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THE CLASS SEPARATION OF NITROGEN COMPOUNDS IN COAL TARS BY LIQUID CHROMATOGRAPHY ON A POLAR BONDED-PHASE SILICA

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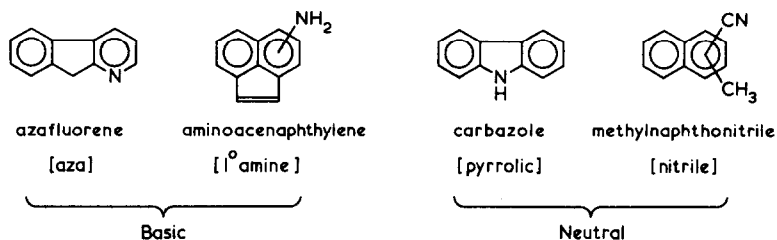
SUMMARY

The use of OPN/Porasil-C, a porous silica with polar *o*-phthalonitrile groups chemically bonded to the Porasil-C support medium, for the class separation of nitrogen compounds in coal tars is described. Sequential elution of an anthracene oil with solvents of increasing polarity yielded clearly-defined neutral and basic nitrogen fractions which were characterised by gas chromatography, mass spectrometry and elemental analyses. The neutral and basic nitrogen fractions contained predominantly pyrrolic compounds and aza heterocycles, respectively, but the presence of nitriles in the neutral fraction was confirmed by infrared spectroscopy. The class separation has made it possible to distinguish more easily between isomeric compound types, and has facilitated the identification of peaks in the complex chromatogram of the unfractionated anthracene oil recorded using nitrogen-selective alkali flame detection.

INTRODUCTION

Nitrogen is a universal component of fossil fuels, being associated almost exclusively with the organic portion of the crude materials, and although its level is usually less than 0.5% in crude petroleum, higher levels (1–2%) are found in shale oil and coal. Nitrogen compounds occur as minor components in the pyrolysis, extraction and combustion products, principally as heterocyclic pyrrolic and pyridinic (aza) species, although aromatic primary amines are now recognised as important components of some coal liquefaction materials[1–4]. With the possible exception of some coal tar products of commercial value, nitrogen compounds are generally regarded as undesirable because of the problems which they pose in refining. A number of the basic compounds are toxic, several of the aza heterocycles[5–7] and aromatic primary amines[1,8–10] being known, or suspected carcinogens. The neutral nitrogen compounds appear, in general, to be less toxic than the basic compounds, but several dibenzocarbazoles have been reported to show carcinogenic activity[7]. A detailed knowledge of the types and concentrations of nitrogen compounds present in coal-derived products is clearly desirable in order to optimise methods for their removal and specify methods for the safe handling of such materials.

In two earlier papers we have described the use of the nitrogen-selective alkali flame detector for the direct gas chromatographic (GC) determination of nitrogen compounds in unfractionated coal tar[11] and liquefaction products[12]. This sensitive and highly specific detector permitted the rapid quantification of the peaks in the complex nitrogen profiles, but it does not yield identifications directly, and unless the chromatographic pattern can be recognised, further analyses by gas chromatography–mass spectrometry (GC–MS) may be necessary. The massive hydrocarbon background caused problems in the GC–MS identification of nitrogen compounds in the unfractionated coal tars[11]; in particular the molecular ions of the aza heterocycles were subject to interference from the ^{13}C isotopes of the corresponding parent aromatic hydrocarbons, which had the same nominal mass and similar chromatographic retention times. The available MS resolution was insufficient to resolve the $^{13}CH-^{14}N$ doublet, which has a mass difference of only 8.1 mmu, and unless the peaks were adequately separated chromatographically, it was not possible to make an unequivocal statement that the nitrogen compound was present.

In some cases a number of isomeric compound types were possible for a given atomic composition; examples are shown below for $C_{12}H_9N$, m/z 167.

azafluorene   aminoacenaphthylene   carbazole   methylnaphthonitrile

[aza]   [1°amine]   [pyrrolic]   [nitrile]

Basic   Neutral

Some of the ambiguities were resolved by the use of boiling point characteristics[11], but it was evident that the preparation of hydrocarbon-free fractions would be necessary for the satisfactory GC–MS identification of nitrogen compounds in these complex materials, and that the most useful fractionation would be a class separation of the nitrogen compounds into basic (principally aza) and neutral (principally pyrrolic) species.

The isolation of basic nitrogen compounds is comparatively straightforward and techniques such as aqueous acid extraction[12–15], precipitation with gaseous hydrogen chloride[16,17] and cation-exchange chromatography[2,18] have all been used successfully for this purpose. These methods involve protonation of the basic nitrogen atom, and the compounds thus isolated are those which can act as proton acceptors, *i.e.* pyridinic (aza) compounds and primary and secondary amines.

The isolation of a neutral nitrogen fraction is much more difficult, since no specific chemical method is available, and consequently these compounds have not been characterised as fully as the basic compounds. The neutral compounds are non-basic because the lone pair of non-bonding electrons on the nitrogen atom is unavailable for protonation; in the case of pyrrolic compounds this is due to interaction of the electron pair with the π-electron system of the five-membered ring to give a stable pseudo-aromatic sextet. Consequently the pyrrolic compounds, together

with the homologous thiophenes and furans, behave similarly to polynuclear aromatic hydrocarbons.

Nevertheless, Drushel and Sommers[19] have achieved the separation of indoles and carbazoles from petroleum using a combination of adsorption chromatography and chemical extraction. Snook *et al.*[20,21] have also isolated indoles and carbazoles from cigarette smoke condensate by sequential elution from a silica column followed by gel-filtration chromatography on Bio Beads SX-12. More recently Ho *et al.*[22] have used a modification of this method to isolate neutral nitrogen compounds from shale and coal-derived oils. However, these separation schemes are complex and time-consuming, involving many experimental steps with the attendant risk of sample loss.

Bonded-phase silicas, particularly those with polar amino or nitrile functional groups, have been used successfully for the separation of hydrocarbons, nitrogen compounds and other heteroatomic species in fossil fuel samples by high-performance liquid chromatography[23-26]. The separations have generally been carried out on analytical or semi-preparative columns containing microparticulate packings. However, the sample capacity of such columns is low, and since the high cost and low permeability of 5–10 μm diameter microparticulates has restricted their use in larger, gravity-fed or low-pressure liquid chromatographic columns, true preparative scale separations using bonded-phase media have been much less frequent.

