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GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF COMPOUNDS GENERATED UPON THERMAL DEGRADATION OF SOME STATIONARY PHASES IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The thermal degradation products of some immobilized stationary phases for gas chromatography were studied. Column bleed products were analyzed by gas chromatography-mass spectrometry (GC-MS); pyrolysis GC-MS was also utilized in this study. The phases studied were: SE-30; methyltolyl silicone (33% tolyl); cyanopropyl(methyl)tolylsilicone (50% cyanopropyl, 25% methyl, 25% tolyl); Carbowax 40M. Cyanopropyl- and tolyl-substituted silicones were degraded mainly to three- to five-membered cyclics, but the cleavage of substituent groups seems to be relatively limited. The degradation products of Carbowax 40M consisted of homologous series of polyethylene glycol derivatives.

INTRODUCTION

Column deterioration was often experienced earlier as a consequence of a physical rearrangement of the stationary phase on the capillary surface at elevated temperatures. Due to stationary-phase immobilization, this is no longer a restricting factor. At present, the thermal stability is determined mainly by the polymer being used as the stationary phase, and the observed column bleed is in most cases due to the elution of stationary-phase degradation products. Such degradation is influenced by several factors: (a) The composition of the supporting surface. Alkali metals catalyze silicone degradation, and silanol groups or certain siloxane bridges also promote silicone degradation. (b) Stationary-phase structure. For a silicone, the stability is greatly influenced by the nature of the side groups and type of chain termination. (c) Stationary-phase purity. Silicones should not contain residues of alkali-metal catalysts. (d) Purity of carrier gas. Traces of oxygen may oxidize Carbowax and also some silicones that have easily oxidized side groups, *e.g.*, tolyl. (e) Injection of reactive solutes, *e.g.* samples containing residues of certain derivatization reagents. (f) Column geometry and film thickness, *i.e.*, the amount of phase present in the column and the area being exposed to carrier gas. (g) Carrier gas flow-rate. However, this factor may be of minor importance¹.

Methods for quantitation of column bleed have been described^{1,2}. However,

it may be of interest to study column bleed also from a qualitative aspect. It was thought that such a study could yield knowledge that could serve as a basis for improvements in thermal stability of capillary columns. This has been studied to some extent for packed column gas chromatography (GC) by Paramasigamani and Aue³. Further, there is a vast amount of information in the literature about the thermal degradation of common polymers.

Several new types of polymers are now being developed for use as stationary phases, and it is of interest to evaluate their thermal stabilities under typical chromatographic conditions, in order to determine whether or not they are suitable as phases for GC. In this introductory work, the column bleed from some new and older types of stationary phases has been studied under realistic conditions.

EXPERIMENTAL

Fused-silica capillary tubing, 10 m × 0.25 mm I.D. (Hewlett-Packard, Avondale, PA, U.S.A.), was deactivated, coated with phase, cured and rinsed as published elsewhere⁴⁻⁸. The phases used for bleeding tests and the separation of bleed products were: methylsilicones⁴; tolyl(methyl) silicones⁵; cyanopropyl(methyl)tolylsilicones⁶; Carbowax 40M⁷ and silarylene/methyl phenylsiloxane block copolymer⁸. Deactivation was omitted for columns coated with cyanosilicone. Bleeding from columns was studied in a Carlo Erba 2150 gas chromatograph, equipped with an especially clean inlet system for the hydrogen carrier gas, the injector system not being connected. In order to collect bleed products, the end of the column was taken out through the opening for the thermometer, and allowed to dip into a small vial containing *ca.* 2 ml of freshly distilled benzene or, in some cases, methylene chloride. Bleeding was effected by heating at 300°C during 3.5 h for SE-30, tolyl/methylsilicone and immobilized Carbowax 40M. For cyanosilicone, the bleeding was allowed to take place at 275°C. After bleeding, column bleed products that might have been trapped on the last 20 cm of the column were rinsed out with benzene or methylene chloride, whichever the vial contained. The solutions of stationary-phase degradation products were concentrated before gas chromatographic-mass spectrometric (GC-MS) analysis. Blanks were prepared by carrying out the above procedure at a low column temperature (40°C).

A Carlo Erba 2150 or a Hewlett-Packard 5790 gas chromatograph was connected to a JEOL JMS-D300 mass spectrometer equipped with a Finnigan INCOS data system. The bleed products were separated on columns, coated with immobilized SE-52 or silphenylene/methylphenylsiloxane block copolymer. Cyclic siloxanes may be formed from the septum, therefore a low-bleed septum, Stabiline (Pierce Eurochemie, Rotterdam, The Netherlands), was used in combination with a relatively intensive septum flush. Further, in order to avoid pyrolysis of bleed products in the GC injector, a relatively low injector temperature was used for the Carbowax bleed products. Injector pyrolysis of Carbowax has been demonstrated by Grob⁹.

