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SOME ASPECTS OF CURRENT TECHNIQUES FOR THE PREPARATION OF CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

L. BLOMBERG*, J. BUIJTEN, K. MARKIDES and T. WÄNNMAN

Department of Analytical Chemistry, University of Stockholm, Arrhenius Laboratory, S-106 91 Stockholm (Sweden)

SUMMARY

Desirable column properties and their relation to different steps in column preparation are discussed. The properties of different capillary materials are compared, the different methods for high-temperature silylation, which are being used to achieve deactivation and wettability, are considered and the advantages of immobilized silicone stationary phases are described. Immobilization leads primarily to improved stationary phase film stability and this is of particular utility in connection with polar columns; some polar silicone gums have a high temperature coefficient of viscosity and may therefore be redistributed on a capillary surface at elevated temperatures, leading to deterioration in column performance. Immobilization very efficiently counteracts such an effect. Silicones containing cyanopropyl and phenyl substitution cannot readily be cross-linked. It is demonstrated that a convenient way to solve this problem is to include some tolyl substitution in the gum that is to be cross-linked.

INTRODUCTION

Gas chromatography (GC) is an analytical technique that has been very much improved in recent years. The improvements include instrumental aspects such as on-column injection and mass-selective detection, as well as new types of capillary columns coated with non-polar or polar immobilized stationary phases. Much work has been devoted to column development¹, since good column properties are a basic requirement for reliable analysis. In this article, the preparation and properties of current types of capillary columns will be described.

The quality of a capillary column may be described by several factors: separation efficiency, deactivation and stability²⁻⁴. First, we strive to attain the highest possible separation efficiency, which will facilitate the use of shorter columns and thereby shorten analysis times. A prerequisite for high efficiency is that the stationary phase occurs as an even, homogeneous film on the column wall. This can be achieved with non-polar stationary phases, but the wettability that is necessary for the formation of even films of *polar* phases will be obtained only after some surface modification. Secondly, polar solutes may be reversibly or irreversibly adsorbed on the

column wall, and unstable compounds may form artefacts due to catalytically active sites in the column. These effects may preclude quantitative elution of such compounds. It is thus important to deactivate the columns. Further, there is an increasing interest in the analysis of polar compounds, *e.g.*, of metabolites rather than non-polar precursors in toxicological studies. Moreover, since derivatization may introduce uncertainties in an analysis, the separation of underivatized polar solutes is in many cases desirable. Thirdly, the column properties should remain constant, even when the column is exposed to strains, such as high temperature or injection of large amounts of polar solutes.

CAPILLARY MATERIAL

Fused silica

Borosilicate and soda glass were for many years the predominant capillary tubing materials, and several column preparation procedures have been developed for these materials. This situation dramatically changed with the introduction of flexible fused-silica capillaries⁵⁻⁷. These are highly inert towards typical solutes, but some adsorption of bases has been observed⁸. Further, fused silica is quite inert towards silicone stationary phases; when coated on a fused-silica capillary, a silicone can thus be heated to much higher temperatures without noticeable degradation, than when coated on a soda-glass capillary. Borosilicate glass, however, shows lower catalytic activity than soda glass. The foremost advantage of fused-silica capillaries is their flexibility, which facilitates handling. There are now several manufacturers of fused-silica capillary tubing, and according to our experience the quality of the material varies considerably; even different batches from one manufacturer may vary markedly. Fused-silica capillaries for GC have recently been marketed and the quality will probably be much improved; this applies to both the inside and the outside. As an example of the variations in properties, some capillaries are acidic in character while others are basic. Further, on some batches, medium-polar silicone gums such as methyl(tolyl)silicone gum (50% tolyl) form even films while, on other batches, droplets are formed under otherwise identical conditions. Desirable properties would be good wettability for medium-polar stationary phases and polar surface-modifying reagents and, if possible, a neutral surface. The outer coating should withstand the high temperatures used upon silanization: some of the capillary types now available tend to become sticky upon heating. During the high-temperature silylation, we protect the capillaries by enveloping them in aluminium-foil, and before heating, purging with nitrogen. Such a system was described by Verzele *et al.*⁹.

