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SEPARATION OF AROMATIC SPECIES IN COAL-DERIVED OILS BY ALUMINA ADSORPTION CHROMATOGRAPHY

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SUMMARY

An alumina adsorption chromatographic method for separating aromatic species in petroleum heavy ends into mono- (single ring), di- (two rings) and poly-aromatic (≥ 3 rings) compounds has been modified to improve the separation of coal-derived oils (boiling point range *ca.* 250–450°C). The overlap of the different aromatic species that occurs for coal-derived oils has been reduced by lowering the polarity of the eluents used. The fractionation thus achieved aids the characterization of coal-derived oils by gas chromatographic–mass spectrometric and nuclear magnetic resonance methods.

INTRODUCTION

Solvents used in direct coal liquefaction processes are complex mixtures of aromatic and hydroaromatic compounds boiling in the range *ca.* 250–450°C^{1–3}. In characterization studies, it is advantageous to fractionate these oils by aromatic ring size, for example, to aid gas chromatography–mass spectrometry (GC–MS) for measuring individual compounds⁴ and nuclear magnetic resonance (NMR) for investigating hydroaromatic groups^{3,5}. Fractionation can be achieved by either alumina adsorption chromatography⁶ or by high-performance liquid chromatography (HPLC) using, for example, NH₂-bonded silica columns^{7–9}. However, HPLC is generally only semi-preparative and where amounts of greater than *ca.* 50 mg are required, for example for NMR, adsorption chromatography has to be used.

The alumina adsorption chromatographic method developed by Hirsch *et al.*⁶ for separating petroleum heavy ends into mono- (single ring), di- (two rings) and poly-aromatic (≥ 3 rings) compounds has found widespread use and, as well as petroleum heavy ends^{6,10}, it has been applied to tar sand bitumen¹¹ and oils from coal liquefaction processes¹². However, our attempts to separate model compounds and coal-derived oils using this method have not been entirely satisfactory in that significant overlap of mono-, di- and polyaromatic compounds occurred; inspection of the analytical data reported by Hirsch *et al.*⁶ suggests that these workers also experienced some overlap of the different aromatic types. In this study, the elution scheme devised by Hirsch *et al.* has been modified to give more satisfactory separations for coal-derived oils. To demonstrate the improved method, a synthetic mixture of model compounds and the

aromatic material in two coal-derived oils, namely hydrogenated anthracene oils (HAOs; anthracene oils are mainly neutral material derived from coal-tar), have been separated and the compositions of the resultant fractions assessed using ^1H NMR spectroscopy and gas chromatography (GC).

EXPERIMENTAL

Separations

The aromatics in the HAOs were first separated from the saturated and polar compounds using silica gel adsorption chromatography¹³. These and the mixture of model compounds were then separated on alumina in 25- or 50-cm glass columns of about 1 cm I.D.

Neutral alumina (Woelm, activity grade super 1, 90% > 60 μm) was used after activation at 400°C for 16 h, being stored in an air oven at 160°C to exclude moisture. The standard Brockmann test¹⁴ was used to confirm the activity of the alumina.

After pre-wetting the alumina with *n*-pentane and applying neat aromatic material (*ca.* 0.5 and 1.0 g for the 25- and 50-cm columns, respectively, *i.e.* alumina to sample mass ratio *ca.* 70:1), the columns were eluted with the benzene-*n*-pentane and dichloromethane-*n*-pentane mixtures detailed in Table I. The eluents used by Hirsch *et al.*⁶ (first column, Table I) gave unsatisfactory results and therefore less polar eluents were tried (second column, Table I); the eluent volumes used are similar to those in the Hirsch *et al.* scheme (Table I). The eluents were divided into either two or three portions and aromatic fractions recovered by evaporating the solvent on a water-bath.

