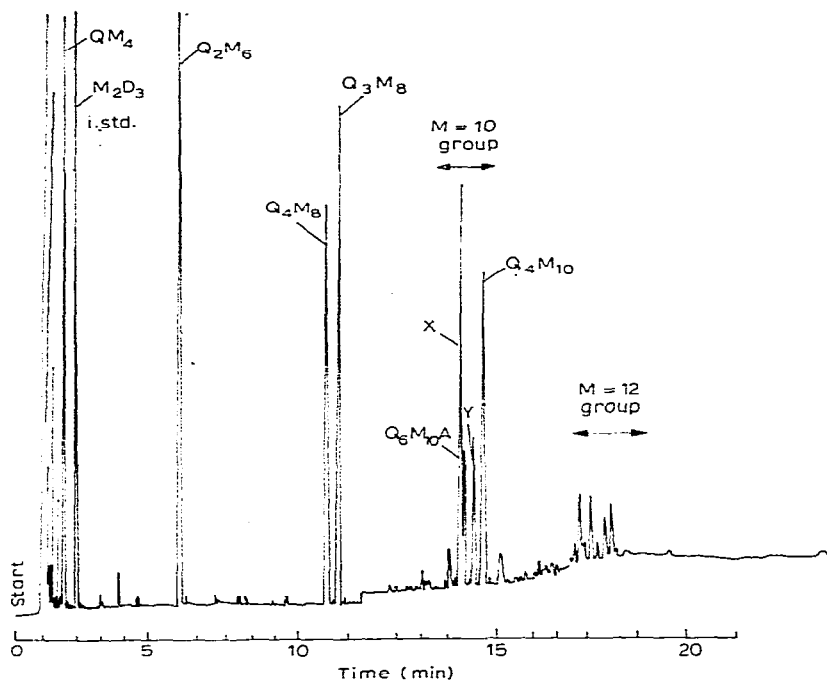


Fig. 1. Capillary gas chromatogram of a 0.5 M di-SA sample silylated with BSA in the eighth h after the formation of the SA. Column: 16 m  $\times$  0.25 mm I.D. glass capillary. Stationary phase: OV-1; phase ratio *ca.* 600. Carrier gas: nitrogen; linear velocity, *ca.* 30 cm/sec. Splitting ratio: *ca.* 25. Detector: FID, make-up gas, N<sub>2</sub> (20 ml/min). Injection port temperature: 330–380°. Detector block temperature: 350°. Electrometer range: 1. Electrometer attenuation: 16. Chart speed: programmed. Column temperature: initial 115°, programmed at 10°/min to 300°. Open identifications: X = Q<sub>4</sub>M<sub>10</sub> branched?; Y = Q<sub>6</sub>M<sub>10</sub>, "B" or Q<sub>5</sub>M<sub>10</sub>.

All peaks marked with compound names were positively identified, partly with help of reference substances, partly by gas chromatography–mass spectrometry (GC–MS), or both. The presence of only small amounts of Q<sub>3</sub>M<sub>6</sub> and the absence of incompletely silylated molecules in the systems silylated by the BSA method are proved.

The identity of peak X has not been determined unambiguously. It represents most probably a branched chain, Q<sub>4</sub>M<sub>10</sub>. This statement is based on (a) retention correlations, (b) MS identification following incomplete GC resolution and (c) provisional informations on the polymerization mechanism of the SA solutions (to be published later). Peak Y is assumed to be Q<sub>6</sub>M<sub>10</sub> "B" or Q<sub>5</sub>M<sub>10</sub> (ref. 19).

On the basis of the retention–peak identity correlations briefly discussed in a previous paper<sup>14</sup>, further tentative identifications are possible. The double peak at RT = 14.13 represents M = 10 polycycles, most probably Q<sub>7</sub>M<sub>10</sub> and/or compounds in the Q<sub>8</sub>M<sub>10</sub>–Q<sub>10</sub>M<sub>10</sub> range. Peaks in the fifth peak group (RT = 17–19) represent M = 12 compounds, but based on the referred retention rules Q<sub>6</sub>M<sub>12</sub> (hexacyclic) and Q<sub>5</sub>M<sub>12</sub> (pentameric chain) are probably missing.

