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INFLUENCE OF FUNCTIONAL GROUPS ON THE GAS CHROMATOGRAPHIC RETENTION BEHAVIOUR OF QM-SILOXANES

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SUMMARY

The retention time sequences of QM-siloxane derivatives (derivatives of trimethylsilyl esters of silicic acids) of the formula $Q_mM_{2m+2-n}X_n$ ($X = H, Cl, C_2H_5O$; $m, n = 1, 2, 3$) and of siloxane derivatives containing M, D and T groups were investigated by capillary gas chromatography. The investigation showed that in compounds of the same structural type the retention times increase in the order of the substituents $H < Cl < C_2H_5O$. A linear correlation between retention time and molecular weight was observed only within groups of QM derivatives of the same structural type.

The retention sequence rule obtained from QM-siloxanes was modified so that it became valid for the investigated compounds, and so that it should be possible to identify unknown siloxane derivatives by the use of gas chromatography.

INTRODUCTION

Earlier gas chromatographic investigations on trimethylsilylated silicic acids[1], also known as QM-siloxanes*, showed that the retention of silicic acid esters of different structures is mainly dependent on the number of trimethylsiloxy (M) groups in the molecule. Six retention areas are known, which show with increasing retention time, silicic acid esters with 4, 6, 8, 10, 12 and 14 M groups[1–4]. A direct relationship between retention and the constitution or molecular weight of the QM esters was not observed.

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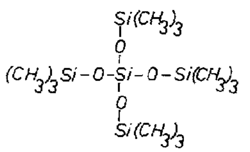
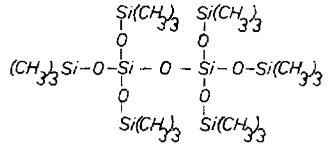
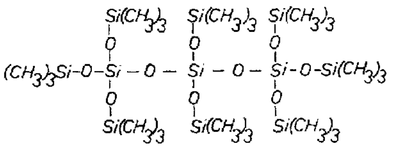
* In this article, the following abbreviations are used: $Q = SiO_{(0.5)4}$; $T = RSiO_{(0.5)3}$; $D = R_2SiO_{(0.5)2}$; $M = R_3SiO_{0.5}$.

TABLE I

FORMULAE OF QM-SILOXANES

Symbol	*Formula*
QM_4	 $(CH_3)_3Si{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}Si(CH_3)_3$
Q_2M_6	 $(CH_3)_3Si{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}Si(CH_3)_3$
Q_3M_8	 $(CH_3)_3Si{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}\underset{\substack{\vert\\O\\\vert\\Si(CH_3)_3}}{\overset{\substack{Si(CH_3)_3\\\vert\\O\\\vert}}{Si}}{-}O{-}Si(CH_3)_3$

Trimethylsilylsilicic acid esters with odd numbers of M groups are produced by incomplete silylation of the silicates or from fluorosilicates[5–9]. They appear in the gas chromatogram between esters of even numbers of M groups.

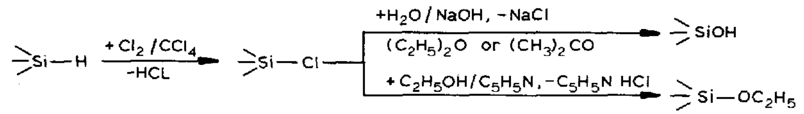
In this investigation, the influence of substituting one or more $(CH_3)_3SiO$ groups of QM_4, Q_2M_6 and Q_3M_8 (Table I) by H, Cl and C_2H_5O was studied in order to obtain a better understanding of the influence of substituents on retention behaviour. Furthermore, the effect on the retention behaviour of substituting a methyl group within the trimethylsiloxy unit by propyl, phenyl and benzyl or of exchanging the Q groups for D or T groups is discussed.

EXPERIMENTAL

Synthesis of siloxanes

The siloxanes used in this investigation are presented in Tables II and III.

