QUALITATIVE DETERMINATION OF POLYAROMATIC HYDROCARBONS IN THE AIR NEAR GAS-WORKS RETORTS

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SUMMARY

An extract of air particulates from a gas-works was separated by two-dimensional thin-layer chromatography. Thirty-five different fractions could be readily observed. Retention values, UV-visible absorption spectra and mass spectra of 14 of the fractions were all very close to corresponding experimental data of standard polyaromatic hydrocarbons. For nonhydrogenated polyaromatic hydrocarbons, a linear relationship was observed between molecular weight and retention value in the first dimension of the thin-layer chromatographic system used.

INTRODUCTION

Because of the extreme complexity of the samples containing polyaromatic hydrocarbons (PAH) associated with air particulates, chromatographic methods are required for the analysis of PAH. In 1965, GUNTHER AND BUZZETTI[1] comprehensively reviewed the occurrence, isolation, identification and determination of PAH. Since then, many methods for PAH analysis have been described based on column chromatography[2-4], thin-layer chromatography (TLC)[5-12] and gas chromatography[13-19]. The fairly short analysis time and selectivity make TLC generally superior to other chromatographic methods, and the system described by KÖHLER et al.[5], with slight modifications, was used in this study. Within 2.5 h the air particulate extract gave a chromatogram in which thirty-five spots were readily visible in UV light.

Identification studies of PAH at present are generally based on comparison with standards. For air pollution samples, the unknown PAH can generally be isolated only in submicrogram quantities so that previously only comparisons of retention values and of absorption and fluorescence spectra have been possible. In this study, however, comparison with standards is based not only on retention values and UV-absorption spectra but also on mass spectra. The method has been tested by applying it to the particularly complex mixture of organic matter extracted from air particulates collected from air near gas-works retorts. The UV spectra of isomeric PAH are usually readily distinguishable, but the spectra of a given PAH and its alkyl derivatives can be very similar. Clear differences are shown, however, between the mass spectra of

unsubstituted PAH and alkyl derivatives. In particular, the number of rings and the number of carbon atoms in side chains can generally be calculated from the molecular weight for nonhydrogenated PAH containing up to six rings. Thus, the UV–MS combination appears to be a useful tool for the identification of PAH.

MATERIALS AND METHODS

Reagents

Benzene P.A., toluene P.A., methanol P.A., and Aluminium Oxide G were obtained from Merck; n-hexane (puriss. min. 99 %) from Kebo; ether anhydrous A.R. from Mallinkrodt; and cellulose powder MN 300 G/Ac. (acetyl content approx. 40 %) from Macherey, Nagel & Co. Ethyl alcohol 99.5 % spect. grade and ethyl alcohol 95 % were used. All solvents were redistilled before use, and the first and last 10 % fractions were discarded.

Apparatus

The apparatus used consisted of the following: a Desaga–Stahl kit for the preparation of thin layers on 20 × 20 cm glass plates; a Beckman DBG UV–visual spectrophotometer equipped with recorder S.03507H, spectrosil semimicro cells of 1 cm path length and variable beam attenuators; an LKB 9000 mass spectrometer.

Procedure

A dust sample was collected 1.6 m above a retort by sucking 60 m³ of air through a glass fiber filter for 1 h. The filter was then extracted overnight in a Soxhlet apparatus with benzene. The extract was finally concentrated and stored in the dark until analysis.

A slurry for the preparation of 5 thin-layer plates 0.25-mm thick was prepared from 20 g of aluminium oxide, 10 g of cellulose acetate powder and 40 g of 95 % ethyl alcohol by mechanical stirring at about 1000 r.p.m. for 5 min. After drying in air for 10 min, the layers were heated in an oven at 100° for 15 min.

