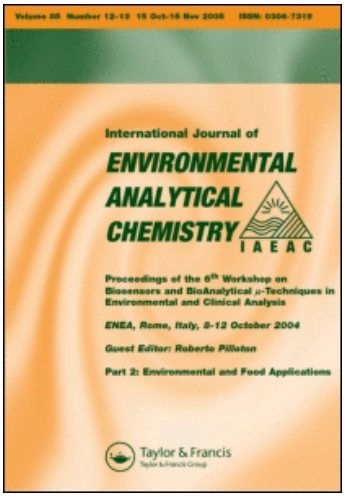

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Selective Gas Chromatographic Stationary Phases for Nitrogen-Containing Polycyclic Aromatic Compounds

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Several selective polysiloxane stationary phases were evaluated for the resolution of nitrogen-containing polycyclic aromatic compounds (N-PAC) in coal tar fractions by capillary column gas chromatography. A new liquid crystalline polysiloxane exhibited the highest selectivity for isomeric alkylated 3- and 4-ring N-PAC, whereas a polarizable biphenyl polysiloxane and a moderately polar crown ether-substituted polysiloxane were more applicable for the analysis of 2- and 3-ring N-PAC. The thermal stabilities of these phases made them suitable for GC-MS applications.

KEY WORDS: Capillary gas chromatography, stationary phases, nitrogen heterocycles, polycyclic aromatic compounds, coal tar, polysiloxanes.

INTRODUCTION

Nitrogen-containing polycyclic aromatic compounds (N-PAC) are ubiquitous in the environment and may originate from a variety of sources.[1,2] The widespread interest in the analysis of N-PAC stems from the demonstrated genotoxicities of many of these compounds

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which are dependent on their nitrogen functionalities and molecular structures.[3,4] Therefore, chemical class characterization, and isomer identification as well, are required in order to properly assess the risks associated with exposure to these materials in the environment. Since secondary and tertiary N-PAC (2° and 3° N-PAC) are among the most abundant chemical classes of N-PAC in the environment, much attention has been devoted to their characterization.[5-7] However, the characterization of these compounds is incomplete because of the large number of possible isomers.[8]

High resolution chromatographic techniques are needed for identification of these N-PAC. Capillary column gas chromatography (GC) provides the highest separation efficiencies compared to other chromatographic techniques. The coupling of selective detectors such as the thermionic ionization detector (TID or NPD), chemiluminescence detector (CD), and mass spectrometer (MS) with capillary GC gives the most selective analytical technique for the characterization of complex N-PAC mixtures.

Polysiloxane polymers provide the best performance as stationary phases in GC.[9] The nonpolar methylpolysiloxanes have sufficient efficiencies to solve most analytical separations, however, many N-PAC isomers cannot be resolved on the methylsilicones. A wide range of commercial stationary phases of different polarities have been used to improve the resolution of components of N-PAC mixtures. The separations of low-molecular-weight coal tar azaarenes (1 to 3 rings)[10] and some environmental N-PAC[11] were improved using polar phases. However, alkylated azaarenes from oil samples required at least 3 phases of differing polarities to effect complete separation.[12] High-molecular-weight (6- to 7-ring azaarenes), on the other hand, were analyzed with a nonpolar phase because of the improved thermal stability and lower elution temperatures obtained on the non-polar phase in comparison to separations on commercially available polar phases.[13]

Recently, new polar-substituted stationary phases were reported in which different organic materials were substituted on the polysiloxane backbone. These polar side groups gave specific selectivities to the polymers. Also, these new polysiloxanes contained small amounts of crosslinkable substituents (i.e. vinyl, octyl, or tolyl) which enabled them to be crosslinked, thereby improving their thermal stabilities. Polarizable biphenyl[14] and mesomorphic liquid

crystalline[15] polysiloxane phases have shown improved selectivities for the resolution of PAC isomers. Applications of these tailor-made stationary phases for the analysis of 2° and 3° N-PAC, which were isolated from a crude coal tar, are discussed in this paper. In addition, a new crown ether-substituted polysiloxane stationary phase is also reported for the first time, and its selectivity is compared with the other two phases and with SE-54.