In a few cases, stationary phase degradation was studied also by pyrolysis GC-MS. The pyrolysis products were trapped on silanized glass beads at liquid nitrogen temperatures before GC separation on a capillary column, coated with immobilized SE-54. The column was connected to the mass spectrometer, as mentioned above. This system has been described recently¹⁰. The polymer (*ca.* 10 mg) was thus

placed in the pyrolysis tube, and the sample was rapidly heated in a flow of helium to 300°C, isothermal for 5 min.

RESULTS

The purpose of this work was to study the stationary-phase degradation products which are formed in a capillary column at elevated temperatures. Several products may be formed, but all we can detect are the stable compounds.

Generally, in GC analysis, a certain part of what is seen as column bleed may come from plasticisers, etc., present in the system. In order to avoid any contribution from such compounds, a gas chromatograph was equipped with a special clean carrier gas inlet system. Bleed products were trapped in a vial, containing benzene, at the end of the column. The most volatile compounds could not, however, be trapped in this system. Such compounds may be of interest since their presence can indicate changes in column polarity. An example of this is the formation of toluene from tolyl-substituted silicones. Pyrolysis GC is a method commonly used for polymer characterization^{11,12}, and it was found that such a system was suitable for the study of low-boiling degradation products. Some stationary phases are degraded to products of a wide range of molecular weights; for the elution of the high-boiling components of the degradation products, a system temperature of 330°C is often required. Such rather extreme conditions could not be met with the pyrolysis unit, but they were easily attained when degradation products trapped in benzene were subjected to GC-MS. In this investigation, the two methods thus complement each other.

The MS characterization of methylsiloxanes was relatively easy, since reference substances were available and/or spectra have been published¹³⁻¹⁵. To our knowledge, no reference substances or spectra are available for tolylcyclosiloxanes and cyanopropylcyclosiloxanes. Acid hydrolysis of corresponding dichlorosilanes gives a mixture of cyclics, which may serve as standard substances. These cyclics were characterized only by GC-MS. The peak assignments given in the chromatograms are thus not to be considered as identification in the very strictest sense.

Thermal degradation of methylsilicones

Thermal degradation of methylsilicones has been extensively studied. In an inert atmosphere at 300-500°C, dimethylsilicones decompose to cyclics. Somewhat different proportions of the different cyclics have been reported¹⁶⁻¹⁸. D₃, hexamethylcyclotrisiloxane, is always the main degradation product, but the proportion of D₄ may be slightly increased when degradation occurs in the presence of potassium hydroxide¹⁸. Fig. 1 shows the trapped degradation products from immobilized SE-30, when bleeding was performed at 300°C. The formation of dicyclic products has been suggested^{18,19}, but no such compounds could be detected in this sample.

The thermal degradation of a methylsilicone may proceed according to two different mechanisms²⁰. The first, referred to as backbiting, is initiated by terminal silanol groups. A post-silanization of the column may be an effective means of blocking such residual silanol groups¹ and give increased thermal stability. The second mechanism is a random chain scission, as suggested by Thomas and Kendrick²¹. Such a degradation would be counteracted by a diminished mobility of the chains. This may be achieved by cross-linking, but a fairly high degree of cross-linking would

