Journal of Chromatography, 265 (1983) 223–238
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,895

COMPARISON OF METHODS FOR THE ISOLATION OF BASIC NITROGEN COMPOUNDS FROM COAL TARS

PAUL BURCHILL*, ALAN A. HEROD, JUDITH P. MAHON and ERNEST PRITCHARD
National Coal Board, Coal Research Establishment, Stoke Orchard, Cheltenham, Gloucestershire GL52 4RZ (Great Britain)
(Received March 31st, 1983)

SUMMARY

A comparison of aqueous acid extraction, cation-exchange chromatography, liquid chromatography on a polar, bonded-phase silica and organometallic co-ordination chromatography for the isolation of basic nitrogen compounds from coal tars is reported. Basic fractions from an anthracene oil have been characterised by gas chromatography, mass spectrometry and elemental analyses, and the extraction procedures are compared in terms of basic nitrogen recovery, concentrations of specific components and the types of compounds present in the basic fractions. Agreement between the methods is generally good, and all appear capable of yielding fractions which will allow the quantitative determination of an environmentally important group of compounds by gas chromatography with flame ionization detection.

INTRODUCTION

Recent work at several laboratories in the U.S.A. has shown that basic nitrogen compounds are major contributors to the mutagenic activity of some coal products, in particular unrefined and partially refined oils[1–3]. This is in marked contrast to products derived from crude petroleum, where the somewhat lower mutagenicity is associated almost exclusively with neutral compounds such as polynuclear aromatic hydrocarbons (PAH)[4]. The high mutagenicity of some of the coal liquefaction products is ascribed to the presence of significant amounts of primary aromatic amines, but a number of the aza heterocycles, which are generally the major basic nitrogen compounds in coal-derived materials, are also recognised carcinogens[5–7].

Although we have successfully used nitrogen-selective alkali-flame detection (AFD) for the gas chromatographic (GC) determination of nitrogen compounds in unfractionated coal tars[8] and liquefaction products[9], the technique does not yield identifications directly, and prior chemical fractionation has generally been found necessary for the identification and quantification of these compounds. Aqueous acid extraction, followed by neutralization and back extraction into an organic solvent, has been the method most widely used for the isolation of basic nitrogen com-

0021-9673/83/$03.00

pounds[1,9–12]. However, the procedure possesses a number of disadvantages; in particular it is dependent upon the solubilities of the protonated bases in the aqueous acid, and such solubilities decrease markedly with increasing molecular weight[13]. The method is therefore unlikely to be quantitative for high-molecular-weight material, although it is quite satisfactory for those compounds which lie within the normal range of GC (molecular weight approximately 50–300)[12]. Further disadvantages of the method are its time-consuming nature, due to the number of experimental steps, and its strong tendency to result in the formation of intractable emulsions with higher-molecular-weight samples. It is therefore desirable to consider other methods for the isolation of basic nitrogen compounds, and in this paper we compare aqueous acid extraction with three alternative techniques, involving the use of open-column liquid chromatography on a cation-exchange resin, a silica with a polar, chemically-bonded stationary phase and an organometallic co-ordination column. The sample examined was an anthracene oil; this typical high-temperature coal tar product had a boiling range of approximately 200–450°C.

Cation-exchange chromatography, using strongly acidic macroreticular resins with $-SO_3H$ functional groups bonded to a polystyrene matrix, has been widely used in the petroleum industry for the isolation of basic components of oils. Rigid, cross-linked polystyrene based resins, such as the Amberlyst 15 used in the present work, have been found particularly suitable for such non-aqueous applications, and cation-exchange chromatography forms part of the SARA (saturates, aromatics, resins, asphaltenes) and USBM-API (U.S. Bureau of Mines, American Petroleum Institute) integrated separation schemes for petroleum products. These standard separation schemes have been reviewed by Altgelt *et al.*[13]. Typically, cation-exchange resins are used in the hydrogen form for petrochemical applications, proton transfer to a basic nitrogen atom forming a positively charged ammonium ion which is strongly held by the sulphonate anion on the resin. Weaker bases and some neutral compounds may also be retained on the resin by alternative mechanisms such as dipole–dipole interactions, hydrogen bonding and weak covalent bonding, but the strength of these intermolecular forces is solvent-dependent, being greatest in non-polar solvents. In practice these weak bases may be desorbed with a polar solvent such as tetrahydrofuran, whereas the ionically bound compounds can only be released by chemical displacement with an even stronger base.

A technique involving the use of liquid chromatography (LC) on a polar, bonded-phase silica was developed as an alternative to the standard silica adsorption LC method used in this Establishment. The silica adsorption method, which is based on an ASTM standard[14], yields nominal saturate, aromatic and polar fractions, but shows a poor selectivity for heteroatomic species, which are arbitrarily distributed between the aromatic and polar fractions. Other adsorption methods[15,16], which use a more extensive range of eluting solvents, give a more effective separation of heteroatomic components, but still result in a considerable overlap between compound classes. On the other hand, bonded-phase silicas, particularly those with polar amino and nitrile functional groups, have been used successfully for the class separation of hydrocarbons and heteroatomic species in coal-derived materials by high-pressure liquid chromatography (HPLC). Such separations have generally been carried out on analytical or semi-preparative columns containing microparticulate packings[17–19]. However, the sample capacity of the columns is low, and since microparticulates of

5–10 μm diameter are both costly and not sufficiently permeable to allow their use in larger gravity-fed or low-pressure LC columns, true preparative scale separations using bonded-phase media have been much less frequent.

The method described herein involves the sequential elution of the sample from an *o*-phthalonitrile (OPN) stationary phase, chemically bonded to a Porasil C support medium, using a series of solvents of increasing polarity. This technique is intermediate in character between adsorption and partition chromatography, but is probably closer to the latter, since it has been noted that the retention characteristics of chemically-bonded stationary phases resemble those of unbonded stationary (liquid) phases in equivalent systems[20]. The partition shows a transition from the normal-phase mode (less polar solvent/more polar stationary phase) to reversed phase (more polar solvent/less polar stationary phase) with increasing solvent polarity. The OPN/Porasil C packing material (80–100 mesh) was developed initially for GC but was found to be of a suitable particle size for open-column liquid chromatography. This method permits a very effective class separation of the heteroatomic components of coal-derived materials, but only the ether eluate, containing the basic nitrogen compounds, is considered in this paper. The complete fractionation scheme will be described in detail elsewhere[21].

