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DETERMINATION OF TRIMETHYLSILYL DERIVATIVES OF SILICATE ANIONS BY GAS CHROMATOGRAPHY USING A HYDROGEN FLAME-IONIZATION DETECTOR

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SUMMARY

Eight trimethylsilyl (TMS) derivatives were used as standard substances in studies of the determination of TMS derivatives of silicate anions. The internal standard method was used for the determination of TMS derivatives with a gas chromatograph equipped with a hydrogen flame-ionization detector and *n*-tetradecane as internal standard. TMS derivatives and *n*-tetradecane were dissolved with chloroform. The relative peak intensities of the eight TMS derivatives on the gas chromatogram were a linear function of their molar concentration and of silicon concentration.

It was found that a linear relationship exists between the relative peak intensities and the atomic composition of the TMS molecules (C/Si) at equivalent concentrations with respect to silicon. By using this linear relationship and linear calibration graphs for TMS derivatives with respect to silicon concentration, a method for the determination of TMS derivatives of low-molecular-weight silicic acids was established.

INTRODUCTION

Trimethylsilylation has been used for the elucidation of the composition of silicate anions in various silicates¹⁻³ and silicic acid solutions⁴⁻⁶. The determination of trimethylsilyl (TMS) derivatives of silicate anions by gas chromatography (GC) has been performed using calibration graphs prepared by employing pure TMS derivatives derived from various silicates of the known structures^{1,7,8}. However, it is difficult to determine the concentration of TMS derivatives that are not available in a pure state. For the determination of these derivatives, Garzó *et al.*⁵ demonstrated an empirical relationship between the flame-ionization detector (FID) response factors and the atomic composition of the molecules (C/Si), using four TMS derivatives as standard substances, and obtained the FID response factors of two TMS derivatives that were difficult to prepare in a pure state. However, we have found that their empirical relationship is not always applicable to every TMS derivative.

In this work, some empirical relationships applicable to the determination of TMS derivatives were studied by measuring the FID response intensities of eight pure

TMS derivatives that had been isolated by gel permeation chromatography (GPC) in our previous work⁹. A method for GC determination of TMS derivatives is proposed. By using this method, the anionic compositions of sodium silicate solution and hemimorphite were investigated.

EXPERIMENTAL

*Preparation of standard stock solutions of TMS derivatives and *n*-tetradecane*

Individual TMS derivatives were prepared by the GPC separation of the TMS products of silicate minerals, tetraalkylammonium silicates and silicon oxychlorides, as described previously⁹. Each TMS derivative was dissolved in chloroform to make a 1000 ppm Si standard stock solution. *n*-Tetradecane was also dissolved in chloroform to give a volume ratio of 1:500.

Gas chromatography

A Yanaco G-180 gas chromatograph equipped with a hydrogen FID was used. The column was a 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 at a flow-rate of 20 ml/min. Samples (1–2 μl) were injected and the oven was programmed from 100 to 300°C at 5°C/min. The chart speed was 10 mm/min.

The internal standard method was used for the quantitative evaluation of the intensities of the TMS derivatives on the gas chromatograms with *n*-tetradecane as the internal standard substance. Sample solutions were prepared by diluting each standard stock solution of the TMS derivatives with chloroform and the *n*-tetradecane standard stock solution was then added to give a volume ratio of 1:1000. The relative peak intensity for each TMS derivative was calculated as the ratio A_s/A_r , where A_s and A_r are the peak areas on the chromatogram for the TMS derivative and *n*-tetradecane, respectively.

Trimethylsilylation

The silicate samples investigated were sodium silicate solution (4889 ppm as SiO₂) prepared by dissolving anhydrous silica (Mallinckrodt, St. Louis, MO, U.S.A.) in sodium hydroxide solution and hemimorphite, Zn₄(Si₂O₇)(OH)₂·H₂O. Sodium silicate solution (5 ml) or powdered hemimorphite (<100 mesh, ca. 0.1 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 1 h and filtered. The siloxane layer was separated and washed with water. The water was vigorously shaken with HMDS (10 ml) to extract the remaining TMS derivatives and the siloxane layer was separated and washed with water, then the two siloxane layers were combined. The siloxane layer was stirred for 4 h at room temperature in the presence of Amberlyst 15 cation-exchange resin (2 g). After filtration, the filtrate was evaporated to about 10 ml by distillation at 120–130°C. The TMS product was analysed quantitatively by GC.

