Preparation of Thermostable, Phenyl Silicone Coated, Glass Capillary Columns for Separation of Polyaromatic Hydrocarbons

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Summary

A procedure for the preparation of glass capillary columns coated with non-extractable phenyl polysiloxanes has been developed, the phenyl silicone being synthesised in situ in the column. The non-extractability can be explained in terms of a certain degree of crosslinking in the polymer and possibly also by some chemical bonding to the capillary glass wall. Rearrangement of the film at higher temperatures is counteracted by crosslinking in the phase. Column bleeding is thus decreased, and column efficiency is maintained even at higher temperatures. Such capillary columns showed suitable selectivities for separation of polyaromatic hydrocarbons, and the high temperatures necessary for these analyses could be attained.

Introduction

The frequent detection of carcinogenic polyaromatic hydrocarbons (PAH) in the environment has created the necessity for a qualitative and quantitative method capable of rapidly resolving components in complex mixtures of polyaromatic hydrocarbons. In this paper, we present a gas chromatographic method for this analysis, utilising glass capillary columns. The polymer coating was prepared *in situ* in such a way that temperature stability and good column life were obtained.

In a previous paper [1] we demonstrated the separation of a PAH mixture. Good separation was obtained on a Carbowax deactivated glass capillary column coated with a methyl silicone; however, some of the isomers such as chrysene/triphenylene could not be resolved.

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An attempt was then made to separate the PAH mixture on a capillary coated with a thin layer of non-extractable Carbowax only. Due to the selectivity of this phase, a considerable improvement was obtained in the separation of certain isomers. This encouraged us to prepare a capillary column coated with a methyl phenyl silicone, as an attempt to attain still better selectivity for the unseparated isomers.

Capillaries coated in our laboratory with a commercial methyl phenyl silicone, OV-17, possessed insufficient film stability at the temperatures required for PAH analysis. Film stability can be improved by chemically bonding the phase to the support material [2], also a slight degree of crosslinking in the stationary phase polymer is known to counteract rearrangements of the film at elevated temperatures [3]. For the preparation of columns suitable for PAH analysis we sought to combine these two approaches. A starting point for this work was the procedure of *Madani* et al. [4] for the preparation of chemically bonded phases.

Experimental

Capillaries. Pyrex and AR-glass capillaries were drawn as described earlier [5]. The AR-glass capillaries were double-etched with HCl according to the methods of *Parker* and *Marshall* [6, 7]. We obtained the most evenly etched surfaces with commercial HCl gas (Matheson). The Pyrex capillaries were surface-deactivated with Carbowax by the method reported previously [1].

Coating Materials. The methyl phenyl silicone pre-polymer was prepared by hydrolysis of a 10:1 (v/v) mixture of dichlorophenylmethyl silane (ICN Pharmaceuticals) and trichloromethyl silane (Merck) with aqueous ammonia [4], The cleanup and drying of the pre-polymer was also performed according to *Madani* et al. [4].

Preparation and Testing of the Columns. All columns were coated by the dynamic method [5] using a 20, 10 or 5 % (v/v) solution of the coating materials (pre-polymer or OV-17) in chloroform. The coating velocity used was 20 mm/s.

Three methods were tried for the *in situ* polymerisation of the methyl phenyl silicone pre-polymer. In one method the etched, coated column was filled with dry ammonia (Matheson). In the second method the etched, coated capillary was flushed with water-saturated

nitrogen for 60 min. In the third method the etched, coated capillary was filled with dry nitrogen. The capillaries were then sealed and placed in the oven of a gas chromatograph. Polymerisation was attempted by programming the temperature to 320 °C at 2°/min, and maintaining this temperature at 320 °C for 18 h. After removal from the oven, the columns were extracted with 20 cm^3 of dichloromethane, and then conditioned at 250 °C for 12 hours before testing.