TABLE I
ELUENTS USED FOR ALUMINA SEPARATIONS

<i>Eluate</i>	<i>Hirsch et al.</i> ⁶ <i>method</i>	<i>This study</i>
Eluate 1 (monoaromatic compounds)	Benzene- <i>n</i> -pentane (5:95) (50* or 120** cm ³)	Benzene- <i>n</i> -pentane (3:97)*** (50* or 120 ** cm ³) <i>n</i> -pentane** (180 cm ³)
Eluate 2 (diaromatic compounds)	Benzene- <i>n</i> -pentane (15:85) (50* or 120** cm ³)	Benzene- <i>n</i> -pentane (10:90) Benzene- <i>n</i> -pentane (7:93) Dichloromethane- <i>n</i> -pentane (3:97)*** (60* or 150** cm ³)
Eluate 3 [§] (polyaromatic compounds)	Benzene-diethyl ether-methanol (25* or 60** cm ³)	Dichloromethane- <i>n</i> -pentane (20:80) or dichloromethane (60* or 150** cm ³)

* 25-cm column.

** 50-cm column.

*** Most satisfactory for elution of compound class (see text).

[§] Elution of polyaromatic compounds is relatively straightforward and polar eluents containing alcohols are required only if acidic or basic compounds also have to be eluted.

Analyses

The compositions of the aromatic fractions from both the mixture of model compounds and the HAOs were assessed by ^1H NMR spectroscopy using a Hitachi-Perkin-Elmer R24B instrument and [^2H]chloroform as solvent. Monoaromatics give aromatic

hydrogen resonances in the chemical shift range 6.5–7.2 ppm, diaromatics in the range 7.1–8.0 ppm and polyaromatics in the range 7.4–8.7 ppm.

GC was used to provide detailed information on the composition of the HAO fractions. A Carlo-Erba 4160 Fractovap gas chromatograph, equipped with a 25-m OV-1 wall-coated open tubular column, temperature-programmed from 80 to 320°C at 5°C/min, and a flame-ionization detector, was used. Peak identifications were made either by using commercially available compounds or from the results of GC-MS analysis (Perkin-Elmer F17/Kratos MS-30 system).

RESULTS AND DISCUSSION

Separation of mono- and diaromatic compounds

The benzene-*n*-pentane (5:95) mixture used to elute monoaromatic compounds gave fractions containing some diaromatic compounds for both the synthetic mixture and the HAOs. For the mixture of model compounds, naphthalene and dibenzyl were found (Table II), while NMR showed the presence of diaromatics in the eluates from the HAOs. The ¹H NMR spectra of the two fractions (first and second half of the eluate) obtained from one of the HAOs are shown in Fig. 1a and b, where signals between 7.2 and 8.0 ppm, attributable to diaromatic compounds (mainly naphthalenes), are readily discernible in both parts of this eluate, although more prominent in the fraction obtained from the second half of the eluate. It was calculated from ¹H NMR that 20 and 50% of the diaromatic species in the HAOs were to be found in this eluate.

The less polar mixture benzene-*n*-pentane (3:97) proved to be much more satisfactory for eluting only monoaromatics. For the mixture of model compounds, only tetralin, *n*-octylbenzene and 1-8-octahydroanthracene were now eluted (see Table II). Also for the HAOs, the bulk of the monoaromatic compounds was found in the first halves of the benzene-*n*-pentane (3:97) eluates (see Table III) and the ¹H NMR spectra shown in Fig. 1a and b suggest that significant amounts of diaromatic species were not eluted by this mixture even in the second half of the eluates. Their absence was confirmed by GC analysis. Fig. 2a shows the chromatogram of the total monoaromatic fraction [whole of the benzene-*n*-pentane (3:97) eluate] from one of the oils. The major peaks in the chromatogram in Fig. 2a are due to octahydrophenanthrenes, alkyltetralins and decahydropyrenes. Although over 80% of this complex fraction was identified by GC-MS, no diaromatic compounds were found.