Several trimethylsilylated silicate systems (*e.g.*, sodium silicate solutions, tetraethylammonium silicate, the mineral diopside) have already been investigated using

the same or similar GC conditions. We did not succeed in detecting TMS-cyclohexasilicate in any of the three systems investigated. As there are positive indications that all three systems contain cyclohexasilicates, it is probable that intermolecular condensation resulting in  $Q_6M_{10}$  and occurring either during silylation (*e.g.*, with diophtase<sup>19</sup>) or in the original solutions (*e.g.*, with the silicate solutions) may account for the absence of this peak. However, failure of evaporation or elution in the course of GC cannot be excluded either.

In addition to routinely accessible quantities, FID response values of the individual compounds in the mixture are essential for the exact quantitative evaluation of the chromatograms. As has already been pointed out by Götzt<sup>20</sup>, these values are significantly different for the common types of silicate anions.  $QM_4$ ,  $Q_2M_6$ ,  $Q_4M_8$  and  $Q_6M_{10}$  were available as pure standard substances, and response factors relative to  $M_2D_3$  (the internal standard) were therefore directly determined. In order to obtain reliable data for the relative response factors of the remaining two main components,  $Q_3M_8$  and  $Q_4M_{10}$  (which are difficult to prepare in a pure state), the correlation shown in Fig. 2 was used. The empirical correlation is fairly reliable and regarding mechanism of the FID operation rather acceptable.

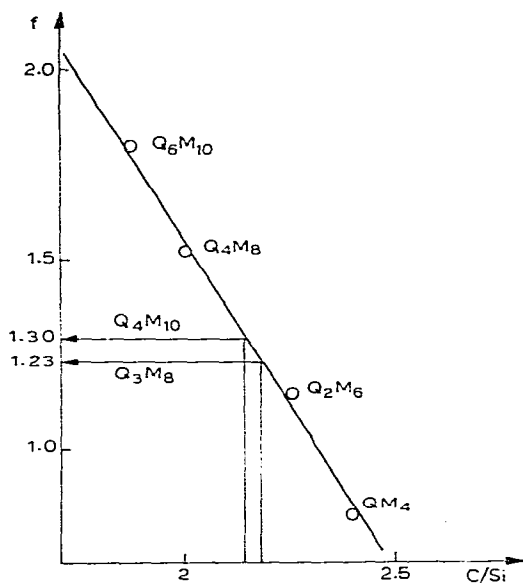


Fig. 2. Correlation between the FID response factors and the atomic composition of the molecules.

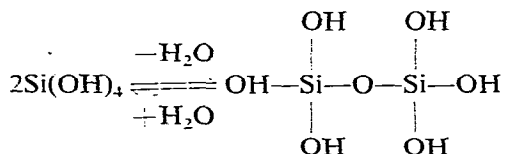
The following FID response factors were therefore used:  $M_4Q$  0.83 (measured),  $M_2D_3$  1.00 (internal standard),  $Q_2M_6$  1.14 (measured),  $Q_3M_8$  1.23 (interpolated),  $Q_4M_{10}$  1.30 (interpolated),  $Q_4M_8$  1.52 (measured) and  $Q_6M_{10}$  1.79 (measured).

The precision of the results calculated from 3–5 replicate GC determinations was <5% for the major and <20% for the minor components in terms of relative standard deviation.

The accuracy of the composition data of the main components is limited mainly by the silylation reaction. The accuracy of the cumulative relative amount of the minor by-products, however, has a further limitation. As both the elemental composition (stoichiometric factors) and FID response factors of these compounds were unknown, percentage  $\text{SiO}_2$  values equivalent to their summarized GC signals were calculated by applying probable approximations for these values. This treatment has introduced a definite source of error into the quantitative evaluation. The reproducibility of the retention times indicated in the chromatograms was excellent even with the unidentified minor peaks.

