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Analysis of a mixture of linear and cyclic siloxanes by cryo-gas chromatography–Fourier transform infrared spectroscopy and gas chromatography–mass spectrometry

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Abstract

A mixture of linear and cyclic methylsiloxanes was analysed to characterize the different types of siloxane structures using gas chromatography (GC), mass spectrometry (MS) and Fourier transform infrared (FT-IR) spectroscopy. Siloxane structures are formed by hydrolysis of dimethyldichlorosilane under controlled conditions in technical applications. In the presence of methyltrichlorosilane or even trimethylchlorosilane, linear polydimethylsiloxanes and mono-, bi- or polycyclic methylsiloxanes are synthesized depending on the reaction conditions. The main structural units are $(CH_3)_3SiO_{1/2}$, $(CH_3)_2SiO$ and $(CH_3)SiO_{3/2}$. GC–MS may provide molecular mass information, but it is not able to identify isomeric structures, which are also formed in lower quantities by the mentioned reactions. Coupling GC with FT-IR enables the determination of group frequencies to assign specific structures. Thus, combination of GC with MS and FT-IR may be used in elucidating complex cyclosiloxane compounds. FT-IR measurements were performed with a Tracer unit.

1. Introduction

Hydrolysis and following condensation reactions of $(CH_3)_2SiCl_2$ in the presence of small amounts of CH_3SiCl_3 lead to the formation of monocyclic polydimethylsiloxanes (PDMSs); a greater amount of the latter component is the reason for the formation of also bicyclic or even polycyclic methylsiloxanes with ladder or cage structures [1–3]. Mixtures of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$ lead to mainly linear PDMSs, $(CH_3)_3SiCl$ acting as a chain stopper in forming siloxanes with the general formula M_2D_n [where $D = (CH_3)_2SiO$].

Cyclic methylsiloxanes were analysed as products of the pyrolysis of silicone resins to reveal the mechanisms of thermal rearrangements [4]; also structural investigations were made considering the additivity of retention index values in GC [5].

The identification of a complex siloxane mix-

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ture should be possible using the coupling of GC with MS and Fourier transform (FT) IR.

2. Experimental

2.1. Samples

A mixture of cyclic $\{[(CH_3)_2SiO]_m$, D_m, $m = 5–12\}$ and linear $\{(CH_3)_3SiO–[(CH_3)_2SiO]_n–Si(CH_3)_3$, MD_nM, $n = 3–10$; $M = (CH_3)_3SiO_{1/2}\}$ PMDSs was obtained by hydrolysis of a mixture of 400 g dimethyldichlorosiloxane (from Chemiewerk Nünchritz, containing approximately 100 ppm methyltrichlorosilane) and 100 g trimethylchlorosilane (Chemiewerk Nünchritz) in 1300 g water. The organic phase was separated, then washed neutrally with a saturated solution of $NaHCO_3$ in water and distilled over a 1 m Vigreux column under reduced pressure (20 Torr; 1 Torr = 133.322 Pa) up to 200°C. The fraction from 100 to 180°C (approximately 50 g) was used for our investigations.

2.2. GC–FT-IR

The measurements were made with a Bio-Rad Digilab FTS-45A spectrometer equipped with a liquid nitrogen-cooled narrow-band MCT detector and a Tracer connected with the gas chromatograph. Using a Fisons gas chromatograph GC 8130 the sample was separated on an HP Ultra 2 column (5% phenyl methylsilicone, 25 m × 0.2 mm, 0.33 μm film thickness). The helium (5.6) gas flow was 0.6 ml/min (24 cm/s). A 1-μl volume of the siloxane mixture, diluted 1:2.5 with dichloromethane, was injected with a split ratio of 1:30. The GC oven temperature was initially 80°C (1 min isothermal), then increased at 12°C/min to 250°C, with 20 min isothermal at 250°C for removing the last components from the column. A heated transfer line connects the column with evacuated Tracer chamber. The GC eluates are deposited onto a liquid nitrogen-cooled ZnSe window, which is computer-controlled moved by stepper motors. The deposition tip and the transfer line temperatures were 250°C in each case. The diameter of the deposited spots is about 0.1 mm. Recent studies have shown the advantages of using of the Tracer compared with the light-pipe interface for providing IR spectra of low-molecular-mass substances [6,7]. The window accommodates chromatographic separations of nearly 30 h, before a cleaning of the crystal of previous depositions at room temperature will be necessary. The function of the Tracer is depicted in Fig. 1.

The focused IR beam transmits the frozen eluate spots. After passing a microscope optic the beam enters the MCT detector. Therefore the recorded spectra show sharp bands by using the Tracer, which may be compared with those measured in condensed phase, and the sensitivity was improved significantly contrary to the light-pipe interface and for that reason GC–FT-IR is comparable to GC–MS. The advantages are described in, e.g., Ref. [8]. Absorbance spectra were recorded in the 4000–700 cm^{-1} region with a spectral resolution of 8 cm^{-1}. Four scans/s were coadded by a MCT frequency of 20 kHz. The data collection time was 20 min.