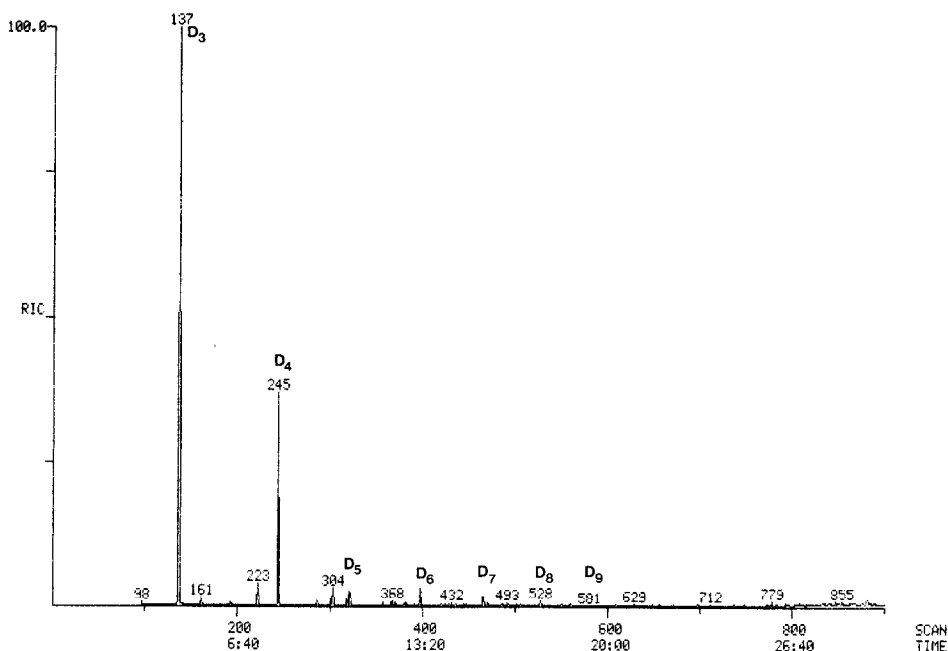


Fig. 1. Reconstructed ion chromatogram (RIC) of the degradation products from a capillary column coated with immobilized SE-30. The separation was performed on a 10-m fused-silica column coated with immobilized SE-52. Injector temperature: 275°C. Injection at 40°C, programmed at 5°/min to 300°C. Peaks: dimethylcyclosiloxanes, D = (CH₃)₂SiO.

be required, and such a polymer would be unsuitable for chromatography. The cross-linking that we introduce on stationary phase immobilization is much too dispersed, *ca.* 100–400 units between cross-links²², to influence chain scission markedly. In fact, when the support is inert and the silicone phase does not contain harmful catalyst residues or silanol groups, the thermal stability cannot be much further improved. However, an additional increase in thermal stability would be possible by strengthening the polymer backbone, which may be achieved in silarylene/siloxane block copolymers⁸.

Thermal degradation of methyltolylsilicones

Tolylsilicones have recently become of interest as stationary phases for GC^{5,23,24}. It was found by Richter *et al.*²⁴ that heating to 175°C of a methyltolylsilicone, doped with 5 wt.% dicumyl peroxide (DCP), resulted in some chemical reactions leading to carbonyl as observed by IR spectroscopy. Tolylsilicones are however very easily cured, and in our work only 0.5 wt.% of DCP is needed for the immobilization of such phases⁵. When such a low concentration of peroxide is used, the curing conditions may be considered as mild. Columns prepared in this way show very good deactivation, and no change in the phase composition could be detected chromatographically after curing⁵. It was considered to be of interest to determine whether the bleed products from such columns contained any oxygenated compounds. Several types of cyclics were found (Fig. 2), but no oxygenated compounds

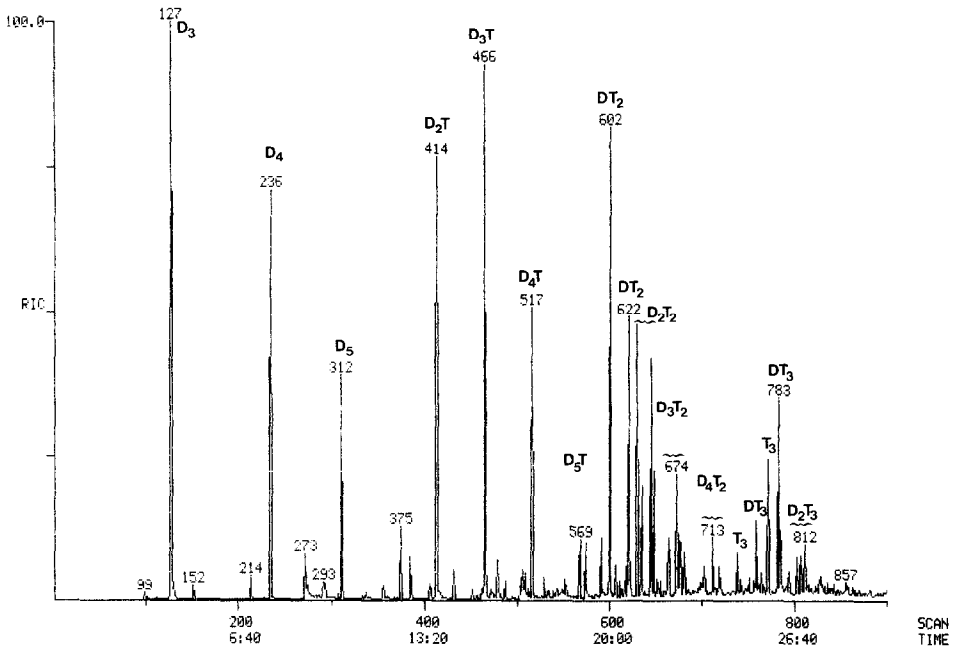


Fig. 2. Reconstructed ion chromatogram of the degradation products from a capillary column coated with immobilized methyltolylsilicone (33% tolyl). Conditions as in Fig. 1. Peaks: cyclosiloxanes, D = $(\text{CH}_3)_2\text{SiO}$; T = tolylmethyl SiO.

