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GLASS CAPILLARY COLUMNS COATED WITH NON-SOLUBLE METHYL SILICONE GUMS

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SUMMARY

When used as stationary phases in glass capillary columns, films formed from gums are generally more stable than liquid phases. The stability indicates that a high column efficiency can be maintained at elevated temperatures, column bleeding is low and the column lifetime is long. In this paper we present a method for increasing further the gum film stability by using gums with a higher degree of cross-linking. Such gums are not soluble in commonly used solvents and are therefore synthesized *in situ*. In addition, measures have been taken to promote chemical bonding between glass and polymer. The columns have been used successfully for the routine analysis of polyaromatic hydrocarbons.

INTRODUCTION

In glass capillary column gas chromatography, the presence of a stable film as the stationary phase in the column is a prerequisite for the separation of complex samples. Firstly, physical stability is desirable, from which it follows that the stationary phase will remain unaltered as a smooth homogeneous film on the glass surface when the column temperature is increased. A second requirement is for chemical stability, which counteracts chemical decomposition of the stationary phase at elevated temperatures. Initially we attempted to prepare chemically bonded methyl polysiloxanes according to Madani and co-workers[1,2], but did not succeed in obtaining non-extractable stationary phase films using their methods. Gum phases are known to be more stable than liquid stationary phases[3,4]. It occurred to us that a combination of the two approaches, chemical bonding and gum formation, would be rewarding[5,6].

Tetrachlorosilane is known as a powerful agent for the chlorination of glass surfaces (*e.g.*, ref. 7). We therefore allowed Pyrex glass to react with tetrachlorosilane in order to prepare a surface suitable for bonding of siloxanes[6]. This surface was coated with a methyl siloxane pre-polymer containing a number of trifunctional groups and the final polymerization was found to proceed rather violently and some rearrangement of the film seemed inevitable, leading to a column efficiency lower than expected. Further, when preparing highly cross-linked gums, it was difficult to stop the

polymerization; polymerization tended to continue when the column was put into use. Such polymers became hard and brittle after some time and they were then unsuitable for gas–liquid chromatography. Consequently, further development of this procedure would involve modifications to the conditions for polymerization.

EXPERIMENTAL

Capillaries

Pyrex glass capillaries were drawn as described earlier[8]. Carbowax deactivation was performed according to our own method[9] and leaching with hydrochloric acid was executed according to Grob et al.[10]. Some capillaries were treated with tetrachlorosilane. A 2-m long plug of tetrachlorosilane was drawn into the glass capillary and transferred by dry nitrogen along the capillary at the rate of 100 mm/sec. The capillaries were sealed, placed in an oven at 300° for 15 h and then flushed with dry nitrogen for 1 h at room temperature.

Coating materials

An α,ω-hydroxypoly(methylsiloxane) pre-polymer was prepared by hydrolysis of dimethyldichlorosilane (DMCS) according to Patnode and Wilcock[11]. To 60 ml of ice-chilled 25% ammonia solution 20 ml of DMCS were added slowly with stirring. The siloxane phase was then separated, carefully washed with water, dried with magnesium sulphate, filtered and distilled at 90° and 15 mmHg, the residue in the distillation flask subsequently being used.

Preparation and testing of the columns

All of the columns were coated by the dynamic method at a speed of 20 mm/sec using a solution of the coating materials in chloroform[8]. After coating, the column was filled with nitrogen saturated with tetrachlorosilane, sealed and left at room temperature overnight. Tetrachlorosilane was then flushed out with dry nitrogen for 3 h, and the columns were filled with nitrogen saturated with water, nitrogen saturated with concentrated ammonia solution or with ammonia gas (Matheson Gas Products, East Rutherford, N.J., U.S.A.). They were then sealed and placed directly in the oven of a gas chromatograph, the temperature of which was programmed to 320° at 5°/min and maintained at this temperature for 18 h. Before making a preliminary test, the columns were conditioned for 30 min at 300°, then for 48 h at 300° and tested again.

The capillaries were tested in a Carlo Erba 2350 gas chromatograph, using hydrogen as the carrier gas. The capacity ratio, k, was measured for dodecane at 100° and tetradecane at 220°. Kováts retention indices for octanol and naphthalene were determined at 100°. The shapes of the octanol and naphthalene peaks indicated the degree of adsorption taking place on the columns. Further, the HETP was measured for C_{24} for comparison of the efficiencies of the different columns used in this investigation.

After testing, the columns were extracted for 24 h with 25 ml of dichloromethane. This procedure should not be carried out too rapidly, as the solvent must be allowed to penetrate the film thoroughly.