EXPERIMENTAL SECTION

Fractionation of coal tar

Coal tar (1.3 g) (medium crude coke oven), which was obtained from the National Bureau of Standards (Washington, D.C.), was separated into chemical classes by column adsorption chromatography using neutral alumina (Fisher A-950, Fair Lawn, NJ) according to the procedure described elsewhere,[16] yielding three fractions: (a) aliphatic hydrocarbons (*n*-hexane, 20 mL), (b) neutral polycyclic aromatic hydrocarbons (PAH/PASH) (benzene, 50 mL), and (c) nitrogen containing compounds (N-PAC) (chloroform, 70 mL). The N-PAC were further fractionated into three subfractions by column chromatography using silicic acid (Baker Chemical Co., Phillipsburg, NJ): (a) secondary nitrogen heterocycles (2°N-PAC) (*n*-hexane/benzene, 1:1, 50 mL), (b) enriched amino polycyclic aromatic hydrocarbons (APAH) (benzene, 30 mL), and (c) tertiary nitrogen heterocycles (3°N-PAC) (benzene/diethylether, 1:1, 50 mL).

Preparation of 18-crown-6-substituted methylpolysiloxane phases

A 50% hydro methylpolysiloxane was prepared by stirring a mixture of 2.63 g of tetramethylcyclotetrasiloxane (D'4), 0.029 g of hexamethyldisiloxane, and 5 mg of trifluoromethane sulfonic acid for 50 h at room temperature. The mixture was neutralized with 30 mg of hexamethyldisilazane while being stirred for 5 min. The resulting polymer (MW about 25,000) was dissolved in 10 mL of CH_2Cl_2, the polymer was precipitated by adding 30 mL of methanol, the mixture was centrifuged, and the solvents were decanted. The polymer was again dissolved in CH_2Cl_2 and precipitated by methanol for a total

of four more times. The polymer was then dried for 10 h under reduced pressure.

The crown ether-substituted polymer was prepared using a hydrosilylation technique.[17] A mixture of 0.125 g of the above prepared polyhydromethylsiloxane, 1.0 g of allyloxymethyl-18-crown-6[18] and 1.1 g of pure benzene were stirred rapidly at 85°C for 45 min under argon. Speier's catalyst ($H_2PtCl_6 \cdot H_2O$ in a mixture of 98% tetrahydrofuran and 2% ethanol) (10 μL to give about 0.4% Pt) was added, and the mixture was stirred at 85°C for an additional 5 h under argon. An IR analysis showed that only 1–2% of the Si-H remained. 1-Octene (1 g) was added and the mixture was refluxed for an additional 30 min to completely substitute the residual Si-H with *n*-octyl groups. The mixture was cooled and 5 mL of CH_2Cl_2 were added. The organic solution was washed 5 times with 30-mL portions of water to remove the catalyst. The solvents were removed and the gummy polymer was dried under reduced pressure. The 25% 18-crown-6-substituted phase was prepared the same way except a 25% hydro methylpolysiloxane was used instead of the 50% hydro polymer.

Molecular weight distributions of the stationary phases were determined by gel permeation chromatography (GPC) using a Hewlett-Packard 1082B liquid chromatograph (UV absorbance detection at 254 nm) and methylene chloride as the mobile phase at a flow rate of 1 mL min^{-1}. Two chromatographic columns packed with a styrene-divinylbenzene copolymer were connected in series for the analysis. The phases that contained either starting materials or very low-molecular-weight oligomers were further purified by preparative GPC using 10^5–10^6 Ultrastyragel (Waters, Milford, MA) to remove the low-molecular-weight materials.

Column preparation

Fused-silica capillary tubing (200 μm i.d.) (Polymicro Technologies Inc., Phoenix, AZ) was purged with nitrogen gas at 250°C for 2 h. Columns of 10–15 m in length were coated statically at room temperature using 0.3% (w/v) stationary phase solutions in methylene chloride, which were previously filtered through a 0.2-μm Millipore filter, to give film thicknesses of 0.15 μm. The stationary phases used were SE-54 (Applied Science, State College, PA), a 25%