The method reported herein involves sequential elution from an *o*-phthalonitrile (OPN) stationary phase chemically bonded to a Porasil-C support medium, using a series of solvents of increasing polarity. This commercially-available 80–100 mesh material was developed initially for GC, but was found to be of a suitable particle size for open-column liquid chromatography. The technique yielded clearly-defined neutral and basic nitrogen fractions, which were characterised by GC, MS, elemental analyses and infrared (IR) spectroscopy. The application of this method to an anthracene oil, a typical high-temperature coal tar product, is described.

EXPERIMENTAL AND RESULTS

The anthracene oil was a standard commercial coal tar product; elemental analyses for the unfractionated material and the fractions are given in Table I. Basic nitrogen was determined by potentiometric titration with perchloric acid in a glacial acetic acid medium using a procedure similar to that described by Moore *et al.*[27]. IR spectra were recorded as thin films between sodium chloride plates on a Perkin-Elmer 457 spectrophotometer.

Liquid chromatography
Waters 80–100 mesh OPN/Porasil-C GC Durapak (22.7 g), supplied by Phase Separations, was dry-packed into a 45 cm × 15 mm I.D. glass Whatman "Multi-System" chromatographic column, giving a bed depth of 27.5 cm. The PTFE diffusion disc was omitted from the lower sealing piston to avoid possible blockages by insoluble material in the sample or migrating fines from the packing, which was retained by silica wool plugs. The re-usable column was pre-eluted with 100 ml of tetrahydrofuran (THF) then 100 ml of hexane, and the washings were discarded.

The anthracene oil (5.43 g) was applied neat to the column and eluted succes-

TABLE I

ELEMENTAL ANALYSES AND RECOVERY EFFICIENCIES FOR LC FRACTIONATION OF AN ANTHRACENE OIL ON OPN/PORASIL-C

	Weight per cent			
	Whole anthracene oil	Hexane eluate	Hexane– 15% benzene eluate	Ether eluate
C	90.5	91.7	87.1	82.8
H	5.6	6.1	5.6	5.5
N (Total)	0.61	< 0.1	4.8	5.2
N (Basic)	0.46	< 0.1	n.d.**	4.4
O	1.9	2.0	2.7	4.0
S	0.87	0.79	0.32	0.66
Yield (g)		4.327	0.126	0.501
Gross recovery (%)		79.7	2.3	9.2
Total nitrogen recovery (%)		< 13.1*	18.4	78.9
Basic nitrogen recovery (%)		< 17.3*	n.d.**	88.2

 * These values are derived from the figure of <0.1 wt.% quoted for total and basic N in the hexane eluate, 0.1 wt.% being the detection limit for both determinations.
 ** n.d. = not determined (insufficient material).

sively with the following solvents: hexane, 300 ml; hexane–15% benzene, 300 ml; diethyl ether, 200 ml; giving nominal hydrocarbon, neutral nitrogen and basic nitrogen fractions, respectively. The flow was not restricted and the flow-rate varied according to the solvent viscosity, but was typically *ca.* 5 ml/min. The solvent volumes used were those required for exhaustive elution of each fraction; the progress of the elutions was monitored by visual inspection of the UV-excited fluorescence, and the final eluate for each fraction was colourless. The eluates were reduced to a few millilitres under nitrogen on a water bath, then transferred to small phials and evaporated to constant weight at 40°C. Yields of the fractions are given in Table I.

Gas chromatography

The samples were analysed by GC using a Perkin-Elmer F-17 chromatograph fitted with a flame-ionisation detector and a nitrogen-selective alkali flame detector. The latter employed an electrically-heated rubidium glass bead as the source of alkali metal ions, its design following closely that of Kolb and Bischoff[28], and its combustion gas flow-rates and bead-heating current were adjusted for maximum response and selectivity towards nitrogen compounds according to the statistical method of Rubin and Bayne[29]; the optimised flow-rates were 3.0 ml/min for hydrogen and 19 ml/min for air, and a bead-heating current of 5.5 on the arbitrary control box scale was used. Under these conditions a selectivity factor of 700 for acridine:phenanthrene was achieved. Splitless injections (0.2 μl) were made onto a 40 m SGE glass support-coated open tubular (SCOT) capillary column coated with SP-2250 50% methyl, 50% phenyl silicone stationary phase using helium carrier gas with a linear velocity of 39 cm/sec. Other chromatographic conditions are given on the appropriate chromatograms.

The fractions were analysed by gas chromatography–flame ionisation detection (GC–FID) as *ca.* 2% w/v solutions in THF, and chromatograms of the hydrocarbon fraction (hexane eluate), neutral nitrogen fraction (hexane–15% benzene eluate) and basic nitrogen fraction (ether eluate) are shown in Figs. 1–3, respectively. Dibenzyl (430 ng/μl) was added as an internal standard for quantification, and a Hewlett-Packard 3353 chromatographic data system was used to measure peak areas and calculate the results. A response factor of unity relative to the internal standard has been assumed where reference compounds were unavailable; the same approach was adopted for multi-component peaks. Concentrations for the numbered peaks in Figs.
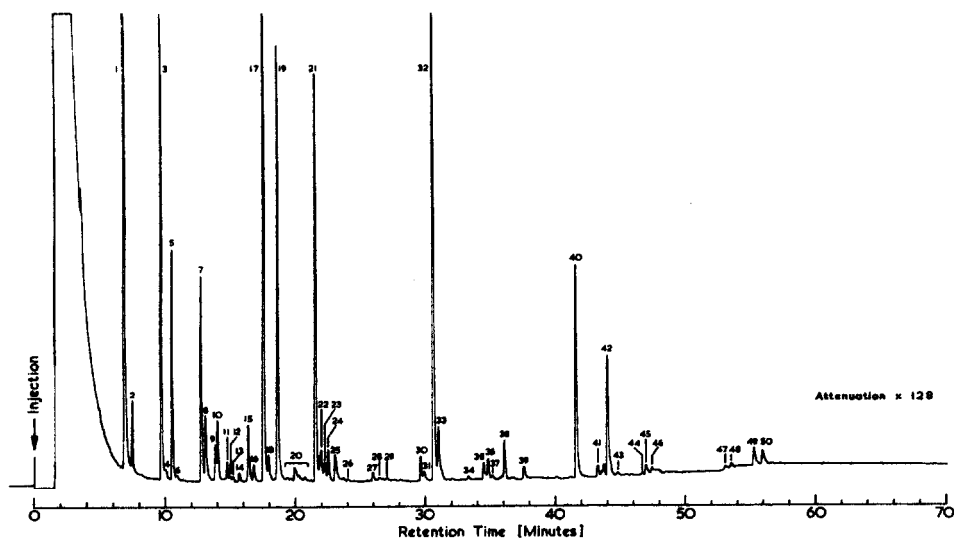

Fig. 1. GC–FID chromatogram of hydrocarbon fraction (hexane eluate) of anthracene oil. Identities of numbered peaks given in Table II. Conditions: 40 m SP-2250 glass SCOT capillary column programmed from 135 to 285°C at 3°C/min with 4-min initial hold.

