Journal of Chromatography, 142 (1977) 339–351

CHROM. 10,392

APPLICATION OF THIN-LAYER AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY TO THE SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN BITUMINOUS MATERIALS

D. W. GRANT and R. B. MEIRIS

The British Carbonization Research Association, Wingerworth, Chesterfield, Derbyshire (Great Britain)

SUMMARY

The application of high-performance liquid chromatography (HPLC) on microparticulate silica gel with selective ultraviolet monitoring at four wavelengths has led to a rapid method for the reliable analysis of polycyclic aromatic hydrocarbons (PAH) in tar and petroleum materials. Preliminary separation of the PAH fraction is accomplished, if necessary, by a new form of thin-layer chromatography which incorporates the organo-clay Bentone 34 and which has been shown to be selective for PAH. This selectivity has been utilised in additional separations of HPLC fractions to facilitate their identification by UV spectroscopy. The operation of a "stop–start" liquid chromatograph is described in which the UV spectra of peaks can be scanned during chromatography for identification purposes.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous in our environment and occur as a result of industrial, domestic and natural processes. Methods for the analytical determination of these compounds have received considerable attention in recent years in view of their toxicological importance. PAH also occur in commercial products, particularly those derived from the petroleum and coal carbonization industries, and a continuing vigilance is necessary to safeguard the health and safety of industrial operatives. Reliable and rapid methods for the analysis of PAH are required to provide data for the maintenance of safe working conditions, and to minimise environmental pollution.

In the coal carbonization industry there is a variety of different situations where the routine determination of PAH is required, ranging from environmental and effluent samples to bulk products such as tar, pitch, and bitumen. To cope with this range of samples a method was required which would conform to the following criteria, *viz:*

(a) All the major PAH in the molecular weight range 200–300 be determined.
(b) The method to be quick, reproducible, and reliable.
(c) The handling of pure PAH for the purpose of calibration to be minimal.

(d) The identity of all the components reported to be confirmed by applying ancillary techniques to a typical sample during an investigation stage.

(e) Applicability to samples from diverse sources.

(f) Ability to upgrade the method as more components are identified and improvements are made.

Modern high-performance liquid chromatography (HPLC) on microparticulate silica gel, with selective UV detection, appeared to fulfill these requirements rather more satisfactorily than any of the other available techniques. With regard to the need to identify compounds a novel form of thin-layer chromatography (TLC) has been developed based on the use of the organo-clay Bentone 34* in the adsorbing layer. This gives a selective separation of PAH which is different in character to that produced by silica gel HPLC. The combination of HPLC and this "Bentone selective TLC" (BSTLC) constitutes a powerful separation technique which can produce virtually pure compounds in sufficient quantity for their subsequent identification by UV spectroscopy. BSTLC is also employed for the preliminary treatment of samples containing a high proportion of non-PAH matter, to obtain a fraction rich in PAH.

The system of lettering used herein to describe the position of fused rings is in accordance with the recommendations of the International Union of Pure and Applied Chemistry[1], but familiar names have been retained in preference to prescribed names in several cases to avoid confusion.

Review of chromatographic methods of PAH analysis

Until very recently gas chromatography (GC) has been the preferred technique for this type of analysis. For instance Liberti *et al.*[2] determined PAH in atmospheric dust using glass capillary columns coated with silicone SE-30 operated at temperatures of over 200°, but no separation was apparently achieved between the important benzopyrene isomers. Wilmshurst[3] has published results from the use of both packed and capillary columns but experienced tailing peaks and poor reproducibility. More recently Grimmer and Bohnke[4] used a stainless steel capillary column coated with silicone OV-1, and a 10-m packed column containing silicone OV-17 but the separations of the benzofluoranthenes and of the benzopyrenes and perylene were poor. Perhaps the most effective application of GC to this problem is due to Lao *et al.*[5,6] involving the use of a GC–MS data processor combination. Results were reported for atmospheric particulates, coal tar volatiles, wood preservation sludge and coke oven emission particulates. However, whilst the technique gave a wealth of detailed information, the validity of data with regard to the identification of geometric isomerides must be in some doubt. Also, as was noted by Lao *et al.* in their first paper[5], quantitative agreement of the results from two different columns was poor. Burchfield *et al.*[7] employed a 6-ft. glass column containing silicone OV-1, and a 3-ft. column containing Dexsil 300, using both electron capture and gas-phase fluorimetry for detection but no separation was achieved between benzo[*e*]pyrene, benzo[*a*]-pyrene and perylene. Electron capture detection has also been employed by Harrison and Powell[8] for the quantitative determination of PAH. Separation was carried out by programmed temperature GC on a 5-ft. column containing polymetaphenoxylene. All of these techniques involve the use of a relatively non-polar stationary phase and

* Dimethyl dioctadecyl ammonium bentonite; trade mark of F. W. Berk & Co. Ltd., London, Great Britain.

the selectivity between isomers is consequently low. This is a particular disadvantage with regard to the separation of the pentacyclic aromatics, which include benzopyrenes, benzofluoranthenes, and perylene, all of which have very similar retention characteristics. Recently, however, a selective stationary phase was described by Janini *et al.*[9,10] consisting of a nematic liquid crystal and which is particularly useful for the determination of benzo[*a*]pyrene.