### *Trimethylsilylation*

Complete elimination of disturbing side-reactions has never been achieved in the course of silylations according to Lentz and Götz-Masson (standard methods). Therefore, the qualitative and quantitative distribution of the TMS-silicates measured by GC has not been completely identical with that of the original sample. The nature of these side reactions can be exemplified by the following equilibrium reaction, which takes place in aqueous medium:



Similar equilibria take place with each protonated silicate anion. The equilibrium constants of these reactions are strongly dependent on pH and the reaction rates of both condensation and hydrolysis have a minimum between pH 2 and 3. Therefore, if any of the silicate anions spends sufficient time in aqueous solution, as a result of several consecutive equilibration reactions a complex mixture is formed and the qualitative and quantitative anion distribution depends on time, concentration and pH.

On the other hand, the standard silylation methods are far too slow, occur in strongly acidic ( $\text{pH} < 1$ ) aqueous solutions and the reaction may be accompanied by changes in concentration.

From these facts it follows that disturbing side-reactions during silylation can be depressed only by slowing down the side-reactions and speeding up the silylation reaction. In our opinion, this can be achieved if the pH during silylation is controlled and a more powerful silylating agent is employed.

In order to accelerate the silylation reaction, weakly acidified BSA was used first as the silylating agent and isopropanol was replaced with acetone. Acetone was added in such an amount that the reaction mixture appeared to be a single homogeneous phase after the addition of the SA solution.

In order to demonstrate that side-reactions were not occurring if silylation was performed with BSA, the quantitative distribution of four main components of the SA solutions ( $\text{QH}_4$ ,  $\text{Q}_2\text{H}_6$ ,  $\text{Q}_3\text{H}_8$  and  $\text{Q}_4\text{H}_8$ ) was first measured, without silylation, by means of  $^{29}\text{Si}$  NMR spectroscopy<sup>21,22</sup>. The results were in acceptable agreement with the GC results obtained after BSA silylation of the same samples.



For a further qualification of this silylation method, freshly prepared (lifetime 1 min) 0.5 M (pH = 2) mono- and disilicic acid solutions were chosen as the silicate systems. It was assumed that hydrolysis (leading to monosilicic acid) or condensation (leading to di- and trimeric or higher silicic acids) had taken place only to a small extent. Consequently, in a 1-min lifetime sample nearly 100% of the weighed  $\text{SiO}_2$  had to appear as  $\text{QM}_4$  (mono-SA sample) and  $\text{Q}_2\text{M}_6$  (di-SA sample) in the chromatograms and all other components indicate hydrolysis or condensation during the silylation process. The sum of the  $\text{SiO}_2$  percentages calculated for each peak in the chromatogram indicates the recovery of the silylation reaction, as the formation of high-MW products in the original SA solution can be excluded after a 1-min hydrolysis time. Table II shows the results obtained with the BSA method on 1-min samples.

TABLE II  
RESULTS OBTAINED WITH THE BSA METHOD FOR 1-min LIFETIME SAMPLES

Sample	$\text{SiO}_2$ (%) occurring as									$\text{SiO}_2$ recovery of the silylation (%)
	$\text{QM}_4$	$\text{Q}_2\text{M}_6$	$\text{Q}_4\text{M}_8$	$\text{Q}_3\text{M}_8$	X	$\text{Q}_6\text{M}_{10}$	Y	$\text{Q}_4\text{M}_{10}$	Unknown by-products	
Mono-SA	77.0	10.0	—	1.2	—	—	—	—	—	88.2
Di-SA	1.0	84.0	—	1.1	—	—	0.4	1.0	1.1	88.6

Table III demonstrates the reproducibility of replicate silylation procedures for SA solutions of different lifetimes by the BSA method. The results are mean values calculated from three GC determinations. Reproducibilities of the replicate silylations calculated from the data in Table III are between 1 and 20% in terms of relative standard deviation. For the long-term samples, the  $\text{SiO}_2$  recovery data include, in addition to reaction recovery, the amount of high-MW silicates that had not become volatile by silylation.

