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GLASS CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY COATED WITH NON-EXTRACTABLE FILMS OF CYANOSILICONE RUBBERS

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SUMMARY

A procedure for the preparation of glass capillary columns using a bonded cyanosilicone rubber as stationary phase is presented. Two types of cyanosilicone pre-polymer were synthesized, with 25% and 100% cyano-substitution, respectively. Glass capillaries that had been leached with HCl or treated with a sodium chloride sol were coated with the pre-polymer, and a rubber was formed *in situ*. Such columns show very good thermal stability up to 300°C; further, activity is low and the efficiency good.

The utility of these thermally stable polar columns is demonstrated by the analysis of aldonitrile derivatives prepared from sugars and also polynuclear aromatics (PNAs), especially aza-PNAs.

INTRODUCTION

Recent interest in gas chromatographic separation of relatively high boiling compounds, such as polynuclear aromatics (PNAs), has encouraged efforts to find thermally stable silicones, both polar and non-polar, to be used as stationary phases.

The merits of high molecular weight, linear polysiloxanes, *i.e.* silicone gums, as stationary phases for glass capillary columns have been recognized by several authors. Major advantages of such phases are the good stability of stationary-phase films, the wide range of film thickness, 0.1–1.5 μm , that can be applied, and the wide temperature range that the gum can be utilized over¹. In gas chromatography (GC), use of silicone gums as stationary phase has been limited principally to the non-polar sphere. Methylsilicone gums and gums showing slight polarity, such as SE-52 and SE-54, have been extensively used, but more polar silicone gums have not been commercially available, except for some very recently marketed types such as OV-215.

In previous papers²⁻⁴, we have shown that the introduction of a slight degree of cross-linking in the siloxane polymer will further increase film stability. Such a polymer, resembling a rubber rather than a gum, is insoluble in commonly-used solvents, but is still suitable for GC. The limited solubility makes conventional column coating impossible; *in situ* preparation, however, facilitates the manufacture of rubber-coated columns.

Good film stability can also be obtained if the stationary phase is bonded to the support. This has been demonstrated for packed columns by Aue *et al.*⁵⁻⁷, for capillary columns by Madani *et al.*⁸⁻¹⁰ and also by the present authors²⁻⁴.

In the work presented here, we have intended to combine the advantages of bonded and rubber phases for the preparation of thermostable cyanosilicone stationary phases for glass capillary columns.

EXPERIMENTAL

Capillaries

Pyrex glass capillaries were drawn as described earlier¹¹. Leaching of the glass capillaries with hydrochloric acid was performed principally according to the method of Grob *et al.*¹². Thus, after heat treatment, 15 h at 180°C, with 20% HCl solution, the capillaries were rinsed with a very dilute HCl solution, pH 3. This pH was selected for rinsing in order to stabilize any silica hydrogel that might possibly have been formed during the leaching¹³. The rinsed capillaries were then dried for 4 h at 250°C, during which time the capillaries were purged with dry nitrogen. Some capillaries were treated with tetrachlorosilane as described earlier³. Sodium chloride deposition for roughening of the glass capillary surface was performed according to the method of De Nijs *et al.*¹⁴. As we used columns with a small diameter, it was necessary to apply pressure to force the suspension through the column. To obtain even deposition, it is important that the liquids move continuously through the column during the deposition and the subsequent rinsing with solvent. Therefore we used a special container (Fig. 1) for these operations. When changing from suspension to solvent, the end of the column is simply drawn up from the suspension reservoir and transferred to the solvent reservoir without alteration in pressure.

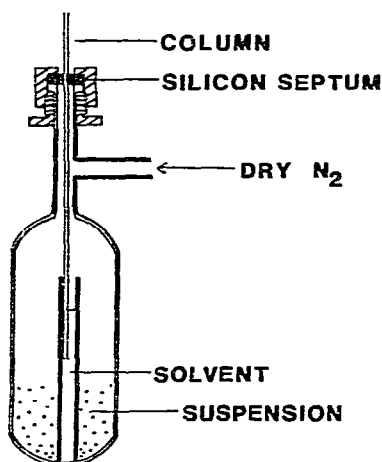


Fig. 1. Glass container for NaCl deposition.