The technique of organometallic co-ordination chromatography is dependent upon the ability of heteroatomic compounds to form highly coloured co-ordination complexes with transition metal ions, in which pairs of non-bonding electrons on nitrogen, oxygen or sulphur atoms co-ordinate with the partially filled *d*-orbitals of the metal ion to give a covalent bond. Co-ordination chemistry in solution is well documented[22], but for the purposes of liquid chromatography it is necessary to immobilize the transition metal salt on an inert support, such as kaolin, or incorporate the metal ion into a macroreticular cation-exchange resin.

In the petrochemical field co-ordination chromatography has generally been used for the isolation of residual neutral nitrogen compounds and other Lewis bases after the removal of the stronger Brønsted acids and bases by anion- and cation-exchange chromatography, respectively[23]. For this purpose a co-ordination chromatography step using anhydrous ferric chloride supported on clay forms a part of the SARA and USBM-API integrated separation schemes[13]. However, it should be appreciated that transition metal salts will also form stable complexes with the stronger acids and bases if these are not pre-removed by ion exchange or other methods. The possibility of the formation of weak π-bonded complexes between the ferric ion and highly condensed aromatic systems has also been noted[23].

The covalent bond between ferric chloride and co-ordinated nitrogen or oxygen ligands is not readily dissociated by polar solvents, although the complexes may be soluble in such solvents. The heteroatomic species must be desorbed by chemical displacement with a ligand which forms a stronger bond with the iron(III) ion, or alternatively by washing the complexes from the support material with a polar solvent, and cleaving them by contact with a strong anion-exchange resin. The latter procedure is employed in the SARA and USBM-API schemes[13], but in the present work, in which we have used anhydrous $FeCl_3$ supported on Chromosorb W, a flux-calcined diatomaceous silica prepared as a solid support for GC, a basic nitrogen fraction was isolated by desorption with an excess of propylamine.

EXPERIMENTAL AND RESULTS

The anthracene oil was a standard commercial coal tar product; elemental analyses for the unfractionated material, the basic fractions and the residues 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.*[24]. Whatman "Multi-System" glass columns were used for the liquid chromatography.

Aqueous acid extraction

4.99 g of the oil was dissolved in 40 ml dichloromethane and extracted with 2 × 20 ml 10% H_2SO_4, then with 2 × 20 ml 20% H_2SO_4. The aqueous acid extracts were combined, cooled and the pH adjusted to 12 by the addition of 8 *M* NaOH. The bases thus regenerated were recovered by back extraction with 40 ml dichloromethane, then with 3 × 20 ml dichloromethane, the combined organic layers being reduced to a few ml under nitrogen at room temperature, then evaporated to constant weight at 40°C. The yield of bases was 0.184 g; the residue was recovered from the initial dichloromethane solution.

Cation-exchange chromatography

Amberlyst 15 was supplied by BDH (Poole, Great Britain), and used in the hydrogen form. Before use 100 g of resin were stirred with 500 ml of 10% aqueous HCl, and washed thoroughly until no Cl^- was present in the washings. The resin was then washed successively with methanol, benzene and *n*-pentane to remove organic impurities and water, and dried under vacuum at 40°C. 10 g of the prepared resin were slurried in tetrahydrofuran (THF) into a 450 × 10 mm I.D. column fitted with

TABLE I

ELEMENTAL ANALYSES AND RECOVERY EFFICIENCIES FOR BASIC NITROGEN

	Elemental analyses (%, w/w)								
	Whole anthracene oil	*Aqueous acid extraction*		*Cation-exchange chromatography*		*Liquid chromatography on OPN/Porasil C*		*Co-ordination chromatography on $FeCl_3$/ Chromosorb W*	
		Basic fraction	*Residue*	*Basic fraction*	*Residue*	*Basic fraction*	*Residue*	*Basic fraction*	*Residue*
C	90.5	83.3	91.3	84.1	91.5	82.8	91.7		
H	5.6	5.5	5.7	5.0	5.8	5.5	6.1		
N	0.84	8.3	0.30	6.15	0.37	5.2	0.17	5.7	0.3
Basic N	0.46		<0.1		0	4.4	<0.1	4.6	0
Recovery of basic nitrogen in basic fractions (%)		67*		95*		88		71	

* Calculated on assumption that all nitrogen in bases is titratable as basic nitrogen —see Discussion.

a water cooling jacket. To allow expansion of the resin bed during desorption of the bases, the column was used without the upper sealing piston, the resin being retained by silica wool plugs. The column was washed with 50 ml THF, and the washings discarded.

2.10 g of the oil were then eluted with THF, at a flow-rate restricted to approximately 1 ml/min, until the eluate was colourless. The bases were desorbed with propylamine–THF (1:2). The desorption reaction was highly exothermic, and water cooling, together with a further reduction in the flow-rate, was necessary to prevent the solvent boiling and disrupting the resin bed. A final elution with THF was then carried out to recover any strongly basic, high-molecular-weight compounds which may not have been completely soluble in the propylamine–THF mixture after desorption. The basic fraction and the initial eluate (residue) were evaporated to constant weight at 40°C; the yield of bases was 0.150 g.

Liquid chromatography on a polar, bonded-phase silica

22.7 g of OPN/Porasil C GC Durapak (80–100 mesh), supplied by Phase Separations (Queensferry, Great Britain), were dry packed into a 450 × 15 mm I.D. column to give a bed depth of 27.5 cm. The column was washed with 100 ml THF then 100 ml hexane, and the washings discarded.

A 5.43-g sample of the oil was eluted with the following solvents: hexane, 300 ml; hexane–15% benzene, 300 ml; diethyl ether, 200 ml; THF, 200 ml; pyridine, 150 ml then THF, 100 ml. The flow was not restricted and the flow-rate varied according to the solvent viscosity, but was typically about 5 ml/min. The eluates were reduced to a few ml under nitrogen on a water-bath then evaporated to constant weight at 40°C. Only the ether eluate, containing the basic nitrogen compounds, is considered in this paper; the yield of this fraction was 0.501 g.

