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EVALUATION OF BONDED METHYLSILICONE RUBBER AS A STATIONARY PHASE FOR GLASS CAPILLARY COLUMNS

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SUMMARY

A detailed description of the preparation of glass capillary columns for gas chromatography, coated with non-extractable methylsilicone rubber, is given. The advantages and disadvantages of such columns are examined and compared with the properties of columns coated with a methylsilicone gum. The excellent qualities of the new columns for the separation of polynuclear aromatics are shown and discussed.

INTRODUCTION

Highly stable separation columns are often a requisite in gas chromatography. Such stability implies that there are no observable changes in column properties, *e.g.*, efficiency, activity, polarity and column bleed, during the analysis of a long series of samples. The risk of column deterioration is high under typically rigorous conditions, *e.g.*, high temperatures and injection of highly polar compounds that may displace a non-polar stationary phase. Glass that has been leached, high temperature-silylated and coated with methylsilicone gum gives highly stable columns[1–5]. The chemical bonding of a silicone to the column glass wall may also increase the stability[6–8].

In previous papers[9–12] we have described a method for the preparation of stable columns having a bonded film of cross-linked siloxanes. This type of stationary phase is insoluble and it is necessary to synthesize it *in situ*, a procedure which also facilitates chemical bonding between glass and silicone. In this paper we present some new developments of the method.

EXPERIMENTAL

Duran or AR-glass capillaries were used. After flame straightening of the capillary ends, the capillaries were leached with 18% HCl according to Grob *et al.*[1,2], *i.e.*, at 180°C overnight for Duran and 140°C for AR. They were then rinsed with slightly acidic water and dried for 2 h at 250°C while flushing with dry nitrogen. The capillaries were then treated with tetrachlorosilane as described previously[11]. After leaching, a few capillaries were deactivated with a mixture of tri- and tetracyclic methylsiloxanes[5], and then coated statically with SE-30.

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An α,ω-hydroxypoly(methylsiloxane) pre-polymer was prepared by hydrolysis of dimethyldichlorosilane (DMCS) according to Patnode and Wilcock[13]. To 60 ml of ice-chilled 25% ammonia solution, 20 ml of DMCS in 100 ml diethyl ether were added slowly with stirring. The siloxane phase was then separated, carefully washed with water and dried over $MgSO_4$ and $CaSO_4$. It was then filtered and low-boiling material distilled off at 90°C and 15 mmHg, leaving a residue of pre-polymer in the distillation flask.

All columns were coated by the static method, using a solution of the coating materials in pentane. After coating, each column was filled with dry nitrogen saturated with fresh tetrachlorosilane, sealed and left at room temperature overnight. Excess of reagent was then flushed out with dry nitrogen for 3 h, and the columns were filled with ammonia gas (Matheson Gas Products, East Rutherford, NJ, U.S.A.). They were then carefully sealed and placed in the oven of a gas chromatograph, the temperature of which was programmed to 320°C at 5°/min and maintained at this temperature for 18 h. Before testing, the columns were conditioned for 48 h at 300°C.

The tests were performed with a Carlo Erba 4160 gas chromatograph, using hydrogen as carrier gas. Column activity was determined according to Grob *et al.*[14].

RESULTS AND DISCUSSION

The preparation procedure

The procedure described involves a number of steps, and we have found it advisable to identify critical moments and, if possible, to check that each step functions as intended.

Leaching is a critical procedure which has to be optimized for each glass type and sometimes even for different batches of glass tubing[4]. For our purposes, it is essential to maintain a smooth surface; a mild leaching is thus desirable. Further, we have found that excessive drying of the capillary is detrimental to the subsequent surface treatment with tetrachlorosilane.

Small variations in pre-polymer synthesis conditions such as the temperature and speed of DMCS addition could result in differences in polymer composition. Using gel permeation chromatography, we found 44 units to be the most frequent chain length of the pre-polymer. Moreover, the pre-polymer must be thoroughly dried. The pre-polymer properties may be monitored by spectroscopy (Fig. 1), *e.g.*, water absorbs in the 3200–3400 cm^{-1} region[15].