2.3. GC–MS

The GC equipment was a HP 5890 series II (Hewlett-Packard, Waldbronn, Germany), the carrier gas helium (5.0), the column inlet pressure was 70 kPa, the gas flow 0.7 ml/min. The column used for separation was a DB-5, 30 m × 0.25 mm, 0.25 μm film thickness; the temperature was initially 80°C (1 min), then increased at 12°C/min to 250°C, and 25 min isothermal at 250°C. The injector temperature was 250°C; splitless injection mode; samples were diluted in chloroform. The temperature of the transfer line to MS was held at 280°C.

The single-stage quadrupole mass spectrometer SSQ700 (Finnigan MAT, Bremen, Germany) was used in the mass range 80–1000 u in the electron impact (EI)/chemical ionization (CI) mode (CI with isobutane), tuning automatically with perfluorotributylamine (FC43), scan time 0.75 s. The manifold heater temperature was 70°C. The ion source temperature was held at 150°C in the EI mode, at 170°C in the CI mode.

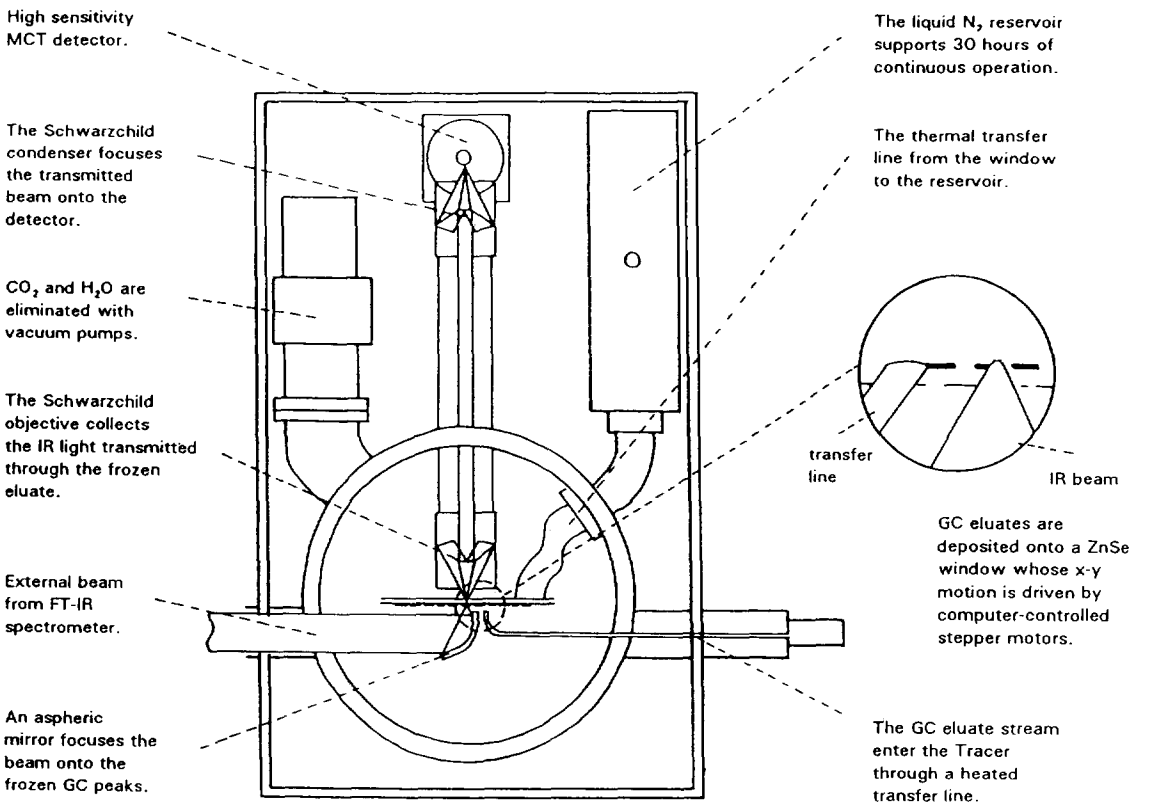

Fig. 1. Structure and function of the Tracer of the FTS-45A (Bio-Rad Digilab).

The ion source pressure in the CI mode was 6500 mTorr.

3. Results and discussion

3.1. GC–MS

Linear PDMSs

Fig. 2 shows the reconstructed ion chromatogram of the mixture containing linear and cyclic components. The mass spectra of all peaks were recorded in the EI and CI mode, where isobutane as reagent gas leads to the determination of MH^+ peaks. All spectra in the CI mode show the expected MH^+ peaks and also the cleavage of CH_4 from the quasi-molecular ion. All linear PDMSs (M_2D_n between M_2D_3 ($MH^+ = 385$) and M_2D_{11} ($MH^+ = 979$) are determined unambiguously. Polycyclic compounds were mainly expected eluting in the range between M_2D_3 and M_2D_5. In fact, the amounts of polycyclic compounds should be very low compared with linear and monocyclic methylsiloxanes.

Monocyclic methylsiloxanes

The cyclic compounds D_m were determined in the range of D_5 to D_{13} considering the MH^+ ions and the cleavage of methane using chemical ionization. Isobutane is useful as a reagent gas in obtaining MH^+ ions because of the capability to generate quasi-molecular ions without following fragmentation reactions.