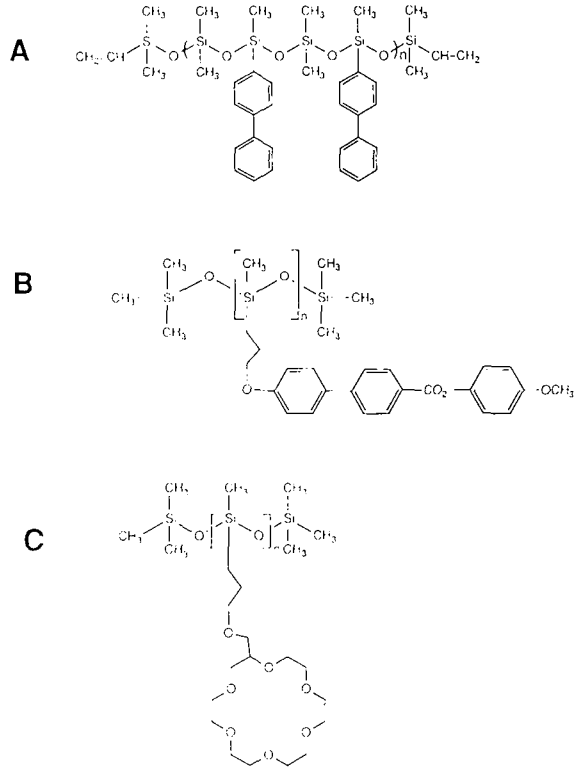


FIGURE 1 Structures of stationary phases: (A) 25% biphenyl, 2% vinyl methylpolysiloxane, (B) 50% biphenylcarboxylate ester liquid-crystalline methylpolysiloxane, and (C) 48% 18-crown-6, 2% octyl methylpolysiloxane.

biphenyl polysiloxane,[14] a 50% biphenylcarboxylate liquid crystalline polysiloxane,[15] and the newly prepared 48% crown ether 2% *n*-octyl polysiloxane reported above. The structures of these phases are shown in Figure 1.

The coated capillary columns were conditioned before crosslinking by heating from 40°C to 240°C at 1°C min^{-1}. The columns to be crosslinked were purged with azo-*t*-butane vapors in argon gas at room temperature for 2 h at a flow rate of 3 mL min^{-1}.[19] Both ends of the columns were sealed and the columns were heated from 40°C to 220°C at 4°C min^{-1} and held at 220°C for 40 min. The columns were then rinsed with 2 mL of methylene chloride using a low flow

rate. The columns were then conditioned at 280°C for 10 h. The liquid crystalline stationary phase was used as a gum without crosslinking.

Gas chromatography

Column evaluations were performed with a Carlo Erba 5160 Mega Series GC at 150°C using hydrogen as carrier gas at 50 cm s^{-1} linear velocity. *n*-Alkanes from *n*-C_{18} to *n*-C_{21} and polycyclic aromatic hydrocarbons (phenanthrene and anthracene) in hexane solutions (1 mg mL^{-1}) were injected using the split mode. Injector and detector temperatures were held at 250°C and 300°C, respectively.

Coal tar fractions were analyzed using a Hewlett Packard 5880 GC equipped with an NPD. Helium was used as carrier gas at 50 cm s^{-1} linear velocity. Splitless injection was performed at 40°C and the temperature was programmed first to 100°C at 15°C min^{-1} and then to 280° at 4°C min^{-1}. Injector and detector temperatures were set at 280°C and 320°C, respectively. Nitrogen at 20 mL min^{-1} was used as auxiliary gas for the NPD. Coinjections with authentic standards were performed in order to achieve positive identification of isomers.

Gas chromatography–mass spectrometry

Analyses were performed using a Hewlett–Packard COM-GC-MS (9133-5890-5970 series) with electron impact ionization at 70 eV. Injection was performed using the splitless mode at 280°C with helium as a carrier gas at 30 cm s^{-1}. The ion source and analyzer temperatures were held at 250°C and 280°C, respectively. The scan speed was set at 300 amu per s^{-1}.

RESULTS AND DISCUSSION

Table I summarizes the chromatographic characteristics of the columns which were used in this study. Efficiencies were greater than 4000 plates per meter for all of the columns coated. The nature of the substituents on the polysiloxane has a moderate effect on column

TABLE I

Capillary column characteristics

Stationary phase	% Substitution[a]	Retention indices[b]		Efficiency[c] (plates/M)
		Biphenyl	Indole	
SE-54	5	1363.4	1299.00	4660
Biphenyl	25	1546.7	1514.00	4607
18-Crown-6	25	1610.4	1961.22	4563
18-Crown-6	50	1802.17	2129.16	4630
liquid crystal[d]	50	–	—	4360

[a]Percent substitutions are given on the basis that each silicon in the polysiloxane backbone can have two substituent groups. SE-54 has 5% phenyl substitution. The unlisted percentage substitutions for all polymers are due primarily to methyl groups.

[b]Measurements were performed at 100 C except for those of the crown ether phases which were performed at 120 C.

[c]Efficiencies were measured at 150 C using n-C_{19} for the isotropic phases and anthracene for the liquid crystal phase.