Borosilicate and soda glass

Conventional borosilicate- and soda-glass capillary columns need to be end-straightened to allow mounting in a gas chromatograph. This may be considered as problematic by some users. Further, the straightening procedure may lead to deterioration of the stationary phase in the straightened part¹⁰. To avoid this, a capillary end-straightening apparatus was constructed¹⁰. A straightening machine is available from Carlo Erba (Milan, Italy). In this apparatus, straightening is achieved by the combined action of a mechanical force and heat; the temperature necessary for the straightening can thereby be minimized. In conclusion, this apparatus simplifies the

end-straightening, and the risk for phase decomposition during straightening is diminished. Some other devices for end-straightening have also been described^{11,12}.

A second approach to improve the versatility of ordinary glass columns is to use pieces of fused silica as a connection between the chromatograph and separation column. The fused-silica capillary and the separation capillary are then connected with screwed or glued joints¹³. A special advantage of this system is that the first fused-silica part can easily be exchanged if contaminated by non-volatile material. In addition, an uncoated, fused-silica capillary may be used as a connection to the injector, thus furnishing a "retention gap" that improves the injection¹³. When hydrogen is used as carrier gas, such joints must, of course, not break. It seems reasonable to protect the joint mechanically by an outer glass tube¹³.

A third approach is the preparation of thin-walled polyimide-coated soda-glass capillaries¹⁴. Although this is relatively untried as yet, capillaries are already available from Quadrex (New Haven, CT, U.S.A.).

Other types of capillary tubing material

Stainless-steel and nickel capillaries have also been used, but these materials seem to have been temporarily abandoned due to their possible catalytic activity. A recently published method for deactivation of metal capillaries may lead to an improvement¹⁵. An interesting approach is the use of etched PTFE as column material¹⁶.

HIGH-TEMPERATURE SILANIZATION

Non-polar columns

Silanization at relatively low temperatures has for many years been a method used for the deactivation of glass capillary columns; the deactivation achieved was, however, not satisfactory¹⁷. Welsch *et al.*¹⁸ showed that high temperatures had to be used if an efficient deactivation was to be obtained. Later, the Grobs¹⁹⁻²² presented a method for persilylation, using hexamethyldisilazane as reagent and a reaction temperature of 400°C. This method is adapted to glass capillaries that have been leached with hydrochloric acid solution. The leaching serves several purposes: first, to provide reactive silanol groups for the subsequent silanization; secondly, to diminish the catalytic and adsorptive activity of the capillary surface; thirdly, to build a barrier of dense xerogel that counteracts further diffusion of metal ions from the bulk to the surface; fourthly, to even out eventual differences between different batches of glass. Further, depending on the drying conditions, some water may remain after drying, and this can take an active part in the silanization. Another silanizing reagent, octamethylcyclotetrasiloxane (D₄) (Ohio Valley Specialty Chemicals, Marietta, OH, U.S.A.) was introduced for GC by Stark *et al.*²³ and by Aue and Wickramanayake²⁴. The reactions between fumed silica and D₄ have recently been studied²⁵⁻²⁷. It was suggested that the silica surface silanol groups initiate a ring opening, and that the thus opened rings may be grafted to the silica surface, forming loops or polymers. Further, the reaction between silica and silicone oils and also rubber was demonstrated. That type of reaction was successfully used by Schomburg *et al.*²⁸ for deactivation of capillaries. The D₄ reaction is performed at 400°C, and it may be speculated that a thin polymeric layer is formed on the surface rather than a "mono-

layer" of methylsiloxy groups. According to our experience, the three methods (Grob, Schomburg *et al.* and Stark *et al.*) for deactivation of non-polar fused-silica, borosilicate- and soda-glass columns by high-temperature silanization result in equally well deactivated columns. Minor differences may occur, though, due to divergences in laboratory practice in different laboratories. Several other silylating reagents have, however, also been used²⁹⁻³².

It may be of interest to find alternative deactivation methods that are milder toward the fused-silica polyimide and also improve the fused silica toward bases. The use of aminols³³ or similar materials³⁴ may be of interest.