The capillaries were tested in a Carlo Erba 2350 gas chromatograph, using hydrogen as carrier gas. The capacity ratio, k, was measured for dodecane at 100 °C and tetradecane at 220 °C. Kováts indices for octanol and naphthalene were determined at 100 °C. The shapes of the octanol and naphthalene peaks indicated the degree of adsorption taking place on the columns. This test is, as mentioned before [1], more sensitive when small samples are injected into the column. Since an FID detector was used, one nanogram was chosen as a suitable sample amount for this test. The film thickness in OV-17 coated columns was calculated from the weight of the stationary phase that could be rinsed out of the column [5]. An estimation of the film thickness in capillary columns with chemically bonded methyl phenyl gum silicone phases was derived from a comparison of dodecane k-values obtained on such columns with corresponding k-values obtained on OV-17 coated columns with known film thickness.

Results and Discussion

Two different glass capillary surfaces were prepared and coated with OV-17. One surface was Carbowax-deactivated Pyrex [1]. Some properties of this column, e.g., surface deactivation and thermal stability at 300 °C, were comparable with those reported for the same surface coated with methyl silicones [1]. However, the efficiency was quite poor, and therefore the selectivity thought possible with this phase could not be achieved. The other surface, HCl-etched AR-glass, gave a higher efficiency, which indicated that a better film formation was obtained on the strongly etched surface. However, the improved wettability of the etched surface was achieved at the expense of increased column activity. Film thickness and its relationship to column activity becomes especially important at high temperatures because the forces on the surface of glass capillaries that maintain the integrity of a normally coated liquid film are relatively weak [8]. A slight, thermally induced rearrangement of the stationary phase in a relatively thinly coated capillary may cause serious deterioration of column properties such as decreased efficiency and increased column activity [9] as was observed with column 1, Table I. A similar rearrangement in a thicker layer may not elicit any effect, column 3, Table I. The bleeding of stationary phase from the AR-glass capillary columns increased appreciably from 280 °C, and column efficiency and deactivation decreased after about 20 analyses.

During our search for a more stable phase for PAH analysis, we studied various methods for the production of methylphenyl polysiloxanes having a small degree of crosslinking in the polymer chains. The crosslinking, it was hoped, would impart thermal stability to chromatographic films of the resulting polymer. A method was found that resulted in the production of dichloromethane-insoluble gums.

Three factors which might influence the formation and/or physical characteristics of these gums were studied. These were, the ratio of dichloromonomer to the trichloromonomer (i.e. degree of crosslinking) used to synthesise the pre-polymer, the catalyst used for the *in situ* polymerisation of the pre-polymer, and the heating of the pre-polymer/catalyst mixture which gave the dichloromethane insoluble phase.

The desired degree of crosslinking (as determined by the formation of an insoluble gum) in the final polymer was obtained by using a 10:1 mixture of dichloromethylphenyl silane and trichloromethyl silane for the preparation of the pre-polymer. Only freshly distilled monomers were used because small amounts of mono-, di-, tri-, and tetrachlorosilane contaminants present in unknown ratios could result in uncontrolled crosslinking and/or chain terminations [10]. These contaminants, if present in varying amounts, would greatly affect the reproducibility of the synthesis. Too much crosslinking leads to hard, brittle, glassy polymers [11] that are unsuitable for gas-liquid chromatography.

In preliminary experiments performed in test tubes, catalysts for the polymerisation of the pre-polymer were tested. Ammonia with a small amount of water,

Table I. Characteristics of some typical 20-m capillary columns.