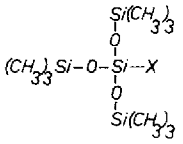
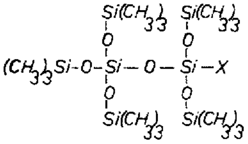
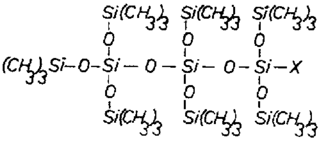
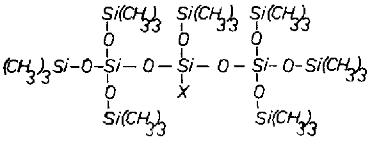
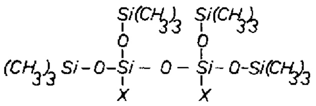
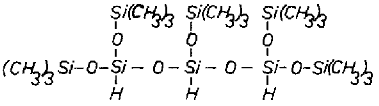
Hydrosilanes were synthesized in accordance with the literature[10,11]. The chlorosiloxanes, ethoxysiloxanes or siloxanols were synthesized from the hydrosilanes according to the following scheme:



The samples were characterized by means of elemental analysis, IR and ^{29}Si NMR spectroscopy.

TABLE II

QM-SILOXANE DERIVATIVES OF THE FORMULA $Q_mM_{2m+2-n}X_n$

Symbol	*Formula*
M_3TX ($X = H, OH, Cl, OC_2H_5$)	 $(CH_3)_3Si{-}O{-}Si(X)(OSi(CH_3)_3)_2$
M_3QM_2TX ($X = H, Cl, OC_2H_5$)	 $(CH_3)_3Si{-}O{-}Si(OSi(CH_3)_3)_2{-}O{-}Si(X)(OSi(CH_3)_3)_2$
$M_3QM_2QM_2TX$ ($X = Cl, OC_2H_5$)	 $(CH_3)_3Si{-}O{-}Si(OSi(CH_3)_3)_2{-}O{-}Si(OSi(CH_3)_3)_2{-}O{-}Si(X)(OSi(CH_3)_3)_2$
$(M_3Q)_2MTX$ ($X = H, Cl, OC_2H_5$)	 $(CH_3)_3Si{-}O{-}Si(OSi(CH_3)_3)_2{-}O{-}Si(X)(OSi(CH_3)_3){-}O{-}Si(OSi(CH_3)_3)_2{-}O{-}Si(CH_3)_3$
$(M_2TX)_2$ ($X = H, Cl$)	 $(CH_3)_3Si{-}O{-}Si(X)(OSi(CH_3)_3){-}O{-}Si(X)(OSi(CH_3)_3){-}O{-}Si(CH_3)_3$
$(M_2TH)_2MTH$	 $(CH_3)_3Si{-}O{-}Si(H)(OSi(CH_3)_3){-}O{-}Si(H)(OSi(CH_3)_3){-}O{-}Si(H)(OSi(CH_3)_3){-}O{-}Si(CH_3)_3$

Chromatographic conditions

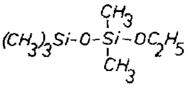
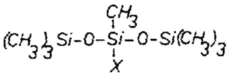
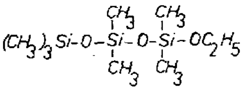
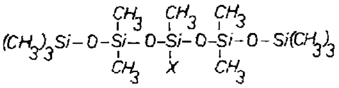
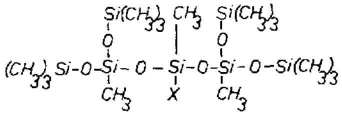
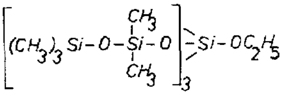
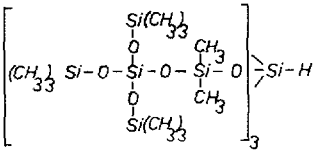
A capillary column of borosilicate glass with an internal diameter of 0.3 mm was used. The column was leached with hydrochloric acid, silylated with hexamethyldisilazane[12] and then static coated with 0.1% OV-1 in pentane.