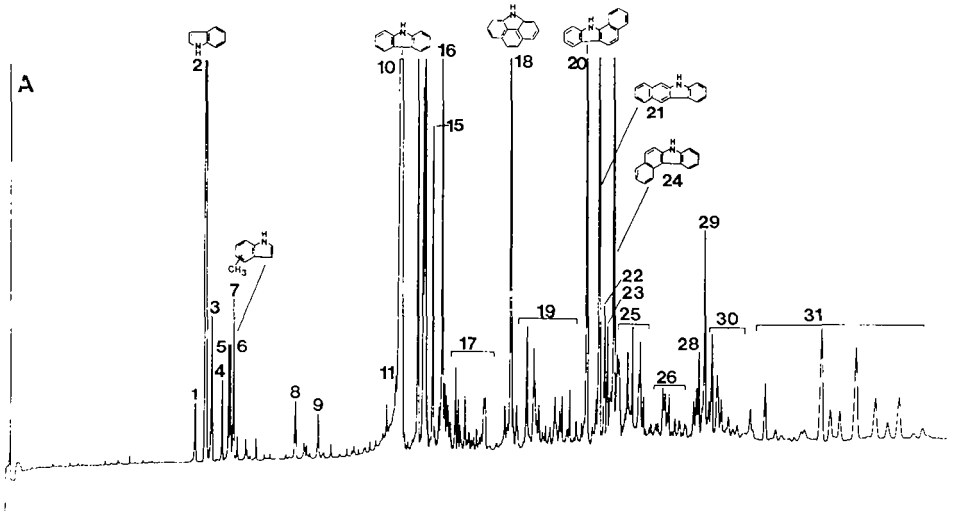
[d]Transition temperatures: g 104 C s 308 C i (g = glassy, s = smectic, and i = isotropic).

efficiency. Columns coated with the liquid crystalline polysiloxane exhibited a lower efficiency than average, because the efficiency measurements were performed in the smectic range, where the ordered structure gives higher resistance to mass transfer. The slightly lower efficiency value for this phase in comparison to the other phases is not important in the resolution of isomeric species where selectivity is the most important contributor to resolution. For instance, the relative retention (α) of the phenanthrene/anthracene pair was 1.6 using the liquid crystalline phase, whereas values on the other phases were lower than 1.1. Moreover, the best selectivity for PAH has been observed in the smectic range.[20,21] Therefore, the use of liquid crystalline polymers for the resolution of wide-molecular-weight range N-PAC mixtures demands phases with wide smectic temperature ranges in addition to good thermal stabilities. The wide smectic range of this liquid crystalline phase (Table I), which is wider than those of the liquid crystalline phases used previously,[22] permits one to perform the whole N-PAC analysis in the smectic range.

Stationary phase polarities were compared by measuring the retention indices of the polarizable biphenyl[14] and polar indole solutes. The 48% crown ether-substituted polysiloxane exhibited the

highest retention indices in comparison with the other stationary phases tested. Obviously, the 48% crown ether phase is more polar than the polarizable biphenyl phase. The biphenyl phase in turn yielded higher R.I. values than SE-54 because of the greater dispersion interactions with the aromatic solute molecules. The higher indole R.I. for the crown ether phase shows the importance of hydrogen bonding as a contribution to selectivity for this phase. Therefore, we can conclude that the hydrogen bonding (dipole–dipole) interactions of the crown ether phase are stronger than the dipole-induced dipole interactions of the biphenyl phase. Gas chromatographic retention on liquid crystalline phases depends on the solute molecular geometry in addition to other solute properties such as vapor pressure and polarity.[23]

Applications of the crown ether, liquid crystal, and biphenyl phases to the analysis of a coal tar 2°N-PAC mixture are shown in Figure 2. The column coated with the crown ether stationary phase shows better chromatographic performance over the whole temperature range, whereas the biphenyl stationary phase provides better resolution for the 3-ring compounds. Coelution of parent and alkylated N-PAC and poor resolution of alkylated N-PAC isomers has been reported for polar phases[12] because the alkylated N-PAC shift toward lower retention. However, the phenyl-substituted