Polar columns

We consider that polar columns will become a powerful tool in GC. It is said that 90% of present day GC analysis can be performed on non-polar columns³⁵. Some of these analyses could certainly be performed more rapidly on polar columns. Moreover, access to polar columns will make it possible to increase the certainty in semi-identification by retention index. It is thus quite convenient to mount two fused-silica columns of different polarities in one injector; by one injection, the desired information can be obtained³⁶. This may be important in routine analysis and for laboratories that cannot afford mass spectrometry. The most interesting aspect of polar columns is, however, that new types of separations will become possible. To utilize the advantages of polar columns fully, it is necessary that they show high efficiency, good deactivation and stability. High efficiency can be obtained when the supporting capillary surface has a surface tension that allows the formation of even films of stationary phase. The wettability required for coating with polar phases may be achieved by physical or chemical methods. Physical surface modification implies roughening, *e.g.*, with hydrogen chloride gas³⁷ or fluoride solution³⁸, or by the deposition of particles, *e.g.*, sodium chloride³⁹ or fumed silica⁴⁰. Chemical modification was tested by Grob in 1968⁴¹. The advantage of this method, as compared with physical modification, is that the surface smoothness may largely be preserved. Further, in most cases, both deactivation and wettability are obtained upon chemical surface modification. Chemical modification was also attempted by Novotný and co-workers^{42,43} who tried to achieve wettability by silanization with silanes that carried polar functional groups. It has been suggested that also Carbowax deactivation should be a chemical type of modification^{44,45}. Carbowax deactivation was used by Cronin⁴⁶ in order to achieve a glass surface suitable for coating with Carbowax. The Grobs¹⁹⁻²¹ have tried to extend the wettability of glass surfaces by reaction with phenyldisilazanes. Modification with diphenyltetramethyldisilazane resulted in a surface suitable for coating with SE-52, SE-54 and OV-73²². Modification with tetraphenyldimethyldisilazane and triphenylsilylamine yielded stable coatings of semi-polar phases²¹. This type of silylation was further investigated by Welsch *et al.*⁴⁷. In order to obtain deactivation and wettability, Schomburg *et al.*²⁸, heated alkali-glass columns that were coated with OV-17 for 20 h at 350°C. Further, for coating with trifluoropropylsilicone gum, PS-286 (Petrarch, Bristol, PA, U.S.A.), Schomburg *et al.*⁴⁸ heated alkali-glass capillaries that were coated with a trifluoropropylsilicone oil of low molecular weight, PS-183 (Petrarch). The PS-183 silicone oil is most likely decomposed at the high temperatures used and fragments are grafted to the glass surface in a manner similar to that described by Li Yu-Fu *et al.*²⁶ for methylsilicone oils.

We have developed methods for chemical surface modification in which modification of surface silanol groups is attempted by reaction with cyclic siloxanes that carry functional side groups of the same kind as the silicone stationary phase with which the surface will subsequently be coated^{49,50}. Our methods have some similarities with Schomburg's polysiloxane degradation treatment²⁸; polysiloxanes decompose to give some cyclics upon heating^{51,52}. We consider, however, that reproducibility may be favoured by the use of defined chemical compounds for the modification. For coating with tolylsilicones having up to 50% tolyl substitution, silanization with phenyl(methyl)cyclosiloxanes gives excellent wettability, but for silicones having a higher degree of phenyl or tolyl substitution, silanization with bis(phenyl)cyclotrisiloxane is needed in order to achieve wettability^{53,54}. On some batches of fused silica, 50% phenyl-substituted silicones can be directly coated⁵⁵.

Further, for cyanopropyl-substituted silicones, silanization with cyanopropyl(methyl)cyclotetrasiloxanes gives excellent wettability for silicones having up to 50% cyanopropyl substitution, and for higher degrees of cyanopropyl substitution silanization with bis(cyanopropyl)cyclotetrasiloxane gives the necessary wettability^{56,57}. Moreover, silanization with 3,3,3-trifluoropropyl(methyl)cyclosiloxanes gives excellent wettability for corresponding silicone gums, *e.g.*, OV-215, PS-286 (Petrarch), and Silastic LS-420 (Analabs, North Haven, CT, U.S.A.)⁵⁸.