Bicyclic methylsiloxanes

In the range between M_2D_3 ($M^+ = 384$) and M_2D_5 ($M^+ = 532$) several bicyclic siloxane structures are expected. These components will contain 6 or 7 silicon atoms, and very different structures are theoretically possible. The com-

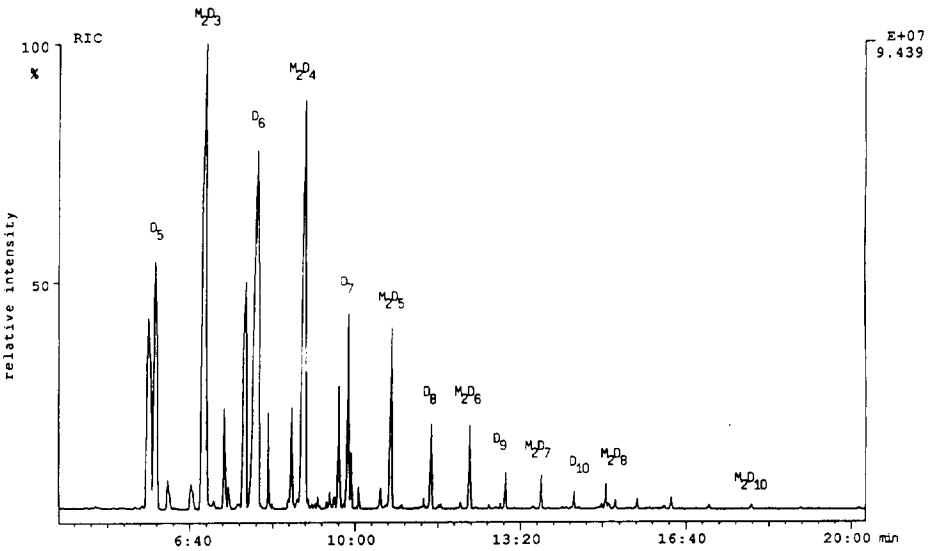

Fig. 2. Reconstructed ion chromatogram of siloxane mixture.

pound at 7.3 min in the GC–MS chromatogram shows a mass spectrum with $MH^+ = 431$ and is correlated to a siloxane with a bicyclic structure containing 6 silicon atoms (Fig. 3). This is to be concluded from the difference of 14 u to the molar mass of monocyclic D_6. FT-IR verifies this conclusion, and it is able to elucidate this compound to the bicyclic siloxane structure of T_2D_4 [$T = (CH_3)SiO_{3/2}$], as described later.

3.2. GC–FT-IR

Using GC–FT-IR real-time information about the cryotrapped components is available by calculating the Gram–Schmidt (GS) or functional group chromatograms [14]. The GS chromatogram shows the total absorbance of the detected peaks (Fig. 4).

By comparing the GS chromatogram with the

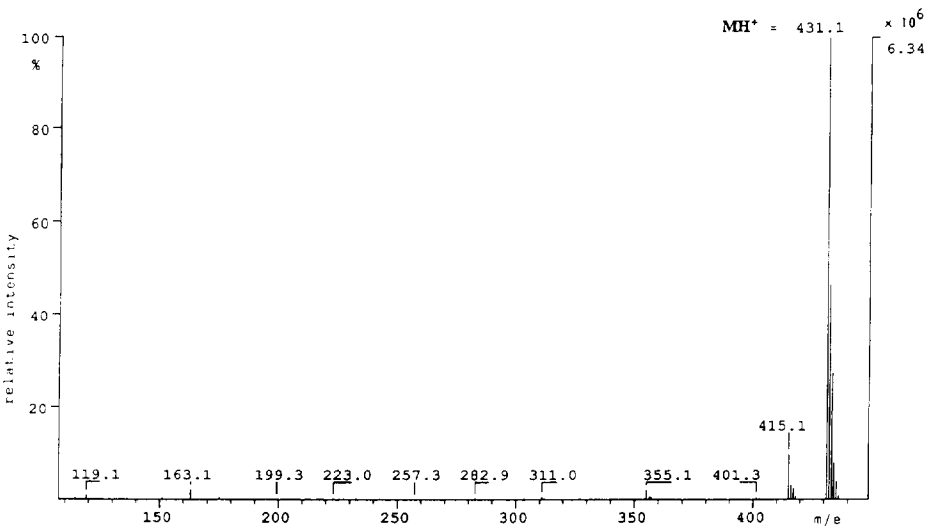

Fig. 3. Mass spectrum of the peak at 7.3 min of the ion chromatogram (CI mode).