1–3 are given in Tables II–IV, respectively, expressed as parts per million or weight per cent of the original, unfractionated anthracene oil.

The unfractionated anthracene oil was analysed by gas chromatography–alkali flame detection (GC–AFD) as an *ca.* 9% w/v solution in THF. The resulting chromatogram is shown in Fig. 4.

Mass spectrometry

Identification of specific compounds in the fractions was achieved using GC–MS. A Perkin-Elmer F-17 chromatograph was interfaced with a Kratos MS-30 double-beam mass spectrometer via a glass jet separator maintained at 250°C. The samples were analysed as *ca.* 3% w/v solutions in THF, and 0.5–1.0 μl splitless injections were applied to a 33 m SGE SP-2250 glass SCOT capillary column under chromatographic conditions closely matched to those used for the GC–FID and GC–AFD analyses. Using 70 eV electron-impact ionisation, up to 760 mass spectral scans were collected at 3 sec per decade of mass over the mass range 50–400, approximately, at a resolution of 3000.
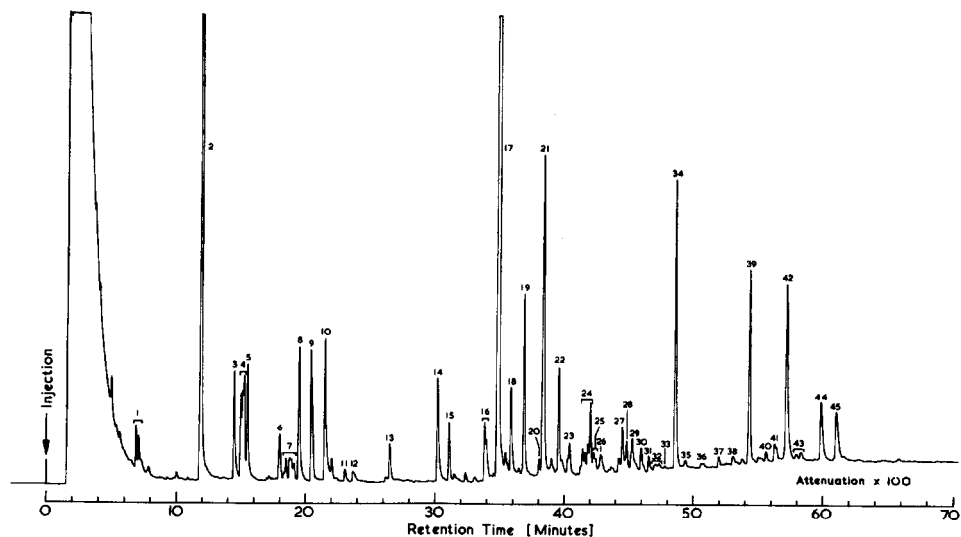
Fig. 2. GC–FID chromatogram of neutral nitrogen fraction (hexane–15% benzene eluate) of anthracene oil. Identities of numbered peaks given in Table III. Conditions as in Fig. 1.

The data system was used to generate total ionisation current (TIC) chromatograms, and single ion chromatograms for specific m/z values. Accurate mass measurement, generally to within ± 5 mmu, permitted the assignment of atomic compositions to the peaks observed in the TIC chromatograms. Visual correlation between the GC–MS TIC and GC–FID chromatograms was excellent, and assignments for the numbered peaks of the GC–FID chromatograms shown in Figs. 1–3 are given in Tables II–IV, respectively. Many of the peaks contain more than one component,
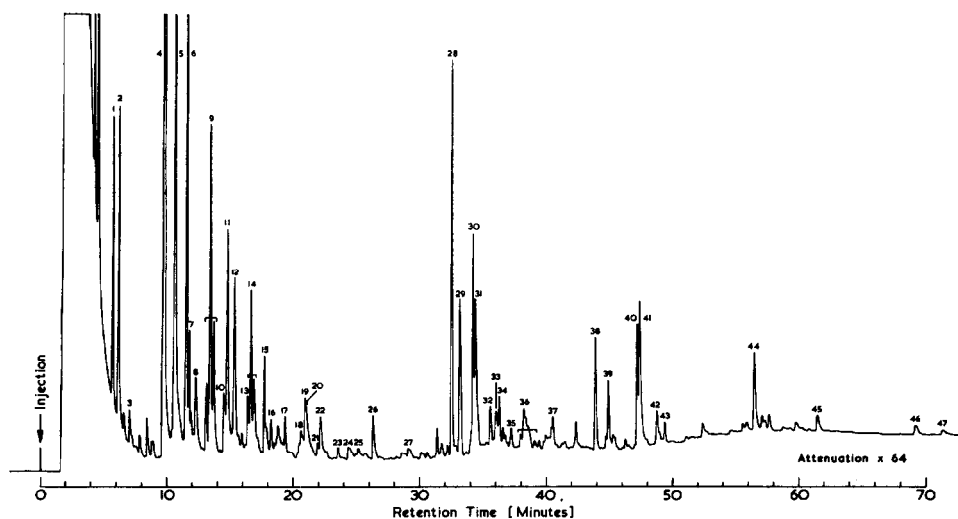