The preparation of polycyclic aromatic hydrocarbon (PAH) samples has been described elsewhere[12].

RESULTS AND DISCUSSION

During the preparation of the pre-polymer, it is desirable to depress the formation of cyclic moieties as these might not readily undergo further polymerization in the column[11]. Acid hydrolysis of DMCS is known to yield cyclic polymers while a basic medium promotes the formation of linear polymers[13]. The synthesis of the pre-polymer was performed by dropwise addition of DMCS to aqueous ammonia, thus maintaining basic conditions during the reaction. However, other factors, such as reagent concentration and temperature, also influence the course of the reaction[13].

A high column efficiency can be obtained if the stationary phase is present as an even, homogeneous film along the entire length of the column. A necessary condition for the formation of such a film is that the glass surface should be smooth and easily wetted by the stationary phase. Four differently treated Pyrex glass surfaces were tested: untreated glass, Carbowax-deactivated glass, tetrachlorosilane-etched glass and glass that was first leached with hydrochloric acid and subsequently etched with tetrachlorosilane. Untreated glass resulted in active, low-efficiency columns, as was also the case for Carbowax-deactivated glass (Fig. 1A and B and Table I). Columns prepared with tetrachlorosilane-etched or hydrochloric acid-leached/tetrachlorosilane-etched glass showed the highest efficiency and a relatively low activity (Fig. 1C and D).
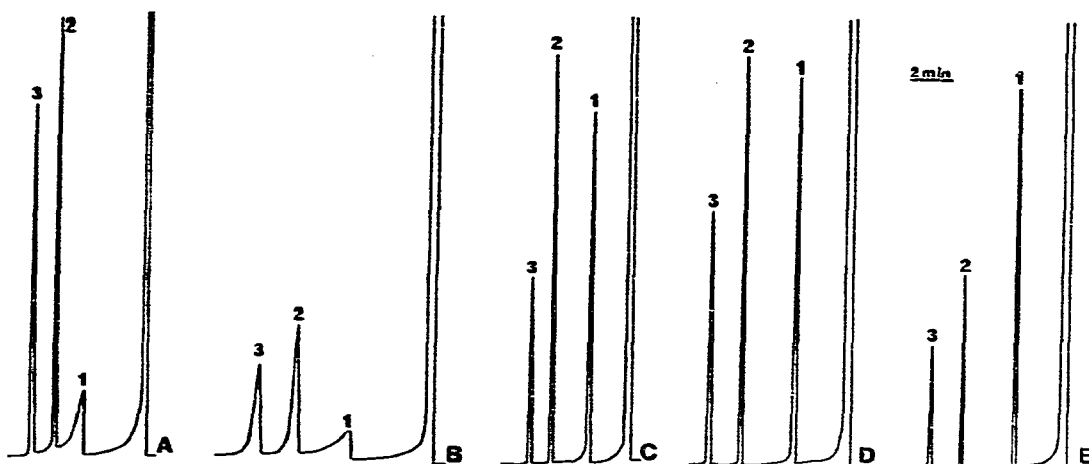

Fig. 1. Gas chromatograms of a polarity mixture on different 20-m Pyrex glass capillary columns. Flame-ionization detector (FID). Column numbers refer to Table I. A = column 1 after extraction; B = column 2 after conditioning; C = column 3 after conditioning; D = column 4 after conditioning; E = column 4 after extraction. Temperature, 100°. Carrier gas (hydrogen) velocity, 70 cm/sec. Peaks: 1 = 1-octanol; 2 = naphthalene; 3 = dodecane. Sample size, ca. 1 ng of each test substance.

The column coating is a critical part of the column preparation and we again stress that the coating must be performed with great care. A special advantage with our method with regard to coating is that it is easy to coat the columns dynamically owing to the low viscosity of the pre-polymer. The preparation of gum columns using the dynamic coating method usually results in low efficiency columns.