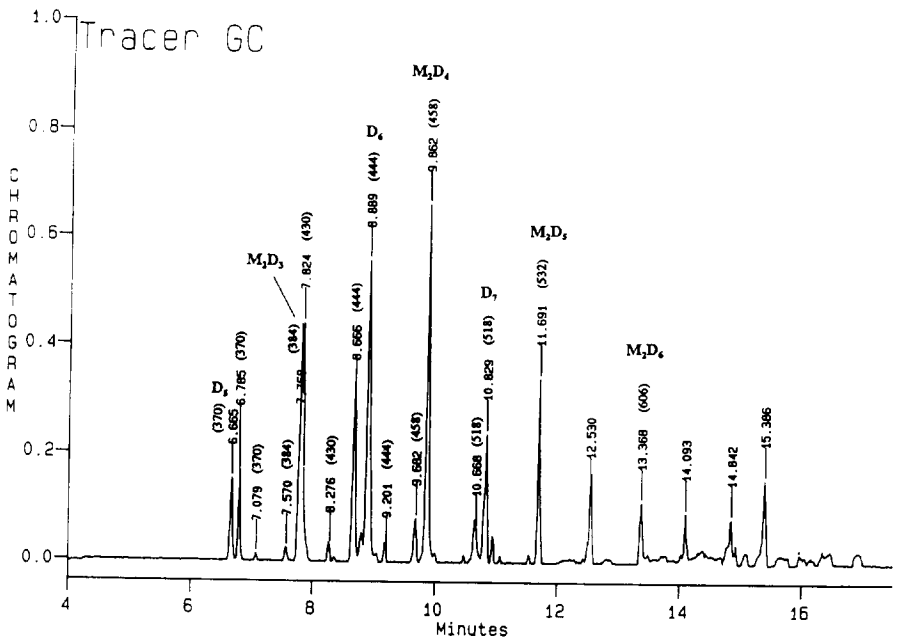

Fig. 4. Gram–Schmidt trace of siloxane mixture. Peaks are labeled (in parentheses) with values of molecular masses determined by GC–MS.

chromatogram of the GC–MS measurement a very good agreement is observed with regard to the retention of eluted compounds. Therefore some of the peaks detected by FT-IR were labeled with their molecular masses found by MS. The knowledge of the masses is very important for further identification.

In addition, the integrated absorptions of spectra created from each interferogram by Fourier transformation with reduced resolution give the special information with respect to characteristic Si–O, Si–CH_3 and CH groups of the sample components in this case, as shown in Fig. 5.

By means of IR spectra it is in principle possible to distinguish between linear chains, rings, branchings or networks in the siloxane framework. While the CH_3 stretching and bending frequencies are nearly the same in all compounds, the CH_3 rocking vibrations as well as the Si–O and Si–C frequencies are influenced by the structure of the molecule; therefore they are very helpful for interpretation of structural units [9]. The identification of the separated siloxane mixture is performed by assigning of the absorption bands and by comparing of the retention times with those from the GC–MS experiments. The GC–MS and GC–FT-IR results were confirmed by comparing the spectra and retention times with those from standards specially synthesized for this purpose. Because of the good agreement of the GS chromatogram with MS chromatogram (compare Fig. 4 with Fig. 1) the molecular masses (M_r) were adopted from the GC–MS experiment. Peaks with the same masses could be assigned to various structural groups for further identification using FT-IR: chains, monocyclic siloxanes, e.g. D_5 (M_r 370), D_6 (M_r 444) and D_7 (M_r 518) with their isomeric structures, or bicyclic siloxanes, e.g. D_4T_2 (M_r 430). GC–MS gives essential information about molecular masses, but cannot usually identify specific isomeric structures. The assignment of some of the separated compounds is suggested in this paper.

Linear PDMSs

Compounds with linear structures such as M_2D_3, M_2D_4, M_2D_5 and M_2D_6 were assigned to the peaks at retention times of 7.8, 9.9, 11.7 and

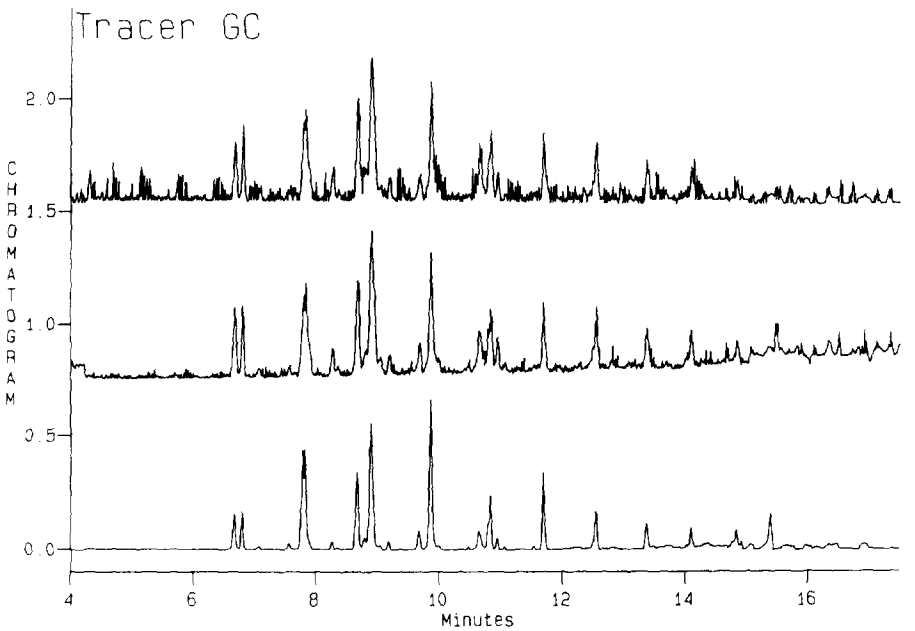

Fig. 5. IR chromatograms representing the integrated absorption of three selected spectral regions: lower trace: 2800–3000 cm^{-1}; middle: 780–900 cm^{-1}; upper: 990–1180 cm^{-1}.