Fig. 3. GC–FID chromatogram of basic nitrogen fraction (ether eluate) of anthracene oil. Identities of numbered peaks given in Table IV. Conditions as in Fig. 1.
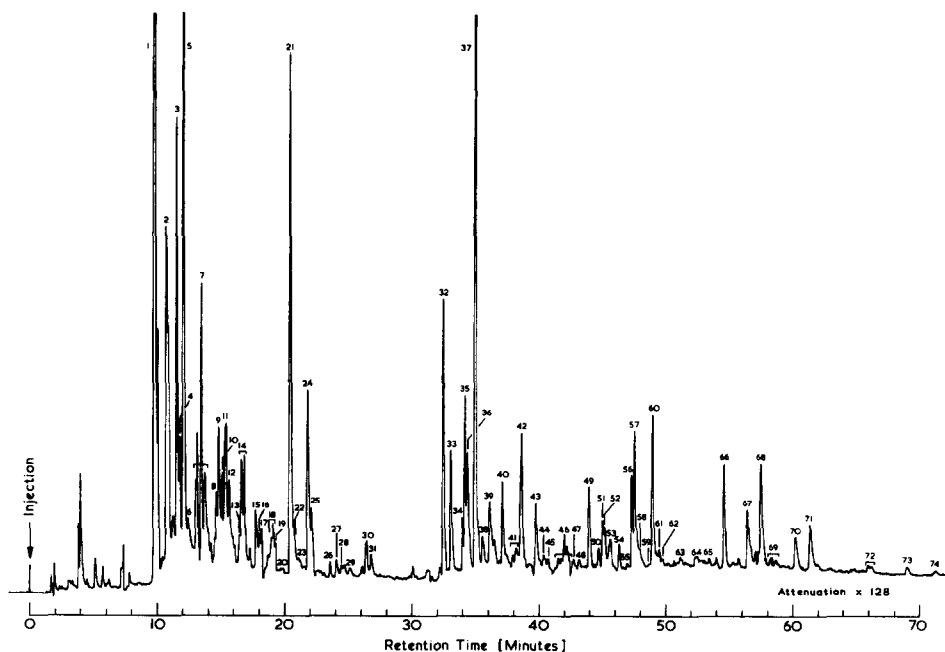
Fig. 4. Nitrogen-selective GC–AFD chromatogram of unfractionated anthracene oil. Identities of numbered peaks given in Tables III and IV for neutral and basic nitrogen species, respectively. Conditions as in Fig. 1.

and in these cases the components are listed in decreasing order of concentration. Where a number of compound types are possible for a given atomic composition, the assignment considered to have greatest validity is listed first.

DISCUSSION

Elemental analyses and nitrogen recoveries

Elemental analyses for the anthracene oil and fractions, and recovery efficiencies for total and basic nitrogen are given in Table I. The gross recovery of material in the three fractions investigated was over 91%, but more material could be recovered by a further elution with a more polar solvent such as THF. However, the additional material was essentially phenolic, having a substantial oxygen content, and did not make a significant contribution to the nitrogen recovery.

The hexane–15% benzene and ether eluates accounted for 97% of the total nitrogen measured in the unfractionated anthracene oil. The hexane–15% benzene eluate was too small to permit a basic nitrogen determination, but the ether eluate contained over 88% of the basic nitrogen measured in the unfractionated material. Basic nitrogen represents 85% of the total nitrogen present in the ether eluate. The shortfall suggests the presence of small amounts of neutral nitrogen compounds in this nominal basic nitrogen fraction. These compounds may result from slight overlap with the neutral nitrogen fraction, but may also reflect the presence of dinitrogen species containing both basic and neutral nitrogen atoms. The elution characteristics of such compounds would be expected to be governed by the more polar basic ni-

TABLE II

COMPOUNDS IDENTIFIED IN HYDROCARBON FRACTION (HEXANE ELUATE) OF AN-
THRACENE OIL

Peak numbers refer to GC–FID chromatogram in Fig. 1. Concentrations determined by GC–FID and
expressed as weight per cent of original, unfractionated sample.

Peak No.	m/z	Atomic composition	Z No.[*]	Conc. (wt.%)	Name or possible type
1	128	$C_{10}H_8$	−12	12.90	Naphthalene
2	134	C_8H_6S	−10.S	0.42	Benzo[*b*]thiophene
3	142	$C_{11}H_{10}$	−12	3.34	2-Methylnaphthalene
4	148	C_9H_8S	−10.S	0.06	Methylbenzothiophene
5	142	$C_{11}H_{10}$	−12	1.69	1-Methylnaphthalene
6	148	C_9H_8S	−10.S	0.08	Methylbenzothiophene
7	154	$C_{12}H_{10}$	−14	1.53	Diphenyl
7	162	$C_{10}H_{10}S$	−10.S		C_2-Alkylbenzothiophene
8	156	$C_{12}H_{12}$	−12	0.75	C_2-Alkylnaphthalene
8	162	$C_{10}H_{10}S$	−10.S		C_2-Alkylbenzothiophene
9	156	$C_{12}H_{12}$	−12	0.33	C_2-Alkylnaphthalene
9	162	$C_{10}H_{10}S$	−10.S		C_2-Alkylbenzothiophene
10	156	$C_{12}H_{12}$	−12	0.69	C_2-Alkylnaphthalene
10	162	$C_{10}H_{10}S$	−10.S		C_2-Alkylbenzothiophene
11	156	$C_{12}H_{12}$	−12	0.17	C_2-Alkylnaphthalene
11	168.	$C_{13}H_{12}$	−14		Methyldiphenyl
12	156	$C_{12}H_{12}$	−12	0.12	C_2-Alkylnaphthalene
13	156	$C_{12}H_{12}$	−12	0.09	C_2-Alkylnaphthalene
14	156	$C_{12}H_{12}$	−12	0.10	C_2-Alkylnaphthalene
15	168	$C_{13}H_{12}$	−14	0.51	Methyldiphenyl
15	170	$C_{13}H_{14}$	−12		C_3-Alkylnaphthalene
15	176	$C_{11}H_{12}S$	−10.S		C_3-Alkylbenzothiophene
16	168	$C_{13}H_{12}$	−14	0.16	Methyldiphenyl
16	170	$C_{13}H_{14}$	−12		C_3-Alkylnaphthalene
16	176	$C_{11}H_{12}S$	−10.S		C_3-Alkylbenzothiophene
17	154	$C_{12}H_{10}$	−14	5.91	Acenaphthene
18	168	$C_{13}H_{12}$	−14	0.30	Methylacenaphthene/diphenyl
19	168	$C_{12}H_8O$	−16.O	3.80	Dibenzofuran
20	182	$C_{14}H_{14}$	−14	0.43	C_2-Alkyldiphenyl/acenaphthene
20	153	$C_{11}H_7N$	−15.N		Naphthonitrile
21	166	$C_{13}H_{10}$	−16	3.58	Fluorene
21	184	$C_{14}H_{16}$	−12		C_4-Alkylnaphthalene
22	182	$C_{14}H_{14}$	−14	0.57	C_2-Alkyldiphenyl/acenaphthene
23	168	$C_{13}H_{12}$	−14	0.26	Methylacenaphthene/diphenyl
24	182	$C_{13}H_{10}O$	−16.O	0.36	Methyldibenzofuran
25	182	$C_{13}H_{10}O$	−16.O	0.43	Methyldibenzofuran
26	182	$C_{13}H_{10}O$	−16.O	0.10	Methyldibenzofuran
27	180	$C_{14}H_{12}$	−16	0.14	Methylfluorene
28	180	$C_{14}H_{12}$	−16	0.09	Methylfluorene
29	196	$C_{14}H_{12}O$	−16.O	0.13	C_2-Alkyldibenzofuran
30	184	$C_{12}H_8S$	−16.S	0.29	Dibenzo[*b,d*]thiophene
31	180	$C_{13}H_8O$	−18.O	0.16	Fluorenone
32	178	$C_{14}H_{10}$	−18	5.72	Phenanthrene
33	178	$C_{14}H_{10}$	−18	1.00	Anthracene
34	210	$C_{15}H_{14}O$	−16.O	0.09	C_3-Alkyldibenzofuran
34	198	$C_{13}H_{10}S$	−16.S		Methyldibenzothiophene