Column number	Glass type	Stationary phase	Pre-treatment	Capacity ratio (dodecane)	Film thickness (μm)	Kováts index naphthalene	HETP (mm)
1	Pyrex	OV-17	Carbowax	3.0	0.03	1328	2.6
2	AR	OV-17	HCl-etched	3.0	0.03	1309	0.54
3	AR	OV-17	HCl-etched	10.2	0.19	1324	0.71
4	AR	"bonded" phenyl silicone	HCl-etched	4.4 *4.2		1329	0.55

* after extraction

water alone, anhydrous ammonia and heating with dry nitrogen were tested in these pilot runs. Insoluble gums were obtained upon heating the pre-polymer with dry nitrogen or with the first two catalysts; no polymerisation was obtained with the anhydrous ammonia. Because the gums formed by the polymerisation and/or thermal setting of the pre-polymer were insoluble in the solvents commonly used for column coating, this step was performed in the column. The above catalysts were applied to the *in situ* formation of the polymer. Those columns prepared using water vapour catalyst followed by sealing and heating had reproducible chromatographic properties. Capillary columns with a polymer phase formed upon heating with dry nitrogen were also useful; it is interesting to note that they showed chromatographic properties differing slightly from those of the above columns. Further, we found it necessary to increase the temperature slowly in the heating step of the polymerisation.

After the *in situ* thermal setting of the phase, the columns still exhibited unacceptable bleeding and polarity (adsorption of alcohols). Extraction of the columns with dichloromethane reduced the bleeding to tolerable levels and reduced the adsorption of alcohols (presumably by the removal of hydroxyls contained in shorter or non-reacted phenyl siloxane chains). The extraction usually resulted in a decrease in dodecane k-values of around 5 %. HCl-etched capillary columns with very thin films of stationary phase showed some activity also after the extraction; this could be partly suppressed by silanisation with hexamethyldisilazane according to *Welsch* et al. [12]. A further possibility of obtaining deactivation would be to bleed Carbowax decomposition products into the capillary column [13, 14]. In this case, however, the bleeding of the deactivated capillary column was too high at temperatures over 250 °C. Most typical polyaromatic hydrocarbons are not inclined to adsorption. Adsorptive components however are usually present in samples from natural sources and our experience is that fairly well deactivated capillary columns are needed for such separations.

The utility of bonded phenyl gum columns prepared with water as catalyst is demonstrated in Figs. 1 and 2. Good separation is achieved of some close isomers such as benzo(b)fluoranthene from benzo(k)fluoranthene, benzo(e)pyrene from benzo(a)pyrene and chrysene from triphenylene, which were either not separated or unresolved by our earlier columns [1]. Columns prepared with wet ammonia or water as catalysts show very similar selectivities; a heat-catalysed polymer however shows somewhat different properties. The elution order of some components is thus altered, anthracene is for instance eluted before phenanthrene. Further, on such columns we obtain a partly resolved peak between peak 9 and 10 in the tar mixture shown in Fig. 1. Using re-

