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Note

Thermostable deactivation reagents for capillary column preparation

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Capillary column preparation with non-polar phases has advanced to the stage where excellent columns may be prepared routinely for such phases as OV-1, OV-101, SE-52 and SE-54[1]. Deactivation of the glass surface prior to coating may be achieved by treatment with Carbowax 20M (which either co-polymerizes or possibly bonds to the surface silanol groups with elimination of water to form a non-extractable layer), or by persilylation[2]. The reagent for persilylation is either hexamethyldisilazane (HMDS) or a mixture of HMDS and diphenyltetramethyldisilazane (DPTMS). More recently[3] the use of peroxides to promote the *in situ* cross-linking of phases which contain a small (*ca.* 1%) number of vinyl groups has yielded columns of high performance and stability.

The temperature limit of the Carbowax 20M deactivating layer is about 250°C and this imposes a limit to its usefulness. Attempts to coat the persilanized glass surface with phases such as OV-17, Dexsil 400 or OV-25 lead to droplet formation. Grob and Grob[2] have reported that extended wettability of the column surface such that OV-17 can be applied may be achieved by the use of phenyl-substituted silyl compounds such as tetraphenyldimethyldisilazane but we have had little success with this technique. Our particular interest in the separation and identification of five- and six-ring polycyclic aromatic hydrocarbons and related alkylated compounds has prompted us to develop techniques for the preparation of capillary columns containing relatively polar phases such as Dexsil 400 and OV-17 which may be routinely used to temperature considerably in excess of 300°C with high amplification. This preliminary paper reports our experiences in preparing columns via deactivation with triphenylchlorosilane (TPCS), octaphenylcyclotetrasiloxane (OPCTS) and diphenyldichlorosilane.

EXPERIMENTAL

A Carlo Erba 4160 Series gas chromatograph fitted with split/splitless and on-

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column injection systems and a flame-ionization detector was used. Hydrogen gas was used as carrier. Chromatograms were recorded on a Pye Unicam SP 4100 computing integrator.

Column preparation

Soda glass and Pyrex capillaries were drawn on Hewlett-Packard Model 1045A or Shimadzu GDM 1 glass drawing machines. Before drawing the capillaries the inside of the tube was washed with concentrated hydrochloric acid and rinsed with distilled water and then acetone. Capillaries were drawn to a nominal internal diameter of 0.3 mm and a length of 15 m. Columns were pretreated by conventional leaching techniques[1]. Hence columns were filled to 95% (soda glass) or 92% (Pyrex glass) with 20% hydrochloric acid, sealed under vacuum and heated to 140 or 180°C, respectively, overnight. After cooling and opening, the columns were flushed with 2% hydrochloric acid, followed by distilled water and then methanol. They were then dehydrated by heating to 300°C for 1 h in a stream of dry nitrogen[4].

Deactivation

With OPCTS. Columns were dynamically coated (2–4 cm sec^{-1}) with a saturated solution of OPCTS in dichloromethane. Both ends of the column were connected to a vacuum (*ca.* 15 mmHg) for 30 min before being sealed. Columns were heated (400°C, 16 h), opened, rinsed with dichloromethane (3 column volumes) and then statically coated by conventional methods.

With TPCS. The silane was purified by recrystallization from light petroleum (b.p. 60–80°C) and dynamically coated (2–4 cm sec^{-1}) as a 1% solution in dry dichloromethane. The ends of the column were connected to a vacuum for 30 min to remove residual dichloromethane, then sealed and heated (400°C, 16 h). Upon opening, excess reagent was removed with dichloromethane.

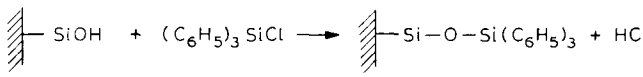
With diphenyldichlorosilane. Columns were dynamically coated with pure diphenyldichlorosilane. The ends were sealed under vacuum and the columns heated (400°C, 16 h). Excess reagent was removed with dichloromethane.

Some columns were treated subsequently with hexamethyldisilazane to cap remaining silanol groups.