Coating materials

Two types of α,ω -hydroxypolycyanosiloxanes were prepared by hydrolysis of different dichlorosilanes as described by Cooper and Prober¹⁵. A pre-polymer with

25% cyano-substitution was made from a mixture of β -cyanoethyl-methyldichlorosilane and dimethyldichlorosilane in the mole ratio 1:1. For a 100% cyano-substituted pre-polymer, the source material was bis(γ -cyanopropyl)dichlorosilane. All silanes were obtained from Silar Labs., Scotia, NY, U.S.A. To 20 ml of ice, the silanes, 13 ml, diluted in 115 ml of ether, were added slowly under vigorous stirring in an atmosphere of nitrogen. After 2 h reaction, the siloxane phase was carefully extracted with water, dried with magnesium sulphate and calcium sulphate, filtered and finally distilled at 170°C and 20 mm. The residue in the distillation flask was examined by infrared (IR) spectroscopy and used as pre-polymer.

Some capillaries were coated with commercially available cyanosilicone phases, AN-600 (Analabs, North Haven, CT, U.S.A.) and XE-60 (General Electric, New York, NY, U.S.A.) both with 25% β -cyanoethyl-substitution, and Silar 10C (distrib. Applied Science Labs., State College, PA, U.S.A.) with 100% γ -cyanopropyl-substitution. The properties of Silar 10C have been shown to differ between batches^{16,17}; nuclear magnetic resonance (NMR) studies showed that the Silar 10C used here is similar to batch "D" mentioned in the paper of Heckers *et al.*¹⁷.

Preparation and testing of the columns

All the columns were coated by the dynamic method using a solution of the coating materials in ethyl acetate. After coating, each column was filled with nitrogen saturated with fresh tetrachlorosilane, and allowed to stand for 12 h at room temperature. The remaining tetrachlorosilane was then flushed out with dry nitrogen during 3 h. Ammonia gas (Matheson Gas Products, East Rutherford, NJ, U.S.A.) was filled into the column, the ends of which were then sealed. The column was placed in a gas chromatograph and polymerization was attempted by programming the temperature to 275°C at 2°/min and then maintaining it at 275°C for 15 h. The columns were conditioned for 15 h at 275°C.

The columns were tested in a Carlo Erba gas chromatograph 2350, using hydrogen as carrier gas. The capacity ratio, k , and the HETP were measured for naphthalene at 100°C and for tetracosane at 150°C. Kováts retention indices for octanol and naphthalene were determined at 100°C. Measurements for Van Deemter curves were made at 100°C for octadecane, 210°C for galactonitrile and 290°C for anthanthrene. Some chromatographic properties of the columns were determined by the test according to Grob, Jr. *et al.*¹⁸.

A Carlo Erba ⁶³Ni electron capture detector (ECD) was used for the analysis of sugar derivatives. The preparation of PNA samples has been described elsewhere¹⁹.

RESULTS AND DISCUSSION

The stability of a cyanosilicone polymer is strongly affected by the structure of the functional groups attached to the silicon atom^{20,21}. Substitution with α -cyanoethyl thus gives a weak silicon-carbon bond whereas β -cyanoethyl and γ -cyanopropyl give highly stable silicones. Further, increased stability is obtained when a phenyl group is bonded to the same silicon atom as a γ -cyanopropyl, *e.g.* Silar 5CP²². Indications of a similar effect are observed with polymers prepared from bis(γ -cyanopropyl)dichlorosilane, *e.g.* Silar 10C²³. In this work we used β -cyanoethyl- and bis(γ -cyanopropyl)silanes to prepare the polymers. The pre-polymer synthesis

should be done with some care; the silane should be added slowly to the reaction vessel, and therefore we added the silane as a solution in ether. Further, the pre-polymer should be thoroughly dried. Before being used, the quality of the pre-