The modern technique of HPLC has presented the analyst with another means of performing this difficult separation and recent advances in this area already suggest that the technique could have considerable advantages over GC in this particular context. The early attempts to apply liquid chromatography to PAH analysis were not very promising because of low column efficiencies and the poor performance at high partition ratios. Nevertheless strongly selective separations of a type that had not previously been achieved by GC were reported. Klimisch[11] showed that benzo[*a*] pyrene could be readily separated from its isomers on low efficiency columns packed with cellulose acetate or polyamide, similar to separations obtained by TLC. The advent of bonded phase packings has led to reverse phase separations of PAH. Vaughan *et al.*[12] employed Corasil C-18 in 1-m columns with aqueous methanol as the mobile phase and with both UV and fluorescence detection. In a later paper these authors described the use of a bonded phase packing prepared from the reaction between microparticulate silica gel and octadecyltrichlorosilane. Interesting results were reported in both cases but, even with the microparticulate material, the separation between benzofluoranthenes and benzopyrenes was dubious. Sleight[14] has examined the retention characteristics of PAH on Permaphase ODS, a commercial bonded material, and a simple relationship between partition ratio and the empirical formulae was suggested.

Clearly the highest level of success in PAH separations has been achieved on microparticulate packings consisting either of bonded phases or of adsorption type materials such as alumina and silica gel. Boden[15] successfully determined benzo[*a*]-pyrene on both types of column with selective UV detection and gave a useful comparison of the various types of column. Krstulovic *et al.*[16] have also used selective UV monitoring of PAH after separation on Partisil 10-ODS and Bondapak C^{18} bonded phase columns by linear gradient elution with aqueous methanol. The procedure involved the use of nine different wavelengths in the UV monitor. The application of selective UV detection clearly enables compounds which are not resolved by the column to be measured separately provided there are sufficient differences in their extinction coefficients. Photometric absorption is of course an established quantitative technique which follows well-defined laws with a high degree of precision and accuracy. Fortunately the majority of PAH absorb strongly in the UV region to give very characteristic spectra and it is this aspect coupled with the improvements in selectivity that gives HPLC a clear advantage over GC for this type of analysis.

EXPERIMENTAL

Thin-layer chromatography

A mixture comprising 50 g silica gel G (Merck, Darmstadt, G.F.R.) and 5 g Bentone 34, previously washed with methanol–water (50:50) until free of chloride ion, was slurried in methanol and used to coat one dozen 200 × 100 mm glass plates with

a 500 μm layer of adsorbent. A Camag TL 200 manual coating apparatus (Camag, Muttenz, Switzerland) was employed for this operation. The plates were left at ambient temperature for 30 min and then dried in an oven for 1 h at 120°. Samples were applied as spots from a microsyringe and the plates were developed in subdued light using "Aristar" grade toluene (BDH, Poole, Great Britain) as mobile phase in an enclosed glass tank. Plates were recovered from the tank when the solvent front had travelled 10 cm and were examined under a UV lamp.

High-performance liquid chromatography

All the work was carried out on stainless steel columns, 25 cm × 6 mm O.D. which were packed by the balanced density slurry method with Partisil 5 microparticulate silica gel (Reeve Angel, London, Great Britain). Aromatic free *n*-hexane (BDH) was used as the mobile phase after drying it over molecular sieve 4A, and the flow rate was adjusted to about 2 ml/min. Two HPLC units were employed during the course of the work. For quantitative purposes the apparatus comprised an electrically driven syringe pump of 500 ml capacity (Metering Pumps, London, Great Britain) and a Cecil Type CE212 variable wavelength UV monitor (Cecil Instruments, Cambridge, Great Britain). For investigational work a Jobling Model JL 911 (Jobling, Staffs, Great Britain) pressure intensifier pump was used together with a modified Optica Model CF4R UV-VIS (Optica UK Ltd.) scanning spectrophotometer modified by the inclusion of a micro-flow cell and separate recorder for generating the chromatogram. The latter instrument could be operated on a stop–start basis to scan UV spectra of selected regions of the chromatogram.

RESULTS AND DISCUSSION

Identification of individual PAH

The Partisil 5 column produced plate efficiencies of 15–20,000 theoretical plates for PAH, with symmetrical peaks and rapid elution times. Fig. 1 shows the separation obtained for a coal tar pitch fraction after extraction in cyclohexane. The elution order corresponds roughly to increasing molecular weight but there is also some selectivity depending on the degree of molecular condensation which can be empirically defined as

$$C_m = \frac{\text{number of C–C bonds shared by two rings}}{\text{number of carbon atoms in molecule}} \times 100$$

This is illustrated in Fig. 2 which shows a relative decrease in retention volume with increasing C_m value.

The separation of the PAH by BSTLC follows a different pattern to the HPLC separation as it does not correlate with the degree of molecular condensation. Table I gives a comparison of k values by BSTLC and by HPLC. There is a considerable displacement of dibenzanthracenes and dibenzopyrenes, pyrene, coronene and benzofluoranthenes by BSTLC with respect to HPLC. For instance, the compounds dibenzo [*a*,*t*]pyrene and dibenzo[*a*,*h*]pyrene are not separated by the HPLC column but were easily resolved by BSTLC. There is also a class separation between dibenzanthracenes and dibenzopyrenes which is not apparent in HPLC.

