Journal of Chromatography, 292 (1984) 355–368
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,656

DETERMINATION OF NITROGEN COMPOUNDS IN HYDROTREATED SHALE OILS BY PREPARATIVE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

L. CHAN, J. ELLIS* and P. T. CRISP
Department of Chemistry, University of Wollongong, P.O. Box 1144, Wollongong, N.S.W. 2500 (Australia)
(First received December 20th, 1983; revised manuscript received February 11th, 1984)

SUMMARY

A simple two-step procedure has been developed for the isolation of trace nitrogen compounds remaining after hydrotreatment of shale oil. Open-column alumina chromatography quickly separates saturates plus monoaromatics from polyaromatics and nitrogen compounds. The nitrogen compounds are then fractionated by preparative high-performance liquid chromatography using an amino bonded-phase column. Individual compounds may then be resolved and identified by gas chromatography–mass spectrometry. The procedure has been applied to whole hydrotreated shale oils prepared using catalysts of different activity and to four distillation fractions of a hydrotreated shale oil.

INTRODUCTION

Shale oils contain substantial quantities of alkenes and a wide range of nitrogen, sulphur and oxygen compounds. Reactions between these compounds lead to a rapid increase in oil viscosity on storage and limit the use of raw shale oil as a fuel and as a chemical feedstock. While most of these hetero atoms can be removed by hydrotreatment (catalytic hydrogenation at high pressure), significant quantities of nitrogen compounds remain and, even at the ppm-level may poison the catalysts used in subsequent catalytic reforming processes. Monitoring the nitrogen compounds present in shale oils and hydrotreated oils will be essential for synfuel production. Moreover, evaluation of the catalysts and conditions used for hydrotreatment will require an ability to identify and quantitate the individual nitrogen compounds which remain.

Strongly basic nitrogen compounds present in fossil fuels have been isolated by extraction with aqueous acid[1–2] or using cation-exchange resin[3]. Nitriles have been isolated from shale oil by complexation with zinc chloride[4]; indoles and carbazoles have been isolated from cracked petroleum by extraction with perchloric acid[5]; and some polycyclic aromatic amines such as aminoquinoline have been isolated from solvent refined coal liquids by derivatisation with trifluoroacetic anhydride[6]. Open-column chromatography using silica and alumina has been widely reported for the

0021-9673/84/$03.00 © 1984 Elsevier Science Publishers B.V.

separation of nitrogenous polycyclic aromatic compounds[7–11]. Semipreparative high-performance liquid chromatography (HPLC) using a C_{18}-bonded silica column separated nitrogenous bases isolated from petroleum by an open silica column modified with hydrochloric acid[12] and an analytical C_{18}-bonded HPLC column has separated benzoquinolines from petroleum[13]. A conventional silica column plus an analytical C_{18}-bonded HPLC column separated benzoquinolines and phenanthridines from shale oil[14] and acid/base extraction followed by semipreparative HPLC on an NH_2-bonded column isolated 2,4,6-trimethylpyridine and acridines from shale oil[15]. Partition chromatography on Sephadex coupled with HPLC on an analytical NH_2-bonded column isolated nitrogen compounds from different synfuels[16].

The isolation and identification of nitrogen compounds in hydrotreated shale oils have received little mention in the literature apart from a reference to the separation of nitrogen compound types from hydrotreated shale oil products by adsorption chromatography on basic and neutral alumina and the identification of pyridine, pyrrole and amide fractions by infrared (IR) spectroscopy[17]. The nitrogen compounds in hydrotreated shale oil are present in only trace amounts and co-elute with aromatic compounds on gas chromatographic (GC) analysis. In order to obtain enough material for characterisation, a system is required for concentrating nitrogen compounds from a large excess of aromatic and aliphatic compounds. We describe here a simple two-step method for the isolation of nitrogen compounds from hydrotreated shale oil. The first step is the concentration of nitrogen compounds and polyaromatic hydrocarbons from the oil by open-column chromatography, and the second is the separation of the two classes by preparative HPLC. Individual compounds may then be resolved and identified by gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Instrumentation

Preparative HPLC. Two Altex 110 metering pumps were coupled in parallel to give a constant flow-rate up to 20 ml/min. The detectors were an Hitachi 155 UV absorption detector operating at 254 nm with an analytical cell of 10-mm path-length and a Waters R-401 differential refractometer connected in series. An Altex 905-42 injector modified with a 1-ml loop was used.

The column was 12.7 mm O.D. (46 cm × 10.2 mm I.D.) 316 stainless-steel tubing terminating in 12.7–1.59 mm Swagelok unions fitted with 5 μm frit. The column was slurry packed with amino bonded-phase using a column packer at 48 MPa.

Analytical HPLC. The HPLC system consisted of a Waters M 6000 A pump, a Waters 450 UV absorption detector operating at 254 nm, a Waters 10-μm μBondapak NH_2 30 cm × 3.9 mm I.D. column or a 10-μm μBondapak CN 30 cm × 3.9 mm I.D. column.

UV and IR spectrophotometry. UV analyses were on a Cary 17 UV spectrophotometer and IR analyses on a Perkin-Elmer 283 IR spectrophotometer.

GC–MS. GC–MS was used for the identification of specific nitrogen compounds. A Varian 2700 chromatograph was interfaced with a Du Pont 21-491B double-focusing magnetic sector mass spectrometer/Nova 3 data system via a glass-jet maintained at 250°C. Approximately 1-μl injections were made onto a 25-m SGE

SE-30 glass SCOT capillary column. Temperature was programmed from 80 to 280°C at 6°C/min unless otherwise stated. Mass spectral scans were collected at 2 sec per decade of mass over the range 40–500 a.m.u., using 70-eV electron-impact ionisation. Compounds were identified by comparison with literature mass spectra from standard sources[18,19]

Materials

Shale oils. Hydrotreated shale oils derived from the Julia Creek oil shale (Toolebuc Formation, Queensland, Australia) were provided by CSR and contained *ca.* 85 ppm nitrogen.