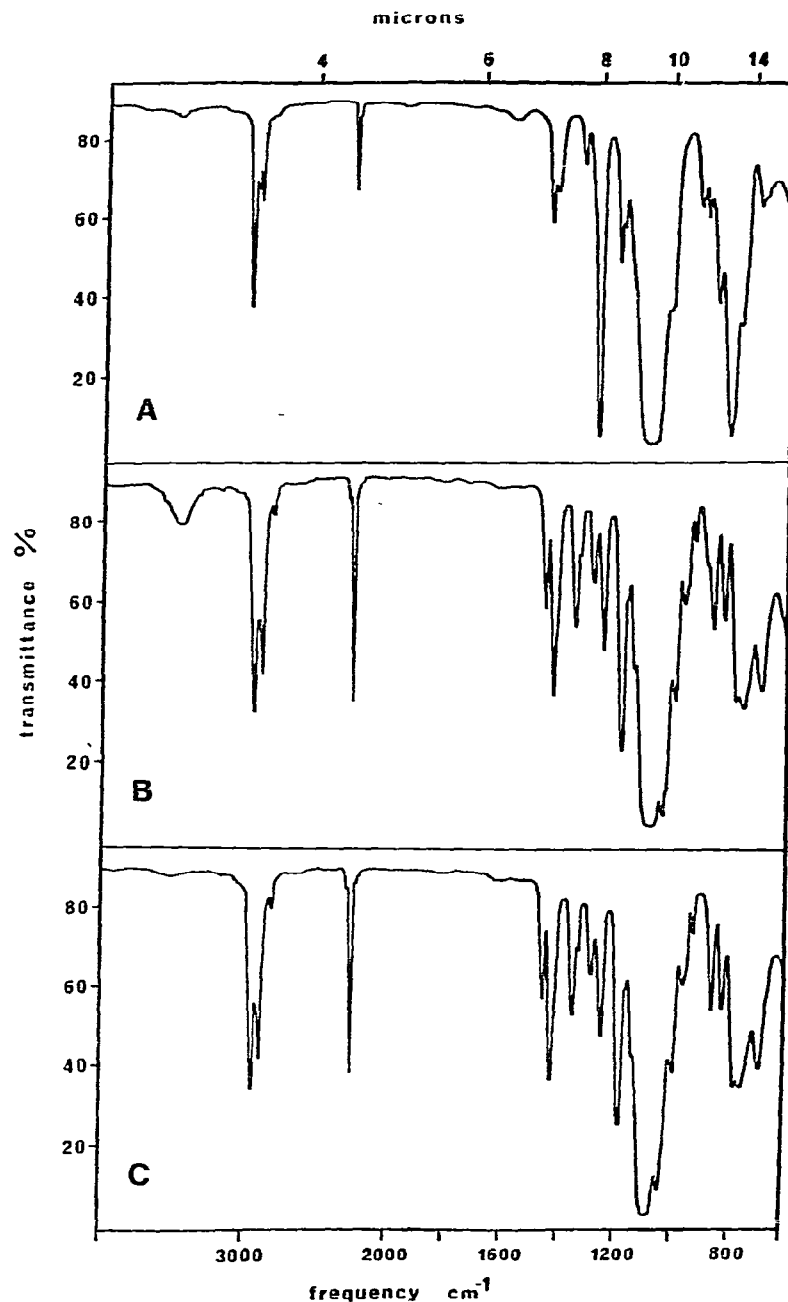


Fig. 2. IR spectrum of siloxanes. A, a pre-polymer with 25% cyano-substitution. B, 100% cyano-substitution; C, Silar 10C.

polymer was controlled by IR spectroscopy. Water content is thus observed in the the 3200–3400 cm^{-1} region and the presence of cyano at 2250 cm^{-1} (Fig. 2)^{24,25}. Gel permeation chromatography and NMR studies suggested that the pre-polymers are composed of three to four monomer units.