An even film of pre-polymer is obtained on static coating, which should not undergo any alteration during the following polymerization; the latter step must thus be performed carefully.

When a column is in use, the stationary phase should not undergo further polymerization, but such effects may occur in cross-linked silicone phases. However, we have found that stable polymers are obtained when the cross-linking is initiated either by a small amount of trichlorosilane[9,10] or by a small amount of $SiCl_4$[11,12]. The hydrochloric acid evolved in such reactions does not seem to have any detrimental effect on the siloxanes, but it is very important to use $SiCl_4$ that has been protected from moisture, otherwise columns which adsorb hydrocarbons will result. After reaction, the column is flushed with dry nitrogen. An indication of appropriate $SiCl_4$

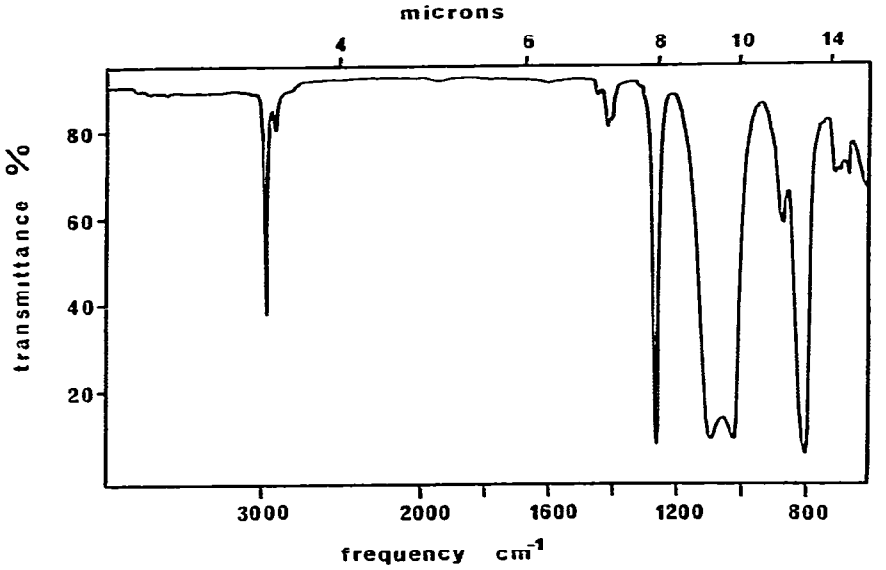

Fig 1 Infrared spectrum of methylsiloxane pre-polymer.

treatment is that the flush gas emerging from the column ceases to give a strong red colour to pH-paper after 15–30 min.

For a final polymerization, the capillary is filled with ammonia gas and its ends are sealed. It is not easy to seal a capillary coated with these silicones, and a check should be made by use of a magnifying glass to ensure that the seal is satisfactory.

Before use, the columns are conditioned in order to remove unreacted fragments and ammonium chloride.

Chromatographic properties

The elution at 300°C of two solutes, a polyaromatic and a normal hydrocarbon, was compared on columns of silicone rubber and gum (Fig. 2). Both columns are more suitable for polynuclear aromatics than for *n*-alkanes. This is in accordance with the results of Hawkes and co-workers[16,17] who found that silicone gums are not suitable for separation of long chain *n*-alkanes, owing to restricted diffusion. Further, the shapes of the curves are similar for the two columns, however, the efficiency is lower for the column of silicone rubber. This may be due to some alteration of the film during polymerization.

Film thickness, d_f, and stationary phase properties have been traded to advantage. Thus, relatively thick films are chosen to obtain sufficient deactivation (Fig. 3). A drawback of such films in high temperature analysis is increased retention. However, the methylsilicone rubbers retain solutes to a much lower extent than the corresponding methylsilicone gums. The retention of hydrocarbons on a column of silicone rubber, $d_f = 0.7$ μm, is in the same range as on a SE-30 column with a film thickness of 0.3 μm. On this basis, we consider a rubber film thickness around 0.7 μm to be suitable as far as retention is concerned.