The concentration of silanol groups in a fused-silica surface is relatively low⁵⁹. For silanization with non-polar reagents this is not a problem, but for polar reagents we have found that the desired wettability cannot be achieved on direct silanization, the degree of coverage evidently being too low. Therefore, we treat the fused silica with hydrochloric acid solution or water at an elevated temperature prior to silanization. After such treatment, silanization can be satisfactorily performed. Borosilicate- and soda-glass capillaries are leached with hydrochloric acid solution according to Grob and Grob²¹ before silanization.

Several methods are available for securing wettability and deactivation. However, we presently consider high-temperature silylation to be preferable for silicone stationary phases and Carbowax treatment for polyethylene glycol phases. An interesting approach is to combine the two methods, *i.e.*, by silanization with silanes carrying epoxy groups⁶⁰.

COATING

Best results are generally achieved when the static coating technique is used. This technique was introduced in 1968 by Bouche and Verzele⁶¹. However, beginners may experience some practical difficulties. A detailed description was recently given by Grob and Grob⁶². In our work, we have noted that it is important to use freshly prepared coating solutions, since some stationary phases may decompose on standing in solution⁴. Further, we prefer to have the column at room temperature during the static coating in a water-bath that is not thermostated. Usually, we employ distilled methylene chloride as a solvent for the stationary phase. We have observed that the use of *n*-pentane can give rise to a slight unevenness in the stationary phase film of SE-52, possibly owing to too rapid evaporation of the pentane at room temperature.

BONDING AND CROSS-LINKING OF STATIONARY PHASES

Early attempts to produce bonding to the surface of capillaries in combination with a cross-linked coating were made by Grob⁴¹ and Bossart⁶³. Later, Madani and co-workers presented a method to immobilize methyl-⁶⁴⁻⁶⁶ and phenylsilicones⁶⁷ by bonding linear α,ω -hydroxypolysiloxanes to the glass surface. On the basis of Madani's work, we have developed a method where immobilization was achieved not only by bonding to the support surface, but also by the introduction of a slight degree of cross-linking in the phase itself⁶⁸⁻⁷¹. The cross-linking was, in fact, of crucial importance for the immobilization. Methods for the preparation of capillaries, coated with methyl-^{69,70}, phenyl-⁶⁸ and cyanopropylsilicones⁷¹, were developed. The method may be further developed, as demonstrated by Lipsky and McMurray⁷². The crosslinking was introduced by tri- or tetrafunctional silanes; the handling of such compounds is fairly delicate due to their tendency to hydrolyze. It is far easier to use peroxides to initiate the formation of crosslinks in a silicone gum. Such methods have been used in the rubber industry for more than 30 years⁷³, and they have now been successfully applied to capillary columns⁷⁴⁻⁸².

Several different types of peroxides may be used for initiation of crosslinking⁸³. Dicumyl peroxide is at present the most commonly used initiator for capillary column preparation, it being considered to give decomposition products that do not catalyze silicone degradation or give rise to column adsorptive activity^{80,84,85}. Further, the decomposition products can easily be removed. Good results were also obtained with *tert.*-butyl peroxide^{72,86}. As an alternative to organic peroxides, azo compounds⁸⁶ or high-energy irradiation^{48,87} have been used. For the curing of polar silicone gums, the irradiation method may imply some special advantages. First, no chemicals are added that may exert a detrimental effect on column performance; polar silicones require relatively high percentages of peroxide. Secondly, reaction takes place at room temperature in a closed system and thirdly, the columns may be tested before they are cured. Several other ways to accomplish crosslinking of silicones have been published^{52,88}. Most of these methods, however, do not fulfil our special requirements. In some methods, catalysts containing metals, such as tin and platinum, are used: one may speculate that residues of such catalysts would have a negative influence on the quantitative elution of sensitive compounds. Attention was paid recently to the effect of platinum in the column when hydrogen is used as carrier gas⁸⁹. Another requirement of a curing method for stationary phases is that a high degree of reproducibility must be achieved. It is of special importance that the curing reaction does not continue during the use of the column in the gas chromatograph. The desired stability would, as a consequence, be lost.