It was also possible to elute monoaromatic species from alumina with *n*-pentane alone. However, this was much more time consuming than using benzene-*n*-pentane (3:97). For example, the monoaromatics in the mixture of model compounds did not start to elute from the 50-cm column in the first ca. 60 cm³ of eluate, whereas 60 cm³ of benzene-*n*-pentane (3:97) eluted ≥60% of the monoaromatic species in the samples investigated.

Separation of di- and polyaromatic species

The benzene-*n*-pentane (15:85) mixture used in the Hirsch *et al.* scheme⁶ gave fractions containing both di- and polyaromatic compounds. For the mixture of model aromatic compounds, phenanthrene and pyrene were eluted (see Table II), while in the ¹H NMR spectra of the fractions obtained from the HAOs (see Fig. 3a) peaks due

TABLE 2
SUMMARY OF ELUTION BEHAVIOUR FOR THE MIXTURE OF MODEL COMPOUNDS

Aromatic compound		1st eluate		2nd eluate		3rd eluate:	
Type	Name	Proportion in mixture (% w/w)	Benzene-n-pentane (5:95)	Benzene-n-pentane (3:97)	Benzene-n-pentane (15:85)	Dichloromethane-n-pentane (3:97)*	dichloromethane-n-pentane (20:80)
					(a)	(b)	
Monoaromatics	Tetralin	14	x	x			
	n-Octylbenzene	11	x	x			
	1-8-Octahydroanthracene	10	x	x			
Diaromatics	Naphthalene	7	x		x	x	
	Diphenyl	8			x	x	
	Dibenzyl	10	x		x	x	
	Fluorene	9			x	x	x
	9,10-Dihydroanthracene	10			x	x	x
Polyaromatics	Phenanthrene	10			x	x	x
	Pyrene	11			x	x	x
	% (w/w) of mixture**	5.5	34	36	24	16	23

* (a) = First half of eluate; (b) second half of eluate.