The chromatograph used was a GCHF 18.3 (Chromatron, G.D.R.) with a flame ionization detector and a home-made on-column injector.

Pure nitrogen with a flow-rate of 1.5 ml/min was used as the carrier gas. The samples were dissolved in *n*-heptane in *ca.* 2 mg/ml concentration. A 1-μl aliquot of the solution was injected into the column at a temperature of 50°C. After elution of the solvent, the column was heated to 320°C at a rate of 12°C/min.

TABLE III

FORMULAE OF M-, D-, T- AND Q-CONTAINING SILOXANES

Symbol	*Formula*
MMOEt	 $(CH_3)_3Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}OC_2H_5$
M_2DX (X = H, Cl, OC_2H_5)	 $(CH_3)_3Si{-}O{-}\overset{CH_3}{\underset{X}{Si}}{-}O{-}Si(CH_3)_3$
MDMOEt	 $(CH_3)_3Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}OC_2H_5$
$(MD)_2DX$ (X = H, Cl, OC_2H_5)	 $(CH_3)_3Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{X}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}Si(CH_3)_3$
$(M_2T)_2DX$ (X = H, Cl)	 $(CH_3)_3Si{-}O{-}\overset{\overset{Si(CH_3)_3}{O}}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{X}{Si}}{-}O{-}\overset{\overset{Si(CH_3)_3}{O}}{\underset{CH_3}{Si}}{-}O{-}Si(CH_3)_3$
$(MD)_3TOEt$	 $\left[(CH_3)_3Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]_3{>}Si{-}OC_2H_5$
$(M_3QD)_3TH$	 $\left[(CH_3)_3Si{-}O{-}\overset{\overset{Si(CH_3)_3}{O}}{\underset{\underset{Si(CH_3)_3}{O}}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]_3{>}Si{-}H$

All samples contained *n*-tetradecane as internal standard. The retention times were measured from the internal standard for maximum accuracy.

RESULTS AND DISCUSSION

The results are shown schematically in Figs. 1–6.

Trimethylsiloxy group substitution

Hydrogen, chloro, ethoxy and, in one case, hydroxyl derivatives of QM_4, Q_2M_6 and Q_3M_8 are shown in Table II. The chromatographic retentions are given in Fig. 1. A decrease in retention time is observed, which correlates with the decrease

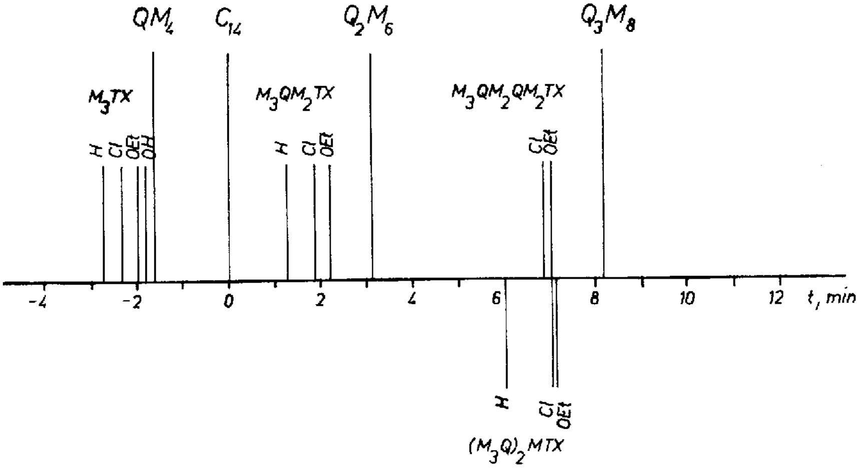


Fig. 1. Retention sequence of singly-substituted QM compounds.

in the molecular weight for each group of compounds: ethoxy, −44 g/mol; chloro, −53.5 g/mol; hydrogen, −88 g/mol.