ADVANTAGES OF CROSS-LINKING

Physical aspects of thermal stability

The stationary phase viscosity is a most important physical factor⁹⁰. If the viscosity becomes low at elevated temperatures, as in the case of silicone oils, the phase will undergo rearrangement on the surface and the stationary phase film will thereby become uneven, *i.e.*, the efficiency will be lowered. Silicone gums are in this respect to be preferred, but even these give low efficiencies above 325°C. The ultimate

film stability is achieved by cross-linking of the stationary phase. For methylsilicones, the temperature coefficient of the viscosity is relatively low when compared with other polymers⁵². This is explained by the fact that the methylsilicone molecules occur in coiled structures⁹¹. The presence of other substituent groups, such as phenyl or cyanopropyl, in silicones, disturbs the helix structures, resulting in an increased temperature dependence of viscosity^{52,58}. Cross-linking of cyanopropyl- and phenylsilicone stationary phases would thus be especially advantageous³⁵. Cross-linked methylsilicones are, furthermore, useful as stationary phases at low temperatures⁹².

Gas chromatographic separation of aqueous solutions is a task of potential interest. Water, when occurring as steam, readily penetrates silicones. It may displace the silicone from the surface of the supporting capillary, and as a consequence the column efficiency will drop. Such a deterioration was already experienced after twenty on-column injections of an aqueous solution on a column coated with SE-54. Capillaries coated with immobilized SE-54 could, on the other hand, withstand water injections quite well⁸⁰. The stability of cured stationary phases towards aqueous solutions was also noted by Sandra *et al.*⁷⁷.

Chemical aspects of thermal stability

The chemical stability is dependent on several factors. Let us first consider methylsilicones. They decompose to give, besides methane, mainly cyclic fragments, which form relatively easily owing to the coiled molecular structure^{93,94}. A primary condition for stability is that the methylsilicones are end-capped; silanol-terminated chains decompose, depending on the conditions, *ca.* 30 times faster than methyl-terminated chains. Owing to the ionic character of the Si-O bond, decomposition is catalyzed by acids and bases. These catalysts may stem from different sources. First, alkali-metal catalysts are sometimes used for the polymerization of siloxanes to gums⁸⁵. It is most important that these catalysts are efficiently removed after the polymerization, since even ppm amounts of these compounds contribute significantly to silicone decomposition at elevated temperatures⁸⁵. According to our experience, it is the presence of such catalyst residues that presently determines the high-temperature stability of silicone stationary phases. Secondly, alkali metals in a soda-glass capillary catalyze decomposition⁹⁵; leaching with hydrochloric acid solution according to Grob leads to improved stationary phase stability on soda glass, but the catalytic effect is still evident. The advantage of fused silica in this respect is obvious, and, in fact, the bleeding of a silicone phase is always much lower when coated on fused silica than when coated on carefully leached soda glass⁵⁸. It should be mentioned that columns made of borosilicate glass show lower bleeding rates than corresponding soda-glass columns. Thirdly, the sample injected on the column may introduce bases and acids. Fourthly, the use of an inappropriate curing agent, *e.g.*, benzoyl peroxide, that gives acidic decomposition products, would lead to decreased stability⁸⁵.

Cross-linking may increase the chemical stability of polymers. Rupture of one silicone-oxygen bond is sufficient for the cleavage of linear macromolecules, but with polymers having a three-dimensional structure it is necessary to rupture bonds at two or three points for cleavage^{94,96}. However, no such improvement has been observed for capillary columns coated with immobilized non-polar silicones^{35,58}.

The presence of electron-accepting side groups in a silicone will affect the bond

strengths. Such substituents will thus weaken Si-C bonds and strengthen Si-O bonds, as compared with methylsilicones⁵². Decomposition of such polar silicones will therefore take place according to mechanisms other than that of methylsilicones. Decomposition of phenylsilicones and also methylsilicones was studied in some detail by Grassie and co-workers⁹⁷⁻¹⁰⁰.