Table IV gives results for the comparison of the BSA silylation method and the standard methods performed without Amberlyst after-treatment applied to mono-SA samples. Let us consider the following three aspects:

(i) extent of side-reactions reflected in the distribution of the main components;

(ii) extent of side-reactions reflected in the amount and quality of additional products;

(iii) recovery of silylation.

(i) With short lifetime (2 min) samples, the low percentage of  $\text{QM}_4$  indicates condensation during derivatization reactions. Therefore, the Götz and Masson method proved to be far inferior with these samples. The BSA method seems to be only slightly better than the Lentz method in this respect. For a medium lifetime (120 min) sample, where the condensation reactions are already progressing ( $\text{Q}_2\text{M}_6$  is the major component in the mixture) the Götz and Masson method seems to

TABLE III  
REPRODUCIBILITY OF REPLICATE SILYLATION PROCEDURES BY THE BSA METHOD

Sample	Hydrolysis time	SiO <sub>2</sub> (%) occurring as										Sum of by-products unknown	Sum of recovered volatiles	Comments
		QM <sub>4</sub>	Q <sub>3</sub> M <sub>6</sub>	Q <sub>4</sub> M <sub>8</sub>	Q <sub>5</sub> M <sub>10</sub>	X*	Q <sub>6</sub> M <sub>10</sub> /I	Y**	Q <sub>4</sub> M <sub>10</sub>					
Mono-SA	2 min	61.3	8.1	—	0.6	—	—	—	0.3	—	—	—	70.3	SiO <sub>2</sub> recovery of the silylation
Mono-SA	2 min	62.8	6.8	—	0.5	—	—	—	0.2	—	—	0.5	70.8	
Mono-SA	120 min	13.6	30.2	6.6	19.1	4.2	—	0.9	2.9	—	—	4.5	81.9	SiO <sub>2</sub> recovery of the silylation
Mono-SA	120 min	10.3	26.9	7.5	18.7	5.1	—	0.6	5.0	—	—	3.5	77.6	
Mono-SA	24 h	2.7	3.5	8.6	3.0	6.6	3.4	3.3	3.1	—	—	9.4	43.6	SiO <sub>2</sub> recovery of the silylation and GC
Mono-SA	24 h	2.8	2.7	7.0	2.5	5.7	3.0	3.2	2.9	—	—	7.8	37.6	
Tri-SA	2 min	0.4	2.6	0.4	53.5	—	—	—	0.5	—	—	3.5	60.9	
Tri-SA	2 min	0.4	2.8	0.4	50.1	—	—	—	0.9	—	—	3.0	57.6	

\* X = Q<sub>4</sub>M<sub>10</sub> branched?

\*\* Y = Q<sub>6</sub>M<sub>10</sub> "B" or Q<sub>3</sub>M<sub>10</sub>.

improve. If  $QM_4$  and  $Q_2M_6$  values are compared, the conditions of the Lentz method appear to favour the hydrolysis of the  $Q_2M_6$  species. The preference for cyclization during both standard silylation procedures is a further striking characteristic ( $O_4M_8:O_3M_8$  ratios). When silylating highly condensed long-term samples (24 h), the results obtained with the two standard silylation procedures become similar.

Consequently, it can be concluded that the chemical conditions during Götze and Masson silylation promote condensation of the mono-SA species, whereas those during Lentz silylation help the same condensation of molecules containing 3, 4, 5 or 6 silicon atoms and hydrolysis. The BSA method seems to suppress all of these disturbing effects to a reliable extent.

(ii) The superiority of the BSA method becomes more evident if the amounts and quality of the additional products are compared. The trace amounts of these in the 2-min sample seem to be an especially important argument in favour of the BSA method. It is important that in condensed long-term samples, where the total amount of additional products was significant also when silylation was performed by the BSA method, the quality of the additional products was different compared with that obtained by applying the two standard methods. The amounts of these individual products did not exceed 1–2% in the BSA silylated samples. As a result of the Götze and Masson and Lentz silylations, however, additional products appear in amounts of up to 2–6% each.