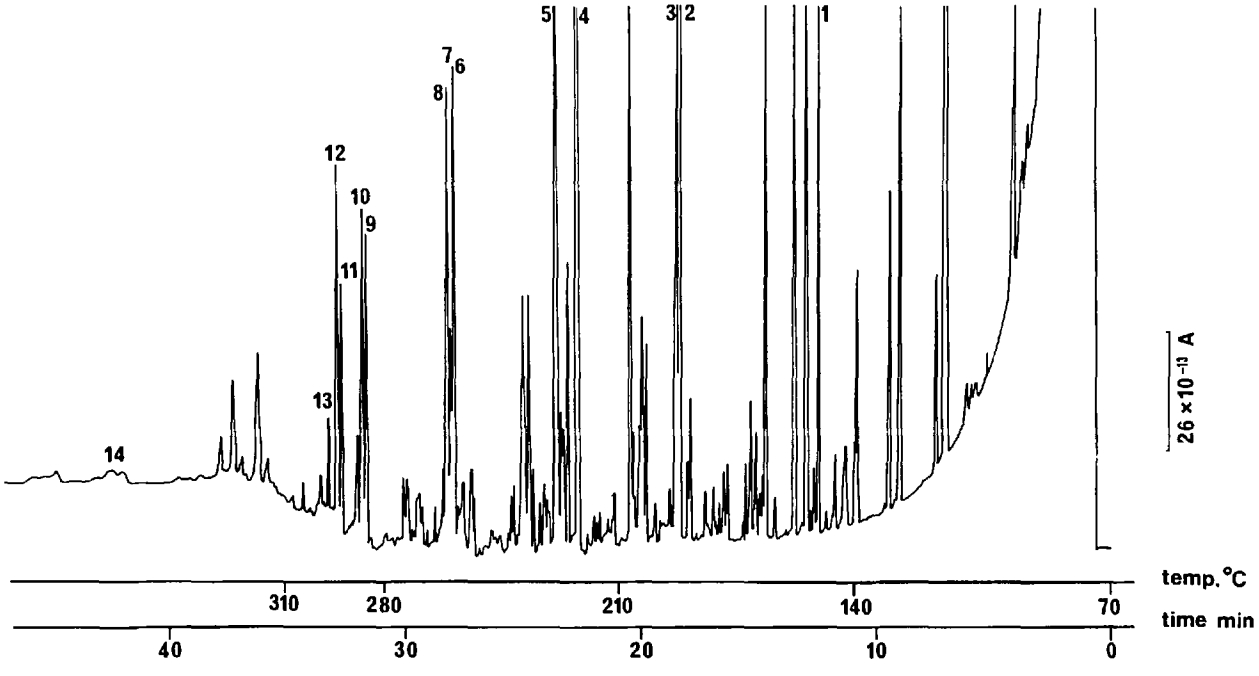

Fig. 1

• Gas chromatogram (FID) of tar sample containing polyaromatic hydrocarbons. HCl-etched AR-glass capillary column (20 m × 0.22 mm ID), coated with chemically bonded phenylmethyl silicone gum. Initial temperature on injection, 70 °C; after 1 min programmed to 310 °C at 7°/min, then isothermal for 12 min. Carrier gas (hydrogen) velocity at 70 °C, 67 cm/s. Inlet splitter opened 1 min after injection. Peaks: 1, acenaphthylene; 2, phenanthrene; 3, anthracene; 4, fluoranthene; 5, pyrene; 6, benz(a)anthracene; 7, triphenylene; 8, chrysene; 9, benzo(b)fluoranthene; 10, benzo(k)fluoranthene; 11, benzo(e)pyrene; 12, benzo(a)pyrene; 13, perylene; 14, coronene.