All columns were coated using conventional static methods. The ends were sealed with either water-glass or silicone rubber. Phases used were Dexsil 400, OV-17, OV-25 and SP2250 at typical concentrations of 0.2% (w/v) to give a nominal film thickness of 0.15 μm.

RESULTS AND DISCUSSION

TPCS was selected as a deactivating reagent in order to obtain the highest possible concentration of phenyl groups on the glass surface. According to eqn. 1 each silanol group is replaced by three phenyl groups:



(1)

Technical problems were encountered with the use of a saturated solution of TPCS in

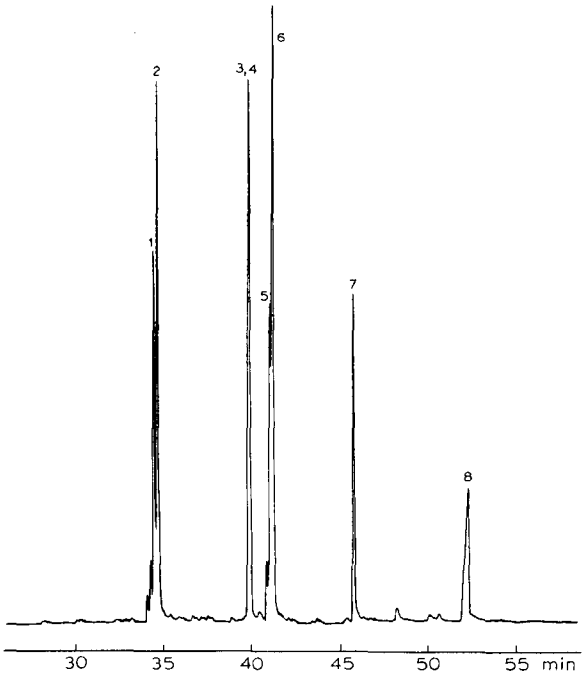


Fig. 1. Separation of standard PAHs on Dexsil 400 (TPCS deactivated). Peaks: 1 = benz[*a*]anthracene; 2 = chrysene; 3 = benzo[*j*]fluoranthene; 4 = benzo[*b*]fluoranthene; 5 = benzo[*e*]pyrene; 6 = benzo[*a*]pyrene; 7 = dibenzanthracene; 8 = dibenzfluoranthene. Temperature programme: 100°C hold 1 min; then 5°C min^{-1} to 320°C hold 20 min. Injection: 1 μl on column.

dichloromethane. Even small losses of solvent resulted in formation of crystals of the silane in the capillary columns causing blockages which could not be erradicated. This difficulty could be overcome by diluting a saturated solution of TPCS with *ca.* 10% of dichloromethane. The wettability of the resultant phenylated surface was such that stable thin films (*ca.* 0.15 μm) of phases such as Dexsil 400 (McReynolds Constant $\Delta I_{benzene}$ = 60) could be applied to yield columns of high efficiency and thermal stability (Fig. 1). Attempts to coat columns treated with TPCS with more polar phases such as OV-17 ($\Delta I_{benzene}$ = 117, 70% phenyl groups) and OV-25 ($\Delta I_{benzene}$ = 178, 75% phenyl groups) led to droplet formation. This lack of wettability suggests that an insufficient number of surface silanol groups were reacting with the TPCS. Presumably the bulky nature of the triphenylsilyl moeity hinders reaction with all the surface silanol groups and thus a significant number of these groups remain on the glass surface.

Extended wettability was achieved if diphenyldichlorosilane was used as the deactivating agent. Presumably less steric hindrance results in increased efficiency of reaction. Columns treated in this way could be coated with OV-17. However, the preparation procedure is complicated by the need to hydrolyse residual Si–Cl groups and then cap them with hexamethyldisilazane of trimethylchlorosilane.

Deactivation of these columns was assessed using a modified Grob test mixture consisting of C_{10} and C_{11} alkanes, octanol, dimethylaniline, dimethylphenol and dicyclohexylamine. Particularly noteworthy was the total elution of the dicyclohexyl-

amine, *i.e.*, there was no loss on the column when compared with the other compounds. Such inertness is usually only observed with high-quality non-polar columns.