The influence of substitution on QM_4 is lower than that observed for the Q_2M_6 and Q_3M_8 derivatives.

When a Q_3M_8 compound is substituted with the same derivative, at the end or middle trimethylsiloxy group, the retention of the end-substituted compound is somewhat lower than that of the middle-substituted compound. This could be due to the stronger shielding of the middle substituent and therefore a smaller influence on the retention time. The investigated QM derivatives of QM_4, Q_2M_6 and Q_3M_8 show, according to the retention sequence rule[1], a retention behaviour of compounds with 3, 5 or 7 M groups.

Substitution by hydrogen and chlorine on two or three trimethylsiloxy groups prduces a further decrease in retention of about twice or three times the singly-substituted compound (Fig. 2). It follows, therefore, that the retention sequence rule is also valid for higher-substituted compounds.

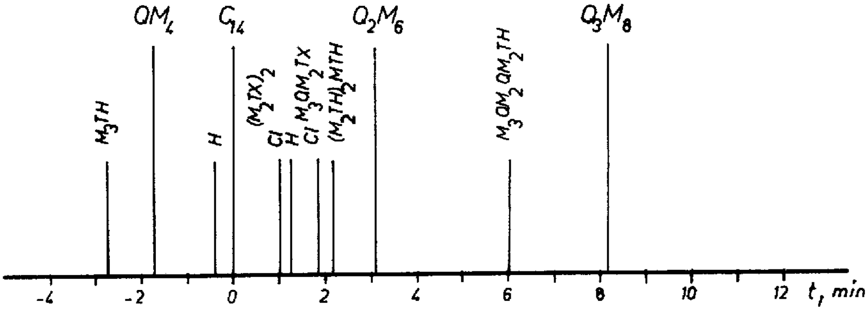


Fig. 2. Retention sequence of multiply-substituted QM compounds.

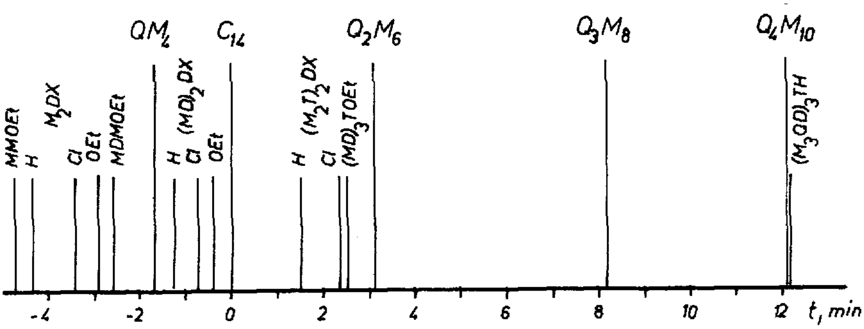


Fig. 3. Retention sequence of M-, D-, T- and Q-containing siloxanes.

Substitution of Q units by D and T groups

The retention data in Figs. 2 and 3 show that the retention sequence for the substituents H < Cl < OC_2H_5 already observed for QM derivatives, also exists for D and T units containing compounds of the same structural type.

The retention seqquence rule obtained from comparing the retention time with the number of M groups in QM compounds is not valid for the D- and T-containing compounds when used in its simplest form. For example, the retention times of compounds of the type $(MD)_2DX$ should be lower than that of QM_4. Probably, the contribution of the D and T units to the retention time should be taken into consideration. No clear correlation is observed between the sum of the building units and their retention when the retention contribution of the D and T units is taken as being the same as for the M unit. For example, compounds of the types $(M_2T)_2DX$,