TABLE II (continued)

Peak No.	m/z	Atomic composition	Z No.	Conc. (wt.%)	Name or possible type
35	192	$C_{15}H_{12}$	−18	0.23	Methylphenanthrene
35	198	$C_{13}H_{10}S$	−16.S		Methyldibenzothiophene
36	192	$C_{15}H_{12}$	−18	0.29	Methylphenanthrene
36	198	$C_{13}H_{10}S$	−16.S		Methyldibenzothiophene
37	192	$C_{15}H_{12}$	−18	0.13	Methylphenanthrene
37	198	$C_{13}H_{10}S$	−16.S		Methyldibenzothiophene
38	190	$C_{15}H_{10}$	−20	0.65	Cyclopenta[d,e,f]phenanthrene
38	192	$C_{15}H_{12}$	−18		Methylphenanthrene
39	204	$C_{16}H_{12}$	−20	0.22	Methylcyclopenta[d,e,f]phenanthrene
39	212	$C_{14}H_{12}S$	−16.S		C_2-Alkyldibenzothiophene
39	206	$C_{16}H_{14}$	−18		C_2-Alkylphenanthrene
40	202	$C_{16}H_{10}$	−22	2.90	Fluoranthene
41	218	$C_{16}H_{10}O$	−22.O	0.29	Naphthobenzofuran
42	202	$C_{16}H_{10}$	−22	1.94	Pyrene
43	216	$C_{17}H_{12}$	−22	0.11	Methylfluoranthene/pyrene
43	218	$C_{16}H_{10}O$	−22.O		Naphthobenzofuran
43	208	$C_{14}H_8S$	−20.S		Phenanthro[b,c,d]thiophene
44	216	$C_{17}H_{12}$	−22	0.09	Methylfluoranthene/pyrene
45	216	$C_{17}H_{12}$	−22	0.19	Benzo[a]fluorene and/or methylfluoranthene/pyrene
45	220	$C_{17}H_{16}$	−18		C_3-Alkylphenanthrene
46	216	$C_{17}H_{12}$	−22	0.15	Benzo[b]fluorene and/or methylfluoranthene/pyrene
46	232	$C_{17}H_{12}O$	−22.O		Methylnaphthobenzofuran
47	230	$C_{17}H_{10}O$	−24.O	0.07	Benzofluorenone
47	234	$C_{16}H_{10}S$	−22.S		Naphthobenzothiophene
48	226	$C_{18}H_{10}$	−26	0.11	Benzo[g,h,i]fluoranthene
48	228	$C_{18}H_{12}$	−24		Benzo[c]phenanthrene
49	228	$C_{18}H_{12}$	−24	0.39	Benz[a]anthracene
50	228	$C_{18}H_{12}$	−24	0.35	Chrysene

* The Z number is derived from the atomic composition according to the general formula C_nH_{2n+z} and reflects the abundance of hydrogen relative to carbon. The more aromatic, or hydrogen-deficient, the molecule, the more negative the Z number. The presence or absence of alkyl side-chains in an aromatic molecule does not affect the Z number. For heterocyclics Z numbers are calculated from C and H contents only.

trogen function, but although compounds such as 1-azacarbazole ($C_{11}H_8N_2$, m/z 168) are known constituents of coal tars[30], no dinitrogen compounds were identified in the ether eluate.

Nature of the compounds identified in the fractions

    Hexane eluate. The GC–FID chromatogram of the hexane eluate is shown in Fig. 1, GC–MS identifications for the numbered peaks being given in Table II. The fraction contained predominantly aromatic hydrocarbons, and no nitrogen compounds were detected. However, many furan and thiophene benzologues were identified as minor components; these low polarity oxygen and sulphur heterocycles are very difficult to separate from the aromatic hydrocarbons because they have similar electronic structures.

TABLE III

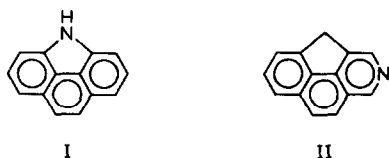COMPOUNDS IDENTIFIED IN NEUTRAL NITROGEN FRACTION (HEXANE–15% BENZENE ELUATE) OF ANTHRACENE OIL

Peak numbers refer to GC–FID chromatogram in Fig. 2 and GC–AFD chromatogram in Fig. 4. Concentrations determined by GC–FID and expressed as parts per million of original, unfractionated sample.