RESULTS AND DISCUSSION

QM₄, Q₂M₆, Q₃M₆, Q₃M₈, Q₄M₈, Q₄M₁₀, Q₈M₈ and Q₈M₁₀ were used as the standard substances for the determination of the TMS derivatives of silicate anions; the names of the TMS derivatives are abbreviated according to Garzó and Hoebbel¹⁰.

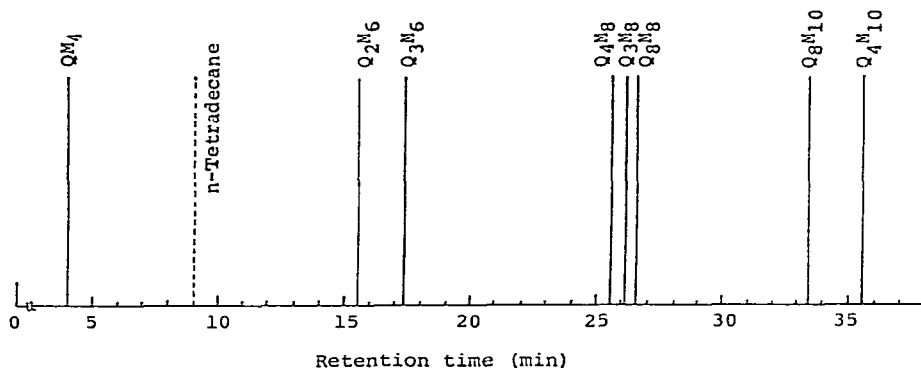


Fig. 1. GC retention times of TMS derivatives and *n*-tetradecane.

The GC retention times of the TMS derivatives and *n*-tetradecane are illustrated in Fig. 1 and the calibration graphs for the TMS derivatives are given in Fig. 2. There are two characteristic tendencies in Fig. 2: (1) the slope of the calibration line increases with increasing *M* (the number of trimethylsilyl groups) in the TMS derivative, and (2) the calibration lines of the TMS derivatives with identical *M* seem to form one group. These characteristics indicate that the peak intensities of the TMS derivatives depend on the number of methyl groups present.