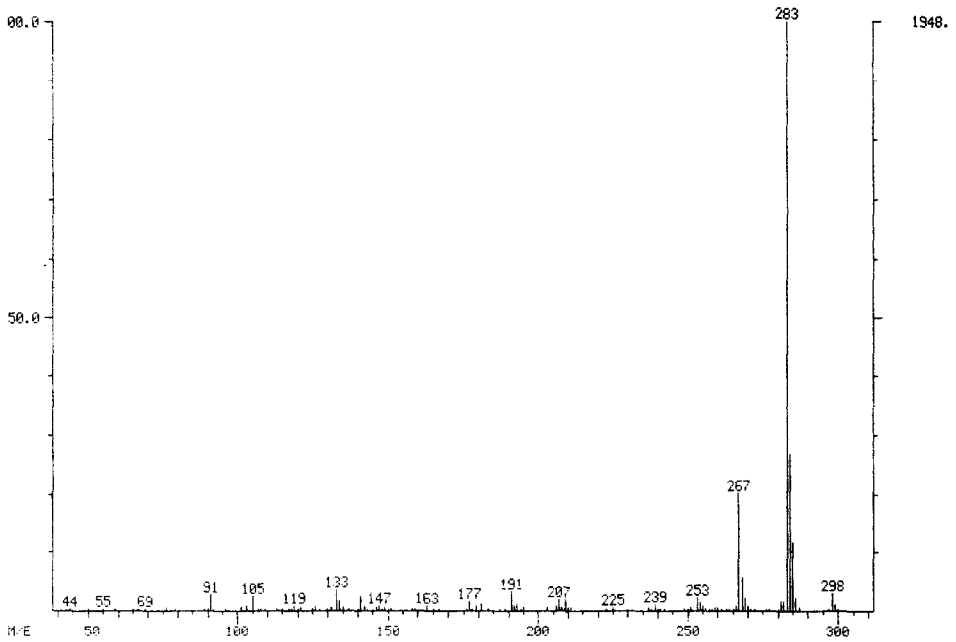


Fig. 3. Mass spectrum of peak D_2T in Fig. 2. Ionization voltage: 70 eV.

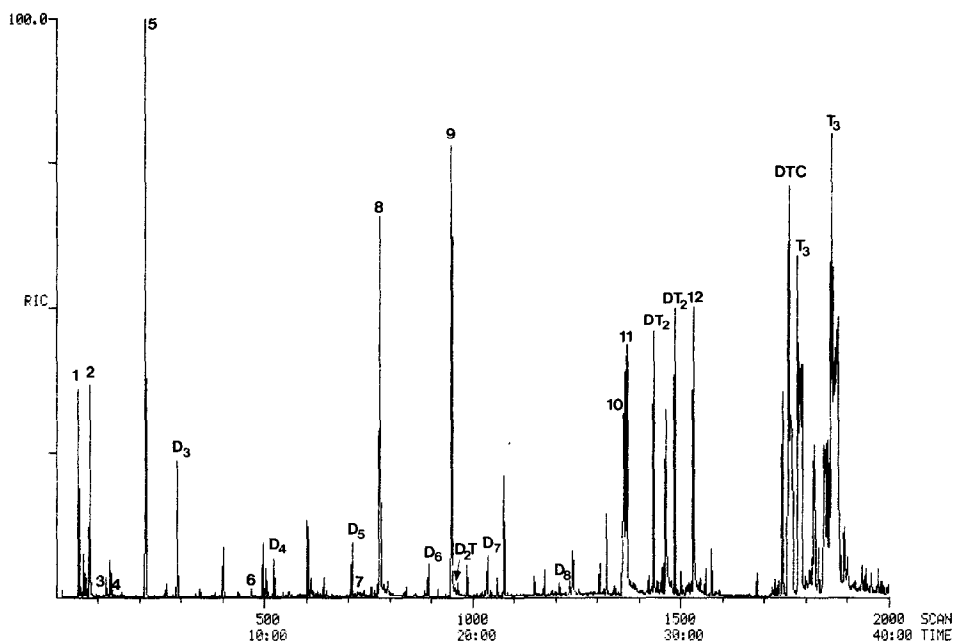


Fig. 4. Reconstructed ion chromatogram from a pyrolysis GC-MS analysis of 10 mg of a cyanosilicone stationary phase containing 50% cyanopropyl, 25% tolyl and 25% methyl groups. Pyrolysis conditions: 5 min at 300°C. After trapping on silanized glass beads at liquid nitrogen temperature, the degradation products were separated on a 20-m fused-silica column, coated with immobilized SE-54. Column programmed from 30 to 270°C at 10°/min. Peaks: 1 = carbon dioxide; 2 = methylene chloride; 3 = 3-butene nitrile?; 4 = butane nitrile?; 5 = toluene; 6 = benzaldehyde; 7 = benzoic acid; 8 = dimethyltolylsilanol; 9 = tetramethyltolylsiloxanol, MW = 240; 10 = trimethylcyanopropylsiloxanol, MW = 270; 11 = hexamethylcyanopropyltrisiloxane, MW = 342; 12 = pentamethyltolyltrisiloxanol, MW = 390. Cyclosiloxanes: D = (CH₃)₂SiO; T = methyltolyl SiO; C = bis(cyanopropyl) SiO.

could be detected in this case. The distribution between the different types of cyclics was somewhat similar to what may be achieved with methylphenylsilicones²⁵⁻²⁷. A mass spectrum of one of the cyclics is shown in Fig. 3. It has been suggested that the fragment M-31 emanates from the formation of an *o*-phenylene bridge between silicon atoms and elimination of methane^{28,29}.