The forces on a glass surface are insufficiently strong to obtain good wetting with cyanosilicones and some glass surface modification is necessary. Ideally, such a modification should give a surface activity which is adjusted so that saturation is effected by the stationary phase itself. In our experience, the intensity of the forces necessary to keep the film in position is very much increased at elevated temperatures, *e.g.* 300°C. This means that if good film stability is to be obtained at 300°C, one has to accept that the column shows some residual activity at 100°C, an activity intended to be utilized for the film fixation at higher temperatures. In the case of bonded phases, the wettability is critical only on coating and bonding. This makes it possible to prepare highly inert, thermally stable columns.

Four types of glass surface modification were tested: etching with tetrachlorosilane, leaching with HCl, deposition of sodium chloride and finally a combination of leaching and salting. The results of these tests are presented in Table I and Fig. 3. Etching with tetrachlorosilane gave a glass surface that was not wetted by the pre-polymer. The other three surfaces were, however, readily wetted by the pre-polymer with 25% cyano-substitution. Leaching gave low column activity, salting gave high; the efficiencies were similar. Of the modifications tested, we consider leaching to be the most suitable for this type of stationary phase. For wetting with the more polar 100% substituted cyanosiloxane, a salted glass surface was necessary. The increased activity achieved on salting could here be partly saturated by the phase itself. A combination of leaching and salting was not successful. We feel that the wetting of the glass surface could be much improved, and are now developing a new method for chemical modification of glass capillaries.

Column bleed from our phases was found to be quite low compared with the bleeding experienced with some commercial cyanosilicones (Fig. 4). The lowest bleeding was obtained from phases having 100% cyano-substitution; possibly a result of the stabilizing effect obtained when two γ -cyanopropyl groups are attached

TABLE I

CHARACTERISTICS OF SOME TYPICAL 20-m PYREX GLASS CAPILLARY COLUMNS

Pretreatment	Stationary phase	Capacity ratio for C_{24}	HETP for naphthalene	Kováts retention index	
				1-Octanol	Naphthalene
Leached	25% CN	9.0	0.7	1400	1493
Leached/salted	25% CN	8.7	0.7	1400	1494
Salted	25% CN	5.6	0.7	1423	1529
Leached/salted	100% CN	5.5	0.8	1616	1822
Salted	100% CN	6.9	0.6	1671	1898
Salted	Silar 10C	4.5	0.8	1629	1844
Salted	XE-60	9.8	0.6	1386	1495
Salted	AN-600	11	0.5	1392	1499