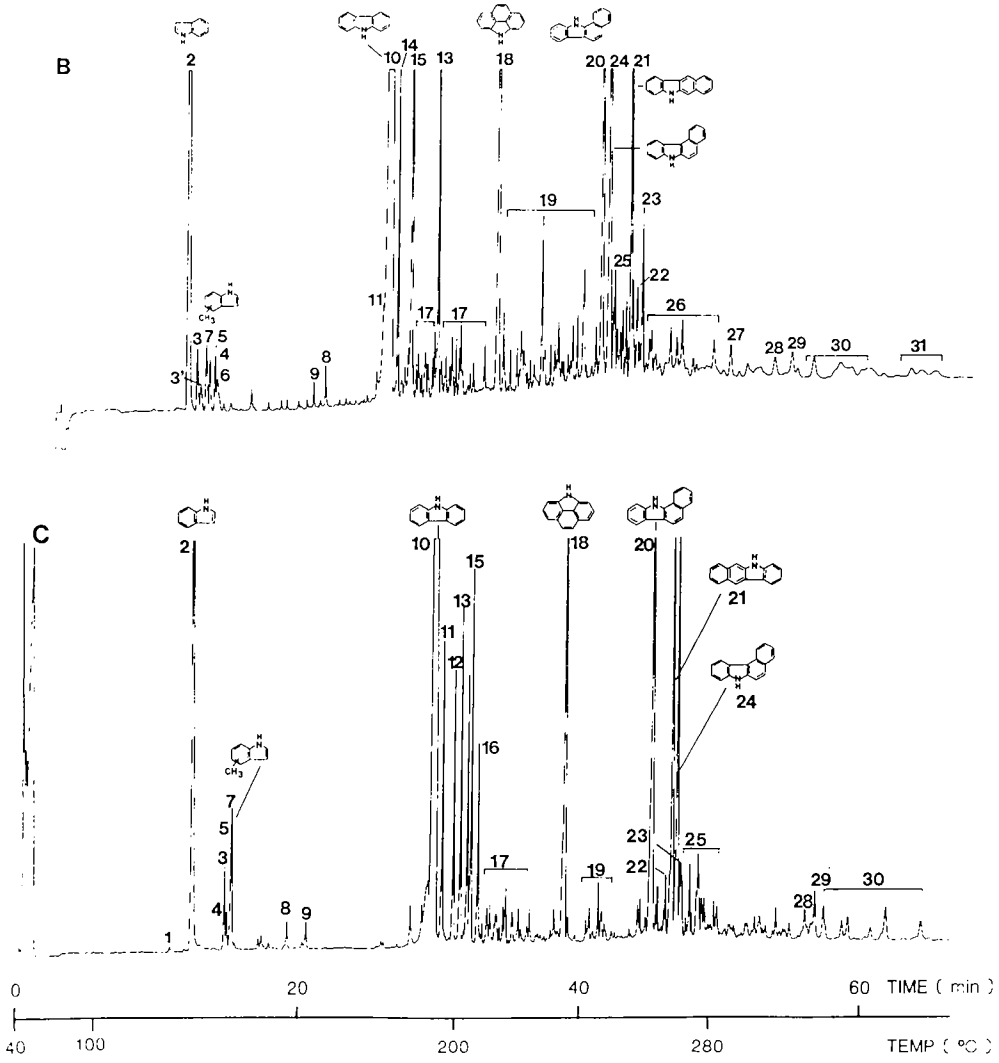


FIGURE 2 Capillary gas chromatograms (NPD) of 2°N-PAC coal tar fraction. (A) 10 m × 0.2 mm i.d. fused silica capillary column coated with 48% 18 crown-6, 2% octyl methylpolysiloxane (0.15 μm film thkckness), (B) 10 m × 0.2 mm i.d. fused silica column coated with 50% biphenylcarboxylate ester methylpolysiloxane, and (C) 15 m × 0.2 mm i.d. fused silica capillary column coated with 25% biphenyl, 2% vinyl methylpolysiloxane. Compound identifications are listed in Table II.

TABLE II

Compounds identified in the 2°N-PAC coal tar fraction

Peak	MW	Compound
1	119	2,3-dihydroindole
2	117	indole
3	131	1-methylindole
4	131	7-methylindole
5	131	3-methylindole
6	131	2-methylindole
7	131	5-methylindole
8	145	dimethylindole isomer
9	145	dimethylindole isomer
10	167	carbazole
11	181	9-methylcarbazole
12	167	benzindole isomer
13	181	2-methylcarbazole
14	181	3-methylcarbazole
15	181	4-methylcarbazole
16	167	benzindole isomer
17	195	dimethylcarbazole isomers
18	191	4*H*-benzo[def]carbazole
19	205	methyl-4*H*-benzo[def]carbazole isomers
20	217	11*H*-benzo[a]carbazole
21	217	5*H*-benzo[b]carbazole
22	231	methylbenzocarbazole isomer
23	231	methylbenzocarbazole isomer
24	217	7*H*-benzo[c]carbazole
25	231	methylbenzocarbazole isomers
26	245	dimethylbenzocarbazole isomers
27	241	11*H*-dibenzo[a,def]carbazole
28	241	4*H*-dibenzo[b,def]carbazole
29	241	naphtho[1,2,3,4-def]carbazole
30	265	phenanthrocarbazole isomers
31	267	dibenzocarbazole isomers