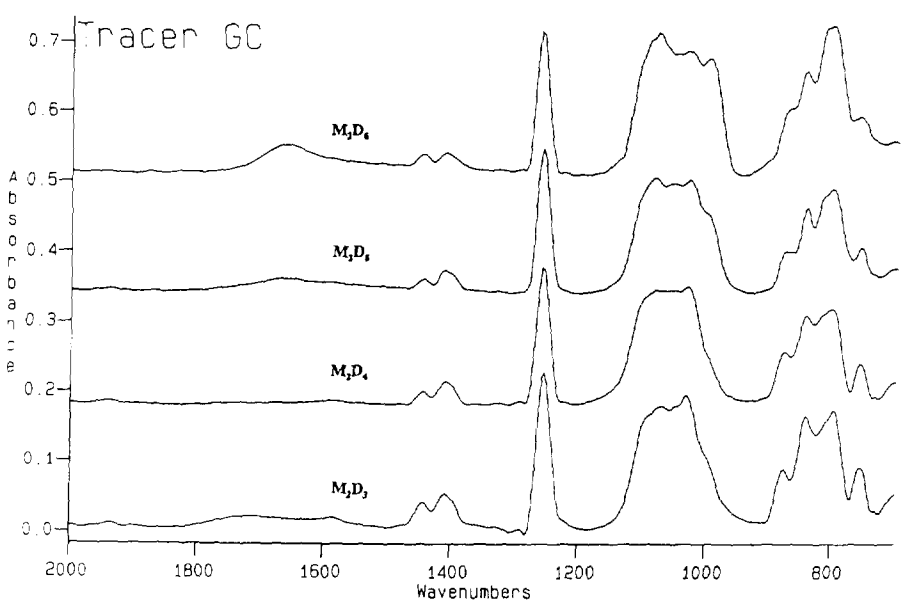

Fig. 6. Spectra of linear PDMSs (n = 3–6). Retention times: M_2D_3 = 7.76 min; M_2D_4 = 9.86 min; M_2D_5 = 11.69 min; M_2D_6 = 13.37 min.

13.4 min by means of the GC–MS results. The recorded subfile spectra are depicted in Fig. 6.

The spectra show the asymmetric Si–O–Si stretching vibrations split in several bands. In the spectra of M_2D_5 an additional band is formed as shoulder (near 1000 cm^{-1}), which is more structured and stronger in the M_2D_6 spectrum. Table 1 shows the frequencies of the spectra of Fig. 6. The assignments correspond to Refs. [9] and [10].

Monocyclic methylsiloxanes

D_6 is the main component of the analysed sample, but siloxanes with more D units and isomeric compounds were formed, too. In the case of D_5 (M_r 370) the GS chromatogram and the reconstructed ion chromatogram (RIC) show three peaks of the same mass. For D_6 and isomeric monocyclic siloxanes (M_r 444), too, three peaks were edited for interpretation, for D_7 (M_r 518) two peaks, for D_8 and also for D_9 one peak. For the higher siloxanes a lot of isomeric structures are possible, and the identification becomes more and more difficult. Fig. 7 shows the spectra of the peaks (M_r 370) at retention times 6.7, 6.8 and 7.1 min.

Some of characteristic vibrations of these compounds shifted by inductive, mechanical or steric effects, are listed in Table 2.

Especially the high absorption band at 1100 cm^{-1} in the spectrum of the peak eluted at 7.1 min points out a branched siloxane with a T unit, whereas the band at 1022 cm^{-1} is characteristic for a cyclotrisiloxane. The siloxane framework is constrained by well defined bond angles and the stretching vibration decreases to 1020 cm^{-1} [11]. M units in straight chains show absorption bands near 1055 cm^{-1}. The rocking vibration near 843 cm^{-1} is missing in cyclic siloxanes. The recorded spectra of the isomeric monocyclic structures (M_r 444) are given in Figs. 8–10. The defined structures are labeled in the figures.

The spectrum in Fig. 8 fully agrees with the spectrum of the cyclic tetramer siloxane MD_4T described by Smith [12] using the GC–FT-IR coupling technique (light-pipe device). The spectrum of the biggest peak of the GC chromatogram with M_r 444 is to be seen in Fig. 9. It consists of two components confirmed by GC–

Table 1
Assignment of stretching, bending and rocking vibrations of linear siloxanes (peaks are labeled in GS chromatogram in Fig. 4)

	M_2D_3, vibration $\tilde{\nu}$ (cm^{-1})	M_2D_4, vibration $\tilde{\nu}$ (cm^{-1})	M_2D_5, vibration $\tilde{\nu}$ (cm^{-1})	M_2D_6, vibration $\tilde{\nu}$ (cm^{-1})
$\nu_{as}CH_3$	2959	2960	2960	2962
ν_sCH_3	2901	2902	2903	2906
$\nu_{as}Si–O–Si$	1075	1079	1081	1080
	1047	1054	1053	1036
	1031	1029	1027	1029
			1000 (sh)	996
$\delta_{as}CH_3$	1444	1444	1444	1444
δ_sCH_3	1255	1256	1258	1260
	1408	1408	1412	1410
$\rho Si–(CH_3)_2$	876	875	874	872
$\rho_{as}Si–(CH_3)_3$	841	843	843	844
$\rho Si–CH3$ and $\nu Si–C$	796, 754	801, 755	802, 755	803, 759