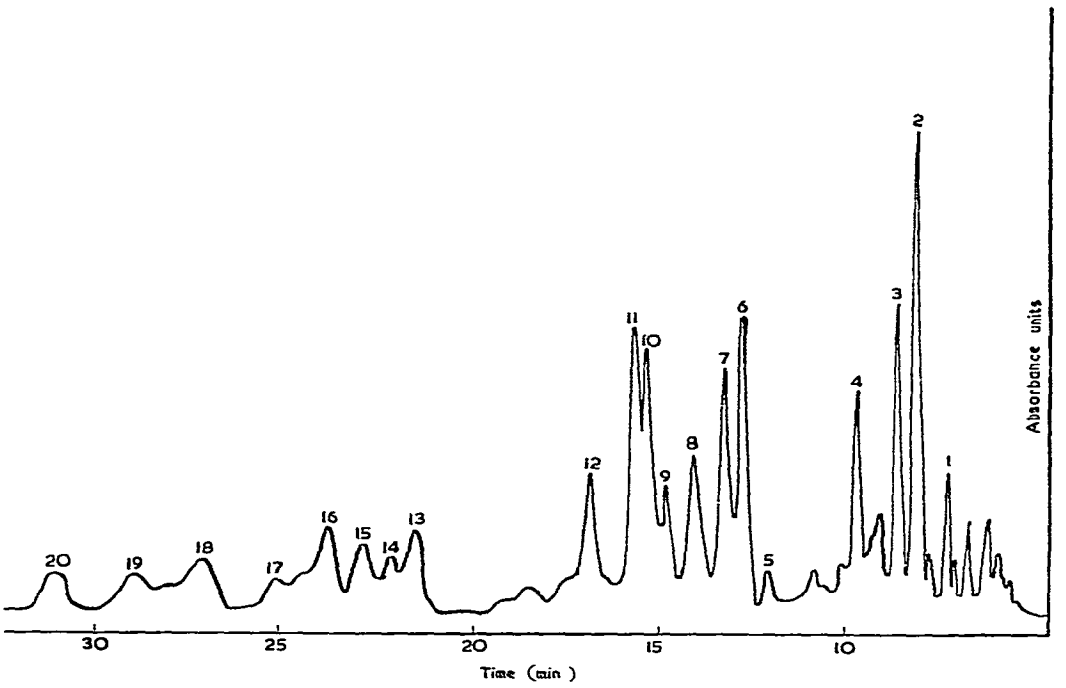

Fig. 1. HPLC of coal tar pitch cyclohexane solubles on 25-cm Partisil 5 column. UV monitor set at 300 nm. (Numbering corresponds to UV spectra run in Fig. 3 and to fractions collected and examined by BSTLC and UV as shown in Table II.)

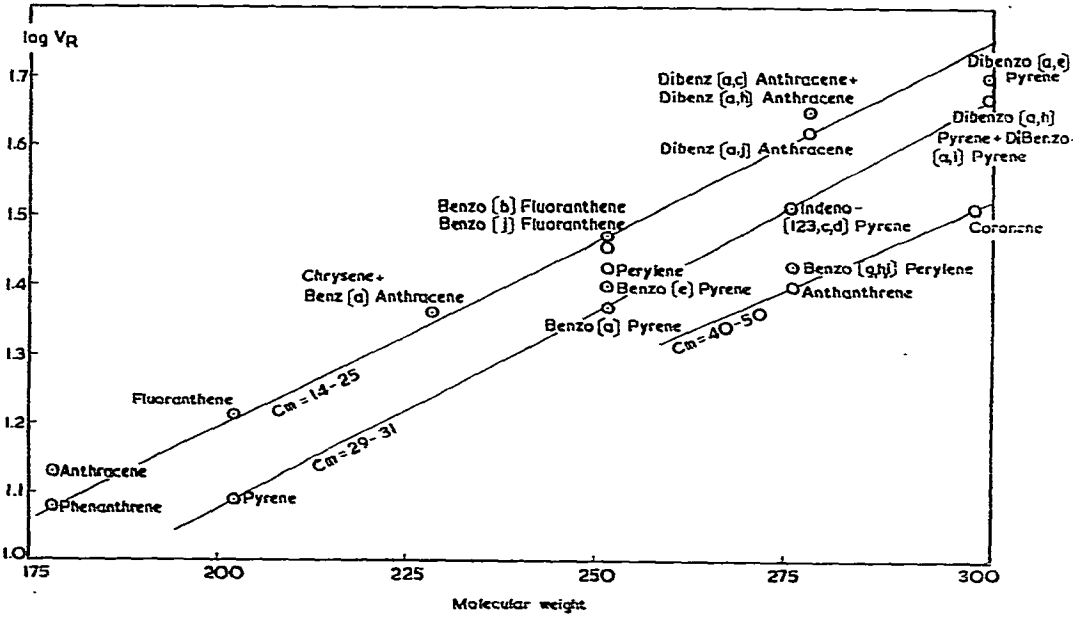

Fig. 2. Relationship between molecular weight and retention volume, showing effect of the degree of molecular condensation. Column, 25 cm Partisil 5; flow-rate, 2.1 ml *n*-hexane per min.