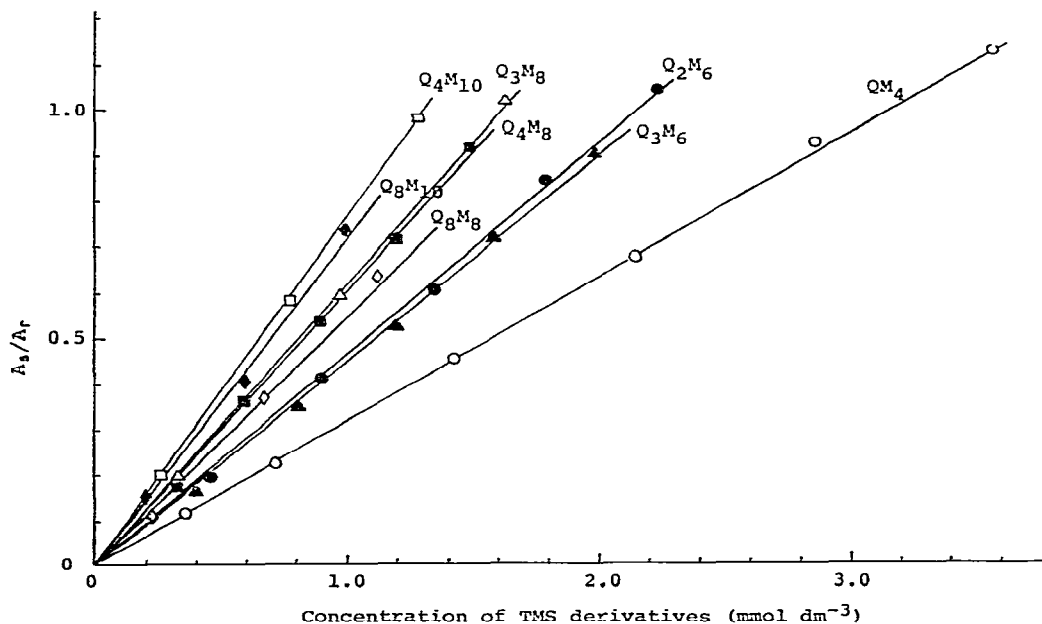


Fig. 2. Calibration graphs for TMS derivatives.

As the FID detects only carbon atoms in an organic molecule, the peak intensity of the TMS derivatives depends approximately on the number of carbon atoms. However, TMS derivatives contain silicon and oxygen heteroatoms. In Fig. 3,

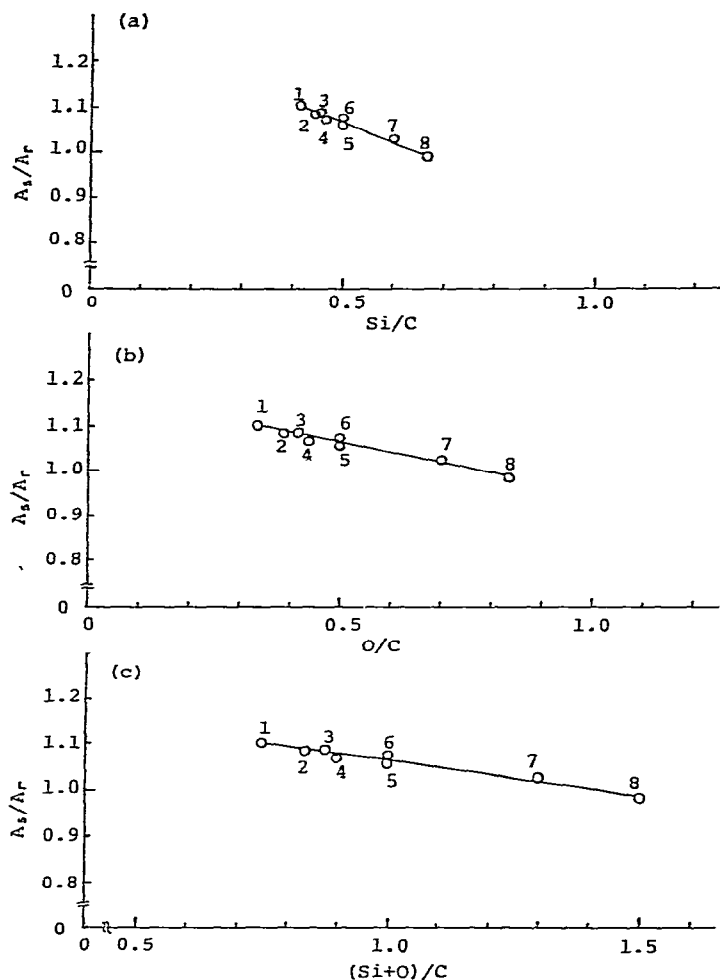


Fig. 3. Relationships between the relative peak intensities (A_s/A_r) and the atomic compositions of the molecules: (a) Si/C, (b) O/C and (c) (Si + O)/C. Concentration of carbon = 500 ppm. 1, QM_4 ; 2, Q_2M_6 ; 3, Q_3M_8 ; 4, Q_4M_{10} ; 5, Q_3M_6 ; 6, Q_4M_8 ; 7, Q_8M_{10} ; 8, Q_3M_8 .

the relative peak intensities (A_s/A_r) for each TMS derivative at a concentration of 500 ppm as carbon are plotted against the atomic compositions of TMS molecules: (a) Si/C, (b) O/C and (c) (Si+O)/C. The plots in Fig. 3 are approximately straight lines in all instances, but the relative peak intensities of the TMS derivatives were different from one another in spite of their having the same carbon content. This indicates that the relative peak intensities of the TMS derivatives are affected by the amounts of silicon and oxygen present in the TMS molecule.