Insolubility of cross-linked stationary phases

Cross-linking makes the stationary phases insoluble in commonly used solvents. This can be advantageous in several respects. First, the stationary phase withstands the huge amounts of liquid solvent from the sample that pass the beginning of the column upon on-column or splitless injection. However, such phase stripping may also be diminished by the use of the "retention-gap" technique¹³. Secondly, columns, the performance of which has deteriorated due to deposition of non-volatile material in the beginning of the column, may be rejuvenated by rinsing with solvent, provided, of course, that the deposited material is soluble¹⁰¹. The merits of such column rejuvenation were clearly demonstrated by Schomburg (see ref. 102). Thirdly, bonded phases facilitate on-column injection of large sample amounts, 100 μ l, as demonstrated by Zlatkis *et al.*¹⁰³.

Precision in retention index determinations

During recent years, improvements in GC techniques have been achieved that jointly facilitate a high precision in retention index determinations. These improvements are high precision in column-oven temperature control¹⁰⁴, modern computer techniques for determination and calculation¹⁰⁵ and virtually non-adsorptive separation capillaries and columns, the properties of which have been stabilized by stationary phase cross-linking. All these factors are of crucial importance. Further, a system for retention index monitoring with different detectors has been described¹⁰⁶. The stability of the retention index was recently demonstrated for some underivatized drugs¹⁰⁷.

IMMOBILIZED MEDIUM-POLAR AND POLAR SILICONES

We consider that capillary columns, coated with stationary phases that separate sample components according to selective mechanisms, may be a powerful tool for the chromatographer. A necessary condition is, however, that these columns show first-rate properties, *i.e.*, high efficiency, a high degree of deactivation, good high-temperature stability and reproducibility in retention characteristics. As indicated above, immobilization of the stationary phase may facilitate preparation of polar capillary columns of the desired high quality. The moderately polar OV-1701 has been cross-linked^{35,48,53,81}.

Immobilization of phenyl- and cyanopropyl-substituted silicones cannot readily be achieved, since such substituents counteract cross-linking¹⁰⁸. This is already observed with a low content of phenyl substitution; the lower reactivity can, however, be compensated for by increasing the percentage of dicumyl peroxide used. The use of high percentages of peroxide may result in columns that show some adsorptive activity^{35,58}. Another approach is to introduce a slight degree of cross-linking in the prepolymer when only few cross-links would have to be formed *in situ* to achieve immobilization. Peaden *et al.*⁵⁵ used 1,4-dimethyl-1,1,4,4-tetrachlorodisilylene for that purpose. This was combined with the incorporation of a certain percentage of vinyl substitution in the prepolymer. Using that method, efficient, ther-

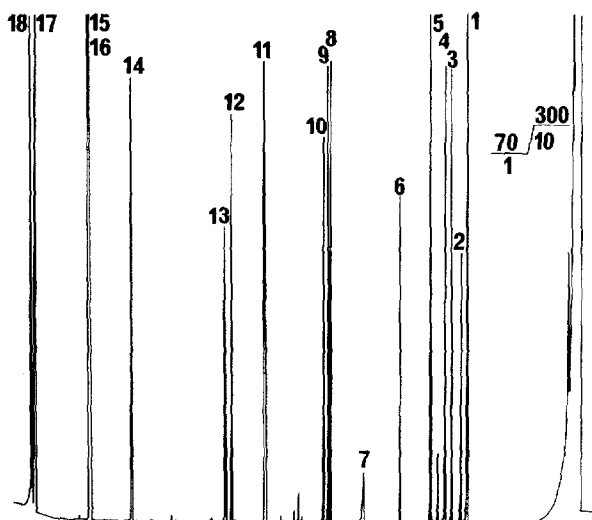


Fig. 1. Gas chromatogram (flame ionization detection) of some underivatized drugs. Column: fused silica, 18 m, HCl-treated, silanized with methyl(phenyl)cyclosiloxane and coated with cross-linked methyl(tolyl)silicone. Peaks: 1 = propylhexedrine; 2 = amphetamine; 3 = phentermine; 4 = methylamphetamine; 5 = ethylamphetamine; 6 = propylamphetamine; 7 = ephedrine; 8 = fendimetraline; 9 = phenmetrazine; 10 = amphetamine; 11 = benzocaine; 12 = methylphenidate; 13 = phenacetine; 14 = procaine; 15 = cocaine; 16 = metaqualone; 17 = codeine; 18 = ethylmorphine. Sample amount: *ca.* 1 ng of each substance.