TABLE I

PAH RETENTION CHARACTERISTICS IN PARTISIL 5 HPLC AND BENTONE-SELECTIVE TLC

Compound		*HPLC*		*BSTLC*	
		Retention volume (ml n-hexane)	*Partition ratio (k)*	R_F	$k = \left\{\frac{1}{R_F} - 1\right\}$
Phenanthrene	($C_{14}H_{10}$)	12.0	2.86	—	—
Pyrene	($C_{16}H_{10}$)	12.2	2.90	0.78	0.28
Anthracene	($C_{14}H_{10}$)	13.4	3.19	—	—
Fluoranthene	($C_{16}H_{10}$)	16.2	3.86	0.59	0.73
Chrysene	($C_{18}H_{12}$)	23.1	5.50	—	—
Benz[*a*]anthracene	($C_{18}H_{12}$)	23.1	5.50	0.80	0.25
Benzo[*a*]pyrene	($C_{20}H_{12}$)	23.5	5.60	0.68	0.47
Benzo[*e*]pyrene	($C_{20}H_{12}$)	25.2	6.00	0.58	0.72
Anthanthrene	($C_{22}H_{12}$)	25.4	6.05	0.57	0.75
Perylene	($C_{20}H_{12}$)	27.1	6.45	0.50	1.00
Benzo[*g,h,i*]perylene	($C_{22}H_{12}$)	27.1	6.45	0.52	0.92
Benzo[*k*]fluoranthene	($C_{20}H_{12}$)	28.8	6.86	0.50	1.00
Benzo[*b*]fluoranthene	($C_{20}H_{12}$)	29.4	7.00	0.57	0.75
Indeno[123,*c,d*]pyrene	($C_{22}H_{12}$)	32.1	7.64	0.40	1.50
Dibenzo[*a,l*]pyrene	($C_{24}H_{14}$)	32.1	7.64	0.43	1.33
Coronene	($C_{24}H_{12}$)	32.1	7.64	0.63	0.59
Dibenz[*a,j*]anthracene	($C_{22}H_{14}$)	42.0	10.00	0.70	0.43
Dibenz[*a,c*]anthracene	($C_{22}H_{14}$)	44.9	10.69	0.70	0.43
Dibenz[*a,h*]anthracene	($C_{22}H_{14}$)	44.9	10.69	0.68	0.47
Dibenzo[*a,h*]pyrene	($C_{24}H_{14}$)	47.0	11.19	0.54	0.85
Dibenzo[*a,i*]pyrene	($C_{24}H_{14}$)	47.0	11.19	0.33	2.03
Dibenzo[*a,e*]pyrene	($C_{24}H_{14}$)	49.8	11.86	0.44	1.27

Before regular analysis could be attempted it was considered to be vital to confirm the identity of all the major components in a typical sample by UV spectroscopy. This identification was carried out by chromatographing a cyclohexane solution of coal tar pitch on the UV scanning HPLC equipment. Fig. 3 shows four sets of spectra obtained by stopping the chromatogram by turning off the flow of mobile phase and scanning the spectra. These were identified as anthracene, benzo[*a*]pyrene, indeno[123,*c,d*]pyrene and dibenzo[*a,e*]pyrene, respectively. It was apparent that several of the peaks contained two or more components, and other peaks could not be identified directly, either because the spectra were too weak or because of a lack of suitable reference spectra. Fractions were therefore collected from a number of replicate injections and equivalent fractions were bulked and concentrated to volumes of a few microlitres each. Each fraction was further subjected to BSTLC and, after measurement of the R_F values, the fluorescent zones were removed, extracted in benzene and re-chromatographed. The UV spectrum was scanned at the peak maximum as before. This technique characterized the peak by (a) the R_F value by BSTLC, (b) the fluorescent colour under UV light, (c) the UV spectrum, and (d) the HPLC retention volume. The comparison of these four characteristics with those of available reference compounds is adequate confirmation of identity where they correspond. Where reference compounds were not available, however, as in the case of benzo[*j*]fluoran-

