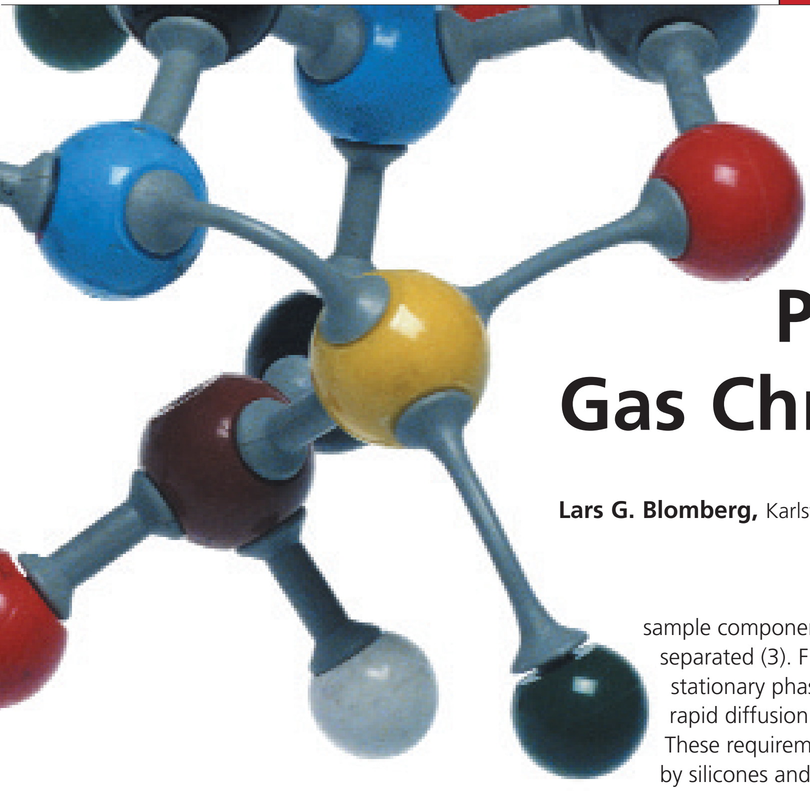


Silicone Stationary Phases for Gas Chromatography

Lars G. Blomberg, Karlstad University, Karlstad, Sweden.

Introduction

Gas chromatography (GC) is generally considered to be a mature technique, sometimes even a technique at a standstill (1). Nevertheless, several new developments have appeared in recent years: high-speed GC, high-temperature GC, solid-phase microextraction GC, large-volume injection and two-dimensional (2D)-GC. However, when it comes to the separation column itself, the very heart of the system, it appears that development has stagnated. Column preparation is now almost totally commercialized, and it seems that column-manufacturing companies do not always have the incentive to perform major new developments. Such developments are of a long-term character, and column-manufacturing companies often view the market with a short-term perspective. In my opinion, it is possible to prepare columns with much improved properties compared with the columns available today. However, users are not always aware of what they are missing, and as a result no motive for major improvements exists. These aspects were discussed in a recent article (2). In this article, I will describe desirable column properties, report on the state of the art, discuss current aspects of silicone synthesis and outline the properties of future columns.

Desirable Column Properties

Silicones: A stationary phase for GC must fulfil certain basic requirements. It must be chemically inert, non-volatile and thermally stable. Furthermore, it must have solvent power and possibly selectivity for the sample components to be separated (3). Finally, the stationary phase must allow rapid diffusion of the analytes. These requirements are met by silicones and, therefore, silicones are preferred as stationary phases for GC.

Separation efficiency: The rapid exchange of analytes between the stationary and mobile phases is a presupposition for high separation efficiency in capillary GC. For this purpose, the stationary phase must, as mentioned above, allow rapid analyte diffusion. Silicones are excellent in this respect because their molecular chains are highly flexible. The degree of flexibility, however, depends on the silicone substituent groups because larger groups suppress chain flexibility. Silicones substituted with phenyl-, cyanopropyl- and similar groups thus supply a somewhat lower diffusivity than, for example, methylsilicones. However, the more polar silicones have other virtues; for example, they provide selective interactions with the analytes. In modern capillary GC, stationary phases are immobilized by cross-linking in order to improve the physical stability of the stationary phase film. However, such cross-linking counteracts chain flexibility, and the degree of cross-linking must be adjusted so that the polymer film is immobilized but sufficient diffusion can still be provided. Finally, it is considered best that the film of stationary phase is uniform along the entire length of the capillary. To obtain an even film, the supporting surface must be wetted by the silicone. For coating with more polar silicones, the fused-silica surface must be modified in order to achieve proper wetting. This leads us to modification of the fused-silica surface — this technique is also used to deactivate adsorptive sites at the capillary surface. In conclusion, the highest separation efficiencies are obtained with methylsilicones, but other types of silicones possess other attractive properties, such as selectivity or high thermal stability.