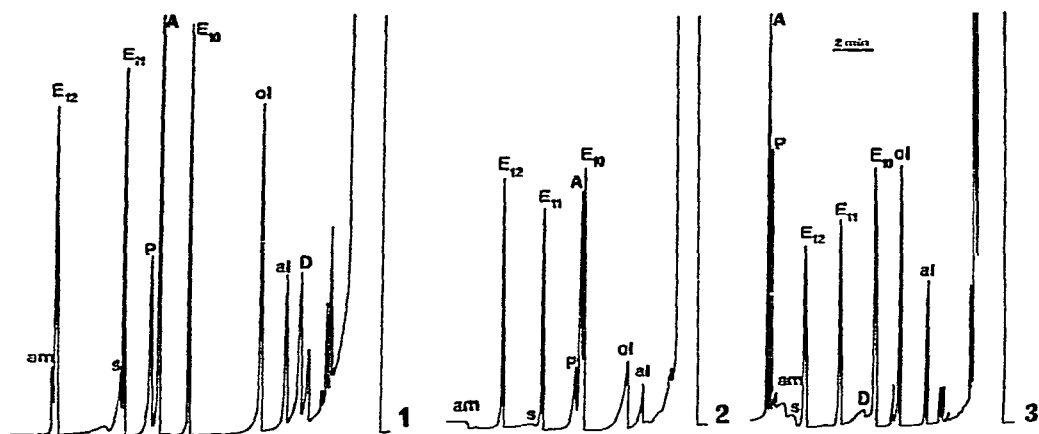


Fig. 3. Gas chromatograms (FID) of a Grob test mixture on different Pyrex glass capillary columns coated with a bonded cyanorubber. Initial temperature, 40°C, programmed to 150°C at 5°/min. Carrier gas flow-rate (hydrogen) at 40°C, 60 cm/sec. Split adjusted to give *ca.* 5 ng of test substance to the column. Peak assignment: D = 2,3-butanediol; al = nonanal; ol = 1-octanol; E₁₀ = C₁₀-acid methyl ester; A = 2,6-dimethylaniline; P = 2,6-dimethylphenol; E₁₁ = C₁₁-acid methyl ester; s = 2-ethylhexanoic acid; E₁₂ = C₁₂-acid methyl ester; am = dicyclohexylamine. Chromatograms: 1, leached glass coated with polymer with 25% cyano-substitution; 2, salted glass coated with the same material as 1; 3, salted glass coated with polymer with 100% cyano-substitution.

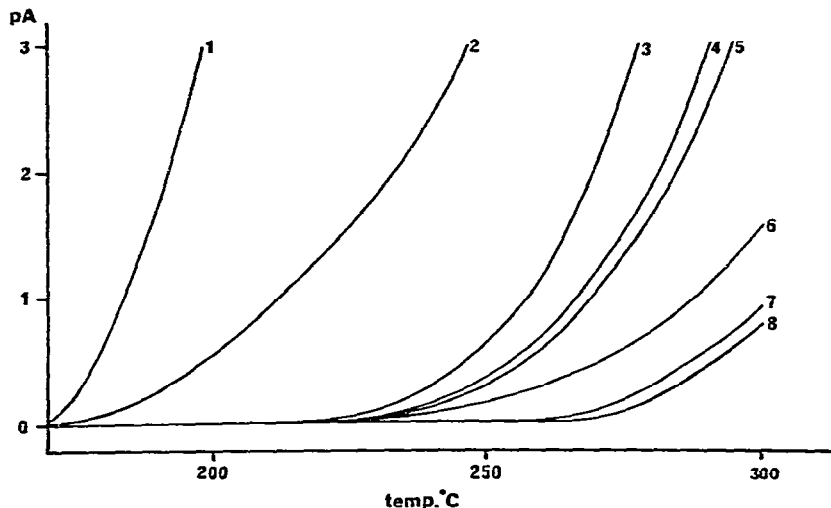


Fig. 4. Relative bleeding rates of 20-m Pyrex glass capillary columns during a temperature programme of 5°/min. Column types: 1 = AN-600 on salted glass; 2 = XE-60 on salted glass; 3 = Silar 10C on salted glass; 4 = 25% CN on leached/salted glass; 5 = 25% CN on salted glass; 6 = 25% CN on leached glass; 7 = 100% CN on leached/salted glass; 8 = 100% CN on salted glass.

to the same silicon atom²³. Further, leached glass gives lower bleed than salted, a probable explanation of this being that substances which could catalyse decomposition of silanes have been removed from the glass surface by the leaching.

The polarities of our cyanosilicone columns are reflected by Kováts retention

indices of octanol and naphthalene (Table I). We find our columns to be slightly more polar than corresponding commercial ones.

Conditioning for 48 h at 250°C results in slightly lower column polarity and k values; further, deactivation is improved on conditioning. Some columns were extracted with solvent, as we have described for methylsilicones^{3,4}. For columns that were conditioned, however, extraction gave no additional improvement of chromatographic properties. The extraction led to a decrease of *ca.* 35% in k values of tetracosane; the main part of the stationary phase was thus found to be insoluble.