Standard mixture. For open-column chromatography (mixture 1): decane (1.97 *M*), decalin (2.03 *M*), tetrahydronaphthalene (0.31 *M*), indan (0.34 *M*), phenanthrene (0.1 *M*), pyrene (0.05 *M*), pyridine (0.02 *M*), isoquinoline (0.01 *M*), carbazole (0.01 *M*), myristonitrile (0.01 *M*), valeramide (0.01 *M*) and phenol (0.05 *M*) in hexadecane.

For analytical and preparative HPLC (mixture 2): biphenyl (0.06 *M*), phenanthrene (0.06 *M*), pyrene (0.05 *M*), benzonitrile (0.19 *M*), carbazole (0.12 *M*), pyridine (0.25 *M*), isoquinoline (0.16 *M*) and benzamide (0.08 *M*) in dichloromethane with 10% (v/v) methanol.

Amino bonded-phase for preparative HPLC. 35 g of LiChroprep Si 60 5–20 μm (Merck) was stored over a saturated lithium chloride solution in a desiccator for 24 h, then 18 ml of triethoxyaminopropylsilane in 180 ml of dried hexane was added with stirring. The mixture was refluxed for 30 min under dried nitrogen with mechanical stirring. The unreacted reagent and the solvent were decanted. The bonded silica was washed with sodium-dried benzene (3 ×), dichloromethane (3 ×), methanol (2 ×), water (2 ×), methanol (2 ×) and dichloromethane (2 ×) by either decantation or filtration. The final product was dried at 35°C for 12 h. Yield 37 g.

Analysis: C, 4.97; H, 1.31; N, 1.72% (w/w), giving a calculated surface coverage[20,21] of 3.3 μmol/m^2 (specific surface of silica was 500 m^2/g).

Solvents. All solvents were purified by fractional distillation and their purities confirmed by GC–MS examination of a 100:1 concentrate. The hexane was freed of benzene by stirring with 18 *M* sulphuric acid for 12 h, washing with 10% sodium carbonate then water and drying over calcium chloride prior to distillation.

Procedure

Open column chromatography. Approx. 4 g of hydrotreated shale oil were dissolved in 20 ml of hexane, then placed on a 40 × 1.2 cm I.D. glass column containing 50 g of neutral alumina (Brockman grade 1, BDH) activated at 350°C for 12 h. The column was pressurised to 10 kPa with nitrogen gas. Hydrocarbons were eluted in 300 ml hexane and the nitrogen compounds in 450 ml of 1% (v/v) ethanol in chloroform.

Preparative HPLC. Nitrogen compounds concentrate (*ca.* 100 mg) was dissolved in 0.5–1 ml of dichloromethane and transferred into the injector with a syringe. The preparative column was eluted with hexane, hexane–dichloromethane (10:3, v/v), dichloromethane–acetonitrile (20:1, v/v) with solvent changes being made manually at the retention times in Figs. 2 and 3.

Extraction of basic nitrogen compounds. Approx. 20 g of hydrotreated oil was dissolved in 40 ml of hexane. The solution was extracted with 2 × 20 ml of 10%

sulphuric acid then with 2 × 20 ml of 20% sulphuric acid. The aqueous acid extracts were combined, washed with 40 ml of dichloromethane, 2 × 40 ml of hexane, cooled and the pH adjusted to 12 with 120–130 ml of 4 *N* sodium hydroxide solution. The bases thus regenerated were recovered by back extraction with 40 ml of dichloromethane then 2 × 20 ml of dichloromethane. The combined extracts were washed with 2 × 40 ml of water, dried over anhydrous magnesium sulphate, filtered and the solvent removed under reduced pressure (4.7 kPa).

RESULTS AND DISCUSSION

Separation of model compounds

Fig. 1 shows the flow diagram for the analytical scheme. A synthetic mixture was used to confirm that the preliminary open alumina column had the ability to eliminate more than 97% of saturated and aromatic hydrocarbons plus acidic compounds without loss of basic or neutral nitrogen compounds. The mixture contained decane, hexadecane, decalin, tetrahydronaphthalene, indan, phenanthrene, pyrene, pyridine, isoquinoline, carbazole, myristonitrile, valeramide and phenol. The stated procedure eluted the saturated hydrocarbons, aromatic hydrocarbons and most of the polycyclic aromatic hydrocarbons (PAHs) with the hexane fraction. The other fraction contained all the nitrogen compounds plus PAHs. Phenol was held by the column.