The concentrated benzene extract from the filter was applied to a corner of a thin-layer plate with a 10-μl microsyringe to give a spot diameter of not more than 4 mm. The capacity of the system was limited by tailing on the aluminium oxide so that up to ten maximally charged layers had to be used to give good absorption spectra for the minor component PAH. Following the method described by KÖHLER et al.[5], the mobile phases were n-hexane–toluene (9:1) for the first direction, and ether–methanol–water (4:4:1) for the second direction. After development, the plates were dried in air for some minutes and then were examined under a 254-nm UV lamp. The fluorescent spots were outlined with a stylus, and Fig. 1 shows their positions. The numbered spots have been analyzed.

In order to improve the separation, the whole chromatographic process was repeated for each individual fraction as follows. The adsorbent in corresponding areas of each of the ten thin-layer plates was collected in suction tubes (Fig. 2a) from which the fractions were washed with four successive 0.25-ml portions of benzene (Fig. 2b). The solvent was finally evaporated from the washings in a stream of nitrogen in evaporators, illustrated in Fig. 2c.

Four thin-layer plates 0.5-mm thick were now prepared. Small holes in the layers

were made by suction with a pipette, to fit the filter paper discs that were placed in the holes and carefully covered with a minimum quantity of a water–aluminium oxide slurry to ensure a normal feed of mobile phase. Six to eight discs were placed about 2 cm from one side of the plates. Chromatography was carried out again in the first dimension, and, after repeated suction, washing and evaporation, the PAH fractions
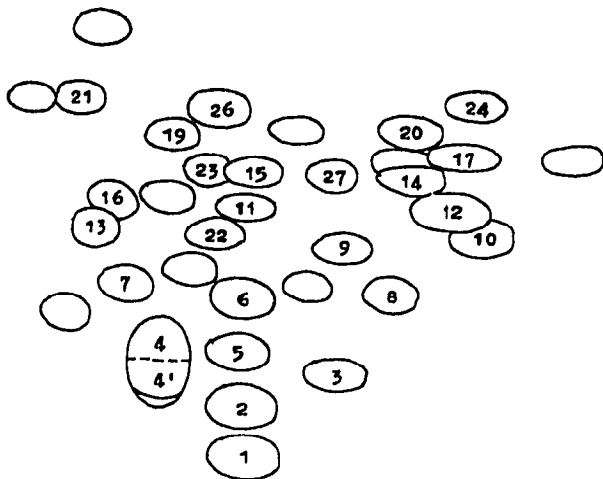
Fig. 1. Spot positions in a thin-layer chromatogram of an air particulate extract.
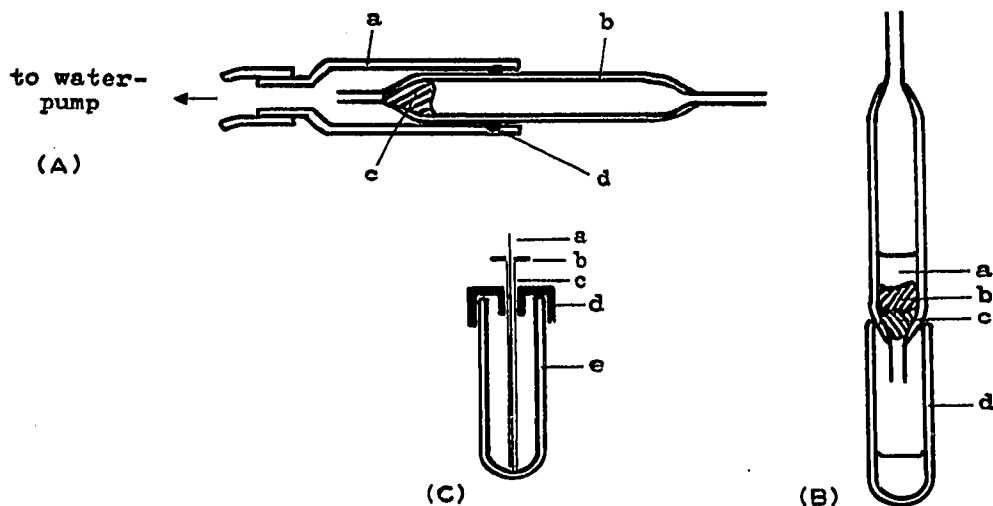
Fig. 2. (A) Suction tube and holder. a = aluminium tube, b = glass tube, c = glass wool plug, d = silicon rubber ring. (B) Washing of PAH fraction. a = benzene, b = adsorbent, c = glass wool plug, d = test tube. (C) In the LINNARSON[23] evaporator, the benzene extract is brought to the filter paper disc by capillary force. When the solvent evaporates, solute will be collected on the disc. a = steel thread, b = 4-mm-diameter filter paper disc, c = glass capillary, d = aluminium cap, e = test tube.