Cross-linked silicone polymers have been used as stationary phases in GC for capillary²⁶ as well as for packed columns²⁷⁻²⁹. It could, however, be questioned whether such phases will possess desired chromatographic properties³⁰. Hawkes and co-workers^{31,32} have shown that silicone gums such as SE-30 are less suitable than a silicone fluid for solutes consisting of long hydrocarbon chains. This would be due to hindered diffusivity of such solutes in SE-30. Low efficiency for straight hydrocarbons was also observed for our columns (Fig. 5). Column polarity and stationary-phase rigidity probably contribute to this hydrocarbon band-broadening, which we experienced for the *n*-alkanes tested, C₁₈ to C₃₄. For galactonitrile and anthanthrene, however, the columns seem to have suitable chromatographic properties.

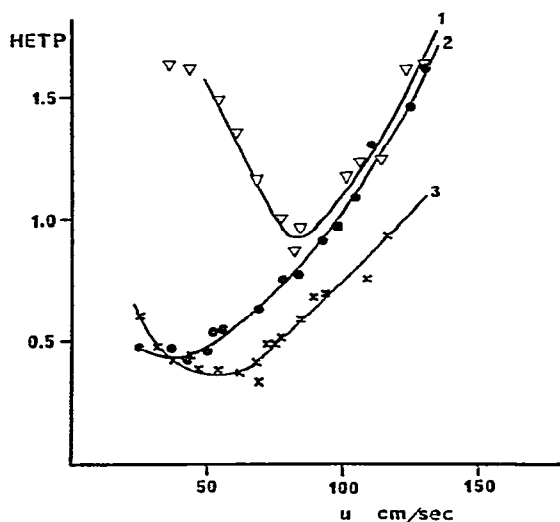


Fig. 5. Van Deemter curves for a 20-m salted Pyrex glass capillary column coated with a bonded rubber with 100% CN. 1 = Octadecane at 100°C; 2 = galactonitrile at 210°C; 3 = anthanthrene at 290°C.

The separation power of our cyanosilicone columns is demonstrated in Figs. 6-8. In Fig. 6, the separation of aldnonitrile acetates prepared from reducing sugars is shown in the nanogram and picogram range. Alditol acetates could also be separated; these gave of course much less response on the ECD than aldnonitriles (Fig. 6D). The advantage of these types of sugar derivative from an analytical point of view is that each sugar forms only one derivative³³. The different elution patterns of a standard mixture of aza-PNA on a cyanopropyl and methylsilicone rubber