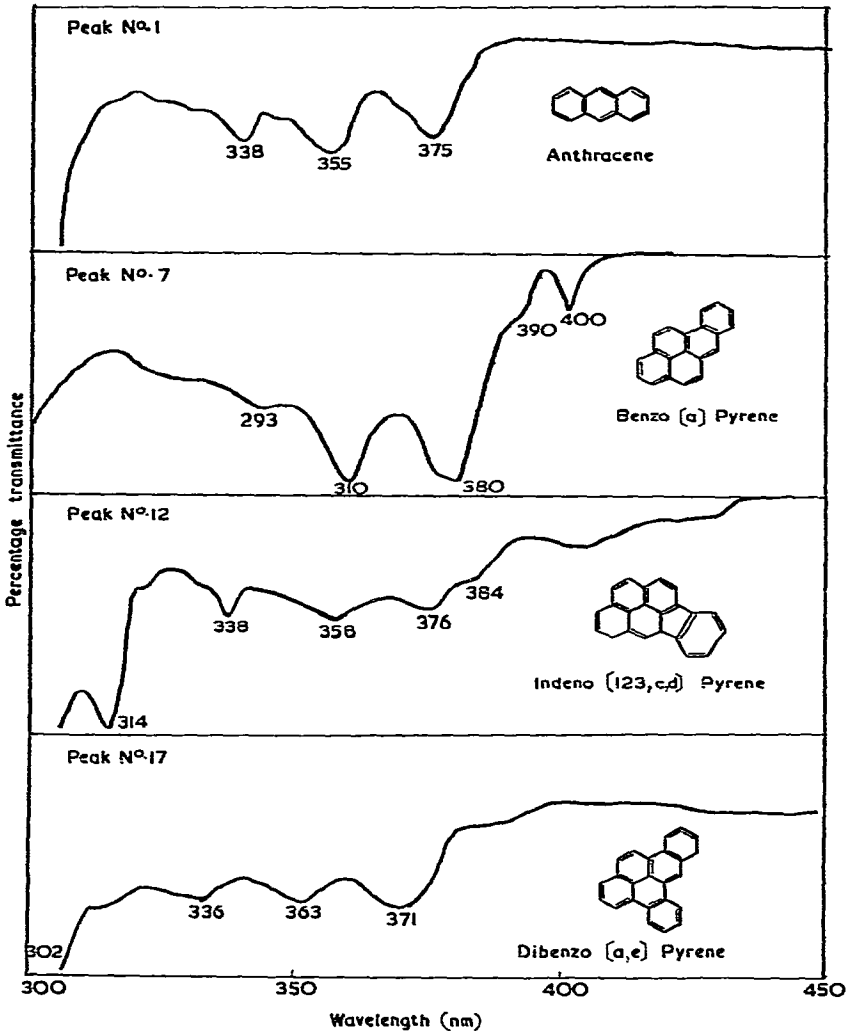

Fig. 3. UV scans of peaks during stop–start HPLC of coal tar pitch fraction.

thene, the identification was made by a comparison with published UV spectra[17]. In other cases no identification was possible and was referred until a more complete library of reference compounds becomes available.

Table II summarises the results of this investigation in relation to coal tar pitch. In a number of cases strongly fluorescent zones were obtained which failed to give significant UV spectra. This indicates that their concentrations would be too low in the original sample to give any significant interference with the identified components using the UV monitor. Their identity is, nevertheless, of interest and will merit further investigation as they may have strongly toxicological properties. Peak 7 for instance gave two BSTLC zones but only one of these was in sufficient quantity to give a UV spectrum, namely benzo[*a*]pyrene. Thus we can assume that there is virtually no inter-

TABLE II

IDENTIFICATION OF MAJOR PAH COMPONENTS OF COAL TAR PITCH CYCLOHEXAN SOLUBLES

NC = not collected, NI = not identified, NR = spectrum not run. Colours: Y = yellow, G = green, B blue, V = violet, BG = blue-green, YG = yellow-green, LB = light blue. Compounds in italics are the major components of peak.

Peak No.	*Identification*				
	HPLC retention	*Stop–start UV scanning*	*BSTLC & UV of HPLC fractions*		
			R_F	*Colour**	*Identification*
1	Anthracene	Anthracene	NC	—	—
2	Pyrene	Pyrene	0.77	BG	*pyrene*
3	NI	NI	0.80	V	1-Methyl pyrene?
4	Fluoranthene	Fluoranthene	0.73	BG	*Fluoranthene*
			0.84	V	3-Methyl pyrene?
5.	NI	Benzo[*a*]fluorene + benzo[*e*]fluorene	NC	—	—
6	Benz[*a*]anthracene + chrysene	Benz[*a*]anthracene** + chrysene***	0.60	LB	Benzo[*a*]pyrene (contamination from peak 7)
			0.75	V	*Benz[a]anthracene*
			0.80	V	Benzo[*b*]fluorene
			(Chrysene not detected because of its low fluorescence)		
7	Benzo[*a*]pyrene	Benzo[*a*]pyrene	0.65	LB	*Benzo[a]pyrene*
			0.80	V	Benzo[*b*]fluorene
8	Benzo[*e*]pyrene + anthanthrene	Benzo[*e*]pyrene + anthanthrene	0.48	BG	*Perylene*
			0.58	B	*Benzo[e]pyrene + anthanthrene*
	+ perylene	+ perylene	0.69	V	Benzo[*a*]pyrene (contamination from peak 7)
9	Benzo[*g,h,i*]perylene	NR	0.45	B	*Benzo[g,h,i]perylene*
			0.63	V	Alkyl benzo[*e*]pyrene?
			0.71	V	NI
10	Benzo[*k*]fluoranthene	Benzo[*k*]fluoranthene	0.45	B	*Benzo[k]fluoranthene*
			0.55	Y	NI
			0.71	V	NI
11	Benzo[*b*]fluoranthene	Benzo[*j*]fluoranthene	0.47	BY	*Benzo[j]fluoranthene*
			0.58	LB	*Benzo[b]fluoranthene*
			0.70	B	NI
			0.81	V	NI
			0.88	LB	NI
12	Indeno[123,*c,d*]pyrene + coronene	Indeno[123,*c,d*]pyrene	0.42	G	*Indeno[123,c,d]pyrene*
			0.61	BG	coronene (v. small)
			0.72	V	NI
			0.83	BG	NI
13	Dibenz[*a,j*]anthracene	weak spectrum	0.75	BG	*Dibenz[a,j]anthracene*
			0.86	BG	NI
			0.80	V	NI
14	NI	weak spectrum	0.70	V	NI
			0.82	G	NI
15	Dibenz[*a,h*]anthracene + dibenz[*a,c*]anthracene	weak spectrum	0.50	V	NI
			0.65	V	NI
			0.74	BG	*Dibenz[a,h]anthracene*