were rechromatographed in the second dimension. Background samples were prepared by suction of PAH-free areas.

In order to correlate mobility with known standards, four 0.25-mm thick thin-layer plates were prepared as described above. To the first three plates a constant small amount of the particulate extract was applied. To the starting points of the second, third and fourth thin-layer plates were added, respectively, 100, 200 and 1000 ng of the standard PAH in question. Two-dimensional chromatography was then carried out as described earlier.

The benzene solution of the PAH fractions resulting from the final chromatographic step were evaporated in a stream of nitrogen. When the tubes appeared to be dry on the inside, the nitrogen stream was maintained for 30 sec to remove the last traces of benzene. Two hundred microliters of spectroscopic grade alcohol were immediately added, and after 2 min the alcoholic solutions were gently shaken and transferred to the cells. PAH fractions and corresponding background samples were then scanned between 500 and 200 nm. Solutions were diluted, if necessary, in order to adjust all absorbance peaks within the chart paper width (absorbance 1.0).

The alcoholic solutions were transferred back to the corresponding tubes and evaporated as described earlier (Fig. 2c), except that glass fiber discs (cut from the filters) were used instead of paper discs. These were then introduced into the ion source of the mass spectrometer via the direct inlet probe. The probe heater control was turned to maximum, and the scan was started near the top of the TIC recorder peak. (TIC, total ionization current.) The ion source temperature was about 230°, the trap current 60 μA and the electron energy 70 eV.

RESULTS AND DISCUSSION

Mobilities

From the thin-layer chromatograms it appeared that R_F values in the first direction were dependent on molecular size. This is demonstrated in Fig. 3. The PAH
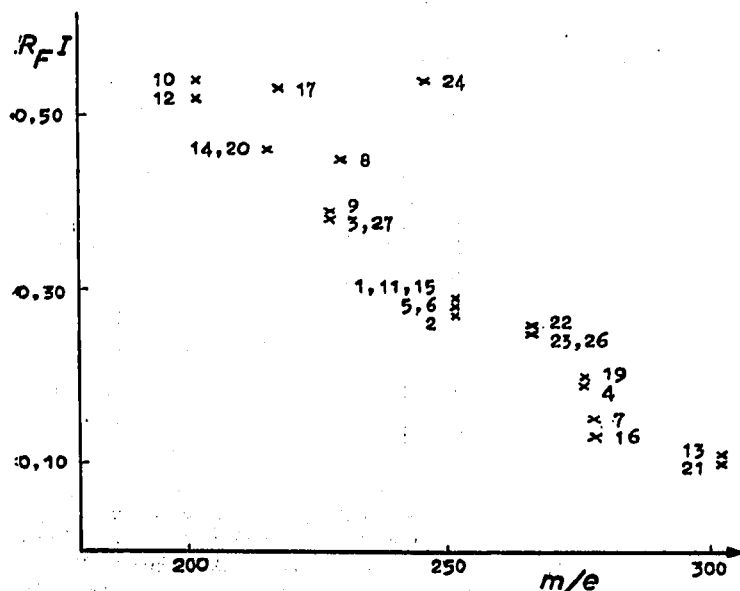

Fig. 3. Plot of R_F values in the aluminium oxide system *vs.* *m*/*e* for the strongest peak of each isolated fraction.

which lie along the line contain no saturated carbons in the nucleus. Therefore, it is considered that the main components of fractions 8, 17 and 24 consist of partially saturated or heterocyclic ring systems. In the second system, the relation appears to be more complicated. Long molecules such as 3,4-benzopyrene and chrysene are strongly retarded, whereas more compact molecules such as 1,2-benzopyrene, triphenylene and 1,12-benzoperylene have high R_F values. This is probably due to the chain structure of the adsorbent (acetyl cellulose).