methylpolysiloxane stationary phases exhibited greater retention of alkylated N-PAC and poor selectivity for the alkylated and parent isomers.[14] The column coated with the crown ether stationary phase provided good resolution of the 2- and 3-ring monoalkylated 2°N-PAC. This selectivity depends on the availability of hydrogen bonding between the pyrrolic hydrogen and macrocyclic ether ring oxygen atoms. For instance, 1-methylindole (peak 3, Figure 2), which

cannot have hydrogen bonding (no N-H group), elutes close to indole, while the 7-, 3-, and 2-methyl isomers (peaks 4, 5, and 6; Figure 2A) in which the methyl group sterically hinders interaction with the N-H, elute later than 1-methylindole, but faster than isomers in which the methyl is away from the N-H (peak 7). However, the same mechanism leads to the coelution of 9-methylcarbazole and carbazole on this phase. These two isomers are resolved only on the column coated with the biphenyl phase.

The liquid crystal phase also exhibited remarkable selectivity for the methylindole isomers, resolving one more isomer than achieved using the crown ether phase (peak between 3 and 7, Figure 2B). However, the different elution orders of the methylindole isomers on the phases showed completely different selectivities. Solute molecular shape was one of the main contributors to the selectivity in the resolution of these monoalkylated isomers on the liquid crystal phase, whereas hydrogen bonding was important on the crown ether phase.

The benzocarbazole isomers (peaks 20, 21, and 24; Figure 2) were resolved using all of these columns. 5*H*-Benzo[b]carbazole (peak 21) and 7*H*-benzo[c]carbazole (peak 24), as well as several methyl-11*H*-benzo[a]carbazole isomers (peaks 22 and 23) were better resolved on the crown ether phase. This improved resolution is a result of the hydrogen bonding contribution with the crown ether phase, which is greater for the isomers in which the nitrogen atom is less hindered (compounds 21 and 24, Figure 2).

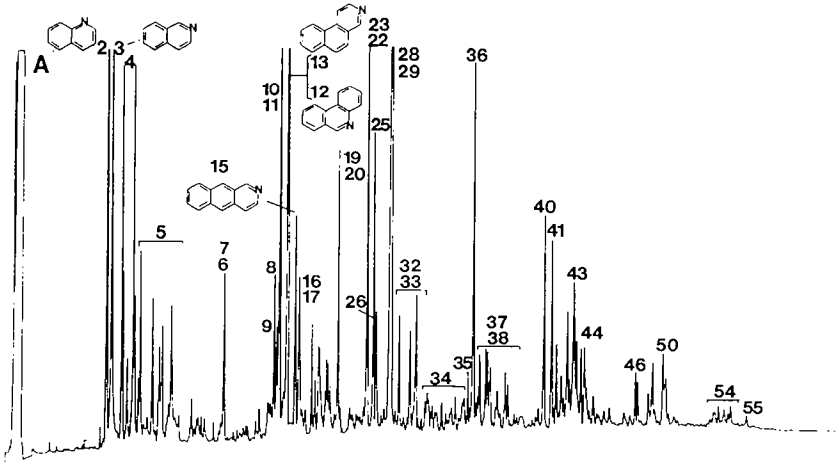
A different selectivity for the resolution of the benzocarbazole isomers was observed using the liquid crystalline phase because the linear fused benzocarbazole (peak 21, Figure 2B) was more retained than the angular fused isomers. With the isotropic phases, the solute vapor pressure was the most important factor affecting solute retention. The most remarkable selectivity demonstrated by the liquid crystalline phase was in the resolution of monoalkylated benzocarbazole isomers (peaks 22, 23, and 25; Figure 2B) where 17 of the 33 possible isomers were found in the reconstructed selected-ion MS chromatogram.

The dibenzocarbazole isomers (31, Figure 2) were not eluted on either the biphenyl or liquid crystal stationary phases, but could be analyzed on the crown ether phase. This can be explained if we consider that hydrogen bonding interactions between the pyrrolic

hydrogens and crown ether oxygens become less intense in the bulkier 2°N-PAC. Simultaneously, the hydrocarbon character of the 2°N-PAC increases with molecular weight; hence, dispersion interactions between the solute and stationary phase are weaker. The lack of dibenzocarbazole reference compounds and the large number of possible isomers make their positive identification impossible; but, the resolution achieved is worthy of mention.