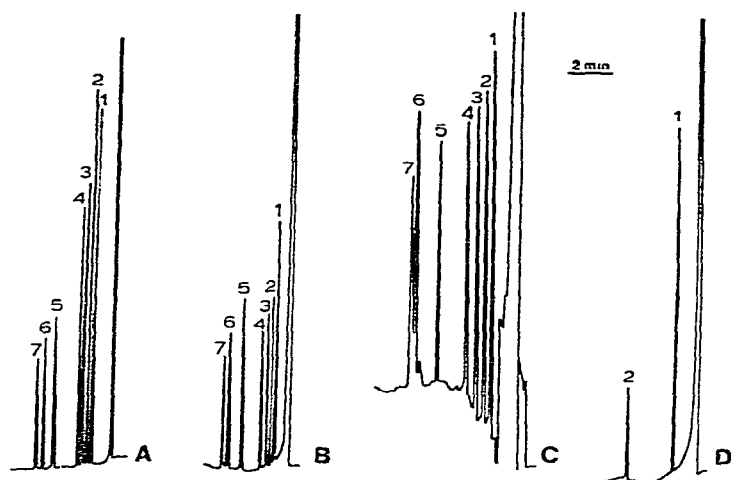


Fig. 6. Gas chromatograms of sugar derivatives on leached Pyrex glass capillary columns coated with bonded silicone rubber with 25% cyano-substitution. A, 33-m column; B-D, 18-m column. A: temperature 226°C; carrier gas (hydrogen) flow-rate, 60 cm/sec; flame ionization detector, split 1:30. Peaks: aldonitriles prepared from (1) rhamnose, (2) fucose, (3) arabinose, (4) xylose, (5) mannose, (6) glucose, (7) galactose. Sample amount *ca.* 3 ng per compound. B: temperature 200°C; electron capture detector; carrier gas, split and peaks as in A. Sample amount *ca.* 30 pg of compounds 1-4, *ca.* 60 pg of compounds 5-7. C: same as B but with splitless injection, 160°C for 1 min, then 10°/min to 180°C. Sample amount 10 and 20 pg, respectively. D: temperature, carrier gas, split and detector as in B. Peaks: 1 = L-arabinitolpentaacetate; 2 = D-glucitolhexaacetate. Sample amount *ca.* 3 ng per compound.

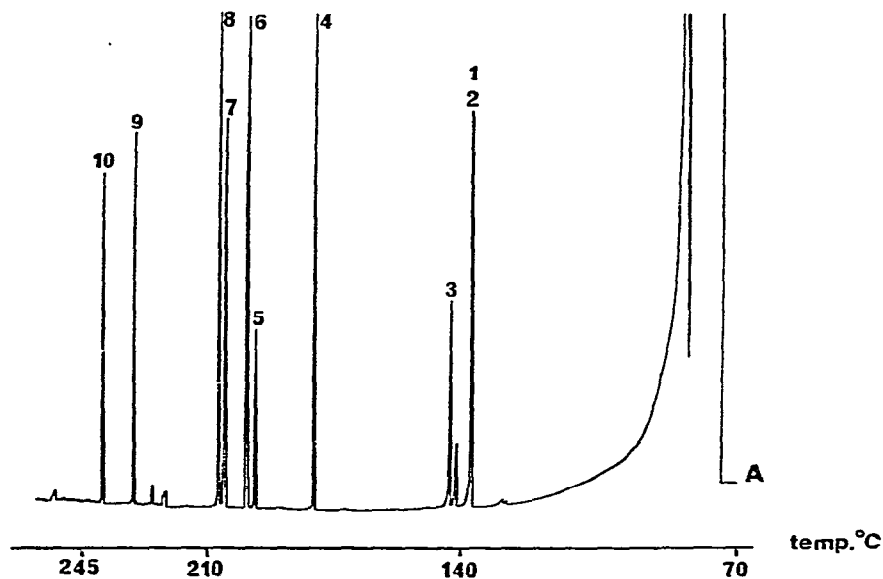


Fig. 7.