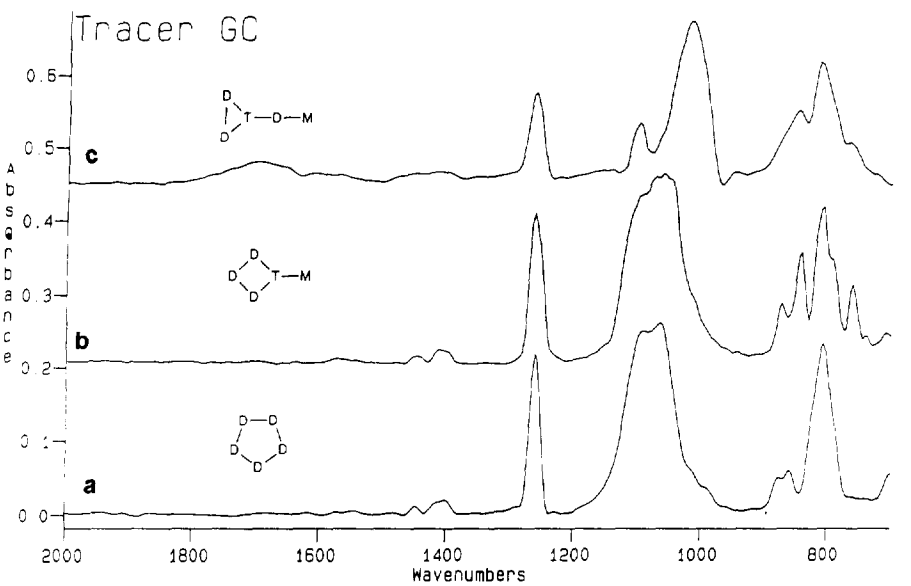

Fig. 7. Spectra of the compounds corresponding to the peaks at (a) 6.7 (6.67), (b) 6.8 (6.78) and (c) 7.1 (7.08) min in the GS chromatogram (M_r 370).

MS results. Therefore a superposed spectrum was observed. The band at 1091 cm^{-1} suggests a cyclic pentamer siloxane, the band at 1080 cm^{-1} a cyclic hexamer siloxane. The methyl rocking vibration band of $(CH_3)_2Si-O$ groups at 858 cm^{-1} represents D units. The 843 cm^{-1} band indicates M units. Together with the band at about 1050 cm^{-1} a linear siloxane structure coupled with the pentamer ring is concluded.

The spectrum in Fig. 10, corresponding to the peak at the retention time of 9.2 min, suggests a cyclotrisiloxane because of the very low Si–O–Si band at 1018 cm^{-1}. Linear parts are indicated by the bands at 847 and 1055 cm^{-1}. The additional band above 1100 cm^{-1} indicates a branched structure (T unit) [9].

Bicyclic methylsiloxanes

As described before, during the synthesis of dimethyldichlorosilanes other chlorosilanes are formed, mainly CH_3SiCl_3. The traces of CH_3SiCl_3 could cause the presence of compounds with molecular masses of $M_r(D_n) - 14$, because T units resulting from the hydrolysis/condensation process can be fitted into the cyclic siloxanes. From D_6, e.g., several T_2D_4 molecules [M_r 430 = $M_r(D_6) - 14$] with different isomeric structures are formed [13], see Fig. 11.

Table 2
Assignment of the IR bands (corresponding to Refs. [9] and [11]) for compounds with M_r 370

Retention time (min)	$\tilde{\nu}_{as}$Si–O–Si (cm^{-1})	Rocking vibrations (cm^{-1})	Structure
6.7	1091, 1065	864, 807	D_5
6.8	1096, 1072, 1060	872, 842, 808, 760	M
7.1	1100, 1055sh, 1020	845, 815	+chain

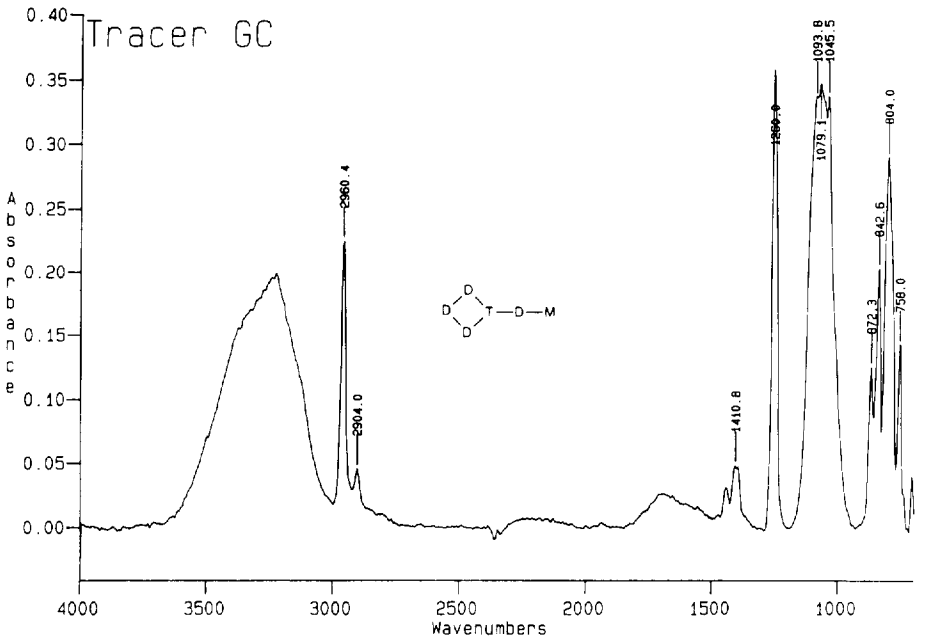

Fig. 8. Spectrum of cyclotetramer siloxane MD_4T (M_r 444).