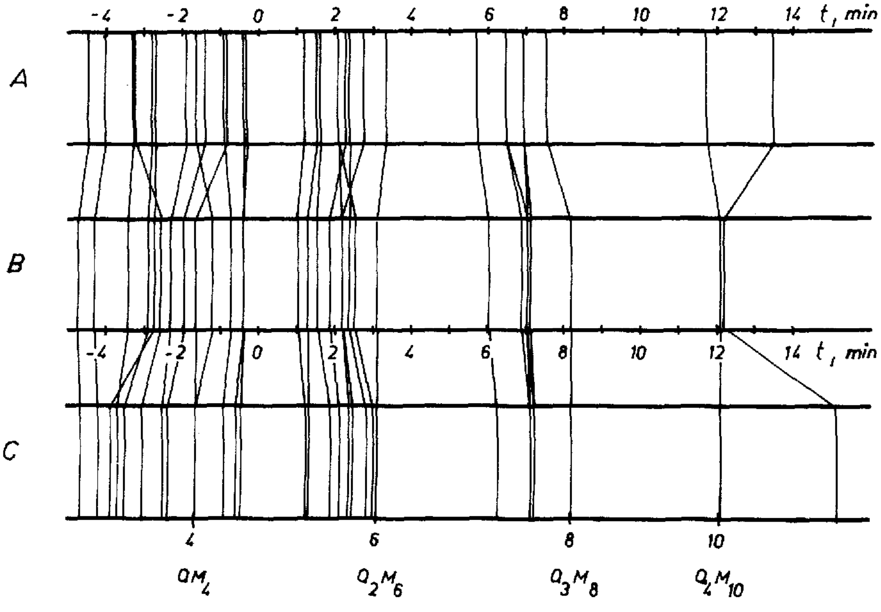
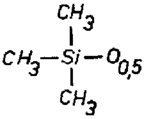
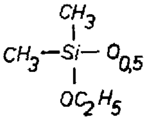
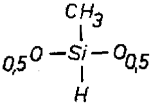
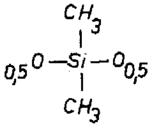
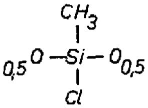
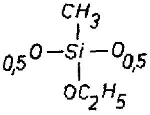
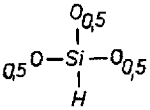
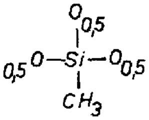
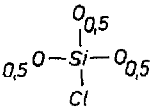
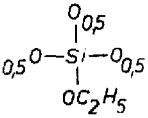


Fig. 4. Comparison of retention sequences: (A) mathematical model; (B) measured retention; (C) empirical model.

TABLE IV

EMPIRICAL RETENTION INCREMENTS OF THE M, D AND T GROUPS

Symbol	*Structural unit*	*Retention increment*
M	 $CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O_{0,5}$	1.0
	 $CH_3-\overset{CH_3}{\underset{OC_2H_5}{Si}}-O_{0,5}$	1.2
D	 $_{0,5}O-\overset{CH_3}{\underset{H}{Si}}-O_{0,5}$	0.5
	 $_{0,5}O-\overset{CH_3}{\underset{CH_3}{Si}}-O_{0,5}$	0.75
	 $_{0,5}O-\overset{CH_3}{\underset{Cl}{Si}}-O_{0,5}$	0.85
	 $_{0,5}O-\overset{CH_3}{\underset{OC_2H_5}{Si}}-O_{0,5}$	0.95
T	 $_{0,5}O-\overset{O_{0,5}}{\underset{H}{Si}}-O_{0,5}$	0.25
	 $_{0,5}O-\overset{O_{0,5}}{\underset{CH_3}{Si}}-O_{0,5}$	0.50
	 $_{0,5}O-\overset{O_{0,5}}{\underset{Cl}{Si}}-O_{0,5}$	0.60
	 $_{0,5}O-\overset{O_{0,5}}{\underset{OC_2H_5}{Si}}-O_{0,5}$	0.70

$(MD)_3$ TOEt and $(M_2TH)_2$ MTH would not fit into the retention scheme of the QM compounds. Therefore, it follows that D or T units have a somewhat lower contribution to the retention time than M groups, whose contribution can be arbitrarily set at 1. The first step in investigating the retention contribution of the D and T groups is based on comparing the different numbers of methyl groups in these units. Counting the number of methyl groups gives a satisfactory correlation with retention time, but compounds of the type $(MD)_2DX$ do not fit into the scheme. Table IV shows empirically determined retention increments for the single building groups. These are based on the somewhat higher values of the real methyl group number of the D and T units in addition to the molecular-weight-dependent influence of the hydrogen, chloro and ethoxy substituents. Using these retention contributions, all the investigated compounds now fit into the retention model produced from the QM compounds. Small inconsistencies are possibly due to unconsidered steric influences or inconsistent instrumental conditions.