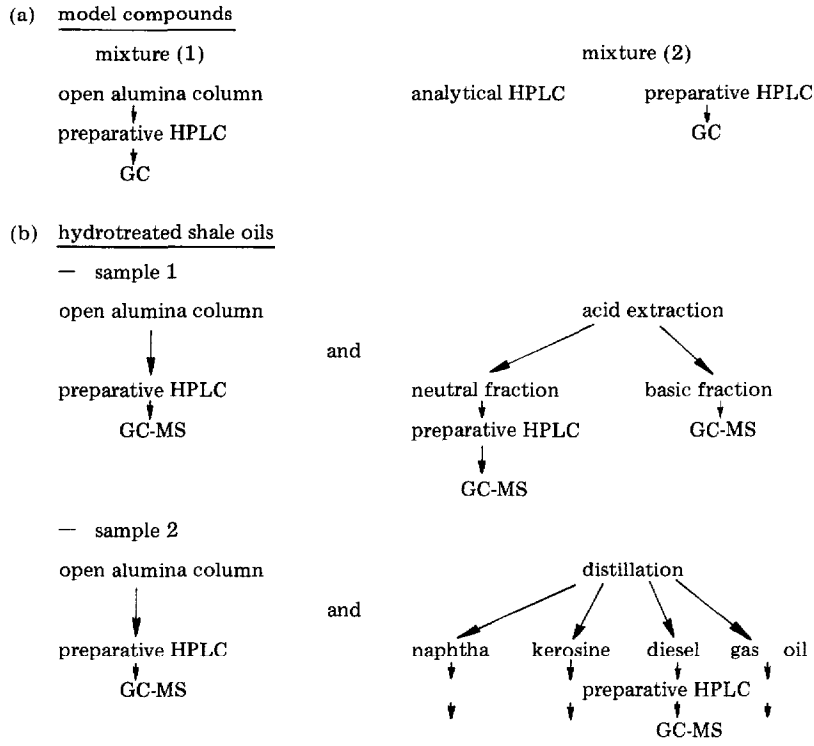

Fig. 1. Flow diagram of analytical scheme for fractionation of model compounds mixture and hydrotreated shale oils.

In order to choose a suitable stationary phase for preparative HPLC, an analytical separation was made of a mixture of biphenyl, pyrene, phenanthrene, benzonitrile, carbazole, pyridine, isoquinoline and benzamide using amino-bonded and cyano-bonded phases. The amino column gave better (baseline) resolution, using the solvent sequence hexane, hexane–dichloromethane (1:1, v/v), dichloromethane–acetonitrile (10:1, v/v). By using a slightly less polar solvent system [hexane, hexane–dichloromethane (10:3, v/v), dichloromethane–acetonitrile (20:1, v/v)], 56 mg of the model compound mixture in 0.4 ml solvent were separated on the preparative HPLC column into PAH, nitrile, pyrrole, pyridine and amide fractions (Fig. 2). After removal of solvent, each fraction from the preparative HPLC was weighed and analysed by GC; the recovery of each compound from the HPLC column was better than 90%.

The capacity of the preparative HPLC column was explored using different loadings. Although 0.4 ml of the standard mixture was well separated (Fig. 2), when the loading was doubled, resolution between pyridine and isoquinoline was lost. However, the separation between different groups of compounds was maintained.

Analysis of hydrotreated oils

The hydrotreated oil samples were separated in two steps; open alumina column then HPLC (Fig. 1). After removing the saturated hydrocarbons and most of the aromatics with hexane, the nitrogen compounds mixed with PAHs were eluted with chloroform (chromatographic time 90 min). The fraction containing the nitrogen compounds was concentrated and separated into seven sub-fractions by preparative HPLC using the same solvent systems and elution parameters as for the model compounds (chromatographic time 2.5 h). An analytical cell was preferred for mon-

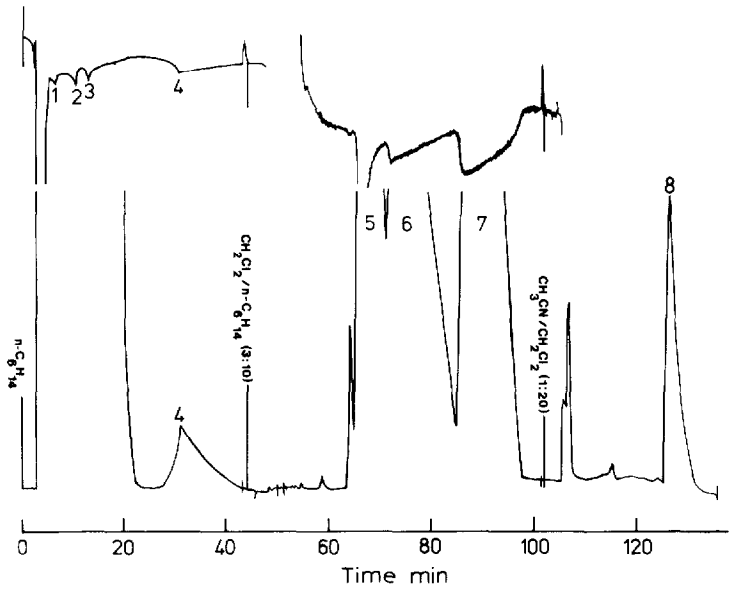

Fig. 2. Preparative HPLC chromatogram of 56 mg of model compounds mixture. 1 = Biphenyl, 2 = phenanthrene, 3 = pyrene, 4 = benzonitrile, 5 = carbazole, 6 = pyridine, 7 = isoquinoline, 8 = benzamide. Upper trace, RI detector; lower trace, UV detector (254 nm).

itoring the minor components although a preparative cell may provide an on-scale HPLC chromatogram and adequate sensitivity for more abundant constituents. After removal of solvent, each sub-fraction was weighed and characterised by IR, UV and GC–MS.

Sample 1. The HPLC trace (UV detector) for sample 1 is shown in Fig. 3. Although both UV and refractive-index detectors were used, the latter did not provide any additional information. This is because the nitrogen compounds in this hydrotreated oil were aromatic. Had some of the nitrogen compounds been aliphatic, these would have been detectable by RI but not by a UV detector operating at 254 nm. The mass of each sub-fraction from sample 1 is shown in Table I. Sub-fractions 1, 2, 4, 5, 6 and 7 were identified by GC–MS (Fig. 4; Table II). Sub-fractions 3 and 8 were monitored for nitrile and amide respectively using UV and IR spectroscopy, but neither of these functional groups were detected.

The major nitrogenous compounds remaining in sample 1 of hydrotreated shale oil were pyridines, indoles, carbazoles, dihydroindoles, tetrahydroquinolines and hexahydrocarbazoles; nitriles and amides were not detected. In order to find the relative amounts of basic and neutral nitrogen compounds, the basic fraction was isolated by extraction of a further portion of sample 1 with aqueous acid and was characterised by GC–MS without further purification (Fig. 4; Table I); it contained mainly pyridines, tetrahydroquinolines and dihydroindoles and accounted for 34% of the total nitrogen compounds. The neutral fraction was separated into seven sub-fractions as before, but these were now not well resolved by GC–MS, despite the loss of GC peaks resulting from the removal of the basic nitrogen compounds by aqueous acid extraction. This suggests that some components of the hydrotreated oil have been isomerised/polymerised by the acid extraction.