It is necessary to evaluate the FID response factors of the TMS derivatives for quantitative analysis. Garzó *et al.*⁵ reported a linear empirical relationship between the FID response factors of QM_4 , Q_2M_6 , Q_4M_8 and Q_6M_{10} relative to dodecamethylpentasiloxane (the internal standard) and the atomic composition of the molecules (C/Si). From this relationship, they obtained the FID response factors of Q_3M_8 and

Q_4M_{10} , which were difficult to prepare in a pure state. In our work, the FID peak intensities of eight TMS derivatives at a concentration of $1.00 \text{ mmol dm}^{-3}$ were measured. The results are shown in Fig. 4. As Q_6M_{10} was difficult to prepare in a pure state, its A_s/A_r value was estimated from the A_s/A_r versus C/Si straight line discussed later. The plots for QM_4 , Q_2M_6 , Q_4M_8 and Q_6M_{10} show a linear relationship, as was reported by Garzó *et al.*⁵. However, the plots for Q_3M_6 , Q_3M_8 , Q_4M_{10} , Q_8M_8 and Q_8M_{10} which were obtained only in our laboratory, deviate considerably from a straight line.

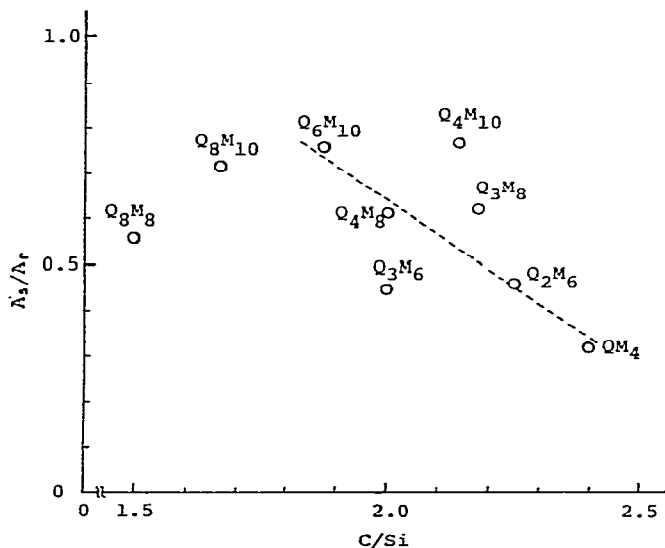


Fig. 4. Relationship between the atomic composition of the molecule and the relative peak intensity of TMS derivatives at a concentration of $1.00 \text{ mmol dm}^{-3}$.

The relative peak intensity of each TMS derivative at equivalent concentrations with respect to silicon ($Si = 500 \text{ ppm}$) was measured and plotted against the atomic composition of the molecules (C/Si). The results, shown in Fig. 5, indicate a linear relationship. The chemical compositions, C/Si ratios and A_s/A_r values for each TMS derivative are listed in Table I. The TMS derivatives with higher C/Si ratios show a higher A_s/A_r values, as shown in Fig. 5. Using this linear relationship, the FID response intensities of the TMS derivatives that are difficult to prepare in a pure state can be calculated exactly.