Using the presented retention model, it should be possible to identify unknown M-, D-, T- and Q-containing siloxanes.

Using the retention sequence model as a basis, retention contributions for the different structural elements were calculated by means of linear regression. Using the equation $Y = A + B_1X_M + B_2X_D + B_3X_T + B_4X_H + B_5X_{Cl} + B_6X_{OC_2H_5}$, the following constants were calculated:

$A = -9.2576$ min
$B_1 = 2.0942$ min
$B_2 = 1.1862$ min
$B_3 = 0.7301$ min
$B_4 = 0.2719$ min
$B_5 = 1.0186$ min
$B_6 = 1.5031$ min

The calculated retention times and their deviations from the measured retention times are given in Fig. 4A and B. Although a few compounds do not show coincidence (shown by crossing of the lines between A and B in Fig. 4), a satisfactory agreement is obtained through mathematic modelling. The agreement, however, is not as good as that obtained by empirical modelling (Fig. 4B and C).

The retention of the investigated compounds is correlated with their molecular weights; the dependence obtained is shown in Fig. 5. A linear dependence is observed for the compounds $Q_mM_{2m+2-n}X_n$, which are obtained by substituting M groups on fully silylated Q_mM_{2m+2} compounds. The gradient of the line produced is practically identical with that of the non-substituted QM-siloxanes Q_mM_{2m+2}. The D- and T-containing compounds show a similar linear correlation between molecular weight and retention time, but with a lower correlation coefficient.

When the gradients of the curves of the investigated Q_mM_{2m+2} compounds and their derivatives are compared with that for QM compounds of another structural type (double rings Q_mM_m), a clear difference is observed. This shows that there is no common linear dependence between retention of QM compounds and their derivatives and the molecular weight. A definite dependence can only be expected between compounds of the same structural type.

Substitution at the M group

The influence of substituting the methyl group of the M unit of ethoxy-tris-

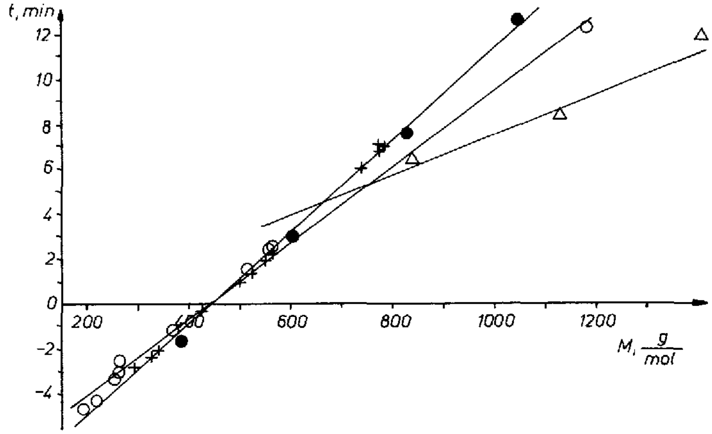


Fig. 5. Correlation between retention and molecular weight. (●) Q_mM_{2m+2}; (+) Q_mM_{2m+2-n} ($y = -5.5083\ \text{min} + 0.0123\ \frac{\text{min} \cdot \text{mol}}{\text{g}} \cdot M$; K (correlation coefficient) = 0.9985; s (standard deviation) = 0.1435 min); (○) D- and T-containing compounds ($y = -4.5218\ \text{min} + 0.0102\ \frac{\text{min} \cdot \text{mol}}{\text{g}} \cdot M$; K = 0.9967; s = 0.2335 min); (△) Q_mM_m (m = 6, 8, 10).