Four additional peaks which appeared in the SA samples in amounts larger than 1% only after silylation according to Lentz and Götze and Masson were also identified positively by GC-MS. GC-MS results are given in Table V.

As a first conclusion from Tables IV and V it can be stated that incomplete silylation ( $Q_2M_5OH$  and  $Q_3M_7OH$ ) occurred only if Lentz or Götze and Masson silylation was used.

The appearance of  $Q_3M_6$  (TMS-cyclotrisilicate) and  $Q_6M_6$  (TMS-bicyclohexasilicate) in certain samples illustrates once again the preference for cyclization (already mentioned in the discussion of the  $Q_4M_8:Q_3M_8$  ratios) in samples silylated by means of the standard methods. MS identification performed on unresolved samples proved the presence of another bicyclic compound ( $Q_6M_8$ ) which can be derived by stepwise inter- and intramolecular condensation starting from  $Q_3M_6$  or  $Q_6M_{12}$ . Therefore, it is probable that the peaks with  $RT = 9.7$  and  $9.8$  are two isomers of  $Q_6M_8$ .

In order to explain the formation of the additional polycyclic products, a scheme showing part of the condensation mechanism of SAs is demonstrated in Fig. 3. In this scheme the molecules appear in their TMS forms, but actually the protonated forms of the SAs react. Therefore,  $M_2$  means  $H_2O$  and  $QM_2$  means  $SiO_2 \cdot H_2O$  in reality.

The reactions in this scheme show that cyclization requires an additional intramolecular condensation step compared with the formation of chains with equal Si numbers.

The chances of cyclization or enlarging the molecule via condensation are probably not equal but depend on concentration, pH and the quality of the molecule. Anyway, the occurrence of subsequent reaction steps needs additional time. In addition, if cyclization is preferred, the range of possible condensation products accessible by GC becomes greater.

TABLE IV  
COMPARISON OF DIFFERENT SILYLATION METHODS USING MONO-SA SAMPLES

Hydrolysis time	Silylation method	$\text{SiO}_2$ (%) occurring as								
		$Q_1M_4$	$Q_2M_6$	$Q_4M_8$	$Q_3M_8$	$X^*$	$Q_6M_{10A}$	$Y^{**}$	$Q_4M_{10}$	Sum of unknown by-products
2 min	Götz and Masson	42.1	35.6	3.5	12.9	1.2	—	—	1.2	5.4
2 min	Lentz	83.1	13.2	0.1	0.2	—	—	—	0.2	3.2
2 min	BSA***	88.1	10.6	—	0.7	—	—	—	0.3	0.3
120 min	Götz and Masson	9.7	27.2	13.4	18.9	8.6	1.8	1.1	3.9	15.4
120 min	Lentz	19.4	29.4	16.5	13.7	4.5	1.4	0.2	0.6	14.3
120 min	BSA***	15.1	36.3	8.9	24.1	5.8	—	1.0	4.6	4.1
24 h	Götz and Masson	4.0	4.8	12.8	3.7	7.8	4.9	2.4	2.2	14.9
24 h	Lentz	3.8	2.8	6.2	0.6	1.0	0.8	0.5	—	14.3
24 h	BSA***	3.6	3.8	8.7	3.1	6.8	3.5	4.2	3.8	11.5

\* X =  $Q_4M_{10}$  branched?.

\*\* Y =  $Q_6M_{10}$  "B" or  $Q_5M_{10}$ .

\*\*\* Mean values derived from replicate silylations.