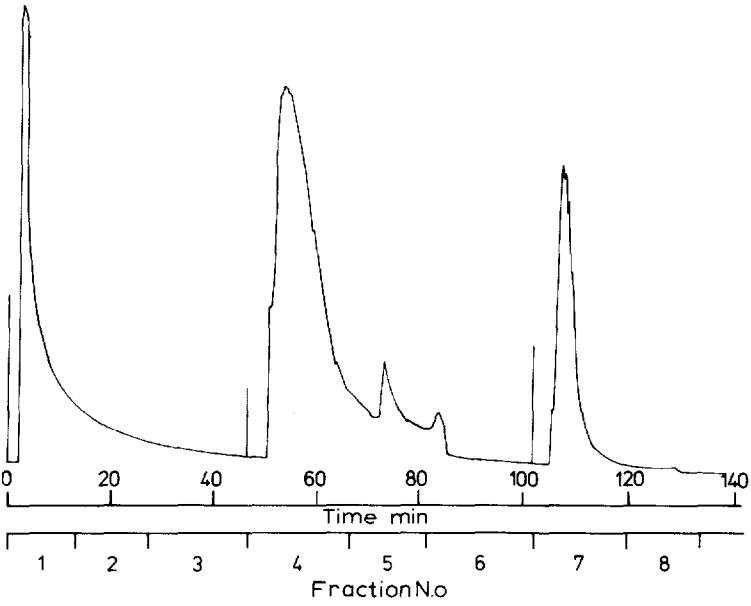

Fig. 3. Preparative HPLC chromatogram of nitrogenous compound fraction from open-column chromatography of 20 g of sample 1. UV detection at 254 nm.

TABLE I

SUB-FRACTIONS* FOR SAMPLE 1

	Sub-fraction						
	1	*2*	*3*	*4*	*5 and 6*	*7*	*8*
Before acidic washing	2150	100	< 50	700	350	700	< 50
After acidic washing	1900	100	< 50	600	250	350	< 50

* Expressed as ppm of original oil sample.

Sample 2. The identical separation procedure (but without acid wash) was applied to a second hydrotreated shale oil prepared from the same shale oil using a different catalyst. The GC–flame ionisation detection (FID) traces of sub-fractions 4, 5 and 6 from HPLC of sample 2 are shown in Fig. 5 and MS of fractions 1–6 in Table III. Sub-fractions 7 and 8 were too poorly resolved to be identified by GC–MS. However, IR excluded the presence of amides. The major nitrogen compounds in sample 2 were benzoquinolines and dihydrobenzocarbazoles *i.e.* less reduced than

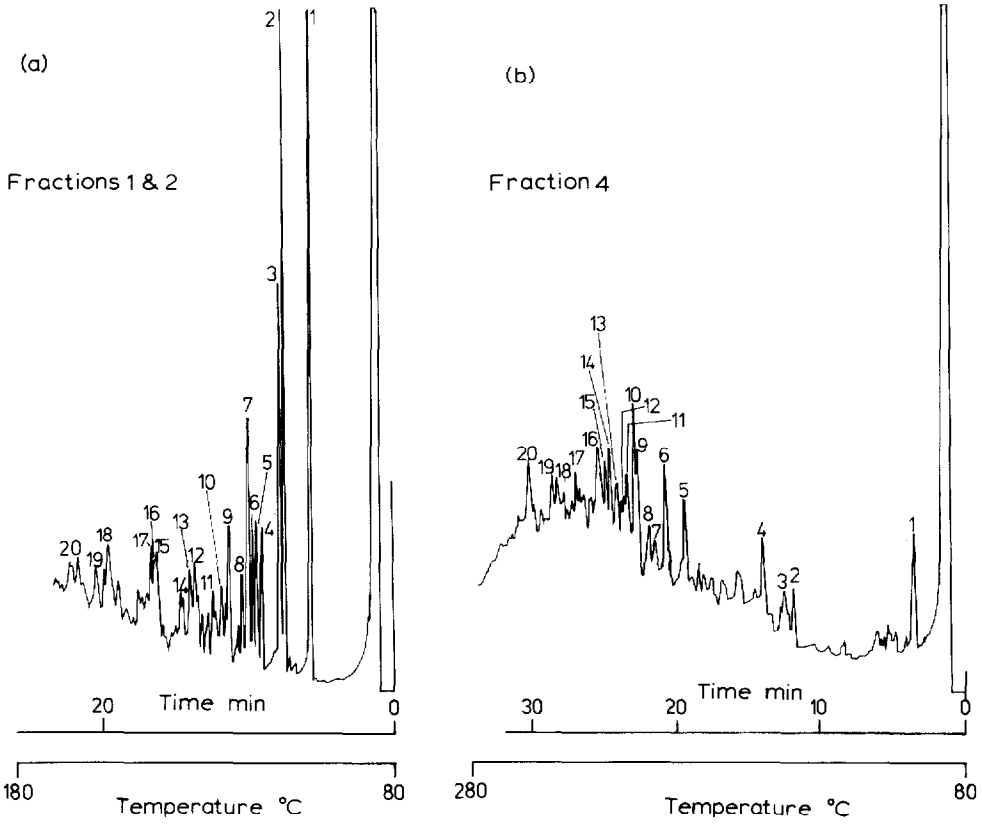

Fig. 4.