Applications of SE-54, crown ether, and biphenyl capillary columns in the resolution of 3°N-PAC (azaarenes) are shown in Figure 3. In this application, the crown ether stationary phase exhibits mainly dipole-dipole solute-stationary phase interactions. The liquid crystalline phase exhibited poor resolution of the isomeric azaarenes because many of the isomeric azaarenes have the same shape and differ only in the position of the nitrogen heteroatom.

The crown ether stationary phase resolved the dihydro-, and the methylquinoline/isoquinoline isomers (peaks 1 and 4, Figure 3). This selectivity was also comparable to the biphenyl phase for the resolution of the benzoquinoline and benzoisoquinoline isomers, and the azafluoranthene and azapyrene isomers; both phases gave improved resolution for these isomers in comparison to separations on SE-54. However, several isomers were still not resolved [i.e., benz[h]- and benz[i]isoquinoline (Peak 16, Figure 3) and 2- and 4-azapyrene (peak 32)]. These isomers probably could be resolved on a more



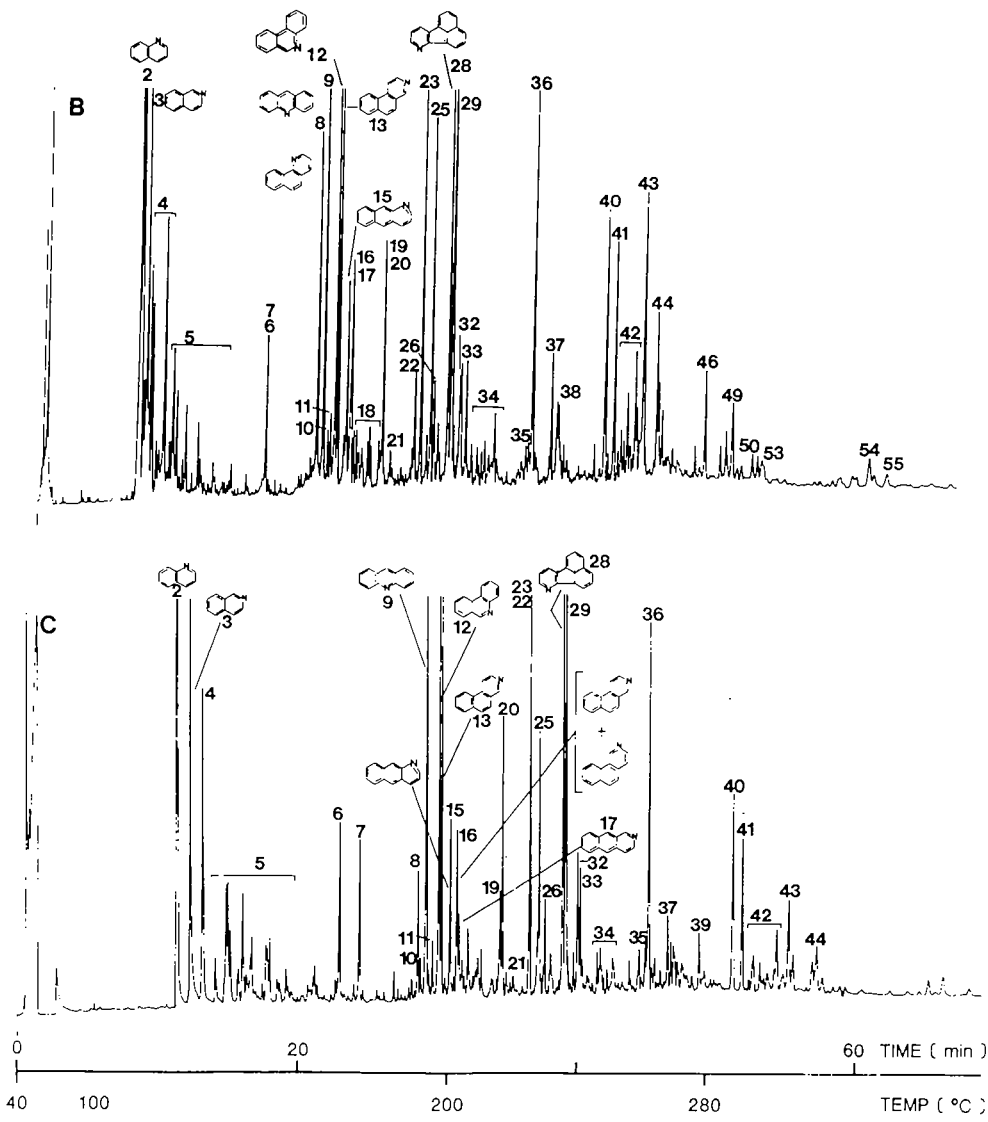


FIGURE 3 Capillary gas chromatograms (NPD) of 3 N-PAC coal tar fraction. (A) 12 m × 0.2 mm i.d. fused silica capillary column coated with 5% phenyl, 1% vinyl methylpolysiloxane (SE-54) (0.15 μm film thickness), (B) 10 m × 0.2 mm i.d. fused silica capillary column coated with 48% 18-crown-6, 2% octyl methylpolysiloxane, and (C) 15 m × 0.2 mm i.d. fused silica capillary coated with 25% biphenyl, 2% vinyl methylpolysiloxane (0.15 μm film thickness). Compound identifications are listed in Table III.

TABLE III

Compounds identified in the 3rd N-PAC coal tar fraction

Peak no.	MW	Compound
1	131	dihydroquinoline isomers
2	129	quinoline
3	129	isoquinoline
4	143	methylquinoline/methylisoquinoline isomers
5	157	dimethylquinoline/dimethylisoquinoline
6	152	unknown
7	152	unknown
8	179	benzo[h]quinoline
9	179	acridine
10	193	methylbenzoquinoline isomer
11	193	methylbenzoquinoline isomer
12	179	phenanthridine
13	179	benzo[f]quinoline
14	181	dihydrobenzoquinoline isomer
15	179	benzo[g]quinoline
16	179	benzo[h]isoquinoline benzo[f]isoquinoline
17	179	benzo[g]isoquinoline
18	193	methylquinoline/methylisoquinoline isomers
19	180	unknown
20	204	unknown
21	207	dimethylquinoline/dimethylisoquinoline isomers
22	203	1-azafluoranthene