TABLE V

RT	Formula
4.8	$Q_2M_5OH$
6.3	$Q_3M_6$
8.9	$Q_3M_7OH + Q_6M_6$

TABLE VI  
EFFECT OF THE TREATMENT WITH AMBERLYST 15 AFTER SILYLATION WITH BSA

Sample	Hydrolysis time (min)	Amberlyst	$\text{SiO}_2$ (%) occurring as							
			$Q_1M_4$	$Q_2M_6$	$Q_4M_8$	$Q_3M_8$	$X^*$	$Q_6M_{10A}$	$Y^{**}$	$Q_4M_{10}$
Mono-SA	2	With	61.3	8.1	—	0.6	—	—	—	0.3
Mono-SA	2	Without	62.8	6.8	—	0.5	—	—	—	0.2
Di-SA	70	With	4.0	33.9	3.8	4.9	0.6	—	0.3	2.7
Di-SA	70	Without	3.8	35.7	4.4	5.7	0.9	—	0.3	3.5
Di-SA	240	With	5.4	22.0	11.1	12.1	5.8	1.2	1.5	4.2
Di-SA	240	Without	5.3	21.4	10.7	11.8	5.8	1.2	1.4	4.3
Di-SA	480	With	4.7	12.3	12.6	9.5	8.3	2.6	2.8	4.7
Di-SA	480	Without	4.7	12.2	13.3	10.0	8.9	2.8	2.9	5.1

\* X:  $Q_4M_{10}$  branched?.

\*\* Y:  $Q_6M_{10}$  "B" or  $Q_5M_{10}$ .

\*\*\* Calculated with approximate response and stoichiometric factors.

§  $\pm \leq 1\%$ .

<i>Approximate amounts (SiO<sub>2</sub>, %) of by-products with RT values and formulae</i>										
<i>Corrected sum of recovered volatiles</i>	<i>Measured recovery of silylation</i>	<i>RT = 4.3</i>	<i>RT = 4.8; Q<sub>2</sub>M<sub>5</sub>OH</i>	<i>RT = 6.3; Q<sub>3</sub>M<sub>6</sub></i>	<i>RT = 8.9 Q<sub>3</sub>M<sub>7</sub>OH + Q<sub>6</sub>M<sub>6</sub></i>	<i>RT = 9.7 + 9.8; Q<sub>6</sub>M<sub>8</sub>?</i>	<i>RT = 12-13; group</i>	<i>RT = 14.3</i>	<i>RT = 16-17; group</i>	<i>RT = 18-19; group</i>
100	76.2	+	2.4	1.6		1.3				
100	77.3		+	+	+					
100	78.0	+	2.3	+						
100	66.7		3.5	4.5		3.5		+		+
100	78.9	+	1.2	1.6	5.8	1.7	4.0			
100	79.0	+		+	+		+	+	+	+
36.3	—		+	+		1.5	5.7	3.9		2.1
30.0	—	+	+	+	5.5	1.2	5.4		+	
49.0	—			+			+	2.0	+	6.5

Considering the quality of the additional products found as a result of Götz and Masson and Lentz silylations, the actual pathway of cyclization is probably the part shown in the box in the scheme. The main components after BSA silylation are circled in the scheme.

The identifications of the additional products together with the reaction pathways in Fig. 3 make it even more probable that the compositions of the original SA

<i>Approximate** amounts (SiO<sub>2</sub>, %) of by-products with RT values and formulae<sup>§</sup></i>							
<i>Sum of unknown by-products***</i>	<i>Sum of recovered volatiles</i>	<i>RT = 4.3</i>	<i>RT = 4.8; Q<sub>2</sub>M<sub>5</sub>OH</i>	<i>RT = 6.3; Q<sub>3</sub>M<sub>6</sub></i>	<i>RT = 8.9; Q<sub>6</sub>M<sub>6</sub> + Q<sub>3</sub>M<sub>7</sub>OH</i>	<i>RT = 12-13</i>	<i>RT = 18-19</i>
—	70.3						
0.5	70.8	+					
0.8	51.0	+					
1.5	55.8	+		+		+	+
2.9	66.2	+		+	+	+	+
3.5	65.9	+		+	+	+	+
5.0	62.5	+		+	+	+	+
5.5	65.3	+		+	+	+	++