Adsorptive activity: In the early days of capillary GC, adsorption of polar analytes at the capillary wall resulted in tailing chromatographic peaks. Surface deactivation can now be successfully achieved, either as a separate deactivation step prior to coating with stationary phase or by adding a deactivating reagent to the coating solution. Furthermore, when using suitable silicones, the stationary phase itself can, upon heating, deactivate the surface. In general, column deactivation is not a problem any more. However, the fused-silica surface is somewhat acidic and this may lead to adsorption of amines. If you want to separate amines, specially deactivated columns are available. It should also be noted that the type of deactivating reagent should be adapted to suit the column temperature. There is no point coating with a highly thermally stable silicone stationary phase when the deactivating layer has a much lower temperature limit.

In essence, the advent of efficient column deactivation was a key issue in the development of modern capillary columns for GC. It made separation of underivatized polar analytes possible and thus increased the need for further development of polar columns, as described later in “Column selectivity.”

Reproducibility of retention time: For the user, it is important that retention times and selectivities can be reproduced over time and from column to column. Let us first consider column stability during use. As a rule of thumb, non-polar columns are much more robust than polar columns.

However, to obtain a long column lifetime the column should be properly treated; that is, oxygen and moisture should not be allowed to enter the column and column temperature should not exceed recommended values. A further stress factor occurs when non-volatile compounds enter the column; for example, in connection with on-column injection.

Column manufacturers often synthesize their stationary phases in-house. To maintain constant silicone properties it is important that the synthesis is performed under carefully controlled conditions. For methylsilicones, the synthesis is relatively straightforward, but for polar silicones, advanced methods must be applied to achieve a reasonable reproducibility. It seems to me that the synthesis of moderately polar and polar silicones is not as reproducible as it could be, as described later in "Silicone Synthesis."

Thermal stability: At elevated temperatures silicones are thermally degraded. By means of a so-called backbiting mechanism cyclic fragments are formed from silanol-terminated silicones (Scheme 1).

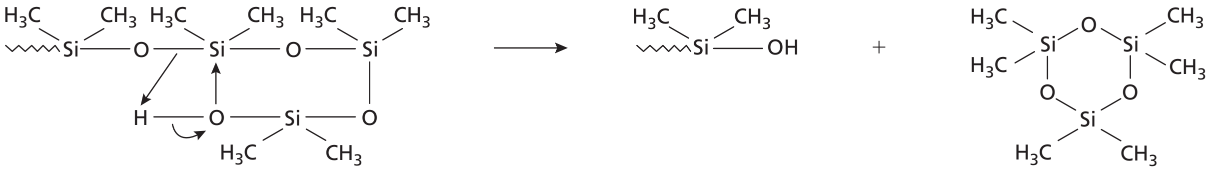
In silanol-terminated polysiloxanes, end-group silanols bend over backwards and attack the backbone. Cyclic polysiloxanes are detached and the end-group silanol is reformed. The degradation will thus continue (Scheme 2).

Cyclics are also formed from endcapped silicones. The dimethyl polysiloxanes generally occur in a helical form and degradation takes place at elevated temperatures when neighbouring coils interact. It is proposed that a siloxane bond rearrangement occurs through the formation of an intramolecular, cyclic, four-centre transition state, which is involved in the rate-determining step of the polysiloxane degradation process (20) (Scheme 3).