(*Continued on p. 362*)

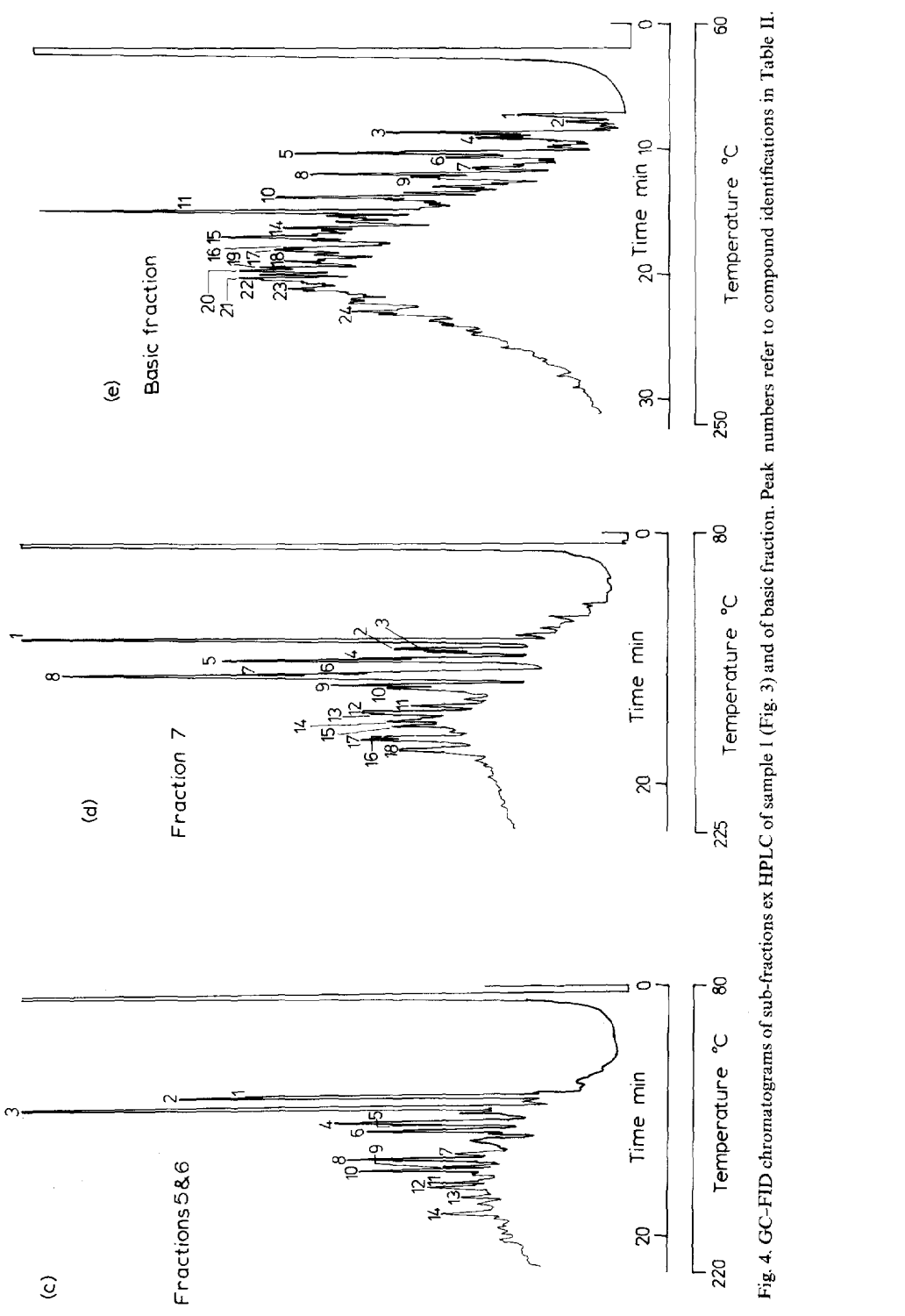

Fig. 4. GC–FID chromatograms of sub-fractions ex HPLC of sample 1 (Fig. 3) and of basic fraction. Peak numbers refer to compound identifications in Table II.

TABLE II

SAMPLE 1: MS IDENTIFICATION OF GC PEAKS FOR HPLC SUB-FRACTIONS

*Sub-fraction**	*Peak No.*	*Name or possible type*	*m/z*
1 and 2	1	Naphthalene	128
	2, 3	Methylnaphthalene	142
	4	Biphenyl	154
	5	Ethylnaphthalene + methylbiphenyl	156 + 168
	6	C_2-Alkylnaphthalene	156
	7	Dimethylnaphthalene	156
	8	C_2-Alkylnaphthalene	156
	9	Methylbiphenyl	168
	10, 11	C_3-Alkylnaphthalene	170
	12	Dimethylbiphenyl	182
	13	C_2-Alkylbiphenyl	182
	14	C_2-Alkylbiphenyl + C_4-alkylnaphthalene	182 + 184
	15	C_3-Alkylbiphenyl	196
	16	Methylfluorene	180
	17	C_3-Alkylbiphenyl	196
	18	C_4-Alkylbiphenyl + C_2-alkylfluorene	210 + 194
	19	C_4-Alkylbiphenyl	210
	20	C_5-Alkylbiphenyl	224
4	1	Dimethylethylpyridine	135
	2, 3	Dimethylindole	145
	4	C_3-Alkylindole	159
	5	Carbazole	167
	6, 7	Methylcarbazole	181
	8–12	C_2-Alkylcarbazole	195
	13–15	C_3-Alkylcarbazole	209
	16	C_3- and C_4-alkylcarbazole	209 + 223
	17	C_4-Alkylcarbazole	223
	18	C_5- and C_6-alkylcarbazole	237 + 251
	19	C_6-Alkylcarbazole	251
5 and 6	1, 2	C_3-Alkyldihydroindole	161
	3	C_4-Alkyldihydroindole	175
	4, 5	C_5-Alkyldihydroindole	189
	6	C_4-Alkyldihydroindole	175
	7	C_6-Alkyldihydroindole	203
	8	C_5-Alkylindole	189
	9, 10	C_6-Alkylindole	203
	11	C_7-Alkylindole	217
	12	Carbazole	167
	13	C_8-Alkylindole	231
	14	Methylcarbazole	181
7	1, 2, 3	C_2-Alkyltetrahydroquinoline	161
	4	C_3-Alkyltetrahydroquinoline	175
	5	Ethyltetrahydroquinoline	161
	6	C_4-Alkyltetrahydroquinoline	189
	7, 8	C_3-Alkyltetrahydroquinoline	175
	9	C_3- and C_4-alkyltetrahydroquinoline	175 + 189
	10	C_4-Alkyltetrahydroquinoline	189
	11	Methylhexahydrocarbazole	187