Thermal degradation of cyanosilicones

Cyanosilicones as stationary phases have been extensively studied by our group^{6,30-32}. Cyanosilicones cannot readily be cross-linked, and in order to make cross-linking possible, copolymers of cyanopropyl- and tolyl-substituted silicones have been prepared. These polymers can be immobilized and are very useful for the separation of fatty acid methyl esters⁶. At 250°C, bleeding becomes apparent, and in some cases a rising baseline is furnished with small peaks. A study of the column bleed was therefore considered to be of interest.

A 10-mg amount of a silicone stationary phase, containing 50% cyanopropyl, 25% methyl and 25% tolyl groups, was pyrolyzed at 300°C (Fig. 4). By this method, the yield of low-boiling material is somewhat favoured, as compared with the higher

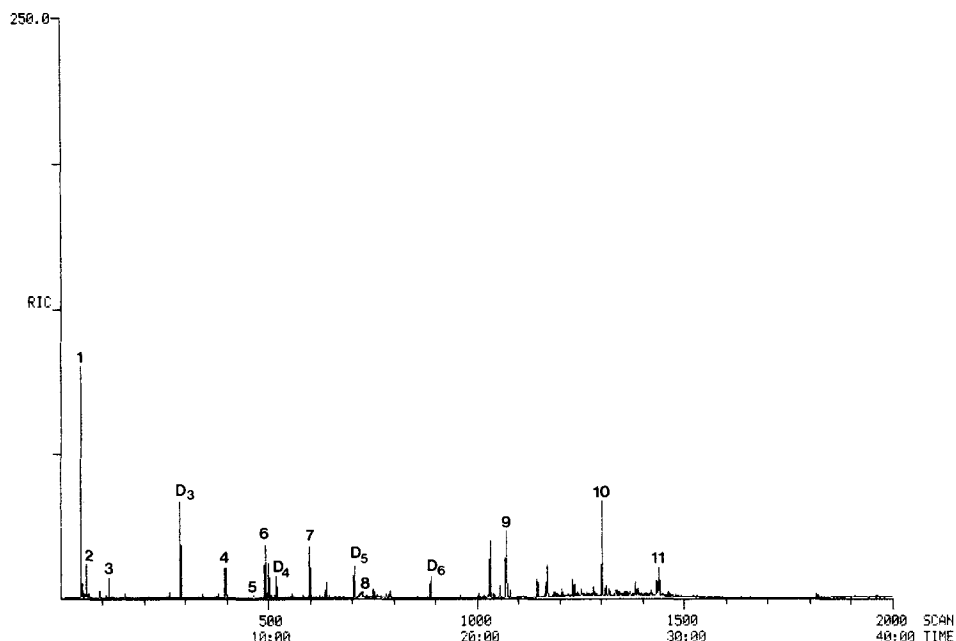


Fig. 5. Blank run of the pyrolysis GC-MS system. Peaks: 1 = carbon dioxide; 2 = acetone; 3 = benzene; 4 = 2-butoxyethanol; 5 = benzaldehyde; 6 = 1-methylethenylbenzene; 7 = 1-phenylethanone; 8 = benzoic acid; 9 = 2,6-bis(1,1-dimethylethyl)-4-methylphenol; 10 = cyclotrisiloxane; 11 = phthalate.

boiling compounds, due to the difficulty in transferring the latter through the system. A blank is shown in Fig. 5.

Although the sample had been subjected to a stream of nitrogen at 200°C for 1 h, it still contained residues of the solvent (Fig. 4, peak 2). Fairly rigorous conditions are thus required for solvent removal. This should be considered when solvent residues are to be evaporated after a static coating, since it is desirable that the solvent is completely removed before the curing step. Further, when a column has been rinsed with solvent after the curing step, it may contain residues of adsorbed solvent for some time. Since it is known that some silicones are degraded in solution³³, it is important that solvent residues be evaporated as quickly as possible.

Toluene is formed upon degradation, but the amount is small compared with the cyclics, *e.g.*, peak T₃ (Fig. 4). It should be noted that the T₃ peaks in the chromatogram are truncated, because the signals to the mass spectrometer data system are intense. Their intensities should be at least ten times higher than those shown in Fig. 4.