TABLE I

CHARACTERISTICS OF SOME TYPICAL 20-m. PYREX GLASS CAPILLARY COLUMNS

Column No.	Pre-treat-ment	Concentration of coating solution (%, v/v)	In situ polymeri-zation promoter	Capacity ratio for C_{24}	Decrease in C_{24} k value after ex-traction (%)	HETP for C_{24} (mm)	Kováts retention index	
							1-Octanol	Naph-thalene
1	—	30	NH_3	21.1	18	0.44	—	1160
2	Carbowax	30	NH_3	18.7	85	0.61	1059	1161
3	$SiCl_4$	30	NH_3	17.2	6.5	0.26	1060	1161
4	$HCl/SiCl_4$	30	NH_3	20.0	10	0.32	1054	1160
5*	$SiCl_4$	5	NH_3	4.5	53	1.0	1075	1159
6**	$SiCl_4$	20	NH_3	18.4	13	0.29	1060	1160
7	$SiCl_4$	30	H_2O	18.4	11	0.26	1057	1161
8	$SiCl_4$	40	H_2O/NH_3	28.1	28	0.35	1083	1160

   * Column coated with Polastosil 16000.
   ** Column coated with Polastosil 200.

We found that treatment with tetrachlorosilane greatly improves the reactivity of the pre-polymer, probably by reaction with end-groups. Tetrachlorosilane also serves the purpose of introducing a suitable degree of cross-linking in the polymer. When ammonia is introduced in a capillary treated in this way, the *in situ* polymerization takes place at room temperature. The advantage of this procedure is that the pre-polymer film seems to remain unaltered during the polymerization. The evenness of the film obtained on coating is thus preserved. The heat treatment step is now considered as being primarily for stabilization of the polymer. Tetrachlorosilane could be added to the coating solution, but because of moisture in the air this is impractical.

Tests were made of three possible methods for *in situ* polymerization. After coating with pre-polymer, the capillaries were filled with nitrogen saturated with water, moisture-saturated ammonia or ammonia gas. The first two methods gave columns that were fairly active (Fig. 2B). Polymerization with ammonia, on the other hand, resulted in fairly low column activity (Fig. 1C). Column bleeding at 300° was very low for all three types of columns, being in the same range as for our previous column type[6].

After testing, the columns prepared in the presence of water or water–ammonia during polymerization were once again subjected to the polymerization step but this time in the presence of dry ammonia. After such a treatment, the column activity was drastically decreased (Fig. 2D). This result we find most interesting, and it will be investigated further. The column efficiency was not altered by this second "polymerization" but the separation characteristics were changed. After treatment with ammonia, these columns acquired separation characteristics similar to those of columns directly polymerized in the presence of ammonia. Such columns could be used to separate some isomers occurring in PAH samples which are very difficult to separate on a non-polar column, *e.g.*, chrysene/triphenylene and benzo[*b*]- and -[*k*]fluoranthene (Figs. 3 and 4). The film thickness in these columns, determined by comparison of *k* values from a statically coated column[8], was approximately 0.7 μm.

For operation up to 260°, the columns could be further deactivated by "pepping-up" according to De Nijs *et al.*[14] (Fig. 2E). Deactivation with hexamethyldisilazane according to Welsch *et al.*[15] was not successful, however (Fig. 2C).
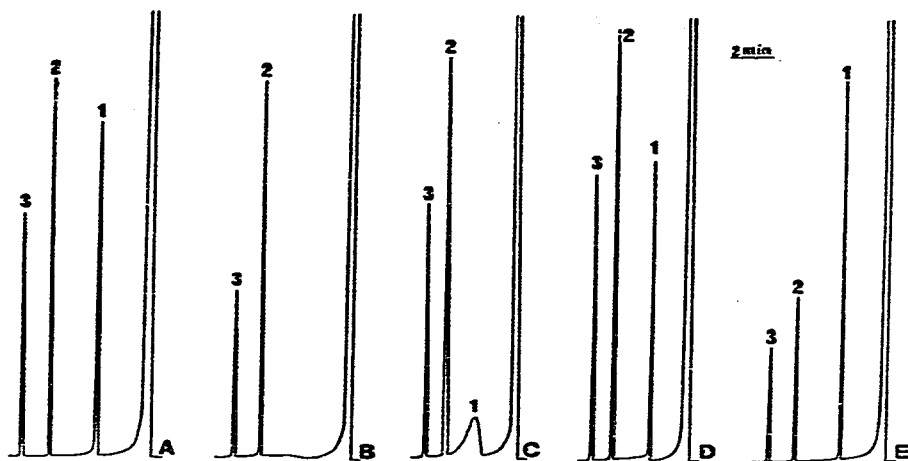
Fig. 2. Gas chromatograms (FID) of a polarity mixture on different 20-m Pyrex glass capillary columns. Column numbers refer to Table I. A = column 6 after conditioning; B = column 7 after conditioning; C = column 7 after silanization; D = column 7 after ammonia treatment; E = column 7 after "pepping-up". Conditions and peak numbers as in Fig. 1.
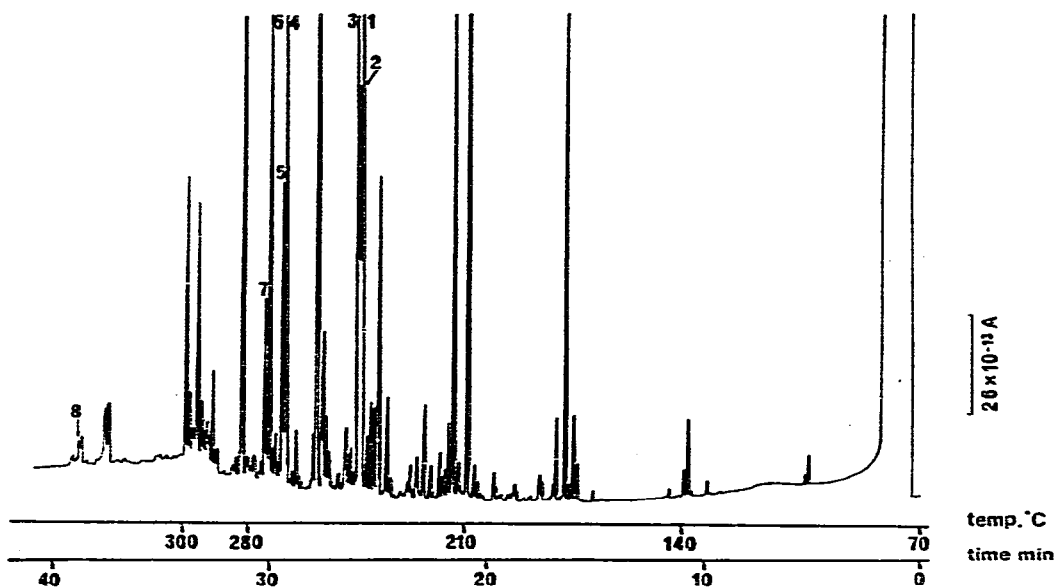