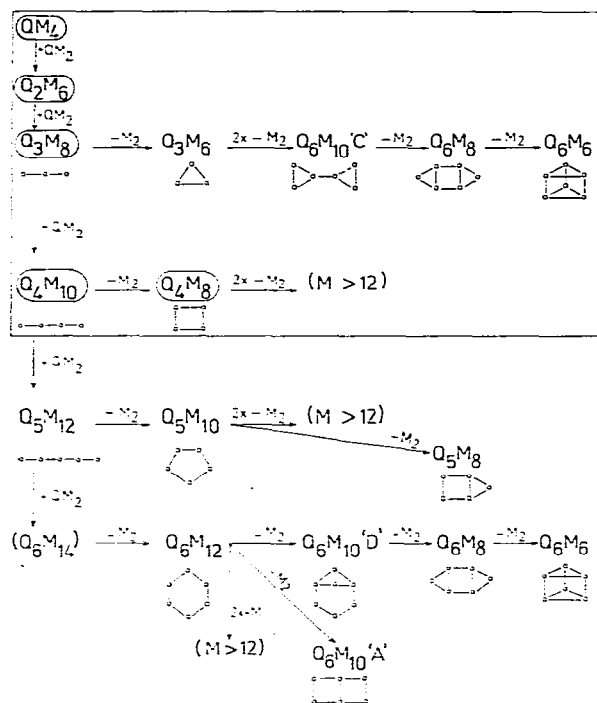


Fig. 3. Scheme showing a part of the condensation mechanism of SA solutions. Key to the structures: ○— =  $QM_3$ ; —○— =  $QM_2$ ; —○— =  $QM$ .

solutions are best reflected in the GC results after BSA silylation. Additional products generated during Götz and Masson and Lentz silylations are the results of erroneous reactions and reflect altered conditions compared to those in the original solutions.

The main components (>1%) of the SA solutions after BSA silylation proved to be molecules, formed from  $QM_4$  by means of a maximum of four condensation steps in the 120-min lifetimes samples.

When 120-min lifetime samples were silylated by the Götz and Masson and Lentz methods, starting from  $QM_4$ , components requiring six condensation steps were formed in more or less significant amounts. On the other hand  $Q_3M_6$ ,  $Q_6M_8$  and  $Q_6M_6$  did not appear, even with the 24-h lifetime samples, when the SA solutions were silylated by the BSA method. These results indicate, in our opinion, a prolonged time of silylation according to Lentz and Götz and Masson compared with that in the BSA derivatization.

(iii) As a further evidence of Table IV it can be stated that the actually measured values of recovery of silylation are similar for the three methods.

Chromatograms for visual comparison are presented in Fig. 4.

#### *The effect of Amberlyst 15 on the silylation reaction*

Results of experiments carried out in order to clear the effect of Amberlyst after-treatment on BSA silylated samples are summarized in Table VI. In the experi-