Co-ordination chromatography

50.3 g of Chromosorb W (100–120 mesh), supplied by Phase Separations, was dried overnight at 150°C then slurried with a filtered solution containing 8.8 g of anhydrous $FeCl_3$ in 200 ml of chloroform [sufficient to give a nominal 6% (w/w) Fe loading]. The bright yellow product was washed exhaustively with benzene then pentane, and dried under vacuum in a rotary evaporator at 40°C. Its iron content was 1.5% (w/w) Fe. 19.6 g of the $FeCl_3$/Chromosorb W adsorbent was dry packed into a 450 × 25 mm I.D. column and pre-wet with hexane.

A 2.23-g sample of the oil was eluted with 500 ml of hexane, at a flow-rate restricted to approximately 2–3 ml/min, until the eluate was colourless. A basic nitrogen fraction was then obtained by eluting the column with 500 ml of hexane–1% propylamine. A further elution with 500 ml of diethyl ether was carried out to recover any desorbed bases which may not have been completely soluble in the hexane–propylamine mixture. The basic fraction and the initial residue (hexane eluate) were reduced to a few ml under nitrogen at room temperature, then evaporated to constant weight at 40°C. The yield of bases was 0.157 g.

Gas chromatography

The four basic fractions obtained as described above were analysed as approximately 2% (w/v) solutions in THF by GC with flame ionization detection

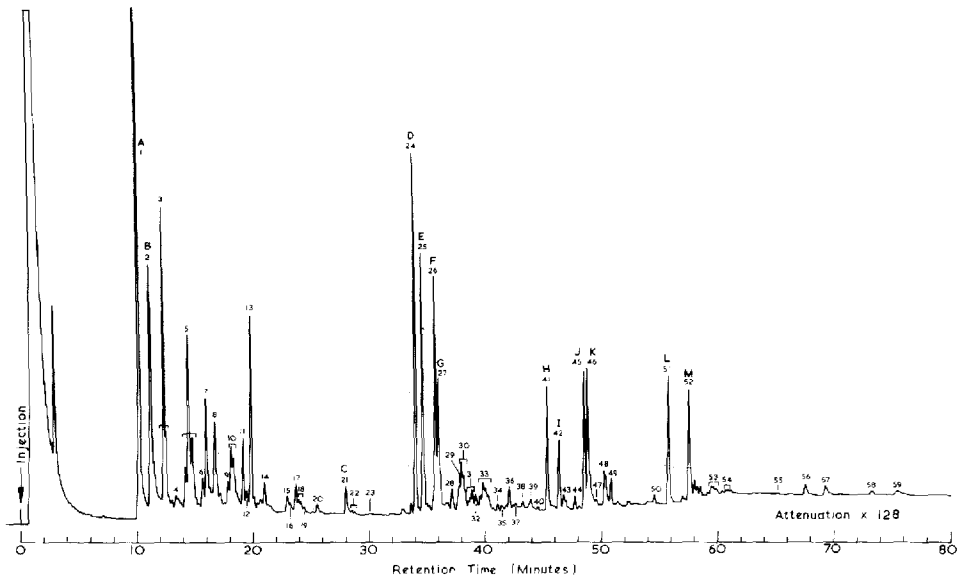


Fig. 1. GC–FID chromatogram of basic fraction isolated from an anthracene oil by aqueous acid extraction. Identities of labelled peaks given in Tables II and III. Conditions: 40-m SP-2250 glass SCOT capillary column programmed from 120 to 285°C at 3°/min with 4-min initial hold.

(GC–FID) using a Perkin-Elmer F-17 chromatograph. 0.2-μl splitless injections were made onto a 40-m SGE glass support-coated open tubular (SCOT) capillary column coated with SP-2250 50% methyl, 50% phenylsilicone stationary phase, using hydrogen carrier gas with a linear velocity of 90 cm/sec. Other chromatographic conditions are given in Fig. 1. The aqueous acid extraction and cation-exchange bases gave almost identical chromatograms, the former being shown in Fig. 1. The GC–

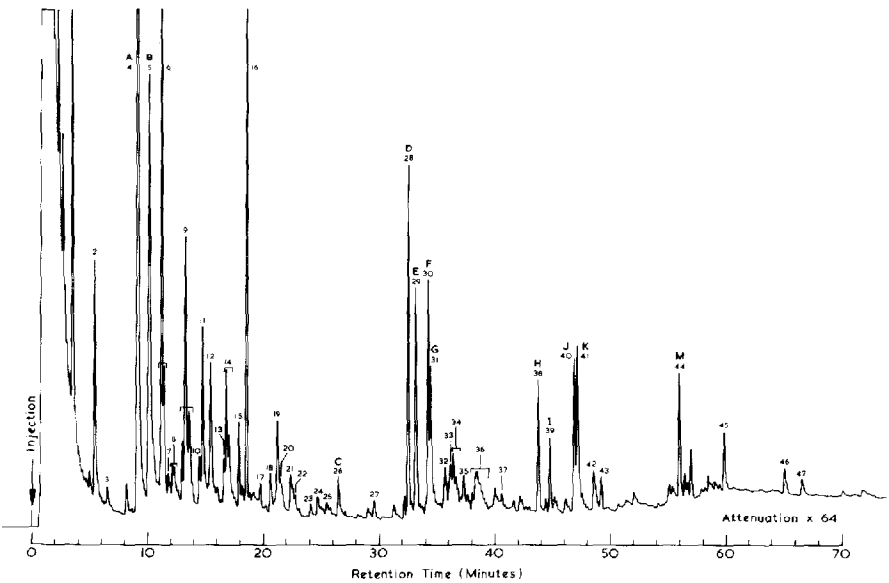


Fig. 2. GC–FID chromatogram of basic fraction isolated from an anthracene oil by liquid chromatography on a polar, bonded-phase silica (OPN/Porasil C). Identities of labelled peaks given in Tables II and IV. Conditions as in Fig. 1.