Peak No.		m/z	Atomic composition	Z No.	Conc. (ppm)	Name or possible type
Fig. 3	Fig. 4					
1	—	136	$C_9H_{12}O$	– 6.O	79	C_3-Alkylphenol
2	5	117	C_8H_7N	– 9.N	2730	Indole
3	8	131	C_9H_9N	– 9.N	186	Methylindole
4	10	131	C_9H_9N	– 9.N	439	Methylindole
5	12	131	C_9H_9N	– 9.N	229	Methylindole
6	16	154	$C_{12}H_{10}$	–14	58	Acenaphthene
6		145	$C_{10}H_{11}N$	– 9.N		C_2-Alkylindole
7	18	145	$C_{10}H_{11}N$	– 9.N	183	C_2-Alkylindole
7		168	$C_{12}H_8O$	–16.O		Dibenzofuran
8	—	170	$C_{12}H_{10}O$	–14.O	246	Hydroxyacenaphthene/diphenyl
9	21	153	$C_{11}H_7N$	–15.N	288	1-Cyanonaphthalene
10	24	153	$C_{11}H_7N$	–15.N	325	2-Cyanonaphthalene
11	—	184	$C_{13}H_{12}O$	–14.O	28	Methylhydroxyacenaphthene/diphenyl
12	—	184	$C_{13}H_{12}O$	–14.O	40	Methylhydroxyacenaphthene/diphenyl
13	31	179	$C_{13}H_9N$	–17.N	87	Cyanoacenaphthene
14	—	180	$C_{13}H_8O$	–18.O	206	Fluorenone
15	—	178	$C_{14}H_{10}$	–18	114	Phenanthrene
16	34	193	$C_{14}H_{11}N$	–17.N	173	Methylbenzoquinoline or methylcyanoacenaphthene
17	37	167	$C_{12}H_9N$	–15.N	4020	Carbazole
18	39	193	$C_{13}H_7NO$	–19.NO	212	Cyanodibenzofuran or azaphenanthro[b,c,d]furan
19	40	181	$C_{13}H_{11}N$	–15.N	350	Methylcarbazole
19		193	$C_{14}H_{11}N$	–17.N		Methylbenzoquinoline
20	41	167	$C_{12}H_9N$	–15.N	29	Naphthopyrrole
21	42	181	$C_{13}H_{11}N$	–15.N	697	Methylcarbazole
22	43	181	$C_{13}H_{11}N$	–15.N	273	Methylcarbazole
23	45	195	$C_{14}H_{13}N$	–15.N	107	C_2-Alkylcarbazole
24	46	202	$C_{16}H_{10}$	–22	246	Fluoranthene
24		195	$C_{14}H_{13}N$	–15.N		C_2-Alkylcarbazole
25	47	193	$C_{14}H_{11}N$	–17.N	86	Methylbenzoquinoline
25		195	$C_{14}H_{13}N$	–15.N		C_2-Alkylcarbazole
26	48	195	$C_{14}H_{13}N$	–15.N	69	C_2-Alkylcarbazole
27	50	202	$C_{16}H_{10}$	–22	151	Pyrene
28	52	203	$C_{15}H_9N$	–21.N	97	Cyanophenanthrene/anthracene
29	53	203	$C_{15}H_9N$	–21.N	114	Cyanophenanthrene/anthracene
30	54	203	$C_{15}H_9N$	–21.N	90	Cyanophenanthrene/anthracene
31	55	203	$C_{15}H_9N$	–21.N	44	Cyanophenanthrene/anthracene
32	58	203	$C_{15}H_9N$	–21.N	36	Cyanophenanthrene/anthracene
32		216	$C_{17}H_{12}$	–22		Methylfluoranthene/pyrene or benzofluorene
33	59	216	$C_{17}H_{12}$	–22	30	Methylfluoranthene/pyrene or benzofluorene
34	60	191	$C_{14}H_9N$	–19.N	654	Phenanthro[b,c,d]pyrrole
35	62	229	$C_{17}H_{11}N$	–23.N	31	Dibenzoquinoline

TABLE III (continued)

Peak No.		m/z	Atomic composition	Z No.	Conc. (ppm)	Name or possible type
Fig. 2	Fig. 4					
36	63	207	$C_{15}H_{13}N$	−17.N	38	C_2-Alkylbenzoquinoline
36		217	$C_{16}H_{11}N$	−21.N		Methylcyanophenanthrene/anthracene
37	64	205	$C_{15}H_{11}N$	−19.N	36	Methylphenanthro[b,c,d]pyrrole
38	65	230	$C_{16}H_{10}N_2$	−22.N_2	40	Diazabenz[a]anthracene/chrysene
39	66	229	$C_{17}H_{11}N$	−23.N	418	3,4-Benzacridine
40	—	228	$C_{18}H_{12}$	−24	35	Benz[a]anthracene
41	—	228	$C_{18}H_{12}$	−24	35	Chrysene
42	68	217	$C_{16}H_{11}N$	−21.N	613	Benzocarbazole
43	69	217	$C_{16}H_{11}N$	−21.N	114	Benzocarbazole
43		243	$C_{18}H_{13}N$	−23.N		Methyldibenzoquinoline
43		231	$C_{17}H_{13}N$	−21.N		Methylbenzocarbazole
43		227	$C_{17}H_9N$	−25.N		Cyanofluoranthene/pyrene or azabenzo[g,h,i]fluoranthene
44	70	217	$C_{16}N_{11}N$	−21.N	350	2,3-Benzocarbazole
44		243	$C_{18}H_{13}N$	−23.N		Methyldibenzoquinoline
45	71	217	$C_{16}H_{11}N$	−21.N	299	Benzocarbazole
45		231	$C_{17}H_{13}N$	−21.N		Methylbenzocarbazole

Hexane–15% benzene eluate. The GC–FID chromatogram of the hexane–15% benzene eluate is shown in Fig. 2, GC–MS identifications for the numbered peaks being given in Table III. The fraction contained almost exclusively neutral nitrogen compounds, and the major components were benzologues of pyrrole, such as indoles and carbazoles. The isolation of a discrete neutral nitrogen fraction in this way has

I

II

confirmed the structures of compounds such as $C_{14}H_{11}N$, m/z 191 (Fig. 2, Peak 34), which was shown to be the neutral phenanthro[b,c,d]pyrrole (I) rather than the isomeric basic compound azacyclopenta[d,e,f]phenanthrene (II).

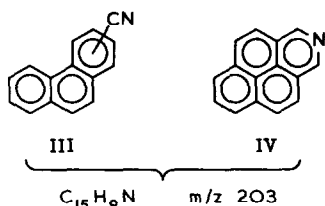Structures containing nitrile (cyano) functions have been postulated for a num-

III

IV

$C_{15}H_9N$ m/z 203

TABLE IV

COMPOUNDS IDENTIFIED IN BASIC NITROGEN FRACTION (ETHER ELUATE) OF AN-
THRACENE OIL

Peak numbers refer to GC–FID chromatogram in Fig. 3 and GC–AFD chromatogram in Fig. 4. Con-
centrations determined by GC–FID and expressed as parts per million of original, unfractionated sample.