The intensities of benzaldehyde and benzoic acid (peaks 6 and 7) were very low, which may indicate that such carbonyl compounds are of minor importance for this type of phase. Moreover, they were present also in the blank. The cyanopropyl group seems to be relatively firmly anchored to the silicon atoms, since only traces of degradation products emanating from that particular group could be found. 3-Butene nitrile and butane nitrile (peaks 3 and 4) were tentatively identified.

Bleed products of higher molecular weight could be analyzed by trapping and

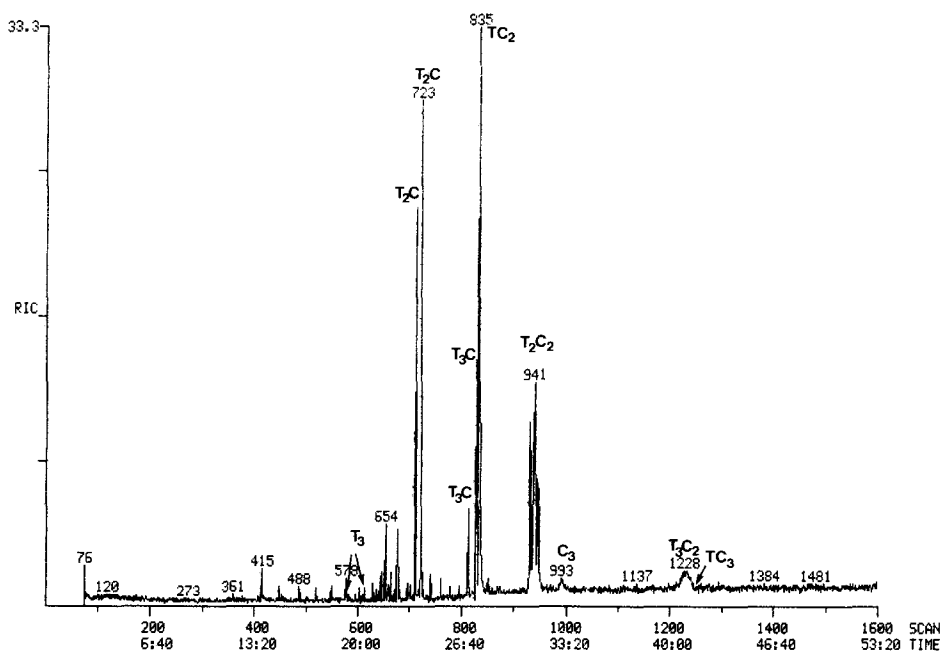


Fig. 6. Reconstructed ion chromatogram of a benzene solution of the degradation products from a capillary column coated with immobilized cyanosilicone stationary phase (same phase as in Fig. 4). The separation was performed on a 10-m fused-silica column coated with immobilized silarylene/di(methylphenyl)siloxane block copolymer. Splitless injection; injector temperature 330°C; injection at 70°C, programmed at 10°/min to 330°C. Peaks: cyclosiloxanes, T = methyltolyl SiO; C = bis(cyanopropyl) SiO.

subjecting to GC-MS. The first peaks appearing in this analysis, *e.g.*, methyltolyl-cyclotrisiloxane (Fig. 6), are the same as the compounds having the highest retention in the chromatogram from the pyrolysis study. The separation of the trapped material was performed on a column coated with silarylene/methylphenylsiloxane block copolymer⁸. Such a column may be used at 350°C, but here it was operated at 330°C, since this was the highest temperature that could be tolerated by the GC-MS interface. The high temperature was necessary for the elution of the highest boiling cyclics. A blank is shown in Fig. 7. The blanks contain bleed products from the injector of the gas-chromatograph used in connection with the mass spectrometer, and also some traces of cyclics from the column from which bleed products were to be collected.

The most abundant degradation products were methyltolyl-di(biscyanopropyl)-cyclotrisiloxane and di(methyltolyl)-di(biscyanopropyl)-cyclotetrasiloxane, Fig. 6. These were obviously the most stable of the degradation products. An attempt was made to find a correlation between the proportion of different cyclics and the curing method used, but no such correlation could be found. A mass spectrum of the cyclotrisiloxane TC₂ is shown in Fig. 8.

Cyclics of higher MW than those shown in Fig. 6 may certainly be formed in a column, but these could not be eluted in our chromatographic system. They require high temperatures and their stability at these temperatures may be questioned.