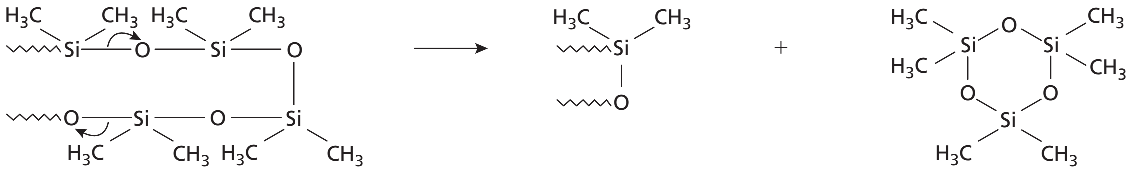
Also, thermal degradation of phenyl-substituted derivatives results in the formation of cyclics (20). However, at high temperatures, the scission of the phenyl group from silicon can predominate leading to the formation of insoluble polymer residues and benzene (20). The column degradation products can give a cumbersome background in the detection system, for example, in a mass spectrometer.

During recent years, columns coated with stationary phases of high thermal stability have become commercially available. These phases are, in general, copolymers of silarylene and polysiloxane in which an aryl group is introduced into the polymer backbone. The backbone thereby becomes more rigid and the above mentioned degradation mechanisms are counteracted. Another type of thermally stable polysiloxanes is the so-called ladder polymers. Both types of thermally stable polysiloxanes were presented many years ago (4–6), but it was not until recently that columns coated with these phases became commercially available.

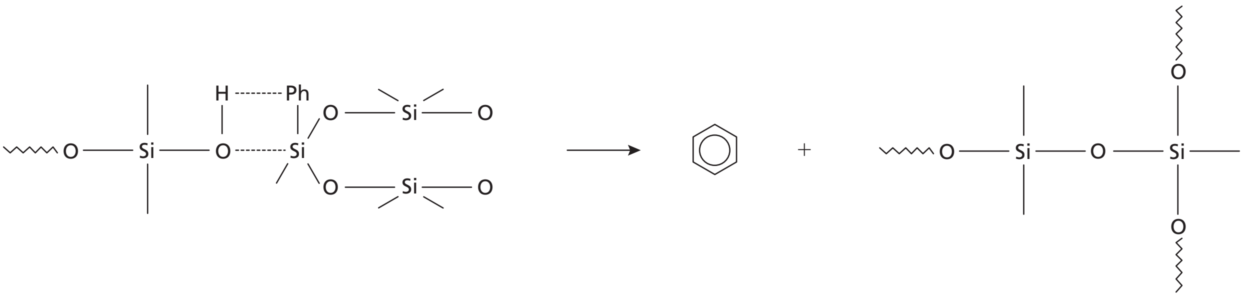
Column selectivity: With capillary columns, high plate numbers can easily be achieved and some experts maintain that about 90% of the analytical tasks for which GC is the method of choice could be solved with the application of non-polar columns. Thus, it was thought that selective stationary phases would be needed only in special instances. However, with the advent of well deactivated columns, interest in the GC separation of



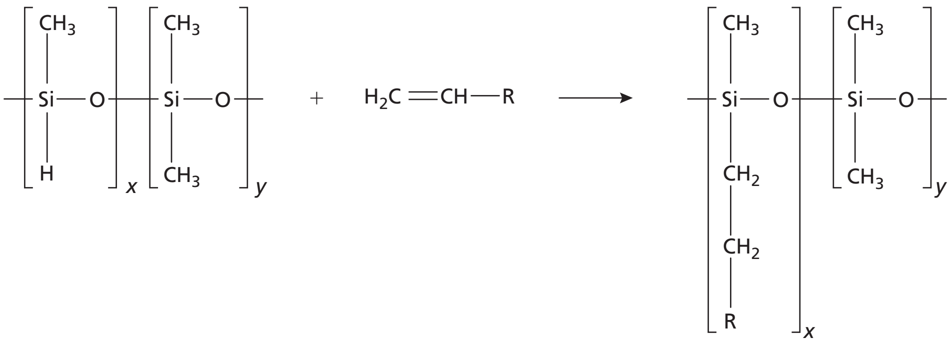
Scheme 1: *Thermal degradation of silanol-terminated dimethyl polysiloxanes.*



Scheme 2: *Thermal degradation of endcapped dimethyl polysiloxanes.*



Scheme 3: *Thermal degradation of phenyl substituted polysiloxanes.*



Scheme 4: *Hydrogen addition.*

polar analytes has grown dramatically. Separation of polar analytes is best performed on moderately polar or polar columns and, in fact, there is an increasing demand for such columns.