Linear calibration graphs for the eight TMS derivatives with respect to silicon concentration were obtained, as shown in Fig. 6. By using these calibration graphs and the linear relationship shown in Fig. 5, determination of the TMS derivatives is possible. A graphical procedure for the determination of TMS derivatives is exemplified in Fig. 7, using QM_4 and Q_8M_8 as standards and Q_2M_6 and Q_3M_6 as samples. The upper abscissa is the atomic composition of the molecules (C/Si) and the lower abscissa the silicon concentration (ppm Si). Firstly, the A_s/A_r values of QM_4 and Q_8M_8 at a concentration of 500 ppm of silicon are determined and the A_s/A_r versus

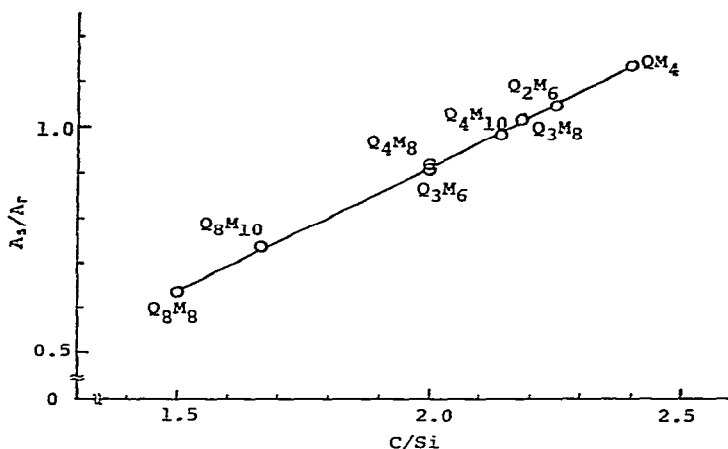


Fig. 5. Relationship between A_s/A_r and C/Si for TMS derivatives. Concentration of total Si = 500 ppm.

TABLE I

CHEMICAL COMPOSITIONS, C/Si RATIOS AND A_s/A_r VALUES (AT 500 ppm Si) FOR EACH TMS DERIVATIVE

Compound	Content (%)				C/Si	A_s/A_r (at 500 ppm Si)
	C	O	Si	H		
QM ₄	37.45	16.62	36.48	9.45	2.40	1.129
Q ₂ M ₆	35.59	18.44	36.99	8.98	2.25	1.041
Q ₃ M ₆	32.39	21.58	37.86	8.17	2.00	0.906
Q ₃ M ₈	34.73	19.29	37.22	8.76	2.18	1.014
Q ₄ M ₈	32.39	21.58	37.86	8.17	2.00	0.919
Q ₄ M ₁₀	34.24	19.76	37.36	8.64	2.14	0.980
Q ₈ M ₈	25.51	28.31	39.76	6.42	1.50	0.632
Q ₈ M ₁₀	27.89	25.98	39.11	7.02	1.67	0.733

TABLE II

ANALYTICAL RESULTS FOR Q₂M₆ AND Q₃M₆

Sample	Si taken (ppm)	A_s/A_r	Si found (ppm)	Difference (%)
Q ₂ M ₆	200	0.402	192	4
	500	1.020	490	2
Q ₃ M ₆	300	0.540	297	1
	500	0.901	495	1

C/Si straight line is drawn. Values of the atomic composition of Q₂M₆ and Q₃M₆ (C/Si) taken from Table I are then plotted on the line. The points "a" and "b" on the line represent Q₂M₆ and Q₃M₆, respectively. As the A_s/A_r values at "a" and "b" are the A_s/A_r values for Q₂M₆ and Q₃M₆, respectively, at concentration of 500 ppm of silicon, the calibration graphs for Q₂M₆ and Q₃M₆ can be prepared as shown in