Fig. 3. Gas chromatogram (FID) of a sample containing polycyclic aromatic hydrocarbons derived from cyclone dust collected at an aluminium plant. Pyrex glass capillary column (20 m × 0.22 mm I.D.) treated with hydrochloric acid/tetrachlorosilane and coated with methylpolysiloxane polymerized under ammonia. Initial temperature on injection, 70°; after 1 min, programmed to 300° at 7°/min, then isothermal for 12 min. Carrier gas velocity (hydrogen) at 70°, 70 cm/sec. Inlet splitter opened 1 min after injection. Peaks: 1 = benzo[a]anthracene; 2 = chrysene; 3 = triphenylene; 4 = benzo[b]fluoranthene; 5 = benzo[k]fluoranthene; 6 = benzo[e]pyrene; 7 = benzo[a]pyrene; 8 = coronene.
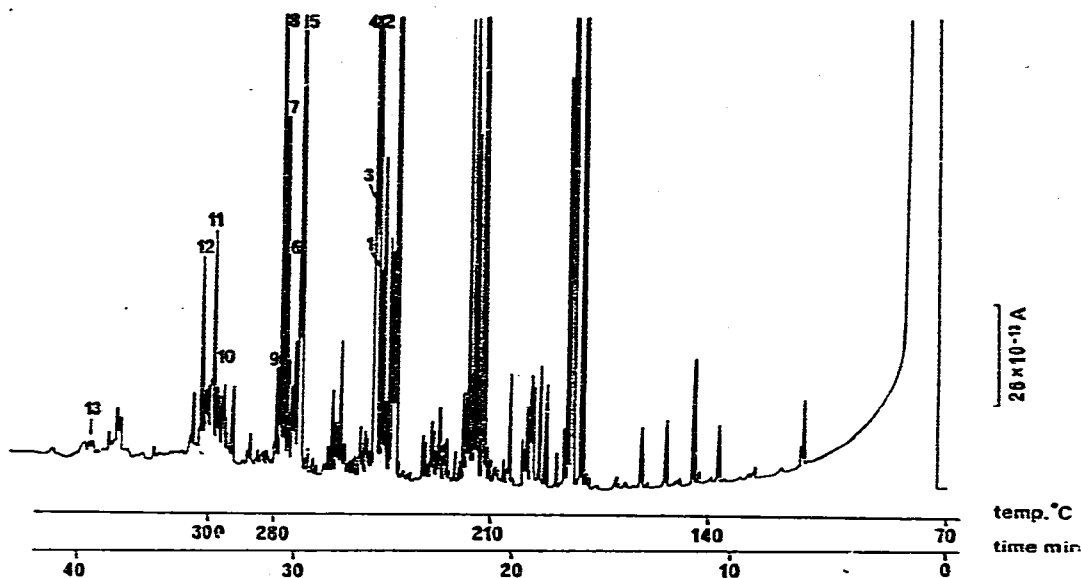
Fig. 4. Gas chromatogram (FID) of a sample obtained from the combustion of a tar intended for cast-iron moulds. Column and conditions as in Fig. 3. Peaks: 1 = cyclopenta[cd]pyrene; 2 = benz[a]-anthracene; 3 = chrysene; 4 = triphenylene; 5 = benzo[b]fluoranthene; 6 = benzo[k]fluoranthene; 7 = benzo[e]pyrene; 8 = benzo[a]pyrene; 9 = perylene; 10 = dibenz[a,j]anthracene; 11 = in-denopyrene; 12 = benzo[ghi]perylene; 13 = coronene.