Silicone Synthesis

General methods: This area has already been discussed by the present author several years ago (7–9). As mentioned previously, it takes advanced synthetic methods to achieve batch-to-batch reproducibility.

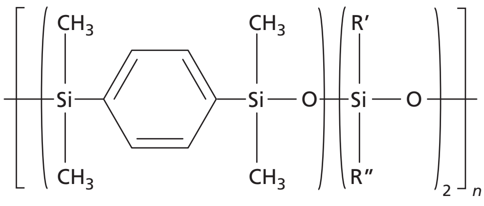
Traditional polymerization reactions involve the formation and breaking of chains, equilibration (10–12). At a certain point in the reaction, the average chain length is at a maximum, thus if the reaction is allowed to proceed further, the average chain length will decrease (10–12). Polymer chain length affects properties, such as support deactivating ability and cross-linking density. However, for non-polar silicones, synthesis can be performed with high reproducibility. This is, as mentioned above, in contrast to more polar silicones, especially in the situations when more than one type of monomer is used for the synthesis. When using two or more types of monomer, the route to reproducibility of the polymer is to prepare regularly alternating polymer structures. To achieve this from, for example, two different monomers or oligomers, the monomers must be terminated so that they can only react with each other and not with themselves. A polymer of this type will, of course, not be equilibrated. In summary, synthesis under controlled conditions is important because this is the only way to achieve a reasonable batch-to-batch reproducibility. Such reproducibility is important because the polymer structure affects (1) the chromatographic properties and (2) the thermal stability of the silicone. Further details are provided in "Methyl/phenol silicones" and "Siloxane/silarylene copolymers."

Hydrogen addition: The monomers or oligomers needed for the polymer synthesis are often not commercially available, and they must be synthesized in house. Such synthesis is sometimes performed by means of hydrogen addition (13). Several applications to stationary phase synthesis have been reported (14–18) (Scheme 4).

For such a reaction, a Pt-salt is used as a catalyst. However, it is not possible to totally remove the catalyst after the reaction and a low concentration always remains. Such residues can have an effect on the column stability, as well as on the analytes. For example, catalyst residues may help to immobilize the polymer in the capillary. This can be regarded as an advantage, but the reaction is not controlled and it cannot be terminated in a controlled way. In addition, it is not unlikely that reactive unsaturated analytes can be hydrogenated in a hot column containing a Pt-catalyst and hydrogen as a carrier gas.

The hydrogen addition approach is also applied for addition of special substituent groups to a silicone polymer. For that purpose, a copolymer consisting of dimethyl units and methyl/hydrogen units is first synthesized or simply obtained from a commercial source. To be able to prepare a reproducible stationary phase, the polymer should have a regularly alternating structure (i.e., the Me–Si–H units should occur at regular intervals). In a random polymer, the H-carrying units may occur close to each other and for sterical and other reasons, all the H-moieties do not react with the substituents (i.e., the degree of substitution will vary from batch to batch). Further, analyte interactions with the stationary phase can be different with isolated substituent groups when compared with vicinal groups.

Methyl/phenyl silicones: The methyl/phenyl silicones are an important group of silicone stationary phases. These silicones have an intermediate polarity and they are quite useful when a sample contains substances from different classes of chemical compounds. Let us consider a polymer having 50% methyl and 50% phenyl substitution. The polymer can be synthesized from one monomer, a methyl/phenyl silane. Another possibility is to prepare a copolymer containing dimethyl units and diphenyl units. Some years ago, we demonstrated that the two types of methyl/phenyl silicones have different properties. The dimethyl/diphenyl type of silicone showed a higher thermal stability than the simple methyl/phenyl polymer. Furthermore, we could show that the two polymers had different retentive properties (19). The observed improvement in thermal stability can be explained as being a consequence of a disturbance, by the phenyl groups, of the helical structure of the silicone



Scheme 5: *Structure of a silarylene/dimethylpolysiloxane copolymer, R′ or R″ = methyl, phenyl or other group of interest.*