(trimethylsiloxy)silane by alkyl and aryl groups (n-C_3H_7, $C_6H_5CH_2$, C_6H_5) was investigated. From the retention scheme in Fig. 6, it can be seen that when methyl is substituted by larger entities a strong increase in retention time is produced, although the increase in molecular weight is only relatively small. The arrangement of these compounds into the previous retention model is not possible. However, the distance between the retention time of methyl- and propyl- and between phenyl- and benzyl-substituted compounds shows that every methylene group has a constant contribution to the retention time. A further systematic investigation is necessary in order to give a more detailed explanation of the contribution of different organic groups to the retention of siloxanes.

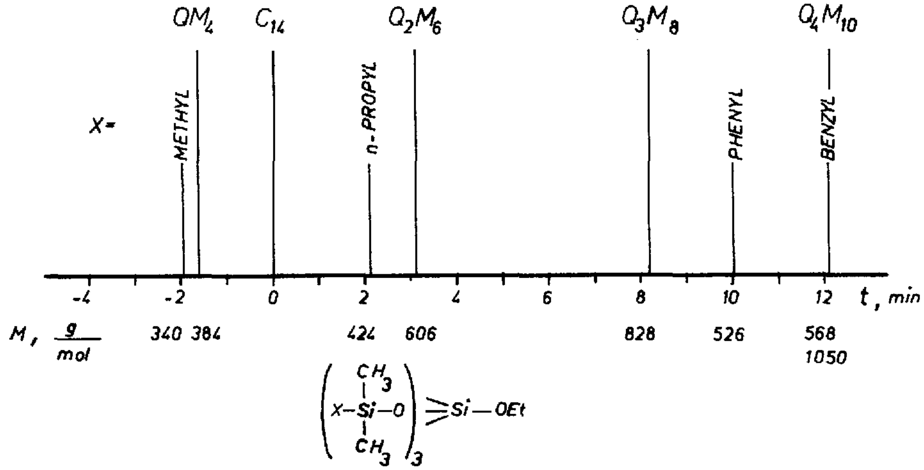


Fig. 6. Retention sequence due to substitution at the M group.

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REFERENCES

1 D. Hoebbel, G. Garzó, G. Engelhardt, H. Jancke, P. Franke and W. Wieker, *Z. Anorg. Allg. Chem.*, 424 (1976) 115.
2 H. P. Calhoun and C. R. Masson, *J. Chem. Soc.*, (1978) 1342.
3 D. Hoebbel, G. Garzó, G. Engelhardt and A. Till, *Z. Anorg. Allg. Chem.*, 450 (1979) 5.
4 A. Winkler, D. Hoebbel, A.-R. Grimmer, W. Wieker, K. Újszászy and M. Mägi, *Rev. Chim. Mineral.*, 20 (1983) 801.
5 J. B. Addison, *Analyst (London)*, 104 (1979) 766.
6 H. P. Calhoun and C. R. Masson, *J. Chem. Soc., Dalton Trans.*, (1980) 1282.
7 J. Götz and C. R. Masson, *J. Chem. Soc.*, (1970) 2684.
8 K. Kuroda and C. Kato, *J. Inorg. Nucl. Chem.*, 41 (1979) 947.
9 H. P. Calhoun, W. D. Jamieson and C. R. Masson, *J. Chem. Soc., Dalton Trans.*, (1979) 454.
10 E. Popowski, N. Holst and M. Kelling, *Z. Anorg. Allg. Chem.*, 494 (1982) 166.
11 E. Popowski, J. Schulz and H. Jancke, *Z. Anorg. Allg. Chem.*, in preparation.
12 K. Grob, G. Grob and K. Grob, Jr., *J. High. Resolut. Chromatogr., Chromatogr. Commun.*, 2 (1979) 677.