In order to correlate R_F values for fractions and standard PAH, particulate extract and standards were chromatographed. Dependence of R_F values on sample size was noted, and irreproducibility may also be due to variation in the activity of the aluminum oxide. The experimental result is illustrated in Fig. 4 showing that for identification purposes R_F values of the TLC system used are comparable only on the same chromatogram.
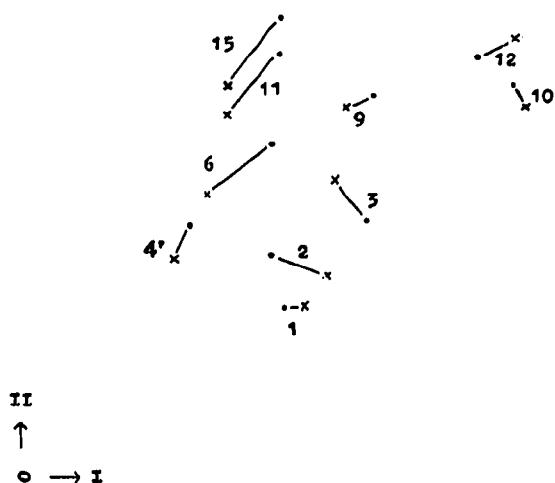

Fig. 4. Spot center positions of some fractions of the particulate extract (dots) compared with those obtained by chromatography of corresponding standard PAH (crosses).

On the second and the third chromatograms mentioned in the procedure for correlating mobilities, the spot intensity of the added PAH increases compared with the spots of the particulate extract and even very small mobility differences could be detected. The true fluorescent colors could be compared on the first and fourth chromatograms. From the latter, standard UV and mass spectra were then obtained. The results of these observations are listed in Table I. R_F values are taken from Fig. 1.

UV–visible spectrophotometry

Experiments with blank thin-layer plates showed that background UV–visible absorption is caused by substrate impurities. In order to study the relation between background absorption and spot position, nine spots from a developed blank thin-layer plate were analyzed as described earlier. The spot positions are shown in Fig. 5. It now appeared that background absorption increased from spot 7 to spot 1, from 8 to 2, etc., whereas it was constant from 1 to 3, from 4 to 6, etc. This shows that the substrate impurities are eluted only by the methanol–ether–water mixture, and thus

TABLE I

R_F VALUES AND FLUORESCENT COLORS OF FRACTIONS AND STANDARDS

Fraction No.	Corresponding standard PAH with no detectable differences in retention values or fluorescent color	Fluorescent color	R_F values	
			I	II
1	3,4-benzopyrene	violet	0.29	0.23
2	3,4-benzofluoranthene	light blue	0.27	0.30
3	chrysene	violet	0.38	0.34
4	2,3-o-phenylenepyrene	yellow	0.19	0.36
5	10,11-benzofluoranthene	yellow	0.28	0.37
6	11,12-benzofluoranthene	violet	0.28	0.44
7		violet	0.15	0.46
8		grey	0.45	0.45
9	1,2-benzanthracene	violet	0.39	0.50
10	pyrene	violet	0.54	0.52
11	perylene	blue	0.29	0.56
12	fluoranthene	bluish grey	0.52	0.55
13		violet	0.11	0.53
14		greenish grey	0.46	0.60
15	1,2-benzopyrene	violet	0.29	0.61
16		grey	0.13	0.57
17		violet	0.53	0.63
19	1,12-benzoperylene	violet	0.20	0.66
20		greenish grey	0.46	0.66
21		light yellow	0.10	0.70
22		violet	0.26	0.53
23		grey	0.25	0.61
24		violet	0.54	0.70
26		blue	0.25	0.69
27	triphenylene	violet	0.38	0.61