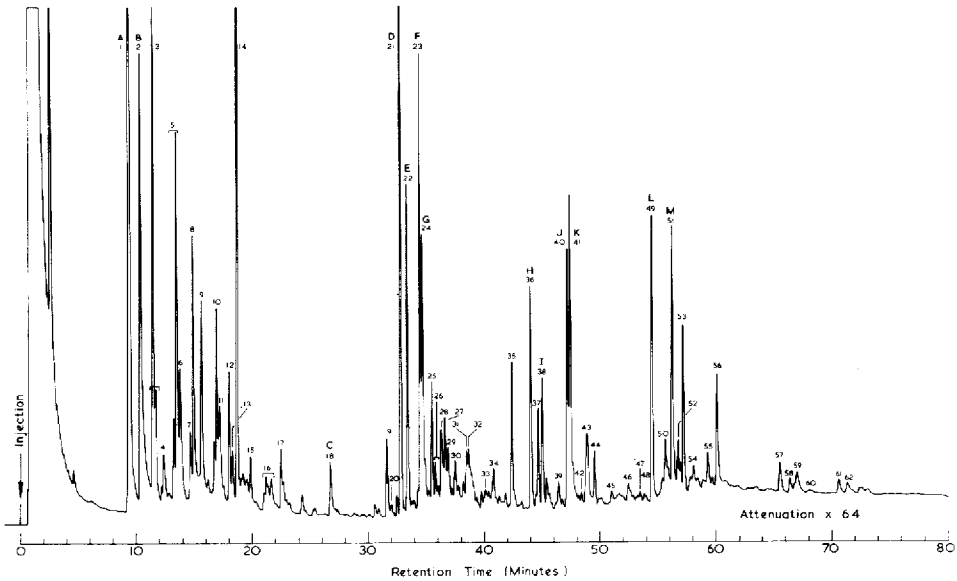


Fig. 3. GC–FID chromatogram of basic fraction isolated from an anthracene oil by organometallic co-ordination chromatography on $FeCl_3$/Chromosorb W. Identities of labelled peaks given in Tables II and V. Conditions as in Fig. 1.

FID chromatogram of the basic fraction obtained by liquid chromatography on OPN/Porasil C is given in Fig. 2, and that for the bases obtained by organometallic co-ordination chromatography in Fig. 3. Dibenzyl (430 ng/μl) was added as an internal standard for quantification, and a Hewlett-Packard 3353 chromatographic data system was used to calculate the results assuming a response factor of unity relative to the internal standard, since few reference compounds were available. The concentrations of thirteen major basic nitrogen compounds in the four fractions are given in Table II, expressed as ppm of the original, unfractionated anthracene oil. The peaks corresponding to these compounds are lettered A–M respectively in Fig. 1–3.

Gas chromatography–mass spectrometry

Gas chromatography–mass spectrometry (GC–MS) was used for the identification of specific compounds in the basic fractions. A Perkin-Elmer F-17 chromatograph was interfaced with a Kratos MS-30 double-beam mass spectrometer/DS-55 data system via a glass jet separator maintained at 250°C. 1 5-μl splitless injections were made on to a 33-m SGE SP-2250 glass SCOT capillary column under chromatographic conditions similar to those used for the GC–FID analyses. Up to 1000 mass spectral scans were collected at 3 sec per decade of mass over the mass range 50–400, approximately, at a resolution of 3000, using 70-eV electron-impact ionization.

The data system was used to generate total ionization current (TIC) chromatograms, and single ion chromatograms for specific m/z values. Accurate mass measurement, generally to within ± 5 m.m.u. using the double beam technique, permitted the assignment of atomic compositions to the peaks observed in the TIC chroma-

TABLE II

QUANTITATIVE GC FID ANALYSES FOR SOME MAJOR COMPONENTS OF BASIC FRACTIONS FROM AN ANTHRACENE OIL

Concentrations expressed as ppm of original, unfractionated anthracene oil. Peak letters refer to GC–FID chromatograms in Figs. 1–3. The Z No. 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 No. The presence or absence of alkyl side chains in an aromatic molecule does not affect the Z No. Z Nos. for heterocyclics are calculated from carbon and hydrogen contents only.

Peak letter	*Component*	*m/z*	*Atomic composition*	*Z No.*	*Concentration (ppm)*			
					Aqueous acid extraction	*Cation-exchange chromatography*	*Liquid chromatography on OPN/Porasil C*	*Co-ordination chromatography on $FeCl_3$/Chromosorb W*
A	Quinoline	129	C_9H_7N	−11.N	3030	2530	7610	4060
B	Isoquinoline	129	C_9H_7N	−11.N	970	853	1730	1070
C	4-Azafluorene	167	$C_{12}H_9N$	−15.N	126	141	197	127
D	7,8-Benzoquinoline	179	$C_{13}H_9N$	−17.N	941	881	1080	1020
E	2,3-Benzoquinoline	179	$C_{13}H_9N$	−17.N	782	758	637	576
F	3,4-Benzoquinoline	179	$C_{13}H_9N$	−17.N	685	600	674	720
G	5,6-Benzoquinoline	179	$C_{13}H_9N$	−17.N	581	571	553	622
H	Azafluoranthene	203	$C_{15}H_9N$	−21.N	359	277	392	385
I	Azafluoranthene	203	$C_{15}H_9N$	−21.N	208	170	254	233
J	Azapyrene	203	$C_{15}H_9N$	−21.N	342	270	410	378
K	Azapyrene	203	$C_{15}H_9N$	−21.N	722	664	573	730
L	3,4-Benzacridine	229	$C_{17}H_{11}N$	−23.N	363	349	418*	473
M	Dibenzoquinoline	229	$C_{17}H_{11}N$	−23.N	373	390	385	457

* Eluted with neutral nitrogen fraction (hexane–15% benzene eluate).