Another drawback of thick film in this context is that column bleed increases

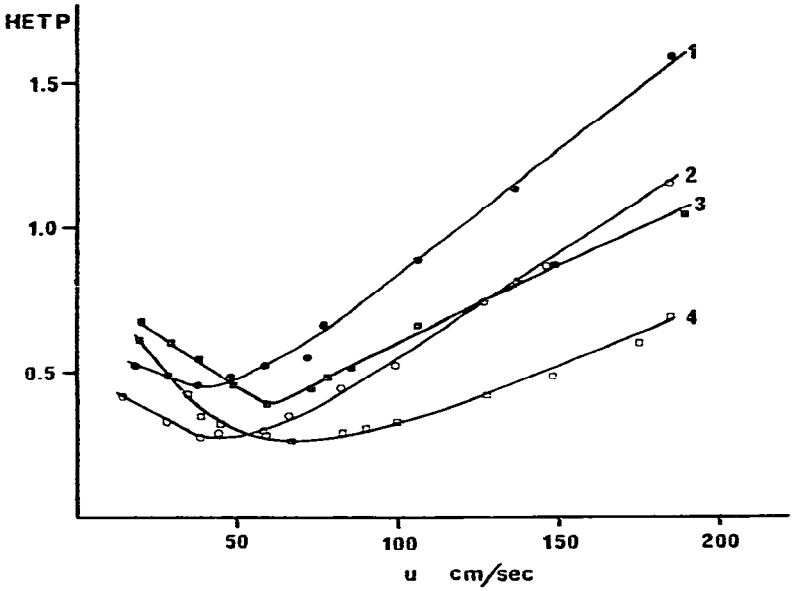

Fig. 2 Van Deemter curves at 300°C. 1 = dotriacontane on a glass capillary column, 0 28 mm I D , coated with methylsilicone rubber, d_f = 0.7 μm; 2 = dotriacontane on a glass capillary column, 0 26 mm I D , coated with SE-30, d_f = 0 3 μm; 3 = anthanthrene on the same column as 1; 4 = anthanthrene on the same column as 2

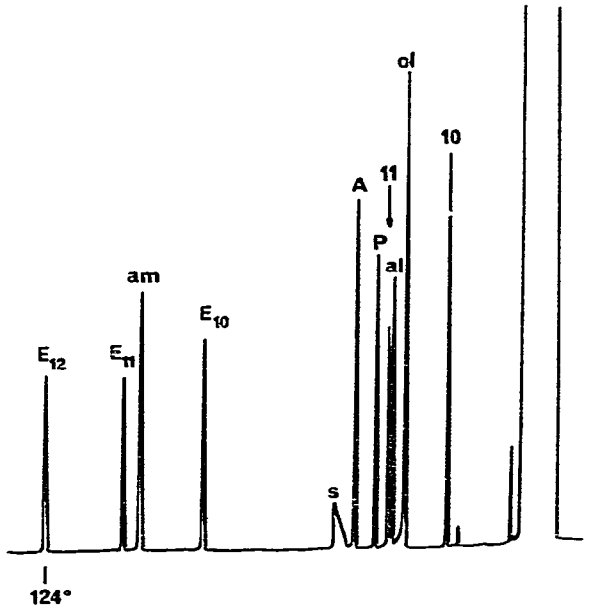

Fig. 3 Gas chromatogram (FID) of a Grob test mixture on a Duran glass capillary column coated with methylsilicone rubber, d_f = 0.7 μm. Initial temperature 40°C, then programmed at 2.5°/min. Peaks: 10 = decane; ol = 1-octanol; al = nonanal; 11 = undecane; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; s = 2-ethylhexanoic acid; E_{10} = C_{10}-acid methyl ester; am = dicyclohexylamine; E_{11} = C_{11}-acid methyl ester; E_{12} = C_{12}-acid methyl ester.

with increase in film thickness. The bleeding of a column of silicone rubber is however much lower than that of a SE-30 column of similar film thickness (Fig. 4). A column coated with a 0.7-μm film of rubber shows acceptable bleeding up to 380°C; programming to this temperature can be performed without observable subsequent deterioration in efficiency, deactivation or bleeding properties.For SE-30, d_f = 0.12 μm, we found 350°C to be the maximum allowable temperature[5]. The lowest bleeding was however obtained on columns coated with methylsilicone rubber where the cross-linking had been initiated by a trichlorosilane as described earlier[10]; such columns possess some adsorptive activity.