background absorption can be compensated for if reference spot positions are chosen as illustrated in Fig. 6.
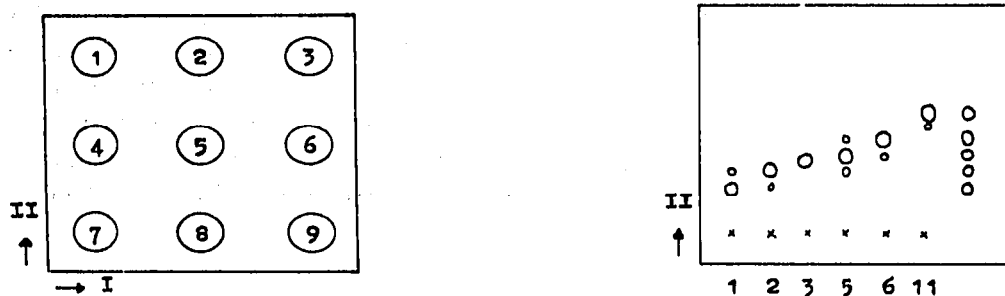

Fig. 5. Positions of reference spots for background absorption study.

Fig. 6. Final chromatogram of fractions 1, 2, 3, 5, 6 and 11. Reference spots are to the right of spot 11.

The UV–visible absorption spectra illustrated in Figs. 7 to 32 were obtained from the isolated fractions of the particulate extract and corresponding standards. The following comments concerning the absorption spectra can be made.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).
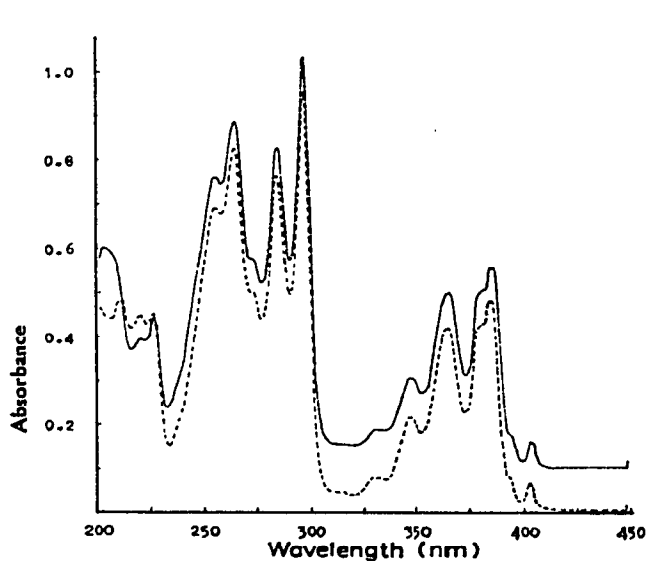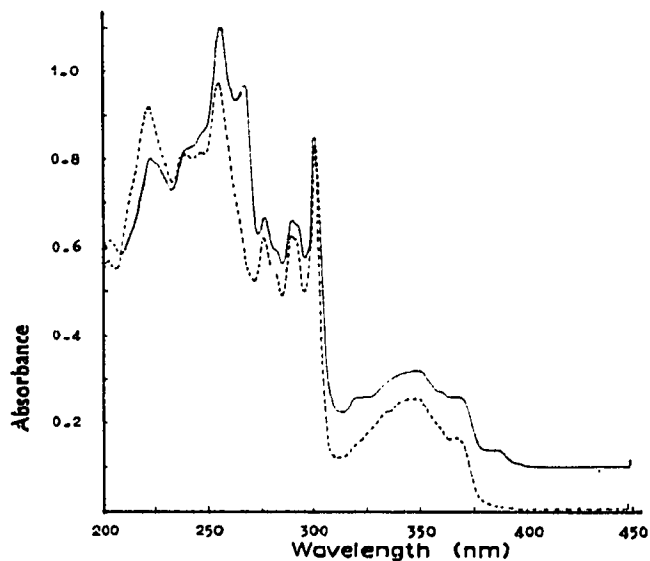

Fig. 7. (————) fraction 1, (— — — —) 3,4-benzopyrene.