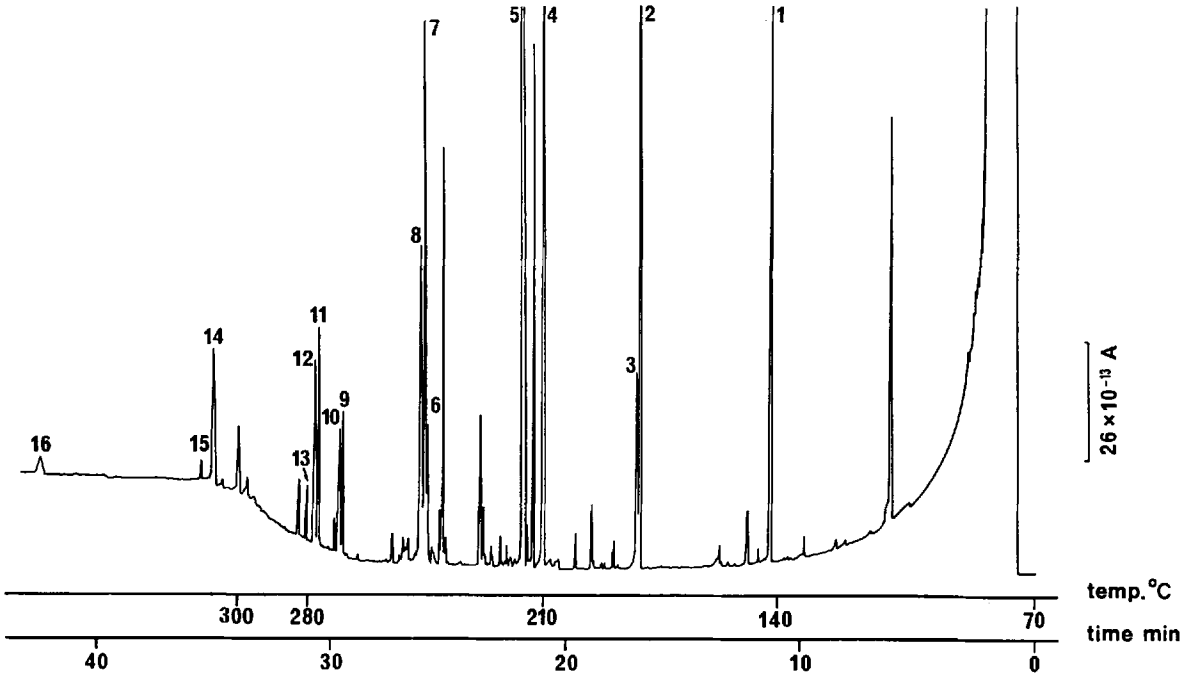

Fig. 2

• Gas chromatogram (FID) of PAH fraction of wood combustion products. HCl-etched AR-glass capillary column (18 m × 0.22 mm ID), coated with chemically bonded phenylmethyl silicone gum. Initial temperature on injection, 70 °C, after 1 min programmed to 300 °C at 7°/min, then isothermal for 10 min. Carrier gas (hydrogen) velocity at 70 °C, 67 cm/s. Inlet splitter opened 1 min after injection. Peaks: 1, acenaphthylene; 2, phenanthrene; 3, anthracene; 4, fluoranthene; 5, pyrene; 6, cyclopenta(cd)pyrene; 7, benz(a)anthracene; 8, chrysene; 9, benzo(b)fluoranthene; 10, benzo(k)fluoranthene; 11, benzo(e)pyrene; 12, benzo(a)pyrene; 13, perylene; 14, benzo(ghi) perylene; 15, anthanthrene; 16, coronene.

ference substances we conclude that this could be benzo(j)fluoranthene.

We are thus able to prepare columns suitable for routine analyses showing different selectivity for PAH; this offers a good possibility of increasing the certitude of such analyses. More variations in phenyl silicone column selectivity can be derived by varying the proportions of monomers for polymer preparation.

The advantages obtained with our bonded gum phases are all connected with increased film stability. First, we obtain better thermal stability, low bleeding up to 310 °C, with chemically bonded phenyl phase capillaries than with normally coated OV-17 columns. Further, we have found that compared with the liquid phenyl silicone phase, the efficiency of bonded phases is less influenced by increasing temperatures. Secondly, the more rigid polymer network in these films facilitates the use of thinner stationary phase layers, column 4, Table I. Such films allow faster elution of the samples, thus increasing the speed of analysis. Our columns are intended for long series of routine analyses of PAH. When it is required to analyse numerous samples, the analysis time becomes an important factor. An emerging drawback is that the phenyl phase retains PAH more strongly than the non-polar phase previously used at this laboratory [1]. The high temperature stability of the bonded phenyl silicones however permits a shortening of this increased retention by the use of thin stationary phase films and extension of the temperature programme to 310 °C. Column life was approximately 3 months, when performing 10 analyses a day.

Grob [3] has recently pointed out the benefits of gum phases for capillary columns and also the needs for more polar gum phases. In this study we found that in some cases, and indeed in the most useful case, the gums produced had a very limited solubility. We therefore had to develop a method for the production of this gum within the column. It is open to speculation whether or not some chemical bonding of the polymer to the glass occurred during the *in situ* polymerisation. However, a major advantage of the *in situ* polymerisation is that this method facilitates the preparation of capillary columns coated with insoluble gums as stationary phases.

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