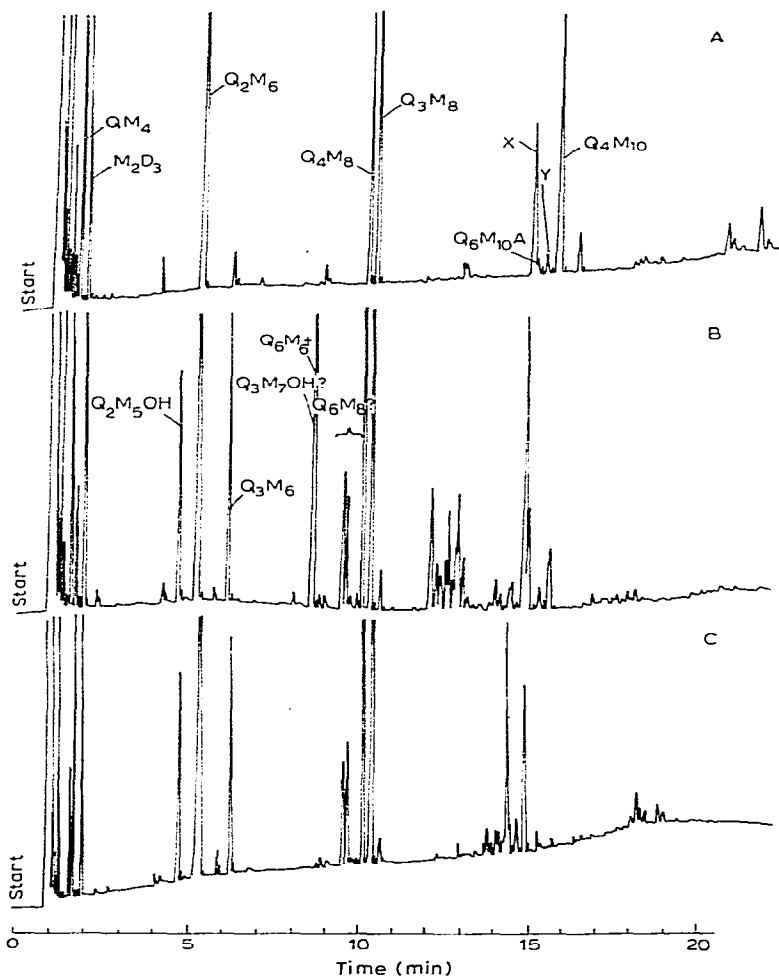


Fig. 4. Comparison of the silylation methods. Sample: 0.5 *M* mono-SA silylated in the 120th min after the formation of the SA: A, by the BSA method; B, by the Lentz method; C, by the Götz and Masson method.

ments involving Amberlyst after-treatment, *n*-tetradecane was used as the internal standard.

It is evident that in the case of mono- and di-SA samples, Amberlyst after-treatment makes no difference.

Amberlyst after-treatment was performed on samples also silylated by the standard methods.

Subsequent GC determinations showed that  $Q_2M_5OH$  and  $Q_3M_7OH$  peaks disappeared, increasing proportionally the quantities of  $Q_3M_6$  and  $Q_3M_8$ . Similarly, the amounts of the components in the RT = 12–13 peak group were added to the  $Q_4M_{10}$  peak suggesting their identity with isomers of incompletely silylated tetrameric chains. This is exemplified by the data in Table VII.

TABLE VII

THE EFFECT OF TREATMENT WITH AMBERLYST 15 AFTER SILYLATION ACCORDING TO GÖTZ

Sample: 10-min di-SA.

Amberlyst	Area (%)									
	Q <sub>4</sub> M <sub>4</sub>	RT = 4.8; Q <sub>2</sub> M <sub>5</sub> OH	Q <sub>2</sub> M <sub>6</sub>	RT = 6.3; Q <sub>3</sub> M <sub>6</sub>	RT = 9.7 + 9.8; Q <sub>6</sub> M <sub>8</sub> ?	Q <sub>4</sub> M <sub>8</sub>	Q <sub>3</sub> M <sub>8</sub>	RT = 12-13; group	X	Q <sub>2</sub> M <sub>10</sub>
Without	3.0	20.2	67.6	0.2	1.0	1.9	2.1	2.5	0.4	1.1
With	3.2	—	85.7	0.3	1.2	2.5	2.6	—	0.4	4.1

Q<sub>3</sub>M<sub>6</sub> and Q<sub>6</sub>M<sub>8</sub>, however, did not disappear by the same Amberlyst after-treatment, verifying the mechanism of the side-reactions proposed in Fig. 3.

As an amazing result of the above experiments we found that even positively identified Q<sub>6</sub>M<sub>6</sub> disappeared in the course of Amberlyst after-treatment and another ( $\bar{M} = 10$ ) peak with similar intensity appeared instead. Experiments are continued in order to give an explanation for this phenomenon.

On the basis of the results we conclude that the BSA silylation is the only GC derivatization method used so far that provides reliable chemical information on SA systems. It seems, however, that further improvements are possible. Consequently, the results presented here should be regarded as the first steps in finding appropriate conditions for the silylation of SA solutions. Other silicate solutions or even solid silicate systems represent different problems.

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