Peak No.		m/z	Atomic composition	Z No.	Conc. (ppm)	Name or possible type
Fig. 3	Fig. 4					
1	—	122	$C_8H_{10}O$	− 6.O	478	Xylenol
2	—	122	$C_8H_{10}O$	− 6.O	607	Xylenol
3	—	122	$C_8H_{10}O$	− 6.O	91	Xylenol
4	1	129	C_9H_7N	−11.N	7610	Quinoline
5	2	129	C_9H_7N	−11.N	1730	Isoquinoline
6	3	143	$C_{10}H_9N$	−11.N	1590	Methylquinoline
7	4	143	$C_{10}H_9N$	−11.N	152	Methylquinoline
8	6	143	$C_{10}H_9N$	−11.N	233	Methylquinoline
8		136	$C_9H_{12}O$	− 6.O		C_3-Alkylphenol
9	7	143	$C_{10}H_9N$	−11.N	1440	Methylquinoline
9		157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
10	8	143	$C_{10}H_9N$	−11.N	126	Methylquinoline
10		156	$C_{12}H_{12}$	−12		C_2-Alkylnaphthalene
11	9	143	$C_{10}H_9N$	−11.N	684	Methylquinoline
12	11	157	$C_{11}H_{11}N$	−11.N	587	C_2-Alkylquinoline
13	13	143	$C_{10}H_9N$	−11.N	140	Methylquinoline
13		157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
13		163	C_9H_9NS	− 9.NS		C_2-Alkylazabenzothiophene
14	14	157	$C_{11}H_{11}N$	−11.N	713	C_2-Alkylquinoline
15	15	155	$C_{11}H_9N$	−13.N	215	Aza-Acenaphthene/diphenyl
15		157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
16	17	157	$C_{11}H_{11}N$	−11.N	80	C_2-Alkylquinoline
16		171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
17	19	169	$C_{12}H_{11}N$	−13.N	126	Methylaza-acenaphthene/diphenyl
17		157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
18	21	171	$C_{12}H_{13}N$	−11.N	116	C_3-Alkylquinoline
19	22	171	$C_{12}H_{13}N$	−11.N ⎫		C_3-Alkylquinoline
19		144	$C_{10}H_8O$	−12.O ⎪ 491		Hydroxynaphthalene
20	23	171	$C_{12}H_{13}N$	−11.N ⎬		C_3-Alkylquinoline
20		144	$C_{10}H_8O$	−12.O ⎭		Hydroxynaphthalene
21	24	169	$C_{11}H_7NO$	−15.NO	133	Azadibenzofuran
21		171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
21		144	$C_{10}H_8O$	−12.O		Hydroxynaphthalene
22	25	169	$C_{12}H_{11}N$	−13.N	124	Methylaza-acenaphthene/diphenyl
22		171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
23	26	183	$C_{13}H_{13}N$	−13.N	54	C_2-Alkylaza-acenaphthene/diphenyl
23		185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
24	28	183	$C_{12}H_9NO$	−15.NO	124	Methylazadibenzofuran
25	—	170	$C_{12}H_{10}O$	−14.O	79	Hydroxyacenaphthene/diphenyl or acetonaphthone
25		158	$C_{11}H_{10}O$	−12.O		Methylhydroxynaphthalene
26	30	167	$C_{12}H_9N$	−15.N	197	4-Azafluorene
26		183	$C_{12}H_9NO$	−15.NO		Methylazadibenzofuran
27	—	181	$C_{13}H_{11}N$	−15.N	89	Methylazafluorene
28	32	179	$C_{13}H_9N$	−17.N	1080	7,8-Benzoquinoline

TABLE IV (*continued*)

Peak No.		m/z	Atomic composition	Z No.	Conc. (ppm)	Name or possible type
Fig. 3	Fig. 4					
28		185	$C_{11}H_7NS$	−15.NS		Azadibenzothiophene
29	33	179	$C_{13}H_9N$	−17.N	637	2,3-Benzoquinoline
30	35	179	$C_{13}H_9N$	−17.N	674	3,4-Benzoquinoline
30		193	$C_{14}H_{11}N$	−17.N		Methylbenzoquinoline
30		199	$C_{12}H_9NS$	−15.NS		Methylazadibenzothiophene
31	36	179	$C_{13}H_9N$	−17.N	553	5,6-Benzoquinoline
31		193	$C_{14}H_{11}N$	−17.N		Methylbenzoquinoline
31		199	$C_{12}H_9NS$	−15.NS		Methylazadibenzothiophene
32	38	179	$C_{13}H_9N$	−17.N	247	Benzoquinoline/isoquinoline
32		185	$C_{11}H_7NS$	−15.NS		Azadibenzothiophene
33	–	179	$C_{13}H_9N$	−17.N	263	Benzoquinoline/isoquinoline
34	39	193	$C_{14}H_{11}N$	−17.N	407	Methylbenzoquinoline
34		199	$C_{12}H_9NS$	−15.NS		Methylazadibenzothiophene
35	40	193	$C_{14}H_{11}N$	−17.N	175	Methylbenzoquinoline
36	41	193	$C_{14}H_{11}N$	−17.N	632	Methylbenzoquinoline
36		207	$C_{15}H_{13}N$	−17.N		C_2-Alkylbenzoquinoline
37	44	193	$C_{14}H_{11}N$	−17.N	185	Methylbenzoquinoline
37		207	$C_{15}H_{13}N$	−17.N		C_2Alkylbenzoquinoline
38	49	203	$C_{15}H_9N$	−21.N	392	Azafluoranthene/pyrene
39	51	203	$C_{15}H_9N$	−21.N	254	Azafluoranthene/pyrene
39		219	$C_{16}H_{13}N$	−19.N		Methylazadihydropyrene or C_2-alkylazacyclopenta-[d,e,f]phenanthrene
40	56	203	$C_{15}H_9N$	−21.N	410	Azapyrene/fluoranthene
41	57	203	$C_{15}H_9N$	−21.N	573	Azapyrene/fluoranthene
42	60	203	$C_{15}H_9N$	−21.N	272	Azapyrene/fluoranthene
42		217	$C_{16}H_{11}N$	−21.N		Methylazafluoranthene/pyrene or azabenzofluorene
43	61	217	$C_{16}H_{11}N$	−21.N	117	Methylazafluoranthene/pyrene or azabenzofluorene
44	67	229	$C_{17}H_{11}N$	−23.N	385	Dibenzoquinoline
45	71	217	$C_{16}H_{11}N$	−21.N	320	Benzocarbazole
45		243	$C_{18}H_{13}N$	−23.N		Methyldibenzoquinoline
46	73	253	$C_{19}H_{11}N$	−27.N	152	Azabenzofluoranthene/pyrene
47	74	253	$C_{19}H_{11}N$	−27.N	87	Azabenzofluoranthene/pyrene

ber of atomic compositions. In some cases alternative compound types involving basic nitrogen functions are possible, *e.g.* cyanophenanthrenes (III) are isomeric with azafluoranthenes/pyrenes (IV).