It was speculated that cyanosilicones were in some way destabilized by the

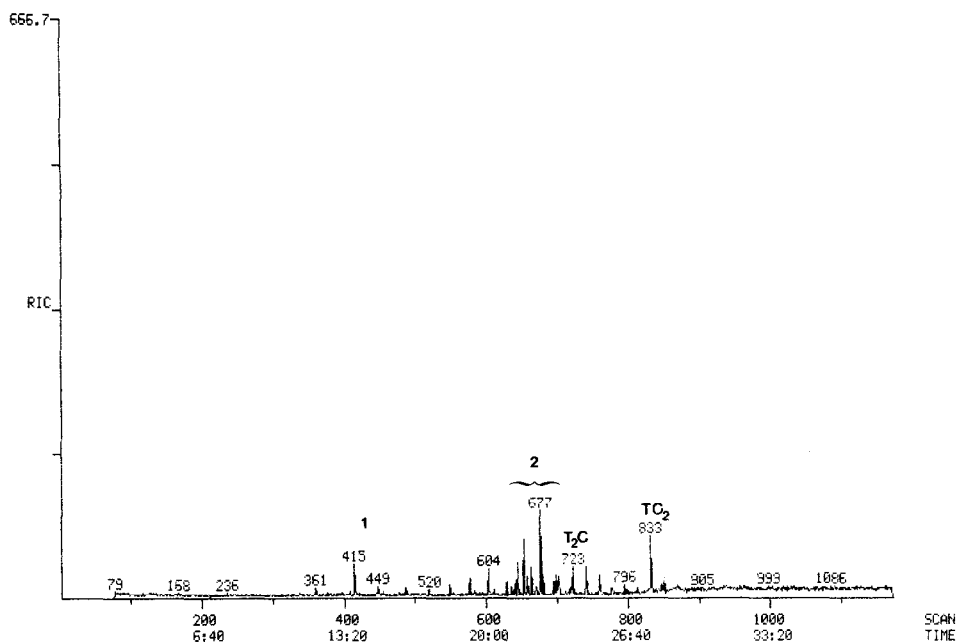


Fig. 7. Blank run of the system used in Fig. 6. Peaks: 1 = phthalates; 2 = bleed products from the injector of the gas chromatograph used in connection with MS. Cyclosiloxanes as in Fig. 6.

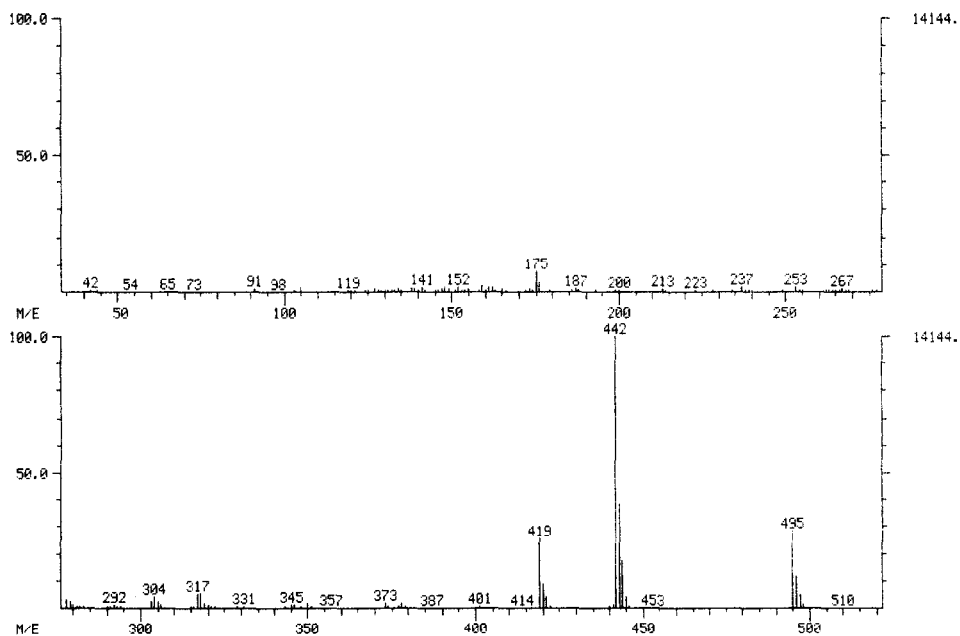


Fig. 8. Mass spectrum of peak TC_2 in Fig. 6. Ionization voltage; 70 eV.

tolyl groups, and it was found that the use of vinyl groups instead of tolyl to facilitate immobilization resulted in an improved thermal stability⁶. Columns coated with such phases showed lower bleed rates than corresponding cyanopropyl/tolyl-coated columns. Further, the bleeding started to appear at somewhat higher temperatures (260°C) and the small peaks that populated the rising baseline of cyanopropyl/tolyl columns were absent from cyanopropyl/vinyl-coated columns.

Thermal degradation of Carbowax 40M

Column bleed products were collected and subjected to GC-MS. Programming to 330°C was necessary for the elution of the high-boiling degradation products, Fig. 9. The molecular weights could be determined by use of the field desorption technique, and these are given in Fig. 10. A maximum around molecular weight 500 was observed. The intense peaks at 45 and 59 were most likely formed as fragments in the mass spectrometer. The rôle of oxygen in the Carbowax degradation was recently discussed³⁴.