The effect of extraction on film thickness, activity, polarity and efficiency was studied. The measure of the extractability was the eventual decrease in the k value for C_{24} caused by the extraction. Firstly, the extractability was dependent on the kind of surface that had been coated with pre-polymer. For columns with which ammonia had been used as a promoter for the polymerization, we found that untreated glass as a support gave an 18% reduction in k values (Table I). A very high extractability was observed for columns that were Carbowax-deactivated prior to coating with pre-polymer. It is evident that the Carbowax surface has a detrimental influence on polymerization; the glass surface thus seems to have a decisive influence on poly-merization. The lowest decrease in k values (6%) was found for columns with a tetra-chlorosilane-etched surface. Secondly, the molecular weight of the pre-polymer in-fluences the completeness of polymerization. Columns coated with a pre-polymer with a molecular weight of 1,200,000, Polastosil 16000 (POCH, Gliwice, Poland) showed a 53% reduction in k values, a result that could be expected for steric reasons. Polastosil 200, with an average molecular weight of 15,000, reacted in a similar manner to our own pre-polymer (Fig. 2A). It can thus be assumed that these two pre-polymers have similar molecular weights. Finally, the choice of promoter for the *in situ* polymerization affected the degree of phase solubility. The best results were obtained with dry ammonia (Table I).

For all columns, extraction resulted in decreased column activity, *e.g.*, octanol is not eluted on columns prepared with untreated glass but extraction makes elution possible (Fig. 1A). Evidently, thorough rinsing removes active components in the phase itself. The remaining activity as observed in Fig. 1A we attribute mainly to the

glass surface. It is presumed that the glass activity is due to action taking place through the stationary phase film. If the glass is not sufficiently wetted by the stationary phase, bare glass surfaces will appear in the column, thus augmenting the adsorption. The adsorption observed in Fig. 1A is probably a result of a combination of high glass activity and poor film formation. Columns prepared on tetrachlorosilane-etched glass showed a decrease in activity after extraction, but too high an activity still remained. Columns prepared on hydrochloric acid-leached/tetrachlorosilane-etched glass, however, showed very low activity after extraction (Fig. 1D and E). It seems that the leaching very effectively removes active components in the glass surface and that it improves wetting. Leaching with hydrochloric acid also serves the purpose of opening up the silica structure, which then offers an optimal number of silanol groups[16]. After further conditioning of these columns (48 h at 300°), the activity was slightly increased as a result of some phase decomposition.

The extraction resulted in a slight decrease in the Kováts retention index for octanol. The column plate number was increased by ca. 25% after extraction.

As a consequence, the best columns are made from Pyrex glass that has been leached with hydrochloric acid and etched with tetrachlorosilane, the final in situ polymerization being performed in the presence of ammonia and the column finally extracted.

This type of glass capillary column was prepared primarily for the routine analysis of polyaromatic hydrocarbons (Figs. 3 and 4). For such analyses, highly stable columns are required. When performing the separations according to our methods, the columns should be stable up to 300°. For routine analysis of PAH, numerous samples have to be analysed, and for good efficiency columns with long-term stability are required. Further, the columns must show high efficiency to make feasible the separation of close-boiling isomers. The presence of adsorptive components in samples from natural sources makes it necessary to use columns of low activity. These demands are well fulfilled by the column type described in this paper. At present, however, knowledge of the toxicity of the many components that we are able to separate is very limited, and we are lacking information as to which PAHs our efforts should be concentrated upon. Further development of our methods for PAH analysis is in progress and will involve mainly instrumental aspects.

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