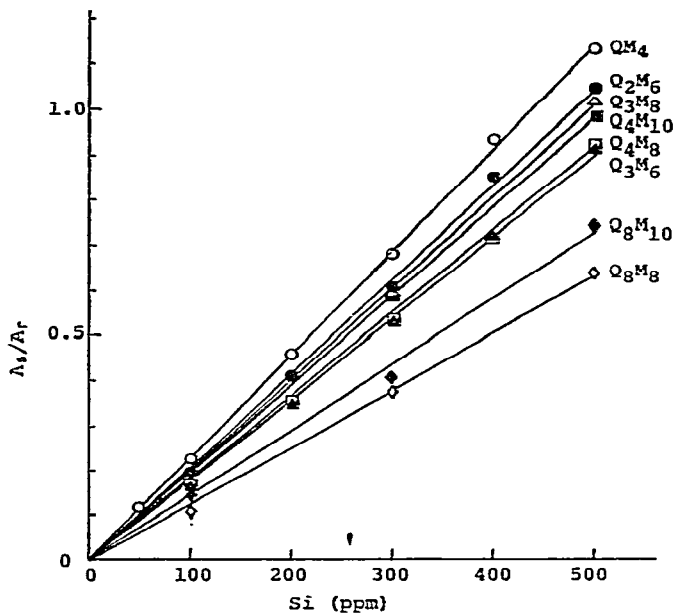


Fig. 6. Calibration graphs for TMS derivatives with respect to silicon concentration.

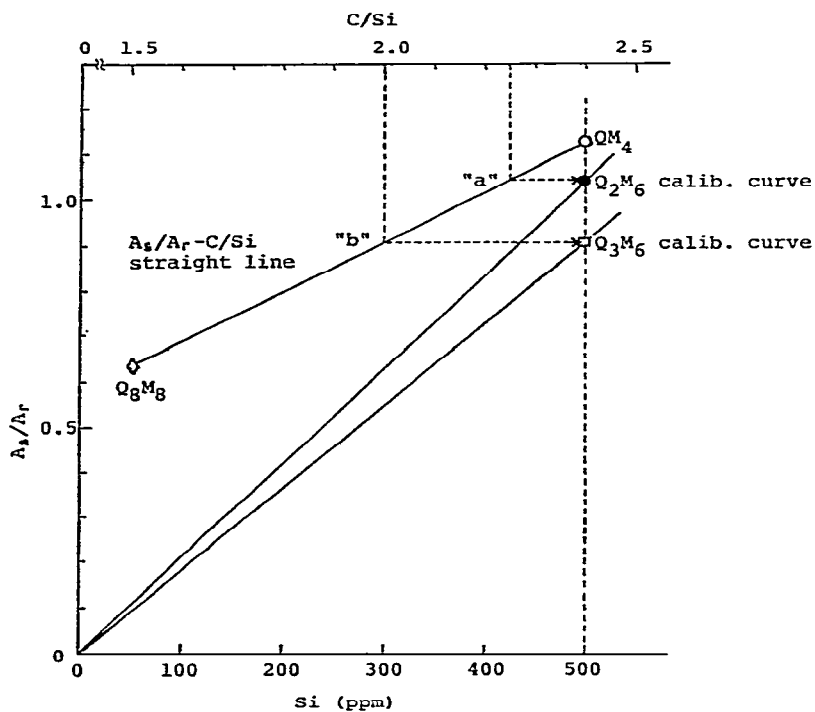


Fig. 7. Graphical procedure for the determination of TMS derivatives using the A_s/A_r versus C/Si linear relationship.

TABLE III

ANALYTICAL RESULTS FOR SODIUM SILICATE SOLUTION AND HEMIMORPHITE

Sample	Run No.	SiO_2 (%) occurring as				
		Q_1M_4	Q_2M_6	Q_3M_8	Q_4M_8	Total
Sodium silicate solution	1	81.9	12.3	1.9	1.4	97.5
	2	79.5	13.1	3.3	1.1	97.0
Hemimorphite	1	16.5	59.5	1.5	6.2	83.7
	2	17.0	59.7	1.4	5.5	83.6

Fig. 7. The analytical results obtained for Q_2M_6 and Q_3M_8 using these calibration graphs are given in Table II. The difference between the amounts of silicon taken and found was within 4%. Hence the proposed method is applicable to the determination of the TMS derivatives of silicate anions.

Sodium silicate solution (4889 ppm as SiO_2) and hemimorphite were trimethylsilylated and subjected to GC analysis using the proposed method. The results are summarized in Table III. Good reproducibility was found for each sample and the recovery of sodium silicate solution was about 97%. It is considered that the low recovery of hemimorphite (84%) is due to the formation of high-molecular-weight TMS derivatives that cannot be determined by GC.

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