TABLE III

MAJOR COMPONENTS OF PEAKS IN GC–FID CHROMATOGRAMS OF BASIC FRACTIONS ISOLATED FROM AN ANTHRACENE OIL BY AQUEOUS ACID EXTRACTION AND CATION-EXCHANGE CHROMATOGRAPHY

Peak numbers refer to GC–FID chromatogram in Fig. 1.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Name or possible type*
1	129	C_9H_7N	−11.N	Quinoline
2	129	C_9H_7N	−11.N	Isoquinoline
3–7	143	$C_{10}H_9N$	−11.N	Methylquinoline
8–10	157	$C_{11}H_{11}N$	−11.N	C_2-Alkylquinoline
11	155	$C_{11}H_9N$	−13.N	Aza-acenaphthene/diphenyl
12	157	$C_{11}H_{11}N$	−11.N	C_2-Alkylquinoline
13	182	$C_{14}H_{14}$	−14	Dibenzyl (internal standard)
14	169	$C_{12}H_{11}N$	−13.N	Methylaza-acenaphthene/diphenyl
15, 16	171	$C_{12}H_{13}N$	−11.N	C_3-Alkylquinoline
17	169	$C_{11}H_7NO$	−15.NO	Azadibenzofuran
18	169	$C_{12}H_{11}N$	−13.N	Methylaza-acenaphthene/diphenyl
19	171	$C_{12}H_{13}N$	−11.N	C_3-Alkylquinoline
20	183	$C_{13}H_{13}N$	−13.N	C_2-Alkylaza-acenaphthene/diphenyl
21	167	$C_{12}H_9N$	−15.N	4-Azafluorene
22	183	$C_{12}H_9NO$	−15.NO	Methylazadibenzofuran
23	181	$C_{13}H_{11}N$	−15.N	Methylazafluorene
24	179	$C_{13}H_9N$	−17.N	7,8-Benzoquinoline
25	179	$C_{13}H_9N$	−17.N	2,3-Benzoquinoline
26	179	$C_{13}H_9N$	−17.N	3,4-Benzoquinoline
27	179	$C_{13}H_9N$	−17.N	5,6-Benzoquinoline
28, 29	179	$C_{13}H_9N$	−17.N	Benzoquinoline/isoquinoline
30–33	193	$C_{14}H_{11}N$	−17.N	Methylbenzoquinoline
34, 35	207	$C_{15}H_{13}N$	−17.N	C_2-Alkylbenzoquinoline
36	205	$C_{15}H_{11}N$	−19.N	Azadihydropyrene or methylazacyclopenteno[*def*]phenanthrene
37–39	207	$C_{15}H_{13}N$	−17.N	C_2-Alkylbenzoquinoline
40	205	$C_{15}H_{11}N$	−19.N	Azadihydropyrene or methylazacyclopenteno[*def*]phenanthrene
41–46	203	$C_{15}H_9N$	−21.N	Azafluoranthene/pyrene
47–50	217	$C_{16}H_{11}N$	−21.N	Methylazafluoranthene/pyrene
51	229	$C_{17}H_{11}N$	−23.N	3,4-Benzacridine
52–54	229	$C_{17}H_{11}N$	−23.N	Dibenzoquinoline
55–59	253	$C_{19}H_{11}N$	−27.N	Azabenzofluoranthene/pyrene

tograms. Visual correlation between the GC–MS TIC and GC–FID chromatograms was excellent, and assignments for the major components of the numbered peaks of the GC–FID chromatograms shown in Figs. 1–3 are given in Tables III–V, respectively. However, many of the peaks contained more than the one component listed; mixed (NO and NS) heteroatomic compounds were prominent amongst the minor components. In some cases a number of compound types are possible for a given atomic composition, and in these circumstances the assignment considered to have greatest validity is listed first.

DISCUSSION

Elemental analyses and estimation of recovery efficiency for basic nitrogen

Elemental analyses for the basic fractions and residues are presented in Table

TABLE IV

MAJOR COMPONENTS OF PEAKS IN GC–FID CHROMATOGRAM OF BASIC FRACTION ISOLATED FROM AN ANTHRACENE OIL BY LIQUID CHROMATOGRAPHY ON A POLAR, BONDED-PHASE SILICA (OPN/PORASIL C)

Peak numbers refer to GC–FID chromatogram in Fig. 2.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Name or possible type*
1	72	C_4H_8O	0.O	Tetrahydrofuran
2	108	C_7H_8O	−6.O	Cresol
3	122	$C_8H_{10}O$	−6.O	C_2-Alkylphenol
4	129	C_9H_7N	−11.N	Quinoline
5	129	C_9H_7N	−11.N	Isoquinoline
6–11	143	$C_{10}H_9N$	−11.N	Methylquinoline
12	157	$C_{11}H_{11}N$	−11.N	C_2-Alkylquinoline
13	143	$C_{10}H_9N$	−11.N	Methylquinoline
14	157	$C_{11}H_{11}N$	−11.N	C_2-Alkylquinoline
15	155	$C_{11}H_9N$	−13.N	Aza-acenaphthene/diphenyl
16	182	$C_{14}H_{14}$	−14	Dibenzyl (internal standard)
17	169	$C_{12}H_{11}N$	−13.N	Methylaza-acenaphthene/diphenyl
18–20	171	$C_{12}H_{13}N$	−11.N	C_3-Alkylquinoline
21	169	$C_{11}H_7NO$	−15.NO	Azadibenzofuran
22	169	$C_{12}H_{11}N$	−13.N	Methylaza-acenaphthene/diphenyl
23	183	$C_{13}H_{13}N$	−13.N	C_2-Alkylaza-acenaphthene/diphenyl
24	183	$C_{12}H_9NO$	−15.NO	Methylazadibenzofuran
25	170	$C_{12}H_{10}O$	−14.O	Acetonaphthone or diphenyl ether
26	167	$C_{12}H_9N$	−15.N	4-Azafluorene
27	181	$C_{13}H_{11}N$	−15.N	Methylazafluorene
28	179	$C_{13}H_9N$	−17.N	7,8-Benzoquinoline
29	179	$C_{13}H_9N$	−17.N	2,3-Benzoquinoline
30	179	$C_{13}H_9N$	−17.N	3,4-Benzoquinoline
31	179	$C_{13}H_9N$	−17.N	5,6-Benzoquinoline
32, 33	179	$C_{13}H_9N$	−17.N	Benzoquinoline/isoquinoline
34–37	193	$C_{14}H_{11}N$	−17.N	Methylbenzoquinoline
38–42	203	$C_{15}H_9N$	−21.N	Azafluoranthene/pyrene
43	217	$C_{16}H_{11}N$	−21.N	Methylazafluoranthene/pyrene
44	229	$C_{17}H_{11}N$	−23.N	Dibenzoquinoline
45	217	$C_{16}H_{11}N$	−21.N	Benzocarbazole
46, 47	253	$C_{19}H_{11}N$	−27.N	Azabenzofluoranthene/pyrene

I. The absence of basic nitrogen in the residues confirms that all the methods are effective in extracting basic nitrogen compounds from anthracene oil. The remaining nitrogen detected in the residues is therefore neutral nitrogen, the lower value obtained for the residue from liquid chromatography on OPN/Porasil C being due to the fact that a separate neutral nitrogen fraction was collected with this scheme.