mostable, non-extractable methylphenylsilicone coated capillary columns could be prepared⁵⁵. However, the columns were not deactivated. The presence of vinyl groups facilitates cross-linking, especially when dicumyl peroxide is used as initiator⁸⁵. We prepared a methyl(phenyl)silicone prepolymer that contained segments of *ca.* five units of methyl(vinyl)siloxane. This gum could be cured with dicumyl peroxide and the capillary columns thus achieved were efficient, deactivated and thermostable⁵³.

A further approach of interest is to end-cap the prepolymer with 1,3-divinyl-tetramethyldisiloxane⁵⁶. Such a capping may facilitate lengthening of polymer chains and thereby give a contribution to immobilization.

The most successful approach was, however, the use of tolyl groups for cross-linking^{53,54,56,57}. Fused-silica capillaries are thus silanized at high temperatures with cyclic siloxanes, carrying sidegroups of the same type as the silicone gum with which the capillary is to be coated⁵⁰. This gives deactivation and wettability. The modified capillary is then statically coated with a silicone gum that may contain different proportions of cyanopropyl, methyl, phenyl and tolyl substitution. Curing is initiated by dicumyl peroxide. Using this method, columns of the desired high quality, possessing useful selectivities, could be prepared. The utility of this type of columns is demonstrated by the separation of a drug test mixture on two capillary columns of different polarities, Figs. 1 and 2.

CONCLUSIONS

The quality of non-polar capillary columns has been vastly increased during the last 2 years; high-quality columns can now be obtained from several companies. These columns are generally prepared from fused-silica capillary tubing which is D₄-deactivated and statically coated with a methylsilicone gum that is finally cross-

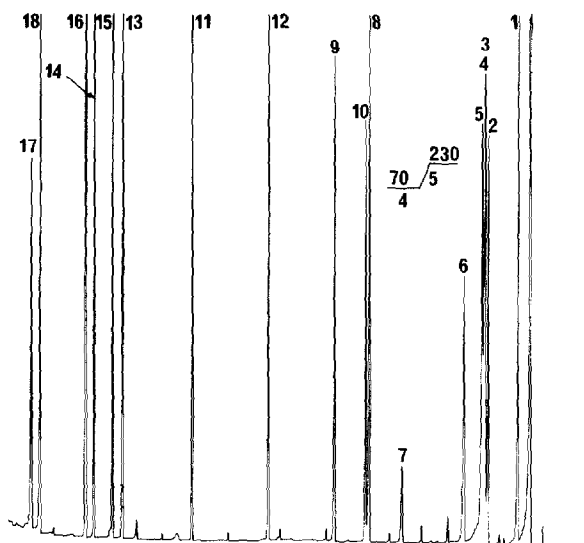


Fig. 2. Gas chromatogram (flame ionization detection) of some underivatized drugs. Column: fused silica, 25 m, HCl-treated, silanized with bis(cyanopropyl)cyclotetrasiloxane and coated with cross-linked cyanopropyl(methyl)tolylsilicone (75% cyano). Peaks as in Fig. 1.

linked *in situ* by a radical-initiated reaction. The success of such columns is due to the flexibility and inertness of fused silica, the high degree of deactivation and good wettability that is achieved upon D₄-silylation and finally the high stability of properties that is achieved by *in situ* cross-linking of the stationary phase.

Methods are now being developed for the preparation of high-quality polar capillary columns. In these methods, deactivation and wettability are achieved by high-temperature silanization with siloxanes carrying polar side groups. The usefulness of polar columns was earlier restricted by their rather low stability. Now, with the advent of cross-linked stationary phases, the desired stability can easily be achieved.

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