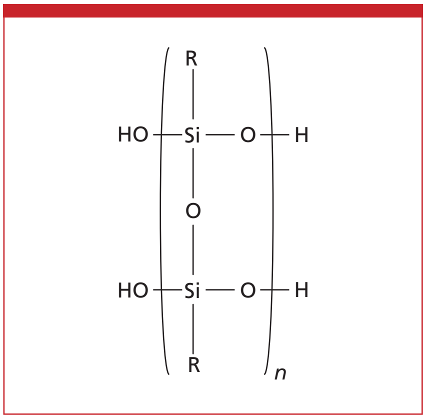
> ***"...for non-polar silicones, synthesis can be performed with high reproducibility."***

molecule, thus counteracting the backbiting mechanism. This disturbance is most effective in a regularly alternating polymer structure (20). In a random polymer there may be long sequences of pure dimethyl substitution, leading to a helical structure in this part and thereby a sensitivity to thermal degradation by scission of one turn, a cyclic polysiloxane, in the helix. In addition, interaction with the analytes may be different with isolated phenyl groups when compared with vicinal groups.

High molecular weight polysiloxanes can be readily prepared by either acid- or base-initiated ring-opening polymerization of cyclic siloxanes (21). The approach can be used to prepare a semiregular structure; for example, a polymer of OV-17 type can be synthesized from two different cyclics, a cyclic dimethyl polysiloxane and a cyclic diphenyl polysiloxane. The method cannot, however, give a truly regularly alternating structure; the reason for this is that the two cyclics involved have different reactivities.

Immobilization of phenyl substituted polysiloxanes can be performed by thermal treatment. Cross-linking takes place via scission of phenyl groups, thus polarity is somewhat decreased after the immobilization (22).

Cyanosilicones: Cyano-substituted silicones are the most polar stationary phases available today. Unfortunately, these phases cannot withstand higher temperatures as substituent groups are not thermally stable enough and the development of a thermally stable alternative would be rewarding.



Scheme 6: *Structure of polyladder organosiloxane, R = methyl.*

Siloxane/silarylene copolymers: Such polymers have a high thermal stability. This was first shown for packed column GC in 1973 by Yudina et al. (23). In 1984 we showed the high thermal stability that can be obtained with silarylene/methylsilicone copolymers in capillary GC (24). Subsequently, the usefulness of this type of stationary phase has been examined in more detail (25). Furthermore, silarylene/phenylsilicone copolymers were shown to be thermally quite stable (26, 27). An increased thermal stability is obtained in a random silarylene/siloxane copolymer, but it must be stressed that the highest thermal stabilities will be obtained with polymers having a regularly alternating structure (Scheme 5).

Also the substituent groups of the arylene moiety can be selected to suit chromatographic needs. During recent years, capillary columns coated with silarylene/siloxane copolymers have become commercially available from several column manufacturers. These columns have an improved thermal stability; however, with the use of stationary phases having a regularly alternating structure, the thermal stabilities would be even better.

As mentioned above, it is of great interest to avoid any thermal degradation of phenyl-containing polysiloxanes when coupled to modern mass spectrometry (MS). This primarily concerns stationary phases of the SE-52 type, which are quite often used in connection with MS. A convenient way to avoid scission of phenyl groups from phenyl-substituted polysiloxanes is to include the phenyl-group in the backbone of the polymer instead. That is, to use an arylene/siloxane copolymer. In such a polymer, the arylene content can be adjusted to give the same polarity as an SE-52 phase (Scheme 6).

Polysiloxanes in ladder form exhibit a high thermal stability, and columns coated with methyl-substituted ladder polysiloxanes are available from Phenomenex (Torrance, California, USA). In such polymers backbiting and unzipping mechanisms are strongly suppressed and, as a result, the thermal stability is quite high. For the future, it would be of interest to develop ladder polymers in which other substituent groups, such as phenyl, are included. However, the synthesis of such polymers would be a demanding task.