TABLE II (*continued*)

Peak No.	*Identification*				
P	*HPLC retention*	*Stop–start UV scanning*	*BSTLC & UV of HPLC fractions*		
			R_F	*Colour**	*Identification*
6	Dibenzo[*a,i*]pyrene + dibenzo[*a,h*]pyrene	NI	0.25	YG	*Dibenzo[a,i]pyrene*
			0.44	BG	*Dibenzo[a,h]pyrene*
			0.55	V	*NI*
			0.70	B	NI
7	Dibenzo[*a,e*]pyrene	Dibenzo[*a,e*]pyrene	0.31	LB	NI
			0.45	Y	*Dibenzo[a,e]pyrene*
			0.67	G	NI
8	NI	NI	0.67	G	NI
9	NI	NI	0.32	G	NI
			0.43	B	*Dibenzo[b,k]perylene*
			0.67	V (faint)	NI
			0.85	V (faint)	NI
0	NI	NI	0.30	BG	NI
			0.45	Y	*Dibenzo[e,k]perylene*

* Colour under UV light.
** First part of peak.
*** Last part of peak.

ference with the measurement of this important compound by the proposed HPLC procedure.

It is evident from Table II that the HPLC/BSTLC/UV procedure has established the identities of most of the major compounds in the range. Several of these emerge in unresolved groups but, by the use of selective wavelengths, it is possible to determine the individual components in most cases.

Preliminary treatment of sample for quantitative analysis

The separation of the PAH fraction from a preponderance of non-aromatic material is usually based on a Rosen type separation[18] or some form of selective solvent extraction[19]. An alternative technique based on BSTLC has been developed which is reasonably quick and effective when applied to petroleum pitch, bitumen and low temperature coal tar.

About 2 g of a representative sample is weighed out and digested in 10 ml freshly distilled tetrahydrofuran (THF) over a water bath until completely dispersed. The solution is cooled and made up to 20 ml in a graduated flask with more THF. Five 10-μl aliquots of the solution are applied to a BSTLC plate from a microsyringe as five separate spots and the plate is developed. When the development is completed the plate is removed from the tank and dried at ambient temperature in air for no longer than 15 min. The total layer between $R_F = 0.15$ and 0.85 is carefully removed with a spatula and transferred to a 100-ml beaker. "Analar" grade benzene (BDH) (20 ml) is added and the mixture is digested over a water bath in a fume cupboard for 30 min and then centrifuged while hot to remove the thin-layer adsorbent. The clear supernatant solution is poured off into a clean covered beaker and the procedure is repeated a further four times. The five extracts are combined, concentrated to about 5 ml and then

centrifuged again. This time the supernatant solution is evaporated to dryness and the residue redissolved in pure cyclohexane. This is concentrated to about 50 μl in a small specially fabricated glass vessel with a tapered base, fitted with a ground glass stopper. The concentrate is weighed and used for the HPLC stage of the separation.

Quantitative analysis of PAH by HPLC

An examination of the UV spectra of the identified PAH listed in Table II indicated that optimum selectivity would be achieved by using the UV monitor set respectively at 300, 330, 385 and 430 nm. Thus for quantitative measurements this would involve four successive runs. Also it was decided to employ a semi-absolute procedure which would not involve frequent recalibration and hence would minimise the need to handle pure PAH. This procedure involved the initial determination of specific extinction coefficients by chromatographing known solutions of pure compounds at the four chosen wavelengths and using the following calculation, derived from simple chromatographic and spectrophotometric theory.

$$K_\lambda = \frac{A_{\lambda(\max)} V_R \sqrt{2\pi}}{1000w\sqrt{N}}$$

where

K_λ = specific extinction coefficient at wavelength λ for compound
$A_{\lambda(\max)}$ = absorbance at peak maximum at wavelength λ
V_R = retention volume (ml) from injection point
N = theoretical plate number of column
w = mass of component chromatographed

Table III lists the values obtained by this method and the wavelengths chosen for the quantitative analysis of each identified component. To determine all the compounds listed in the table would require all four runs, involving an analysis time of about 2 h. However, the data given enables appropriate selections to be made if a more restricted analysis is sufficient. For instance, the determination of benzo[*a*]pyrene alone only requires a single HPLC run, preferably at 385 nm, where the selectivity for this compound with respect to its nearest neighbours is a maximum. The Partisil 5 column gives fused peaks for chrysene and benz[*a*]anthracene; benzo[*e*]pyrene and anthranthrene; perylene and benzo[*g,h,i*] perylene; benzo[*b*]fluoranthene and benzo[*j*] fluoranthene; indeno[123,*c,d*]pyrene, coronene and dibenzo[*a,l*]pyrene; dibenz[*a,h*] anthracene and dibenz[*a,c*]anthracene; and dibenzo[*a,i*]pyrene and dibenzo[*a,h*] pyrene. By using the conditions indicated the components of these groups are all determined separately. In the case of peak 12 coronene has only been detected in trace amounts and dibenzo[*a,l*]pyrene has not yet been detected in actual samples. In peak 16 the BSTLC/UV procedure revealed the presence of a third component which has not been identified but which will cause some interference.