The high nitrogen contents of the basic fractions obtained by aqueous acid extraction and cation-exchange chromatography indicate that these methods are most specific for basic nitrogen compounds. The lower nitrogen contents of the bases isolated by liquid chromatography on OPN/Porasil C and organometallic co-ordination chromatography suggest that these fractions may also contain residual, high-boiling hydrocarbons and possibly other, more polar species as diluents. However, the GC–MS analyses showed little evidence for the presence of such compounds, although it is possible that they may not have been eluted from the GC column.

TABLE V

MAJOR COMPONENTS OF PEAKS IN GC–FID CHROMATOGRAM OF BASIC FRACTION ISOLATED FROM AN ANTHRACENE OIL BY CO-ORDINATION CHROMATOGRAPHY ON $FeCl_3$/CHROMOSORB W

Peak numbers refer to GC–FID chromatogram in Fig. 3.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Name or possible type*
1	129	C_9H_7N	−11.N	Quinoline
2	129	C_9H_7N	−11.N	Isoquinoline
3–7	143	$C_{10}H_9N$	−11.N	Methylquinoline
8–11	157	$C_{11}H_{11}N$	−11.N	C_2-Alkylquinoline
12, 13	155	$C_{11}H_9N$	−13.N	Aza-acenaphthene/diphenyl
14	182	$C_{14}H_{14}$	−14	Dibenzyl (internal standard)
15	169	$C_{12}H_{11}N$	−13.N	Methylaza-acenaphthene/diphenyl
16	171	$C_{12}H_{13}N$	−11.N	C_3-Alkylquinoline
17	166	$C_{13}H_{10}$	−16	Fluorene
18	167	$C_{12}H_9N$	−15.N	4-Azafluorene
19	178	$C_{14}H_{10}$	−18	Phenanthrene
20	181	$C_{13}H_{11}N$	−15.N	Methylazafluorene
21	179	$C_{13}H_9N$	−17.N	7,8-Benzoquinoline
22	179	$C_{13}H_9N$	−17.N	2,3-Benzoquinoline
23	179	$C_{13}H_9N$	−17.N	3,4-Benzoquinoline
24	179	$C_{13}H_9N$	−17.N	5,6-Benzoquinoline
25	185	$C_{11}H_7NS$	−15.NS	Azadibenzothiophene
26	179	$C_{13}H_9N$	−17.N	Benzoquinoline/isoquinoline
27	199	$C_{12}H_9NS$	−15.NS	Methylazadibenzothiophene
28–33	193	$C_{14}H_{11}N$	−17.N	Methylbenzoquinoline
34	205	$C_{15}H_{11}N$	−19.N	Azadihydropyrene or methylazacyclopenteno[*def*]phenanthrene
35	202	$C_{16}H_{10}$	−22	Fluoranthene
36	203	$C_{15}H_9N$	−21.N	Azafluoranthene/pyrene
37	202	$C_{16}H_{10}$	−22	Pyrene
38	203	$C_{15}H_9N$	−21.N	Azafluoranthene/pyrene
39	219	$C_{16}H_{13}N$	−19.N	Methylazadihydropyrene or C_2-alkylazacyclopenteno[*def*]phenanthrene
40, 41	203	$C_{15}H_9N$	−21.N	Azapyrene/fluoranthene
42	216	$C_{17}H_{12}$	−22	Methylfluoranthene/pyrene or benzofluorene
43	191	$C_{14}H_9N$	−19.N	Phenanthro[*bcd*]pyrrole
44	217	$C_{16}H_{11}N$	−21.N	Methylazafluoranthene/pyrene or azabenzofluorene
45	195	$C_{14}H_{13}N$	−15.N	C_2-Alkylcarbazole
46	231	$C_{17}H_{13}N$	−21.N	C_2-Alkylazafluoranthene/pyrene or methylazabenzofluorene
47	No molecular ion detected			Phthalate
48	226	$C_{18}H_{10}$	−26	Benzo[*ghi*]fluoranthene
49	229	$C_{17}H_{11}N$	−23.N	3,4-Benzacridine
50	228	$C_{18}H_{12}$	−24	Benz[*a*]anthracene
51, 52	229	$C_{17}H_{11}N$	−23.N	Dibenzoquinoline
53	217	$C_{16}H_{11}N$	−21.N	Benzocarbazole
54	243	$C_{18}H_{13}N$	−23.N	Methyldibenzoquinoline
55	217	$C_{16}H_{11}N$	−21.N	2,3-Benzocarbazole
56	217	$C_{16}H_{11}N$	−21.N	Benzocarbazole
57–62	253	$C_{19}H_{11}N$	−27.N	Azabenzofluoranthene/pyrene

The basic nitrogen contents of the bases isolated by liquid chromatography on OPN/Porasil C and organometallic co-ordination chromatography represent approximately 80% of the total nitrogen in the fractions. The shortfall is probably due to the overlap of neutral nitrogen species, a number of which were found in these fractions. It is also possible that small amounts of dinitrogen compounds, containing both neutral and basic nitrogen atoms, may be present in the bases; for example 1-azacarbazole ($C_{11}H_8N_2$, m/z 168) is a known constituent of coal tars[25]. However, the only dinitrogen compound identified in the present work was a methyldiazaphenanthrene ($C_{13}H_{10}N_2$, m/z 194) containing two basic nitrogen atoms. The basic nitrogen contents of the basic fractions isolated by aqueous acid extraction and cation-exchange chromatography were not determined, but on the basis of our earlier work[12], the value for the aqueous acid extract would be expected to be close to 100% of its total nitrogen value. A similar percentage figure would be expected for the bases extracted by cation-exchange chromatography, since both extraction methods, together with the acid–base titration technique used to determine basic nitrogen, involve protonation of the basic nitrogen compounds.