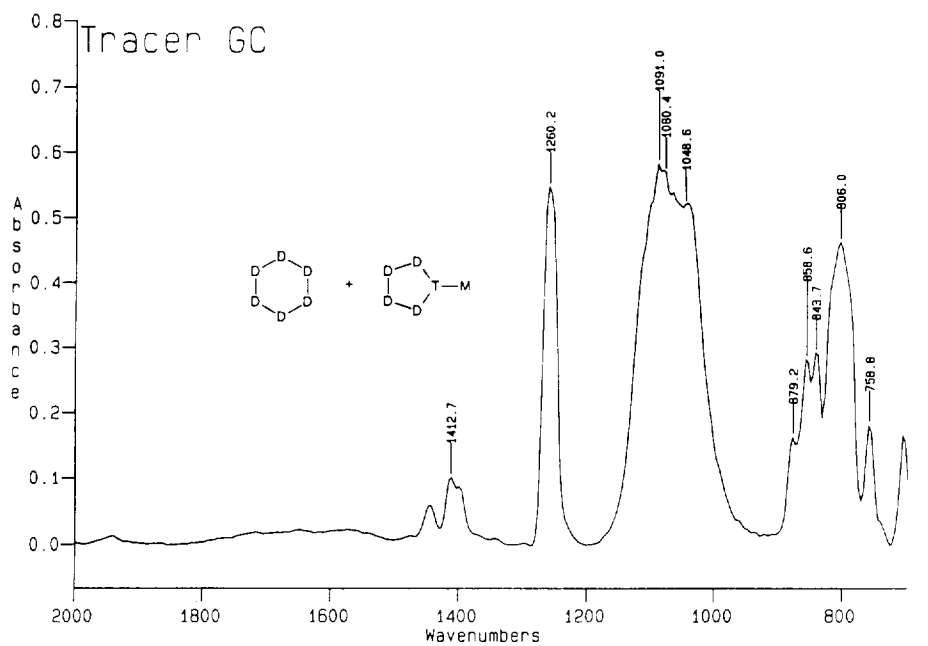

Fig. 9. Spectrum of the compounds corresponding to the unresolved peak at the retention time of 8.9 min in the GS chromatogram, assigned to D_6 and cyclopentamer siloxane MD_4T (M_r 444).

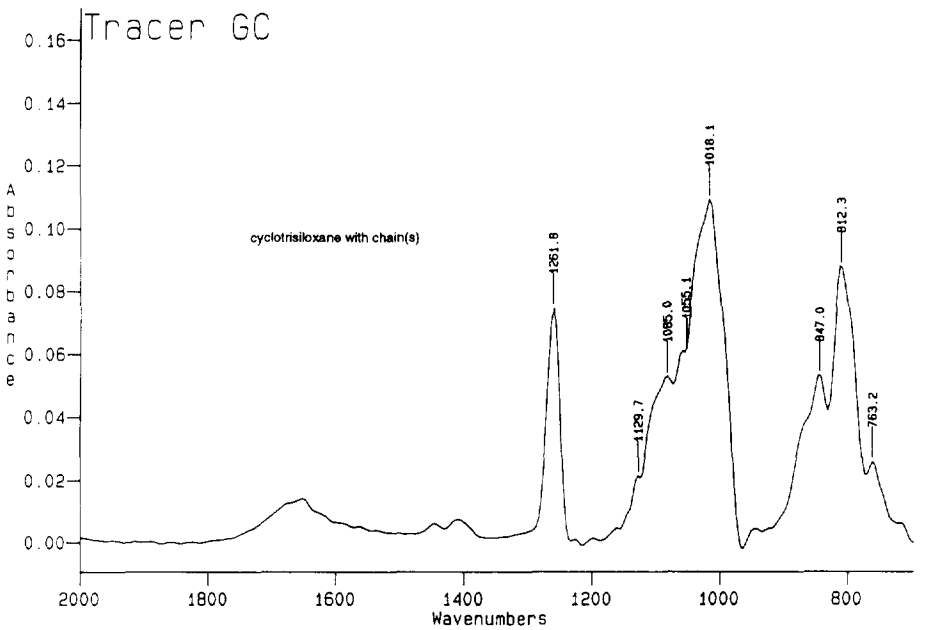

Fig. 10. Spectrum of the compound corresponding to the peak at the retention time of 9.2 min in the GS chromatogram, assigned to cyclotrimeric siloxane (M_r 444).

Fig. 12 shows the spectrum of the compound corresponding to the peak at 8.26 min and the suggested structure 2 of Fig. 11 as a bicyclic siloxane. The bands at 1072 and 1107 cm^{-1} indicate a cyclic tetramer siloxane with T units of a branched siloxane. The structures 1, 3 and 4 for T_2D_4 can be excluded in this case, because the characteristic bands for cyclic trimer siloxanes near 1020 cm^{-1} and for cyclic pentamer siloxanes near 1090 cm^{-1} are missing. Also a linear structure is excluded, because the bands at 843 and 1055 cm^{-1} are not to be seen in the spectrum.