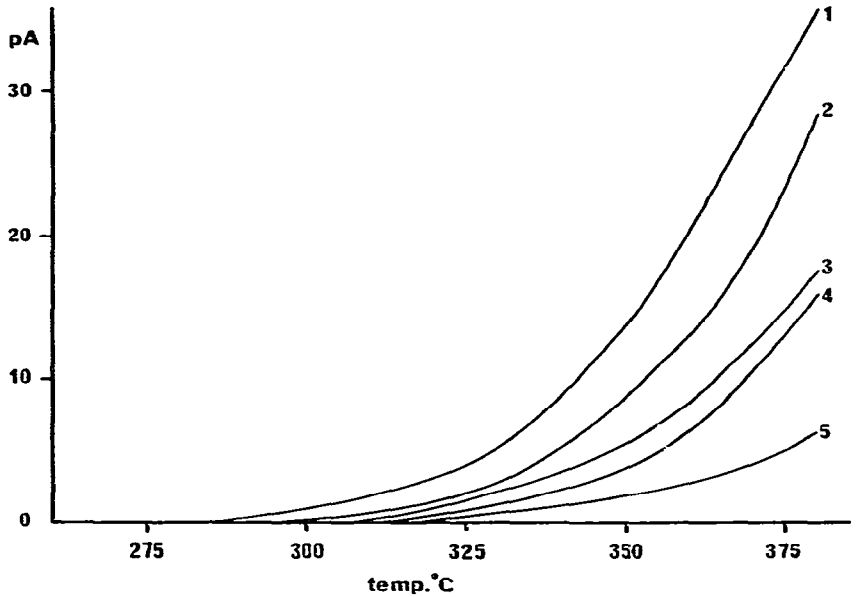

Fig. 4. Bleeding rates of some 20-m Duran glass capillary columns. Carrier gas velocity (hydrogen) at 250°C, 50 cm/sec Programming rate, 5°/min to 380°C. Curves: 1 = SE-30, d_f = 0 36 μm; 2 = bonded methylsilicone rubber, d_f = 0.72 μm; 3 = bonded methylsilicone rubber, d_f = 0 35 μm; 4 = SE-30, d_f = 0 12 μm; 5 = bonded methylsilicone rubber, cross-linked with trichlorosilanes[10], ratio of CH_3/Si = 1 8, d_f = 0.35 μm.

Non-extractability of the stationary phase

The fact that our stationary phase is insoluble has some special advantages. First, a dirty column can be regenerated by rinsing with solvent. This is illustrated in Fig. 5, which shows the elution of a simple polarity mixture before and after rinsing of a column that had been used for more than a year for the separation of aza-polynuclear aromatics.

Further, when using on-column injection techniques with ordinary stationary phases there is a risk that the huge amounts of solvent passing through the column on injection will dissolve some of the stationary phase. To avoid this effect it was recommended that the stationary phase should be rinsed out from the first coils of the column[18]. However, the formation of artefacts is favoured in the first part of a column, since all sample components are trapped there for a relatively long time. We

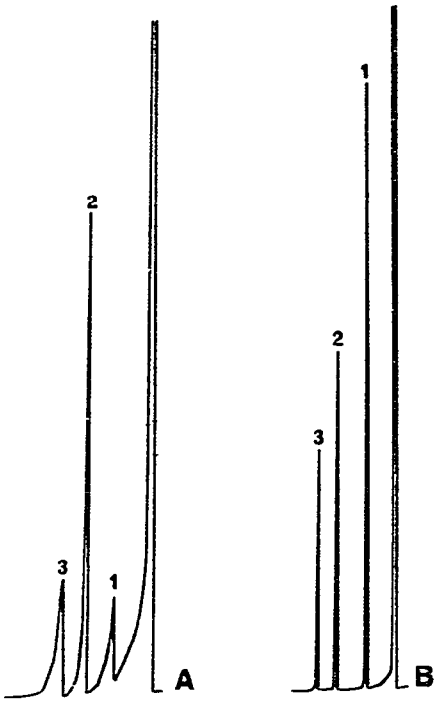

Fig 5. Gas chromatograms (FID) of a test mixture on a Duran glass capillary column coated with bonded methylsilicone rubber. A, after more than a years use for separation of aza-polynuclear aromatics; B, the same column after rinsing Peaks: 1 = 1-octanol; 2 = naphthalene; 3 = dodecane

think that the absence of stationary phase in this part of a column may involve an increased risk of artefact formation. In a column coated with an insoluble stationary phase the film is not rearranged on injection of large amounts of sample solvent: this justifies the presence of a protecting film of stationary phase also in the first column coils.