(*Continued on p. 364*)

TABLE II (*continued*)

*Sub-fraction**	*Peak No.*	*Name or possible type*	*m/z*
	12, 13	C_2-Alkylhexahydrocarbazole	201
	14, 15, 16, 17	C_2- and C_3-alkylhexahydrocarbazole	201 + 215
	18	C_3- and C_4-Alkylhexahydrocarbazole	215 + 229
Basic N	1	C_2-Alkylpyridine	107
	2	C_4-Alkylpyridine	135
	3, 4	C_3-Alkylpyridine	121
	5, 6	C_4-Alkylpyridine	135
	7–9	C_5-Alkylpyridine	149
	10	C_2-Alkyltetrahydroquinoline	161
	11, 12	C_4-Alkyltetrahydroquinoline	189
	13	C_5-Alkyltetrahydroquinoline	203
	14	C_4-Alkyltetrahydroquinoline	189
	15	C_5-Alkyldihydroindole	189
	16–18	C_6-Alkyldihydroindole	203
	19–22	C_7-Alkyldihydroindole	217
	23	C_7-Alkylindole	215
	24	C_8-Alkylindole	229

* See Fig. 4.

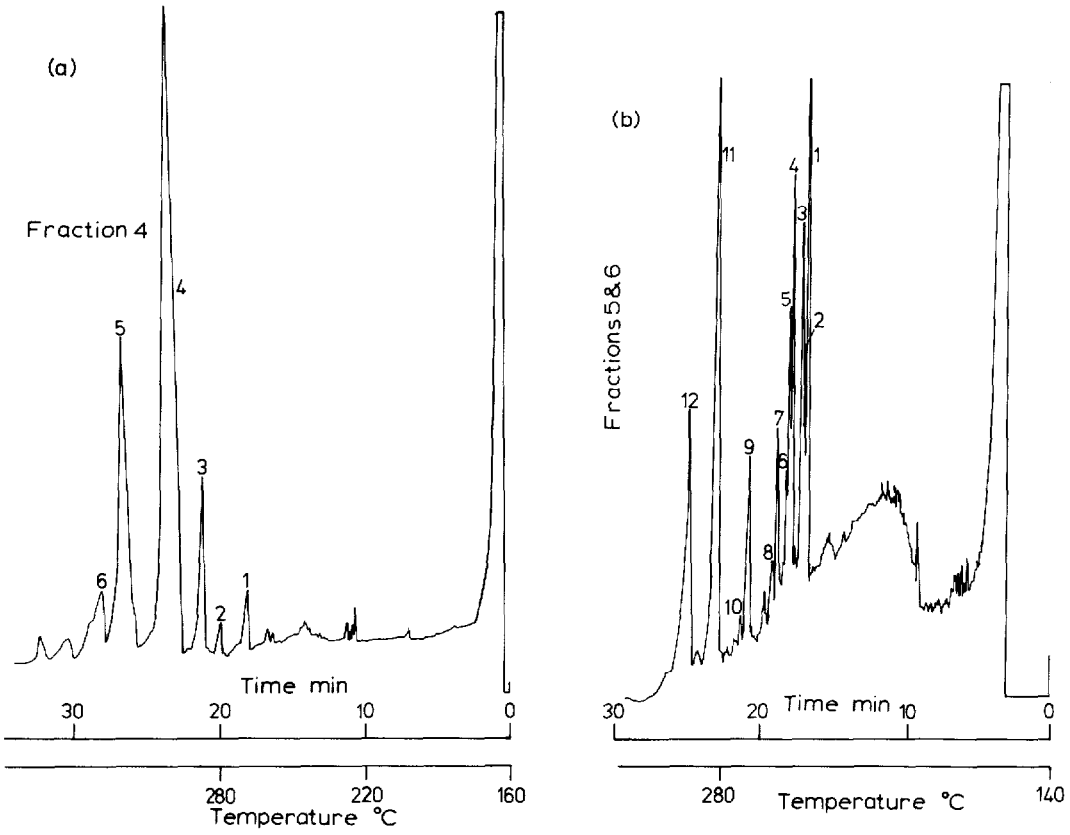

Fig. 5. GC–FID chromatograms of sub-fractions 4, 5 and 6 ex HPLC of sample 2. Peak numbers refer to compound identifications in Table III.