Outlook

In my opinion, stationary phases for capillary GC could be much improved. The stationary phases should have a regularly alternating structure that would lead to both improved reproducibility of chromatographic properties and thermal stability. A highly polar substitute for the cyano-silicones is desirable. Alternatives to phenyl silicones include the silarylene/siloxane copolymers (24–27) and biphenyl siloxanes (28). Furthermore, there is a need for multipurpose columns that are useful for different types of analytes. For that purpose, the silicones should contain different substituent groups; for example, cyanopropyl-, methyl- and phenyl- as in OV-1701 or OV-225 (29). Dicyanobiphenyl siloxane is another example of dual selectivity phases (30).

Acknowledgements

The Swedish Natural Science Research Council financially supported this work. The author thanks Professor R. Tabacchi and Dr S. Claude, Institut de Chimie de l'Université de Neuchâtel, Switzerland, for helpful discussions.

References

(1) B. Erickson, *Anal. Chem.*, **71**, 271A–276A (1999).
(2) L.G. Blomberg, *LC•GC Int.*, **11**, 760–762 (1998).
(3) H. Rotzsche, *Stationary Phases in Gas Chromatography*, J. Chromatogr. Library, **48**, Elsevier, Amsterdam, The Netherlands (1991).
(4) A.J. Barry and H.N. Beck, in F.G.A. Stone and W.A.G. Graham (Eds.), *Inorganic Polymers*, Academic Press, New York, USA, (1962).
(5) J.F. Brown Jr. et al., *J. Am. Chem. Soc.*, **82**, 6194 (1960).
(6) I.P. Yudina, G.N. Semina and K.I. Sakodynskii, *J. Chromatogr.*, **365**, 19–25 (1986).
(7) L.G. Blomberg and K.E. Markides, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **8**, 632–650 (1985).
(8) L.G. Blomberg, *Trends Anal. Chem.*, **6**, 41–45 (1987).
(9) L.G. Blomberg, *J. Microcol. Sep.*, **2**, 62–68 (1990).
(10) K.A. Andrianov, *Metalorganic Polymers*, Interscience Publishers, New York, USA, (1965).
(11) M.G. Voronkov, V.P. Mileshkevich and Yu.A. Yuzhelevskii, *The Siloxane Bond*, Consultants Bureau, New York, USA, (1978).
(12) W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, USA, (1968).
(13) J.L. Speier, *Advances in Organometallic Chemistry*, **17**, 407–447 (1979).
(14) J.C. Kuei et al., *Chromatographia*, **20**, 25–30 (1985).
(15) J.S. Bradshaw et al., *J. Chromatogr.*, **357**, 69–78 (1986).
(16) B.E. Rossiter et al., *Tetrahedron Lett.*, **32**, 3609–3612 (1991).

(17) H. Frank, G.J. Nicholson and E. Bayer, *J. Chromatogr. Sci.*, **15**, 174 (1977).
(18) B. Koppenhoefer and E. Bayer, in F. Bruner (Ed.) The Science of Chromatography, *J. Chromatogr. Library*, **32**, 1, (1985).
(19) I. Hägglund et al., *J. Chromatogr. Sci.*, **29**, 396–402 (1991).
(20) P.R. Dvornic and R.W. Lenz, *High Temperature Siloxane Elastomers*, Hüthig & Wepf, Heidelberg, Germany (1990).
(21) E.E. Bostick, in K.C. Frisch and S.L. Reegen (Eds.), *Ring Opening Polymerization*, Marcel Dekker, New York, USA, (1969).
(22) I. Hägglund et al., *J. Microcol. Sep.*, **3**, 459–465 (1991).
(23) I.P. Yudina et al., *J. Chromatogr.*, **77**, 41 (1973).
(24) J. Buijten et al., *J. Chromatogr.*, **301**, 265–269 (1984).
(25) A. Bemgård et al., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **10**, 302–318 (1987).
(26) A. Bemgård et al., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **11**, 881–890 (1988).
(27) K. Janák et al., *J. Microcol. Sep.*, **3**, 497–503 (1991).
(28) J.C. Kuei et al., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **7**, 13–18 (1984).
(29) I. Hägglund et al., *J. Chromatogr.*, **673**, 93–99 (1994).
(30) A. Malik et al., *Chromatographia*, **46**, 79–84 (1997).

Professor Blomberg has a chair in Analytical Chemistry at the Department of Chemistry, Karlstad University, Karlstad, Sweden. His main research interests concern chromatography and electrophoresis.