Analysis of polynuclear aromatics

The glass capillary columns coated with methylsilicone rubber were developed for separation of polynuclear aromatics PNA. Variables such as the degree of leaching, film thickness and degree of cross-linking have been traded to meet the requirements for advanced routine analysis of PNA. For many applications, columns coated with silicone gums are superior due to their higher efficiency and lower activity, but for PNA we prefer the columns of silicone rubber. Even though they are methylsilicones, they possess some selectivity which enables the resolution of some isomers, *e.g.*, chrysene/triphenylene[11,19] and benzofluoranthenes[10,11,19] (Fig. 6), which are difficult to separate on other columns. A column dedicated to the separation of PNA must have good temperature stability, and it must also show good chromatographic properties at high temperatures. For our purposes, only rubber columns fulfil both these requirements in PNA analysis.

Finally, columns of silicone rubber are very durable and resistant to unmild

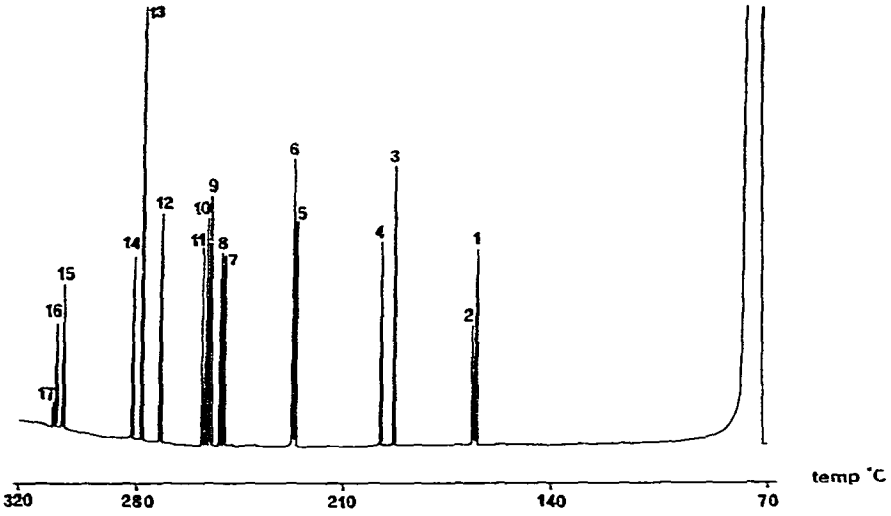

Fig. 6. Gas chromatogram (FID) of a standard mixture of some PNA on a 20-m AR-glass capillary column coated with bonded methylsilicone rubber Initial temperature on injection, 70°C; programmed after 1 min to 320°C at 5°/min Carrier gas velocity at 70°C, 70 cm/sec Inlet split opened 1 min after injection Peaks 1 = phenanthrene; 2 = anthracene; 3 = fluoranthene; 4 = pyrene; 5 = benz[*a*]anthracene; 6 = chrysene, 7 = benzo[*j*]fluoranthene; 8 = benzo[*k*]fluoranthene; 9 = benzo[*e*]pyrene; 10 = benzo[*a*]pyrene; 11 = perylene; 12 = *p*-quaterphenyl; 13 = dibenz[*a*, *c*]anthracene and dibenz[*a*, *h*]anthracene; 14 = benzo-[*g*, *h*, *i*]perylene; 15 = coronene; 16 = dibenzo[*a*, *h*]pyrene, 17 = dibenzo[*a*, *i*]pyrene

treatment; this makes possible a long column lifetime, which can be further extended by a solvent rinse.

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