For quantitative analysis the sample, after applying the BSTLC procedure, is chromatographed in 5 μl quantities on the Partisil 5 column using the four selected wavelengths. The peak absorbances are measured at their maxima and the concentration of each component is calculated from

$$C(\mathrm{w/w}) = 10^5 A_{\lambda(\max)} V_R w_{\mathrm{TLC}} \sqrt{2\pi}/25 K_\lambda \sqrt{N} \cdot \sigma$$

TABLE III

SPECIFIC EXTINCTION COEFFICIENTS FOR PAH BY CALIBRATION AT FOUR WAVELENGTHS

Specific extinction coefficient K_λ calculated from $K_\lambda = A_{\lambda(max)}\, V_R\sqrt{2\pi}/1000\, w\sqrt{N}$ (see text).

Compound	*Specific extinction coefficient*				*Wavelength used for analysis*
	300	*330*	*385*	*430*	
Anthracene	2.7	11.4	1.4	0	300
Phenanthrene	2.9	0.6	0	0	300
Pyrene	31.1	95.8	0	0	330
Fluoranthene	10.8	25.1	2.3	0	330
Chrysene	47.6	4.9	0	0·	300, 330*
Benz[*a*]anthracene	17.2	16.4	1.3	0·	
Benzo[*a*]pyrene	65.6	16.2	73.5	0	385
Benzo[*e*]pyrene	35.0	70.4	0	0	330
Perylene	2.3	2.3	35.9	92.0	430
Anthanthrene	135.2	3.9	30.0	64.3	430
Benzo[*g,h,i*]perylene	87.2	13.3	49.7	0	300
Benzo[*k*]fluoranthene	112.8	18.8	21.1	0	300
Benzo[*j*]fluoranthene**	80.0	32.5	32.5	6	385
Benzo[*b*]fluoranthene	77.6	31.6	1.8	0	330 (diff)***
Coronene	385.0	28.3	0	0	300 (diff)
Indeno[123,*c,d*]pyrene	150.3	25.6	49.3	20.3	385
Dibenz[*a,j*]anthracene	235.0	35.3	0	0	300
Dibenz[*a,c*]anthracene	28.7	19.4	0	0	—
Dibenz[*a,h*]anthracene	144.3	36.4	0	0	300
Dibenzo[*a,i*]pyrene	73.3	40.2	88.9	0	385 (diff)
Dibenzo[*a,h*]pyrene	151.9	5.0	11.0	21.8	430
Dibenzo[*a,e*]pyrene	59.4	7.9	3.1	0	300

* Determined by simultaneous equations at the wavelengths given.
** Data from published spectrum[17].
*** (diff) = determined by difference.

where

w_{TLC} = weight of TLC fraction after concentration to about 50 μl
σ = density of cyclohexane at ambient temperature

Fig. 4 shows chromatograms obtained at the four chosen wavelengths for the PAH fraction isolated from a petroleum pitch sample. The same procedure has been used successfully for bitumens and low temperature coal tar fractions and individual PAH levels as low as 0.0003% (w/w) have been determined. Tar products from the high temperature carbonization of coal are predominantly aromatic in character and are analyzed without the prior BSTLC procedure.

ACKNOWLEDGEMENTS

The authors wish to thank the Council of the British Carbonization Research Association for permission to publish this paper. Thanks are also due to Mr. W. A. Allen for some of the practical measurements.