** Normalized to 100%, yields >95%.

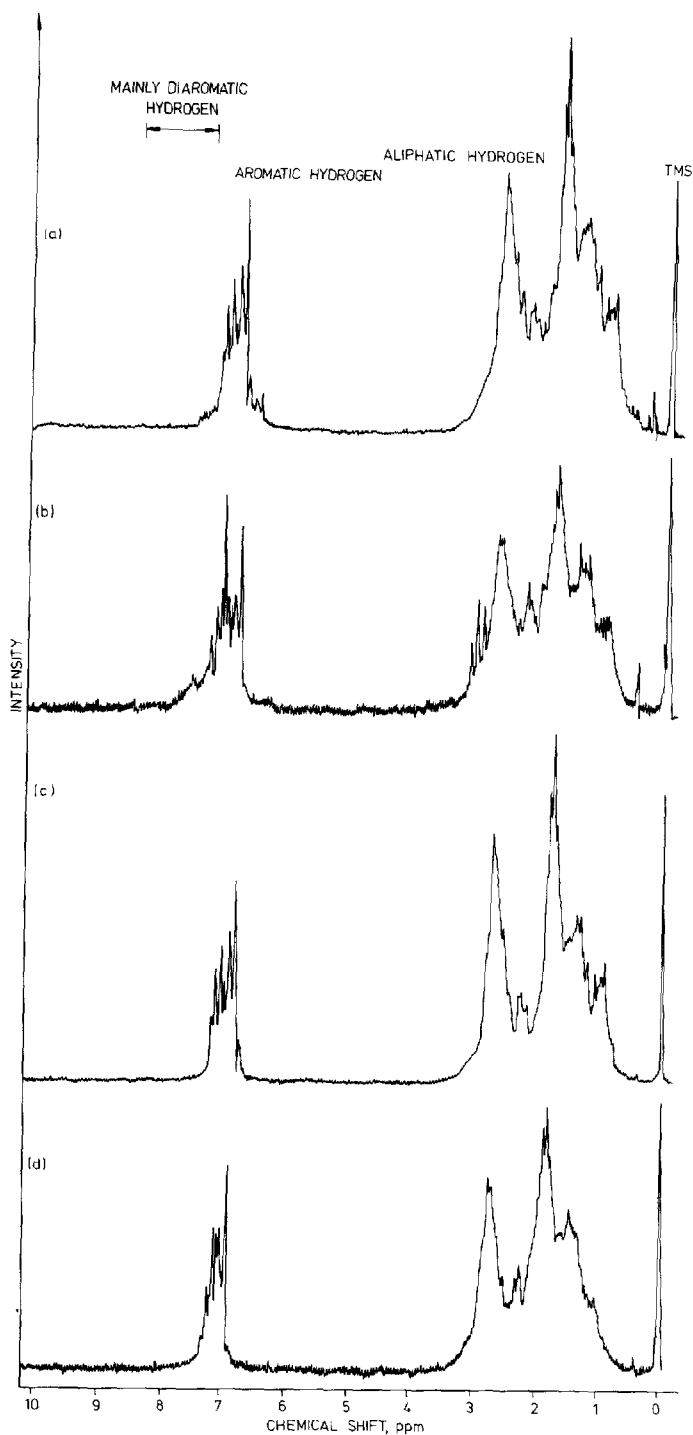


Fig. 1. ^1H NMR spectra of monoaromatic fractions from HAO (No. 1). (a) Benzene-*n*-pentane (5:95), fraction from first half of eluate; (b) benzene-*n*-pentane (5:95), fraction from second half of eluate; (c) benzene-*n*-pentane (3:97), fraction from first half of eluate; (d) benzene-*n*-pentane (3:97), fraction from second half of eluate.

TABLE 3
SUMMARY OF ALUMINA COLUMN SEPARATIONS CARRIED OUT ON COAL SOLVENT SAMPLES

Compound classes eluted	HAO No. 1									
	1st eluate		2nd eluate				3rd eluate: dichloromethane <i>n</i> -pentane (20:80), total eluate			
	Benzene <i>n</i> -pentane (5:95)	Benzene <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (15:85)*	Benzene <i>n</i> -pentane (7:93)**	Dichloromethane <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (15:85)*	Benzene <i>n</i> -pentane (10:90)**	Dichloromethane <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (10:90)**	Dichloromethane <i>n</i> -pentane (3:97)
	(a)***	(b)***	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
	Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)	
Monoaromatics	x	x	x	x	x	x	x	x	x	x
Diaromatics	x	x	x	x	x	x	x	x	x	x
Polyaromatics [§]	54	14	23	13	17	2	8	41	4	10
% (w/w) of aromatic fraction ^{§§}	68		36		37		8		32	
									31	
									32	

Compound classes eluted	HAO No. 2									
	1st eluate		2nd eluate				3rd eluate: dichloromethane <i>n</i> -pentane (20:80)			
	Benzene <i>n</i> -pentane (5:95)	Benzene <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (15:85)*	Benzene <i>n</i> -pentane (10:90)**	Dichloromethane <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (15:85)*	Benzene <i>n</i> -pentane (10:90)**	Dichloromethane <i>n</i> -pentane (3:97)	Benzene <i>n</i> -pentane (10:90)**	Dichloromethane <i>n</i> -pentane (3:97)
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
	Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)		Repeat (total eluate)	
Monoaromatics	x	x	x	x	x	x	x	x	x	x
Diaromatics	x	x	x	x	x	x	x	x	x	x
Polyaromatics [§]	64	11	57	11	11	16	7.5	22.5	7.5	27
% (w/w) of aromatic fraction ^{§§}	75		68		25		30		5	

* Following benzene *n*-pentane (5:95).

** Following benzene *n*-pentane (3:97).

*** (a) = First half or third of eluate; (b) = second half or third of eluate; (c) = last third of eluate.

§ Includes some fluorenes and dibenzofurans.

§§ Normalized to 100%, yields > 90%.