TABLE III

SAMPLE 2: MS IDENTIFICATION OF GC PEAKS OF HPLC SUB-FRACTIONS

*Sub-fraction**	*Peak No.*	*Name or possible type*	*m/z*
1	1	Methylfluorene	180
	2	C_2-Alkylfluorene	194
	3	C_3-Alkylfluorene	208
	4	Phenylnaphthalene	204
	5	Pyrene	202
	6	Methylphenylnaphthalene	218
	7, 8	Methylpyrene	216
	9, 10	C_2-Alkylpyrene	230
	11–14	C_3-Alkylpyrene	244
	15	C_4-Alkylpyrene	258
	16	Methylbenzophenanthrene	242
	17	C_2-Alkylbenzophenanthrene	256
	18	C_3-Alkylbenzophenanthrene	270
2	1	Benzophenanthrene	228
	2, 3	Methylbenzophenanthrene	242
	4, 5	C_2-Alkylbenzophenanthrene	256
3	1	Perylene	252
	2	Methylperylene	266
	3, 4	Dimethylperylene	280
	5, 6	Dibenzanthracene	278
	7	Benzoperylene	276
	8	Methylbenzperylene	290
4	1	Methylperylene	266
	2	Dimethylperylene	280
	3	Benzchrysene or dibenzanthracene	278
	4	Benzoperylene	276
	5, 6	Methylbenzoperylene	290
5 and 6	1, 2	C_2-Alkylbenzoquinoline	207
	3	C_3-Alkylbenzoquinoline	221
	4	C_4-Alkylbenzoquinoline	235
	5	Methyldihydrobenzocarbazole	233
	6	C_2-Alkyldihydrobenzocarbazole	247
	7	C_5-Alkylbenzoquinoline	249
	8, 9	C_2-Alkyldihydrobenzocarbazole	247
	11	C_5-Alkylhexahydrofluorenone	256
	12	C_6-Alkylhexahydrofluorenone	270

* See Fig. 5.

the corresponding ring systems in sample 1. In addition, some oxygen compounds were detected and tentatively identified. These results indicate that different hydrogenation conditions may change greatly the relative proportions of different nitrogen compounds remaining after hydrotreatment and show that the detailed identification of residual nitrogen compounds can be used to probe catalyst activity.

Sample 2 was distilled to give the following fractions: naphtha less than 190°C, kerosine 190–230°C, diesel 230–320°C and gas oil greater than 320°C, each of which

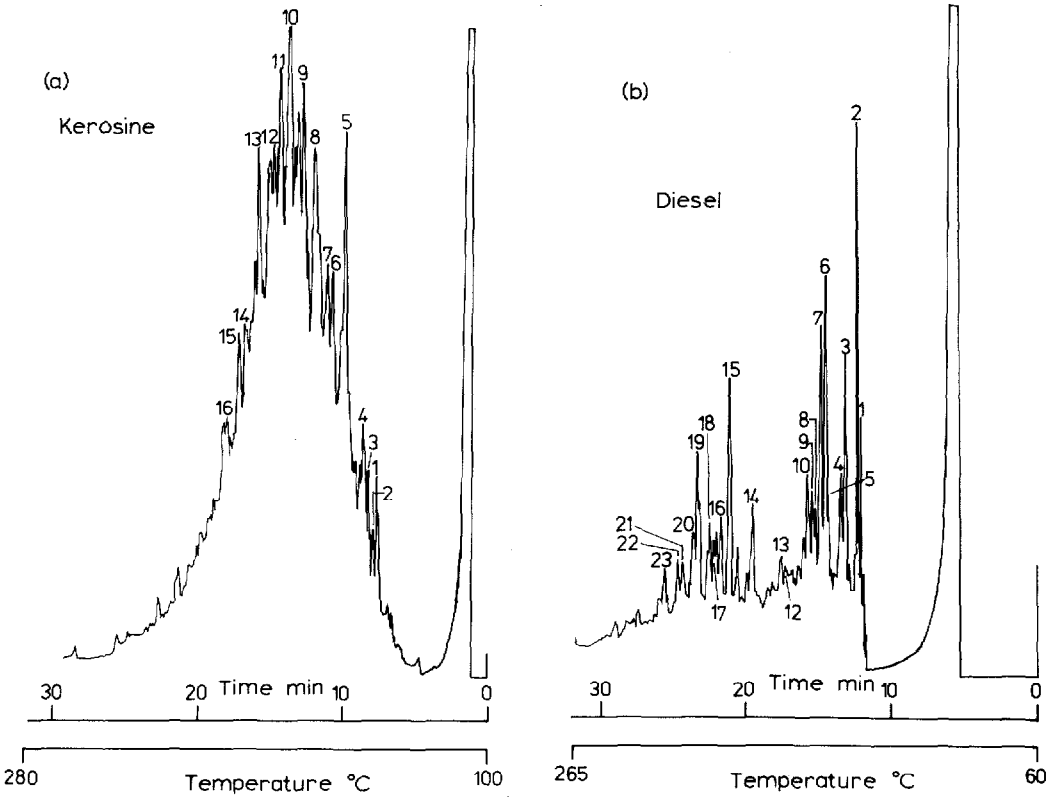

Fig. 6. GC–FID chromatograms of sub-fraction 4 from kerosine and diesel distillation fractions of sample 2. Peak numbers refer to compound identifications in Table V.

was separated and analysed by the above procedure. The masses of each HPLC sub-fraction are listed in Table IV; IR and GC–MS traces showed that all the compounds detected in the whole hydrotreated shale oil (sample 2) were found in the respective distillation fractions. However, some compounds which appeared in sub-fraction 4 of the kerosine and diesel had not been resolved/detected in the whole hydrotreated shale oil. The GC–FID traces for sub-fraction 4 of these two fractions are shown in Fig. 6 and identifications in Table V. These oxygen compounds prob-

TABLE IV

SUB-FRACTIONS* OF SAMPLE 2 AND DISTILLED FRACTIONS FROM SAMPLE 2

	Sub-fraction (ppm)					
	1	*2*	*3*	*4*	*5 and 6*	*7 and 8*
Whole hydrotreated oil	9300	1650	225	750	750	510
Kerosine fraction	120		0	80		120
Diesel fractions	970	30	0	30	30	200
Gas oil fraction	21,330	1000	330	670	670	670

* Expressed as ppm of original oil sample or distillation fraction.