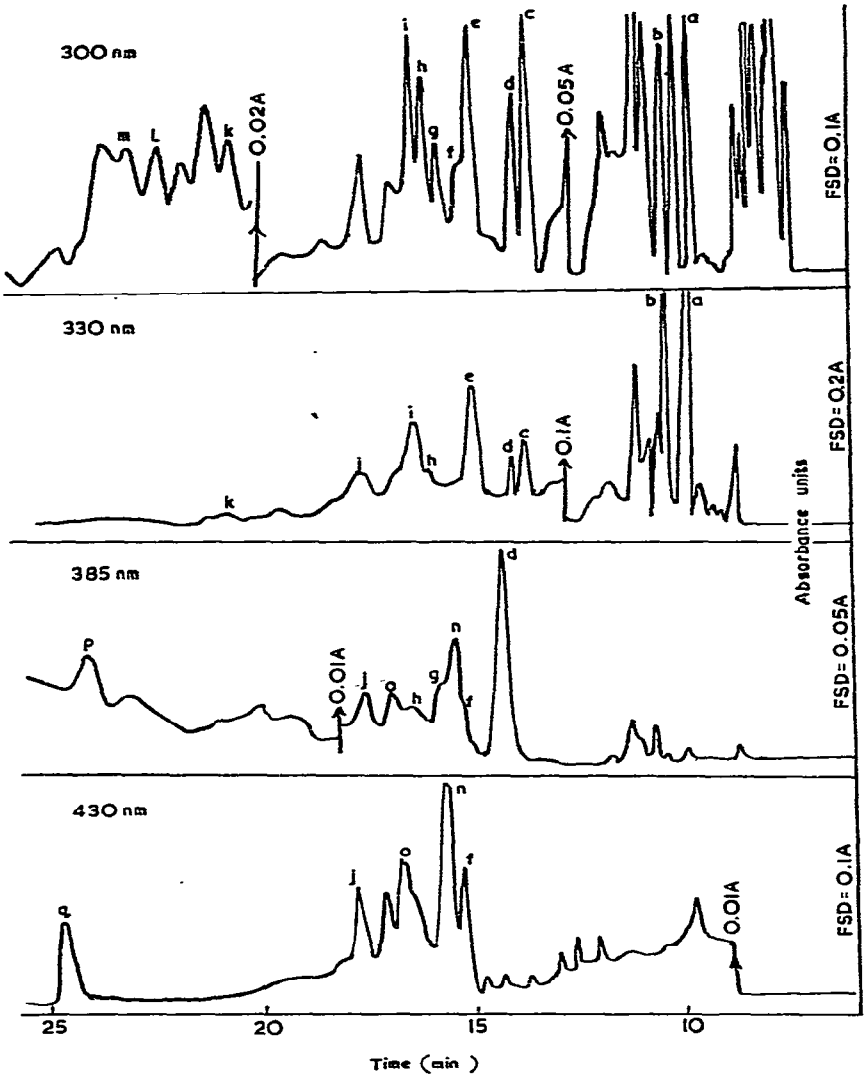

Fig. 4. HPLC on 25-cm Partisil 5 column at selective wavelengths. a = Pyrene, b = fluoranthene, c = chrysene + benz[*a*]anthracene, d = benzo[*a*]pyrene, e = benzo[*e*]pyrene, f = anthanthrene, g = benzo[*g,h,i*]perylene, h = benzo[*k*]fluoranthene, i = benzo[*b*]fluoranthene + benzo[*j*]fluoranthene, j = indeno[123,*c,d*]pyrene, k = dibenz[*a,j*]anthracene, l = dibenz[*a,h*]anthracene, m = dibenzo[*a,h*]pyrene + dibenzo[*a,i*]pyrene + unidentified, n = perylene, o = benzo[*j*]fluoranthene, p = dibenzo[*a,i*]pyrene, q = dibenzo[*a,h*]pyrene.

REFERENCES

1 *IUPAC Nomenclature of Organic Chemistry, Definitive Rules for Hydrocarbons*, Butterworths, London, 3rd ed., 1971.
2 A. Liberti, G. P. Cartoni and V. Cantuti, *J. Chromatogr.*, 15 (1964) 141.
3 J. R. Wilmshurst, *J. Chromatogr.*, 17 (1965) 50.
4 G. Grimmer and K. Bohnke, *Z. Anal. Chem.*, 312 (1972) 261.

5 R. C. Lao, R. S. Thomas, H. Oja and L. Dubois, *Anal. Chem.*, 45 (1973) 908.
6 R. C. Lao, R. S. Thomas and J. L. Monkman, *J. Chromatogr.*, 112 (1975) 681.
7 H. P. Burchfield, E. E. Green, R. J. Wheeler and S. M. Billedeau, *J. Chromatogr.*, 99 (1974) 697.
8 E. K. Harrison and C. I. B. Powell, *Ann. Occup. Hyg.*, 18 (1975) 199.
9 G. M. Janini, K. Johnston and W. L. Zielinski, Jr., *Anal. Chem.*, 47 (1975) 670.
10 G. M. Janini, B. Shaikh and W. L. Zielinski, Jr., *J. Chromatogr.*, 132 (1977) 136.
11 H.-J. Klimisch, *J. Chromatogr.*, 83 (1973) 11.
12 C. G. Vaughan, B. B. Wheals and M. J. Whitehouse, *J. Chromatogr.*, 78 (1973) 203.
13 B. B. Wheals, C. G. Vaughan and M. J. Whitehouse, *J. Chromatogr.*, 106 (1975) 109.
14 R. B. Sleight, *J. Chromatogr.*, 83 (1973) 31.
15 H. Boden, *J. Chromatogr. Sci.*, 14 (1976) 391.
16 A. M. Krstulovic, D. M. Rosie and P. R. Brown, *Anal. Chem.*, 48 (1976) 1383.
17 E. Clar, *Polycyclic Hydrocarbons* (2 Vols.), Academic Press, New York, 1964.
18 A. A. Rosen and F. M. Middleton, *Anal. Chem.*, 27 (1955) 790.
19 D. Hoffman and E. L. Winder, *Natl. Cancer Inst. Monogr.*, 9 (1962) 91.