However, the presence of cyanonaphthalenes was confirmed by their GC retention times, and additional evidence for the presence of nitriles was obtained from the IR spectrum of this fraction (Fig. 5), which shows a significant $C \equiv N$ absorption at 2222 cm^{-1}, in addition to the pyrrolic N–H band at 3420 cm^{-1}.

The only potentially basic species confirmed in the fraction was 3,4-benzacridine (V), the presence of which is attributed to the high degree of steric hindrance of its nitrogen atom.

It was similarly found that an intermediate elution with benzene, between the

V   VI

$C_{17}H_{11}N$ m/z 229 $C_{13}H_9N$ m/z 179
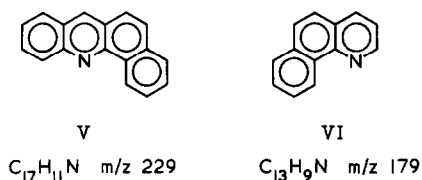
hexane–15% benzene and ether elutions, would selectively displace 7,8-benzoquino-line (VI), the most sterically hindered of the benzoquinolines. However, this compound was too polar to be eluted by the hexane–15% benzene mixture, and in the present scheme it was eluted with the other benzoquinolines in the ether eluate.

Ether eluate. The GC–FID chromatogram of the ether eluate is shown in Fig. 3, GC–MS identifications for the numbered peaks being given in Table IV. The fraction contained almost exclusively basic nitrogen compounds. The compounds identified were principally aza heterocycles, but a number of mixed (NO and NS) heteroatomic compounds, containing a pyridine ring together with an additional furan or thiophene ring, were also detected. Primary and secondary aromatic amines were absent from the anthracene oil, but if present they should be eluted in this fraction, since their basicities are similar to those of the aza heterocycles.

Identification of peaks in the nitrogen-selective GC–AFD chromatogram and general observations on the liquid chromatographic fractionation

The GC–MS analyses demonstrate that liquid chromatography (LC) on OPN/Porasil-C gives a well-defined separation of nitrogen compounds in coal tars into neutral and basic species. The GC–AFD nitrogen profile of the unfractionated anthracene oil shown in Fig. 4 is clearly a composite of the GC–FID chromatograms
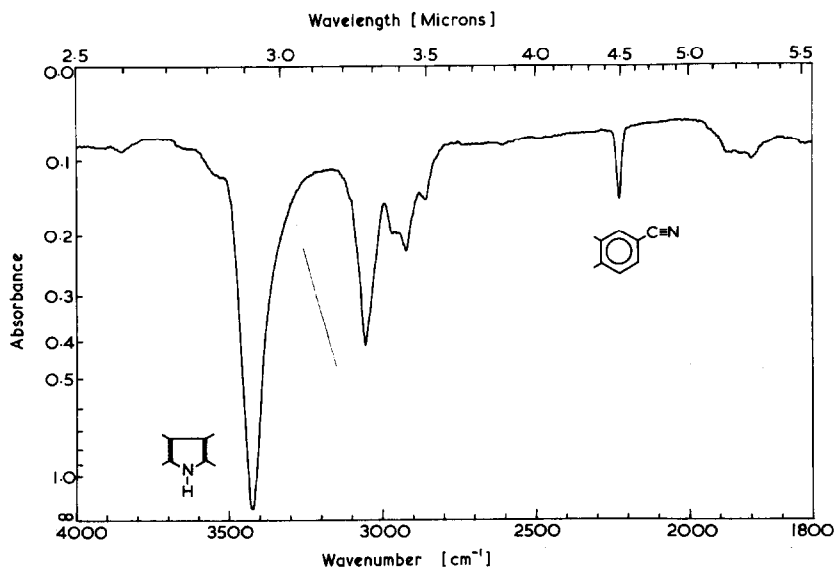

Fig. 5. Infrared spectrum of neutral nitrogen fraction (hexane–15% benzene eluate) of anthracene oil showing nitrile ($-C \equiv N$) and pyrrolic (N—H) absorptions.

given in Figs. 2 and 3 for the neutral and basic nitrogen fractions. Identifications for the numbered peaks in Fig. 4 are given in Tables III and IV for the neutral and basic nitrogen species respectively. In this way many more peaks in the GC–AFD chromatogram could be identified than was possible from GC–MS analysis of the unfractionated material.

The mechanism of the LC separation on OPN/Porasil-C nominally involves partition of the sample components between the chemically-bonded stationary phase and the liquid mobile phase, but in practice adsorption effects such as dipole–dipole interactions, hydrogen bonding, weak covalent bonding and dispersion forces are also likely to be important. The strength of these reversible intermolecular forces will be dependent upon the functional groups and stereochemistry of the sample molecules, the nature of the bonded stationary phase, and the polarity of the eluting solvent (mobile phase). With such a complex system the separation achieved is unlikely to be as selective as those obtained by more specific chemical methods. Nevertheless, the basic nitrogen fraction was very similar to those isolated by cation-exchange chromatography, aqueous acid extraction and organometallic coordination chromatography. A detailed comparison of these methods for the isolation of basic nitrogen compounds from coal tars has been reported elsewhere[31].

The isolation of a discrete neutral nitrogen fraction containing pyrrolic compounds and nitriles on OPN/Porasil-C is particularly important since alternative fractionation schemes are complex and time-consuming. The present method minimises the possibility of sample loss, and has allowed a much more detailed examination of this inaccessible group of compounds than has been possible hitherto.

The OPN/Porasil-C column does not retard aromatic hydrocarbons significantly using hexane as the eluting solvent, and although no saturated hydrocarbons were detected in the anthracene oil, it is unlikely that any useful separation of aromatic and saturated hydrocarbons could be achieved. However, if a class separation is required, the composite hydrocarbon fraction may be subjected to adsorption chromatography on activated silica and/or alumina.

Very little overlap between the neutral and basic nitrogen fractions was observed for the anthracene oil, indicating that the method should be suitable for other high-temperature coal tar products and coke oven effluents. It is possible that more overlap may occur with low-temperature tars and other heavily alkylated samples due to steric hindrance and electron-inductive effects. In this context it should be noted that substitution at the *m*- and *p*-positions by electron-releasing substituents such as alkyl groups will normally increase the basicity of aromatic amines since the electron release tends to stabilise the positive charge on the protonated nitrogen atom. However, when substitution occurs at the *o*-position, a reduction in basicity may result from a combination of steric hindrance and the anomalous *ortho* effect.

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