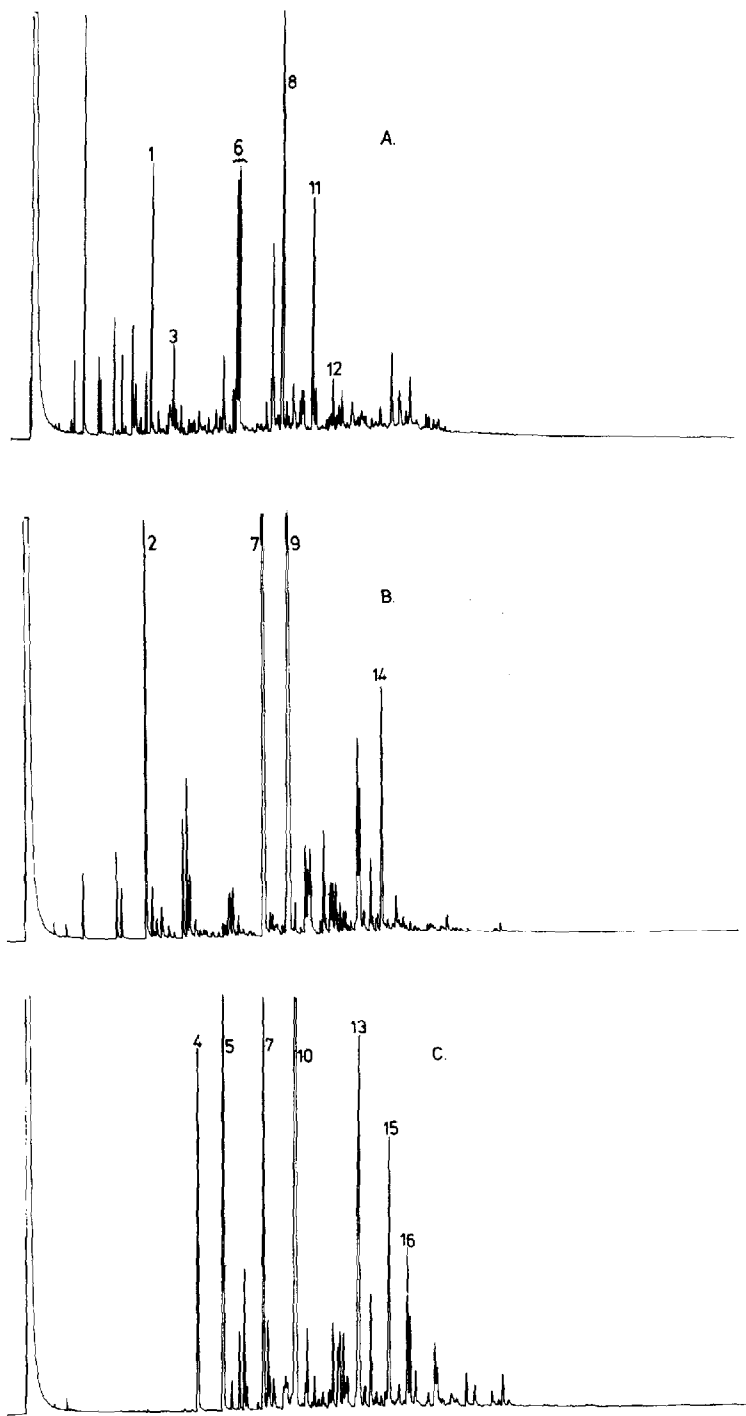


Fig. 2. Gas chromatograms of aromatic fractions from HAO (No. 1). (A) Mono-; (B) di-; (C) polyaromatics. Peaks (in order of elution): 1 = tetrahydroacenaphthene; 2 = diphenyl; 3 = hexahydrofluorene; 4 = dibenzofuran; 5 = fluorene; 6 = 1-4,4a,9,10,10a-octahydrophenanthrene; 7 = dihydrophenanthrene; 8 = 1-8-octahydrophenanthrene; 9 = tetrahydrophenanthrene; 10 = phenanthrene; 11 = decahydropyrene isomer; 12 = decahydropyrene isomer; 13 = tetrahydrofluoranthene; 14 = hexahydropyrene isomer; 15 = dihydropyrene; 16 = pyrene.

to these (7.8–8.0 ppm for pyrene and 7.6 and 8.3–8.6 ppm for phenanthrene) are discernible. Reducing the concentration of benzene in the eluent from 15% to 10% and then to 7% failed to prevent the early elution of the polyaromatic compounds (see Table III and Fig. 3b).