TABLE V

MS IDENTIFICATION OF GC PEAKS FOR HPLC SUB-FRACTION 4 OF (a) KEROSINE AND (b) DIESEL DISTILLATION FRACTIONS

*(a) Peak No.**	*Name or compound type*	*m/z*	*(b) Peak No.**	*Name or compound type*	*m/z*
1	Methylindanone	146	1	Methyltetralone	160
2	Tetralone	146	2–4	C_2-Alkyltetralone	174
3, 4	C_2-Alkylindanone	160	5–7	C_3- and C_4-alkyl-tetralone	188 + 202
5	Dimethylindanone	160	8	C_4- and C_5-alkyl-tetralone	202 + 216
6–8	Methyltetralone	160	9	C_5-Alkyltetralone	216
9–11	C_2-Alkyltetralone	174	10	C_6-Alkyltetralone	230
12, 13	C_3-Alkyltetralone	188	11	Methylhexahydro-fluorenone	200
14	Fluorenone	180	12	C_2-Alkylhexahydro-fluorenone	214
15–17	Methylfluorenone	194	13, 14	Methylfluorenone	194
18–21	C_2-Alkylfluorenone	208	15	C_2-Alkylfluorenone	208
22, 23	C_3-Alkylfluorenone	222	16	C_4-Alkylhexahydro-fluorenone	242

* See Fig. 6.

ably co-eluted with and were obscured by the relatively large amount of high-molecular-weight PAHs present in sub-fraction 4 of whole sample 2. The preparative HPLC showed that the naphtha fraction was almost free of nitrogen and oxygen compounds. The proportion of heterocyclic compounds increased with increasing boiling point of the distillation fractions.

CONCLUSION

The technique described is well suited to analysis of trace amounts of nitrogen compounds in hydrotreated shale oil. Preparative HPLC provides an effective separation in a short time. The preparative HPLC column can be fabricated in the laboratory and is reuseable. The running cost for such a system is low and it would be affordable by most laboratories. The disposable open column is essential to protect the preparative HPLC column and also to raise the ratio of nitrogen compounds to hydrocarbons. The separation scheme described may not necessarily be applied to the fractionation of crude shale oils into specific nitrogen compound types. This is because alkanones are present in some raw shale oils[22] and these are likely to form Schiff bases with the primary amino groups of the stationary phase, thereby degrading its performance. While it may be possible to regenerate the column by hydrolysing the Schiff bases with aqueous acid[23], it would be preferable to remove the alkanones beforehand. A need for further development of an HPLC scheme is indicated in the case of crude shale oils.

ACKNOWLEDGEMENTS

We thank CSR Ltd. for financial support and for the provision of samples of hydrotreated shale oils. We are indebted to Messrs. J. Mandelson, R. Holdgate, B. Marcovich and A. Muradian for helpful information and discussions.

REFERENCES

1 B. A. Tomkins and C. H. Ho, *Anal. Chem.*, 54 (1982) 91–96.
2 P. Burchill, A. A. Herod and E. Pritchard, *J. Chromatogr.*, 246 (1982) 271–295.
3 J. F. McKay, J. H. Weber and D. R. Latham, *Anal. Chem.*, 48 (1976) 891–898.
4 G. K. Hartung and D. M. Jewell, *Anal. Chim. Acta*, 27 (1962) 219–232.
5 H. V. Drushel and A. L. Sommers, *Anal. Chem.*, 38 (1966) 19–28.
6 D. W. Later, M. L. Lee and B. W. Wilson, *Anal. Chem.*, 54 (1982) 117–123.
7 G. U. Dinneen, G. L. Cook and H. B. Jensen, *Anal. Chem.*, 30 (1958) 2026–2030.
8 G. K. Hartung and D. M. Jewell, *Anal. Chim. Acta*, 26 (1962) 514–527.
9 J. E. Schiller, *Anal. Chem.*, 49 (1977) 2292–2294.
10 D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong and D. L. Vassilaros, *Anal. Chem.*, 53 (1981) 1612–1620.
11 M. M. Boduszynski, R. J. Hurtubise and H. F. Silver, *Anal. Chem.*, 54 (1982) 372–375.
12 J. M. Schmitter, Z. Vajta and P. J. Arpino, in A. G. Douglas and J. R. Maxwell (Editors), *Advances in Organic Geochemistry, 1979*, Pergamon, Oxford, 1980, p. 67.
13 J. M. Schmitter, H. Colin, J. L. Excoffier, P. Arpino and G. Guiochon, *Anal. Chem.*, 54 (1982) 769–772.
14 C. D. Ford and R. J. Hurtubise, *Anal. Lett.*, 13 (1980) 485–496.
15 H. S. Hertz, J. M. Brown, S. N. Chesler, F. R. Guenther, L. R. Hilpert, W. E. May, R. M. Parris and S. A. Wise, *Anal. Chem.*, 52 (1980) 1650–1657.
16 A. P. Toste, D. S. Sklarew and R. A. Pelroy, *J. Chromatogr.*, 249 (1982) 267–282.
17 C. D. Ford, S. A. Holmes, L. F. Thompson and D. R. Latham, *Anal. Chem.*, 53 (1981) 831–836.
18 *Eight Peak Index of Mass Spectra*, Mass Spectrometry Data Centre, Reading, 1974, 2nd ed.
19 E. Stenhagen, S. Abrahamsson and F. W. McLafferty, *Registry of Mass Spectral Data*, Wiley, New York, 1974.
20 G. E. Berendsen, K. A. Pikaart and L. de Galan, *J. Liq. Chromatogr.*, 3 (1980) 1437–1464.
21 H. Engelhardt and G. Ahr, *Chromatographia*, 14 (1981) 227–233.
22 R. Regtop, P. T. Crisp and J. Ellis, *Fuel*, 61 (1982) 185–192.
23 D. Karlesky, D. C. Shelly and I. Warner, *Anal. Chem.*, 53 (1981) 2146–2147.