An indication of the recovery efficiency for basic nitrogen compounds may be obtained by expressing the weight of basic nitrogen in the bases as a percentage of the weight of basic nitrogen in the unfractionated anthracene oil; these percentage recoveries are given in Table I. The values for the aqueous acid extraction and cation-exchange bases have been calculated on the assumption that all nitrogen in these fractions was basic. The percentage recoveries thus determined range from 67 to 95%, the highest values being obtained by cation-exchange chromatography and liquid chromatography on OPN/Porasil C.

Quantitative GC–FID analyses

The basic fractions were analysed quantitatively by GC–FID, concentrations of thirteen major components, spanning the boiling range of the samples, being given in Table II. Poor agreement between the separation methods was obtained for the low boiling components, particularly quinoline and isoquinoline, but much better agreement was found for higher boiling constituents. The possibility that the variable results obtained for quinoline and isoquinoline may have been due to partial loss of the more volatile components during evaporation of the small basic fractions to constant weight was investigated by carrying out a direct GC–AFD analysis of the unfractionated anthracene oil using N-phenylcarbazole as an internal standard. This method, which we have described in earlier papers[8,9], gave concentrations of 7290 and 1940 ppm for quinoline and isoquinoline, respectively. It may be significant that the basic fraction isolated by liquid chromatography on OPN/Porasil C, which gave the GC–FID results most closely approaching these figures, was the largest of the four and would be expected to be least vulnerable to evaporative losses. It is therefore possible, because of the relatively high concentrations of quinoline and its alkyl derivatives, that the lower percentage recovery figures for basic nitrogen given in Table I may to some extent reflect losses of light ends rather than any inherent deficiencies in the extraction procedures.

Nature of the compounds identified in the basic fractions

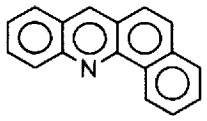
All the techniques examined yielded fractions containing predominantly basic nitrogen compounds. The GC–FID chromatograms in Figs. 1–3 show that the basic

fractions are very similar, but some minor differences are apparent, and these were investigated by GC–MS.

Aqueous acid extraction and cation-exchange chromatography. The basic fractions isolated by these techniques gave almost identical chromatograms, that for the aqueous acid extract being shown in Fig. 1, with peak identifications in Table III. The similarity between the fractions is not unexpected since both methods involve the protonation of basic nitrogen atoms as the first stage of the extraction although the methods used to recover the bases differ. GC–MS analysis of the basic fractions demonstrated that both methods were extremely specific for basic nitrogen compounds since only aza heterocycles were detected, but these included a number of mixed (NO and NS) heterocyclic species containing additional furan or thiophene rings.

Liquid chromatography on a polar, bonded-phase silica. The mechanism of this method is more complex than those of the other techniques examined, which employ relatively simple chemical reactions. It nominally involves partition of the sample components between a chemically-bonded stationary phase and a 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 such as acid extraction. Nevertheless, the GC–FID chromatogram in Fig. 2 shows that liquid chromatography on OPN/Porasil C yields a basic fraction very similar to that obtained by aqueous acid extraction and cation-exchange chromatography (Fig. 1). A few minor differences between the chromatograms were observed, however, and the bases were examined by GC–MS, identifications for the numbered peaks in Fig. 2 being given in Table IV.

A notable omission from the bases isolated by liquid chromatography on OPN/Porasil C was 3,4-benzacridine, which was eluted in the less polar neutral nitrogen fraction (hexane–15% benzene eluate):



3,4-benzacridine

$C_{17}H_{11}N$ m/z 229

This compound was isolated by aqueous acid extraction and cation-exchange chromatography (Fig. 1, peak 51) and by co-ordination chromatography (Fig. 3, peak 49). Its premature elution from OPN/Porasil C is probably due to the high degree of steric hindrance of its nitrogen atom compared with other dibenzoquinolines.

Conversely, an unidentified benzocarbazole ($C_{16}H_{11}N$, *m/z* 217) was eluted from OPN/Porasil C as peak 45 in Fig. 2. This compound should have been eluted with the other carbazole derivatives in the preceding neutral nitrogen fraction, and there is no obvious reason for its elution with the bases. It was not identified in the

basic fractions isolated by aqueous acid extraction or cation-exchange chromatography.

Organometallic co-ordination chromatography. The mechanism of this technique is comparatively simple and well-understood, involving the formation of organometallic complexes by co-ordination of pairs of non-bonding electrons (lone pairs) on Lewis bases with the partially-filled *d*-orbitals of transition metal ions. For chromatographic purposes the transition metal ion has to be supported on an inert medium, and in the present work the iron(III) ion was adsorbed as $FeCl_3$ on to Chromosorb W. In theory, co-ordination chromatography would not be expected to be highly selective for any particular group of compounds, since complex formation with all nitrogen, oxygen and sulphur heteroatomic species appears feasible. In practice, however, after eluting the hydrocarbons with hexane, it was possible to displace the basic nitrogen compounds selectively with propylamine; this moderately weak base did not co-ordinate sufficiently strongly with the iron(III) ion to displace more tightly-held species such as phenols. A 1% propylamine–hexane solution was sufficient to displace the basic nitrogen compounds from $FeCl_3$/Chromosorb W; it is assumed that most of the neutral nitrogen compounds were eluted by hexane alone, together with the hydrocarbons and possibly other weakly co-ordinating species such as furans and thiophenes.

The basic fractions obtained by co-ordination chromatography contained all the basic nitrogen compounds isolated by aqueous acid extraction, cation-exchange and liquid chromatography on OPN/Porasil C, but the GC–FID chromatogram in Fig. 3 also shows the presence of a few additional peaks which were investigated by GC–MS, peak identifications being given in Table V. Prominent amongst these were some residual hydrocarbons, including phenanthrene (peak 19), fluoranthene (peak 35) and pyrene (peak 37). It is not clear whether they are the result of incomplete elution with hexane, adsorption on the support medium or the formation of weak π-bonded complexes with Fe(III). Fig. 3 also shows the presence of some neutral nitrogen compounds including phenanthro[*bcd*]pyrrole (peak 43) and three benzocarbazoles (peaks 53, 55 and 56). It appears that the strength of complexation of pyrrolic nitrogen with Fe(III) increases with ring number, since no indole and only a small proportion of the carbazole was detected in the nominal basic fractions isolated by co-ordination chromatography. However, unlike other secondary amines, pyrrolic compounds would not be expected to form strong co-ordination complexes with transition metals, since the lone pair of electrons on the nitrogen atom interacts with the π-electron system of the five-membered ring to give a stable, pseudo-aromatic sextet, and is not available for co-ordination with the *d*-orbitals of the metal ion. The unavailability of the lone pair of electrons on the nitrogen atom for protonation is likewise responsible for the very low basicities of pyrrolic compounds. The homologous furans and thiophenes have similar, pseudo-aromatic structures.