4. Conclusions

Cryo-GC–FT-IR combined with GC–MS is a powerful tool in the elucidation of siloxane structure. Both techniques are supplementary in identifying cyclosiloxane compounds, especially isomers. A mixture of linear and cyclic siloxanes

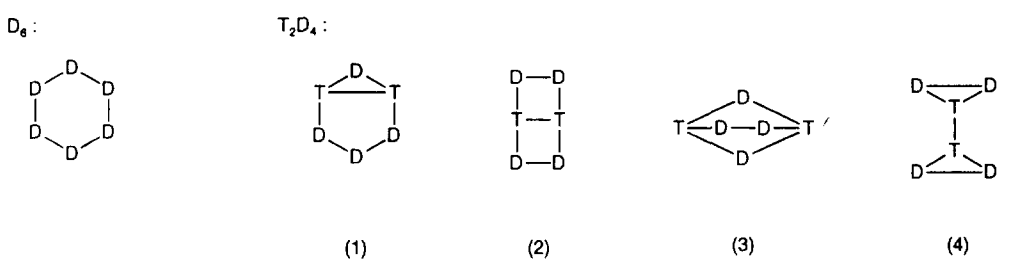

Fig. 11. Symbolic representation of D_6 and of geometric isomers of T_2D_4.

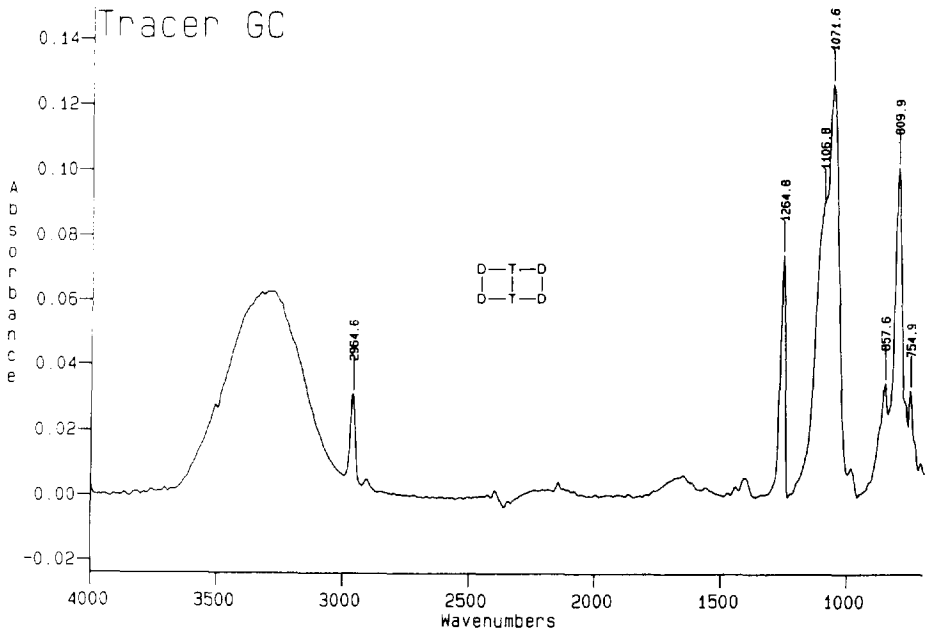

Fig. 12. Spectrum of the compound corresponding to the peak at the retention time of 8.3 min in the GS chromatogram, assigned to T_2D_4 (M_r 430).

assigned by these both techniques may be used as reference material for identifying low-molecular-mass siloxanes.

References

[1] D.W. Scott, *J. Am. Chem. Soc.*, 68 (1946) 356.
[2] W. Patnode and D.F. Wilcock, *J. Am. Chem. Soc.*, 68 (1946) 358.
[3] C.B. Hurd, *J. Am. Chem. Soc.*, 68 (1946) 364.
[4] G. Garzó, J. Tamás, T. Székely and K. Ujszászi, *Acta Chim. (Budapest)*, 69 (1971) 273.
[5] G. Alexander and G. Garzó, *Chromatographia*, 7 (1974) 190.
[6] J. Powell and S. Compton, *Tech. Quart.*, 3 (1991) 123.
[7] N.R. Smyrl, D.H. Hembree, Jr., W.E. Davis, D.M. Williams and J.C. Vance, *Appl. Spectros.*, 46 (1992) 2, 277.
[8] S. Bourne, A.M. Haefner, K.L. Norton and P.R. Griffiths, *Anal. Chem.*, 62 (1990) 2448.
[9] H. Kriegsmann, *Advances in Molecular Spectroscopy*, Pergamon Press, Oxford, 1962, pp. 999–1014.
[10] H. Kriegsmann, *Z. Anorg. Allg. Chem.*, 298 (1959) 232.
[11] E.D. Lipp and A.L. Smith, in A.L. Smith (Editor), *The Analytical Chemistry of Silicones*, Wiley, New York, 1991, p. 323.
[12] A.L. Smith, in J.R. Durig (Editor), *Chemical, Biological and Industrial Applications of Infrared Spectroscopy*, Wiley, New York, 1985, p. 73.
[13] H. Jancke, G. Engelhardt, M. Mägi and E. Lippmaa, *Z. Chem.*, 13 (1973) 392.
[14] G.M. Brissey, D.E. Henry, G.N. Giss, P.W. Yang, P.R. Griffiths and C.L. Wilkins, *Anal. Chem.*, 56 (1984) 2002.