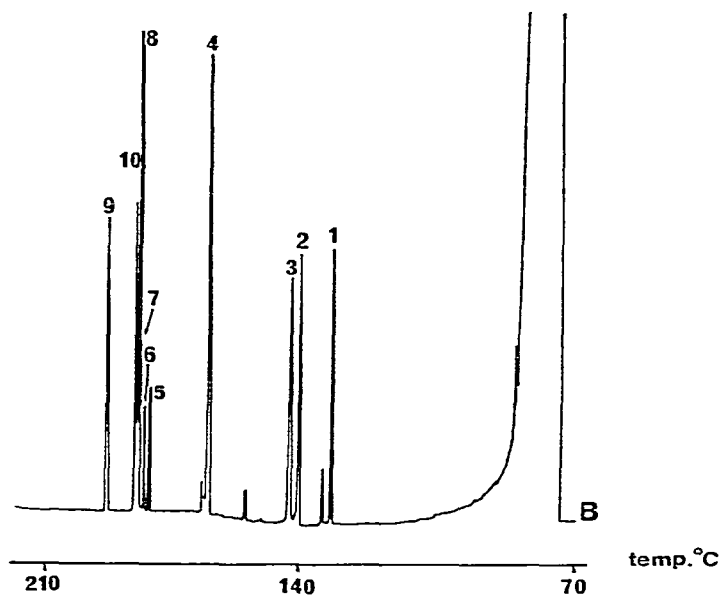


Fig. 7. Gas chromatograms (FID) of a standard mixture of aza-PNA. A, on a salted Pyrex glass capillary column coated with bonded silicone rubber with 100% cyano-substitution. B, on an equivalent column coated with bonded methylsilicone rubber. Initial temperature on injection, 70°C; after 1 min programmed to 275°C at 7°/min. Carrier gas flow-rate at 70°C, 70 cm/sec. Inlet splitter opened 1 min after injection. Peaks: 1 = 7-methylquinoline; 2 = 2,6-dimethylquinoline; 3 = 2,4-dimethylquinoline; 4 = 4-azafluorene; 5 = benzo[*h*]quinoline; 6 = acridine; 7 = benzo[*c*]quinoline; 8 = benzo[*f*]quinoline; 9 = benzo[*c*]cinnoline; 10 = carbazole.

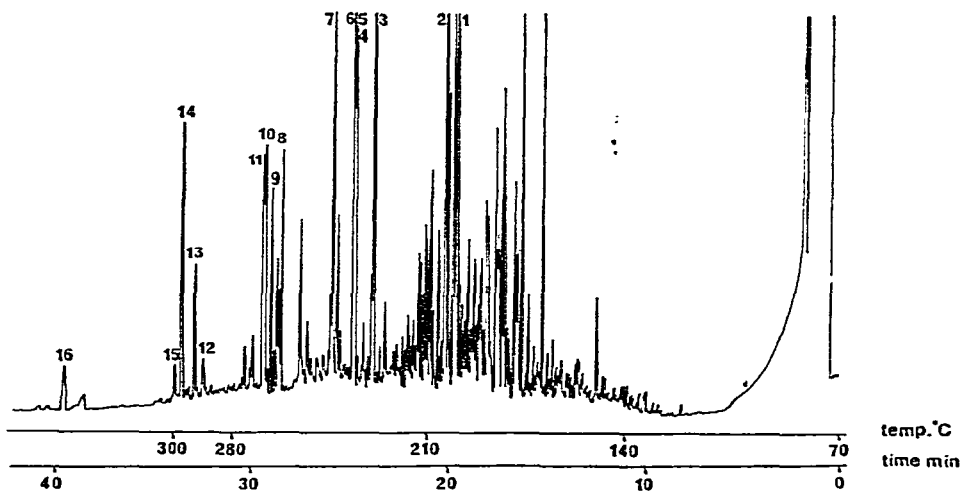


Fig. 8. Gas chromatogram (FID) of PNA from particulate matter in Stockholm city air. Column and conditions as in Fig. 7A, programming extended to 300°C. Peaks: 1 = fluoranthene; 2 = pyrene; 3 = benzo[*ghi*]fluoranthene; 4 = cyclopenteno[*cd*]pyrene; 5 = benz[*a*]anthracene; 6 = chrysene; 7 = β,β' -binaphthyl (I.S.); 8 = benzofluoranthene; 9 = *p*-quaterphenyl (I.S.); 10 = benzo[*e*]pyrene; 11 = benzo[*a*]pyrene; 12 = indeno[*cd*]fluoranthene; 13 = indeno[*cd*]pyrene; 14 = benzo[*ghi*]perylene; 15 = anthanthrene; 16 = coronene.

columns, respectively, is demonstrated in Fig. 7, and Fig. 8 shows the separation of PNAs obtained from particulate matter in Stockholm city air. Samples of this type are routinely analysed on non-polar glass capillary columns at our laboratory. Access to capillary columns of different polarity, stable up to 300°C, increases the precision of such analyses. We consider that this new type of selective glass capillary column will be a versatile tool for the separation of typical close isomers occurring in high boiling samples.

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