CONCLUSIONS

The following conclusions may be drawn concerning the use of aqueous acid extraction, cation-exchange chromatography, liquid chromatography on a polar, bonded-phase silica and organometallic co-ordination chromatography for the isolation of basic nitrogen compounds from coal tars:

(i) All the techniques give similar fractions, containing predominantly basic nitrogen species, which allow the quantitative GC determination of this environmentally important group of compounds. Agreement between the GC–FID analyses of the basic fractions from an anthracene oil was good, except for the lowest boiling components, for which it was apparent that some sample losses had occurred.

(ii) GC–MS analysis of the basic fractions showed that aqueous acid extraction and cation-exchange chromatography were the most specific extraction techniques for basic nitrogen compounds.

(iii) The highest recoveries of basic nitrogen were obtained using cation-exchange chromatography and liquid chromatography on OPN/Porasil C. There was some evidence that the lower recoveries achieved with the other methods may have been due to loss of light ends on evaporating the small basic fractions to constant weight rather than to inefficiency in the extraction procedures.

(iv) The chromatographic methods are all considerably quicker than aqueous acid extraction and avoid the emulsion problems sometimes experienced with the latter technique. They may also be incorporated more readily into integrated separation schemes; liquid chromatography on OPN/Porasil C was particularly promising in this respect and the method will be described in greater detail in a further paper[21].

ACKNOWLEDGEMENTS

The authors thank the National Coal Board for permission to publish this work, which was carried out under the auspices of the International Energy Agency, as part of a coal pyrolysis project. The views expressed are their own, and not necessarily those of the Board.

REFERENCES

1 M. R. Guerin, C. H. Ho, T. K. Rao, B. R. Clark and J. L. Epler, *Environ. Res.*, 23 (1980) 42–53.
2 C. H. Ho, B. R. Clark, M. R. Guerin, B. D. Barkenbus, T. K. Rao and J. L. Epler, *Mutat. Res.*, 85 (1981) 335–345.
3 B. W. Wilson, M. R. Petersen, R. A. Pelroy and J. T. Cresto, *Biomedical Studies on Solvent Refined Coal (SRC-II) Liquefaction Materials: A Status Report, PNL-3189, US DOE Contract EY-76-C-06-1830*, Battelle Pacific Northwest Laboratory, Richland, WA, October 1979; also published, in part, in *Fuel*, 60 (1981) 289–294.
4 M. R. Guerin, I. B. Rubin, T. K. Rao, B. R. Clark and J. L. Epler, *Fuel*, 60 (1981) 282–288.
5 K. Hirao, Y. Shinohara, H. Tsuda, S. Fukushima, M. Takahashi and N. Ito, *Cancer Res.*, 36 (1976) 329–335.
6 M. Dong, I. Schmeltz, E. LaVoie and D. Hoffmann, in P. W. Jones and R. I. Freudenthal (Editors), *Carcinogenesis —A Comprehensive Survey*, Vol. 3: *Polynuclear Aromatic Hydrocarbons*, Raven Press, New York, 1978, pp. 97–108.
7 M. L. Lee, M. V. Novotny and K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, New York, London, 1981, Appendix 5, pp. 441–449.
8 P. Burchill, A. A. Herod and E. Pritchard, *Fuel*, 62 (1983) 11–19.
9 P. Burchill, A. A. Herod and E. Pritchard, *J. Chromatogr.*, 246 (1982) 271–295.
10 M. W. Dong, D. C. Locke and D. Hoffmann, *Environ. Sci. Technol.*, 11 (1977) 612–618.
11 W. W. Paudler and M. Cheplen, *Fuel*, 58 (1979) 775–778.
12 P. Burchill, A. A. Herod and E. Pritchard, *Fuel*, 62 (1983) 20–29.
13 K. H. Altgelt, D. M. Jewell, D. R. Latham and M. L. Selucky, in K. H. Altgelt and T. H. Gouw

(Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, Ch. 9, pp. 185–214.
14 *Annual Book of ASTM Standards*, Part 17, *Petroleum Products*, American Society for Testing and Materials, Philadelphia, 1971, Standard D2549-68, pp. 899–902.
15 M. Farcasiu, *Fuel*, 56 (1977) 9–14.
16 H. Sawatzky, A. E. George, G. T. Smiley and D. S. Montgomery, *Fuel*, 55 (1976) 16–20.
17 G. P. Blumer and M. Zander, *Erdoel Kohle, Erdgas, Petrochem., Compendium 78/79 Suppl.*, (1978) 1472–1483.
18 R. J. Crowley, S. Siggia and P. C. Uden, *Anal. Chem.*, 52 (1980) 1224–1228.
19 R. Miller, *Anal. Chem.*, 54 (1982) 1742–1746.
20 L. R. Snyder and D. L. Saunders, in K. H. Altgelt and T. H. Gouw (Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, Ch. 10, p. 219.
21 P. Burchill, A. A. Herod, J. P. Mahon and E. Pritchard, *J. Chromatogr.*, in preparation.
22 F. Basolo and R. Johnson, *Co-ordination Chemistry*, Benjamin, New York, 1964.
23 D. M. Jewell, in K. H. Altgelt and T. H. Gouw (Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, Ch. 11, pp. 273–286.
24 R. T. Moore, P. McCutchan and D. A. Young, *Anal. Chem.*, 23 (1951) 1639–1641.
25 *Coal Tar Data Book*, Coal Tar Research Association, Gomersal, Leeds, 2nd ed., 1965, Section B1.