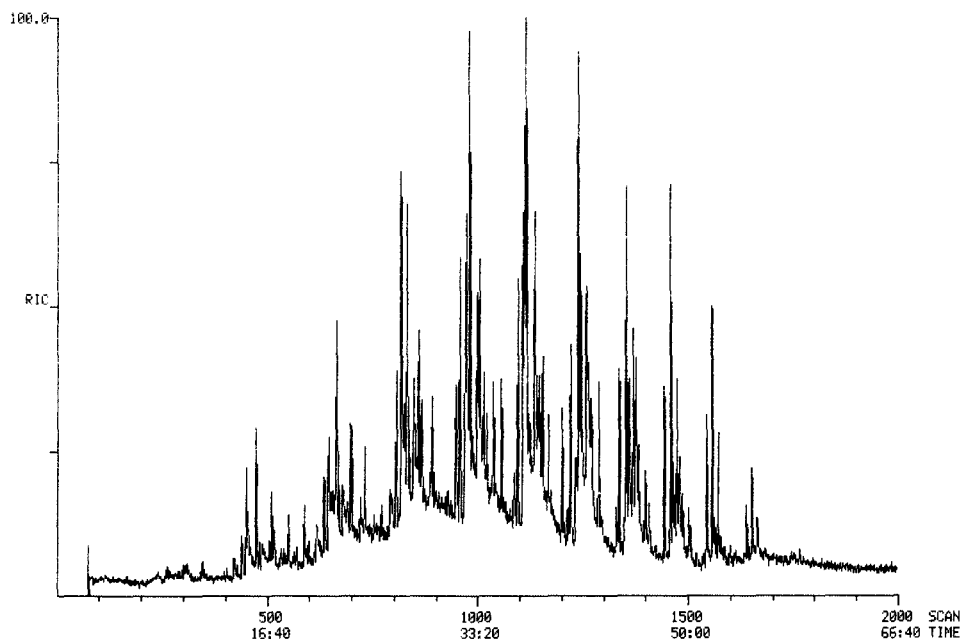


Fig. 9. Reconstructed ion chromatogram of a benzene solution of the degradation products from a capillary column coated with immobilized Carbowax 40M. Column as in Fig. 6. Splitless injection, split closed 2 min. Injector temperature: 275°C. Injection at 70°C, programmed at 10°/min to 330°C. Peaks: homologous series of poly(ethylene glycol) derivatives.

CONCLUSIONS

In recent years, several factors that influence precision and reproducibility in gas chromatography have been improved. The quality of the stationary phase has thereby become a limiting factor, and improved stationary phase grades are desirable. This concerns mainly polar and polarizable phases. First, phases ought to be very

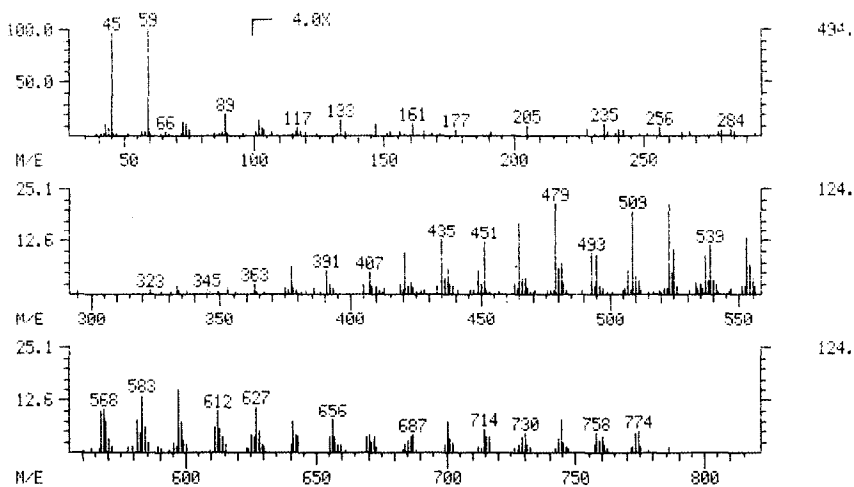


Fig. 10. Field desorption mass spectrum of the sample of degradation products from immobilized Carbowax 40M in Fig. 9. Emitter heating: 0–20 mA at 2 mA/min. Field strength: 7 kV.

similar from batch to batch. Secondly, they ought to maintain their properties during use, even when stressed by, *e.g.*, high temperatures or the injection of polar solutes.

In this work, we have started to acquire fundamental knowledge about the bleed process, which may serve as a basis for improvements. The formation of cyclics on degradation of differently substituted silicones was thus demonstrated. An approach to further increased chemical stability of silicones would be the construction of polymers where degradation through the formation of cyclics is counteracted. For this purpose, ladder polymers^{35,36} and copolymers of silarylene and siloxanes^{37–39} have been prepared. The latter type of polymer is presently being developed for use as a stationary phase in our laboratory, and we will report on this in a future publication.

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