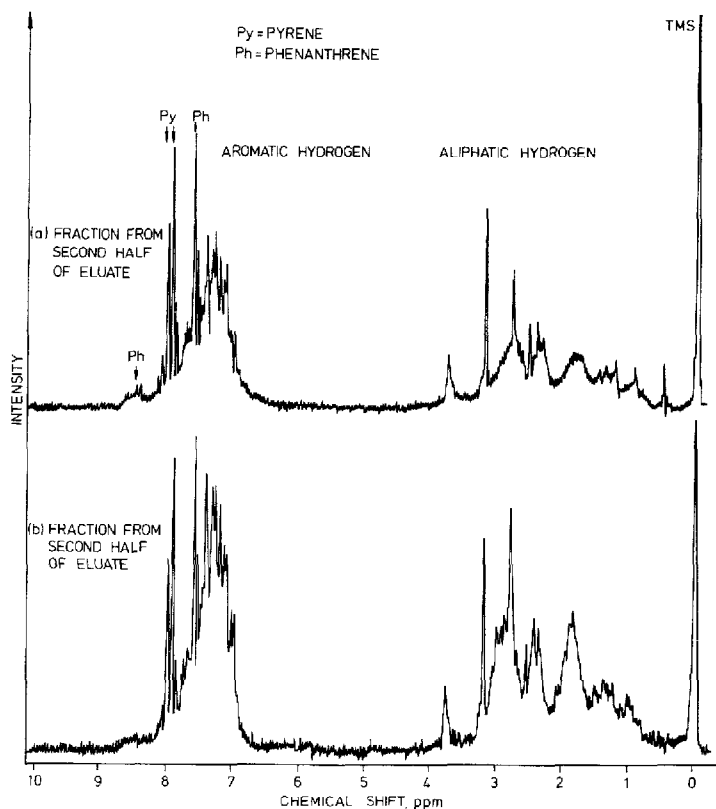


Fig. 3. ^1H NMR spectra of some fractions obtained from HAO (No. 2) using (a) benzene-*n*-pentane (15:85) and (b) benzene-*n*-pentane (10:90) as the eluent. Fraction from second half of eluate in both instances.

Even though dichloromethane is slightly more polar than benzene, an *n*-pentane mixture containing *ca.* 3% of dichloromethane is less polar than one containing 7% of benzene (which failed to prevent the elution of polyaromatic compounds), but more polar than one containing 3% of benzene (which was used to elute monoaromatic compounds). Table II indicates that phenanthrene and pyrene are not eluted by dichloromethane-*n*-pentane (3:97) while naphthalene, dibenzyl and diphenyl are eluted relatively quickly, indicating a good separation between these types of diaromatics and polyaromatics. However, naphthalene, dibenzyl and diphenyl eluted well before the other diaromatics, namely fluorene and 9,10 dihydroanthracene; these started to elute in the second half of the eluent, but mostly with the polyaromatics (Table II). The late elution of fluorene and 9,10-dihydroanthracene was also reported by Hirsch *et al.*⁶ It was also found that, as well as fluorenes, dibenzofurans which are diaromatics in the

HAOs elute mainly with the polyaromatics (Fig. 2b and c). Therefore, if true measures of the concentrations of diaromatic species are required for coal-derived oils, it is recommended that fluorenes and dibenzofurans in the polyaromatic fractions should be determined by GC (Fig. 2).

Although the compositions of the eluates used in this work are not claimed to have been optimized, the results serve to show that, in the separation of aromatics using alumina, overlap of the different compound classes can be reduced by lowering the polarity of the eluents.

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