23	203	2-azafluoranthene
24	203	azafluoranthene isomer
25	203	7-azafluoranthene
26	203	azafluoranthene isomer
27	203	azafluoranthene isomer
28	203	acenaphtho[1,2-b]pyridine
29	203	azapyrene isomers
30	217	methylazafluoranthene/methylazapyrene isomer
31	217	methylazafluoranthene isomer
32	203	2- and 4-azapyrene
33	217	methylazafluoranthene/methylazapyrene isomer
34	217	methylazafluoranthene/methylazapyrene isomers
35	226	unknown
36	229	benzacridine isomer
37	229	benzacridine isomer
38	243	methylbenzacridine isomers
39	231	dimethylazafluoranthene/dimethylazapyrene
40	253	phenanthroquinoline isomers

TABLE III (continued)

Peak no.	MW	Compound
41	253	phenanthroquinoline isomer
42	267	methylphenanthroquinoline isomers
43	253	phenanthroquinoline isomers
44	253	phenanthroquinoline isomers
45	267	methylphenanthroquinoline isomers
46	277, 279	phenalenophenanthridine and phenanthroquinoline isomers
47	279	anthroquinoline isomer
48	279	naphthophenanthridine isomer
49	279	anthraisoquinoline isomers
50	280	unknown
51	277	phenanthrophenanthridine isomer
52	277	phenanthrophenanthridine isomer
53	303	azabenzoperylene isomer
54	293	unknown
55	303	azabenzoperylene isomers

efficient column. However, the 5- and 6-ring azaarene isomers (peaks 40 to 54) were not effectively separated on any of these columns. The best separations for the latter series of compounds were obtained using SE-54 and the crown ether phase. The reduced selectivity for the resolution of isomeric N-PAC at higher temperatures on the crown ether phase can be explained by the fact that dipole-dipole interactions decrease with increasing temperature and approach zero where all orientations are equally probable.[24]

The advantage of the crown ether phase in GC applications in comparison to other polyglycol-containing stationary phases (e.g., Carbowax) is its higher thermal stability which enables the analysis of 6-ring N-PAC on such phases for the first time. High-molecular-weight N-PAC have only been analyzed using nonpolar stationary phases which possess little selectivity for these compounds. The new phases reported here provided unique selectivity for both low- and high-molecular-weight N-PAC mixtures, and they should be the phases of choice for such analyses.

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