Fig. 1 shows the separation of a set of standard polycyclic aromatic hydrocarbons (PAHs). The ability of a column to resolve the pairs of compounds benzanthracene/chrysene, benzo[*b*]-/benzo[*j*]fluoranthene and benzo[*e*]-/benzo[*a*]pyrene and to elute the compounds dibenzanthracene and dibenzpyrene may be taken as a measure of its selectivity towards PAHs and thermal stability. These compounds constitute a suitable test mixture for PAHs. In particular resolution of benzo[*b*]fluoranthene from benzo[*j*]fluoranthene is difficult to achieve. Although relatively involatile compounds such as dibenz[*ah*]anthracene and dibenzpyrene are eluted from this Dexsil 400 column, resolution of the isomeric pair benzo[*b*]- and benzo[*j*]fluoranthene is not achieved. Coating of Dexsil 400 on phenylated glass surfaces thus yields columns of exceptional thermal stability.

By analogy with the reaction of octamethylcyclotetrasiloxane[5,7] OPCTS is thought to undergo a surface-catalysed ring opening and co-polymerization reaction when heated in the column deactivation step. Thus, even if some surface silanol groups do not react directly, they will still be effectively shielded by the resultant polymeric phenylsiloxane layer. In this respect the resultant layer is similar to that given by the *in situ* cross-linking technique recently reported[3,6]. Following deactiva-

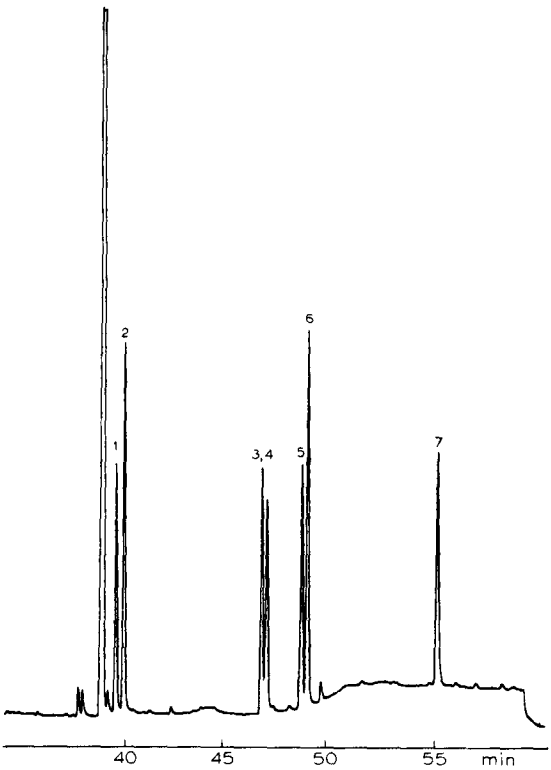


Fig. 2. Separation of standard PAHs on OV-17 (OPCTS deactivated). Identification of peaks and temperature programme as for Fig. 1.

tion with OPCTS we have coated columns with OV-17 (and its equivalent SP2250) and OV-25 (which contains 75% of phenyl groups). These columns have been used for the analysis of PAHs where their greater selectivity permits the complete separation of the pairs of compounds chrysene/benzathracene, benzo[*b*]- and benzo[*j*]fluoranthene, and benzo[*e*]- and benzo[*a*]pyrene (Fig. 2). The temperature stability of these columns is excellent and some have been used at temperatures up to 320°C (with high amplification) for several weeks with no evidence for the loss of phase or column efficiency. Columns prepared in this way have been used to study high-molecular-weight PAHs and alkylated PAHs obtained from tobacco smoke condensate by capillary gas chromatographic–mass spectrometric techniques.

CONCLUSION

Use of OPCTS as a column-deactivating reagent for the preparation of glass capillary columns provides a thermostable layer which will accept a thin coating of liquid phases which contain a high percentage of phenyl groups. Columns so prepared may be routinely used up to 320°C at high amplifier settings. Improved performance for the separation of PAHs is thus achieved. When interfaced to a mass spectrometer, compounds such as polyalkylated dibenzanthracenes and polyalkylated indenopyrenes, present in tobacco smoke subfractions, may be eluted, identified and quantified.

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