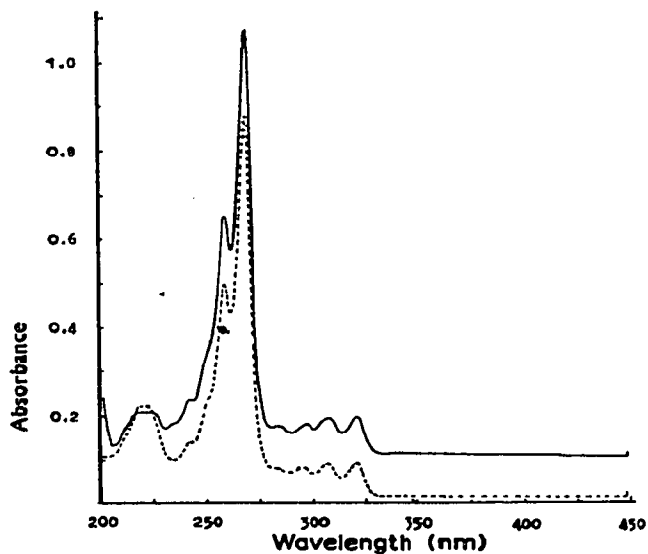Fig. 8. (————) fraction 2, (— — — —) 3,4-benzofluoranthene.

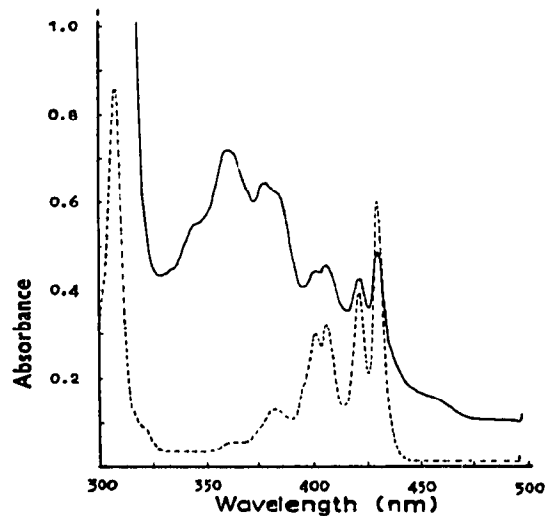Fig. 9. (————) fraction 3, (— — — —) chrysene.

Fig. 10. (————) fraction 4', (— — — —) anthanthrene.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).
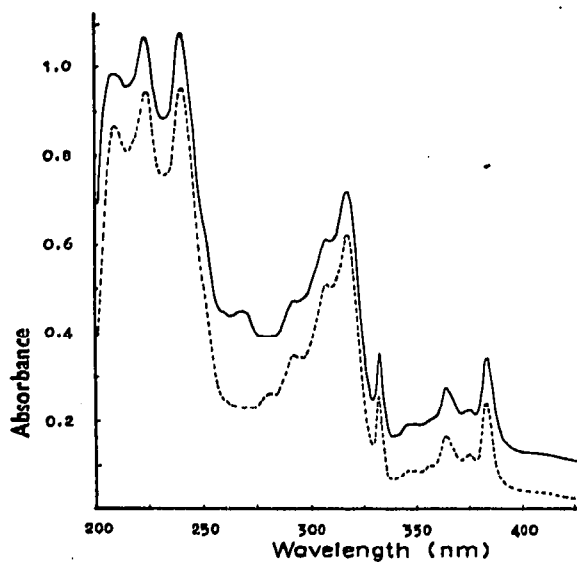

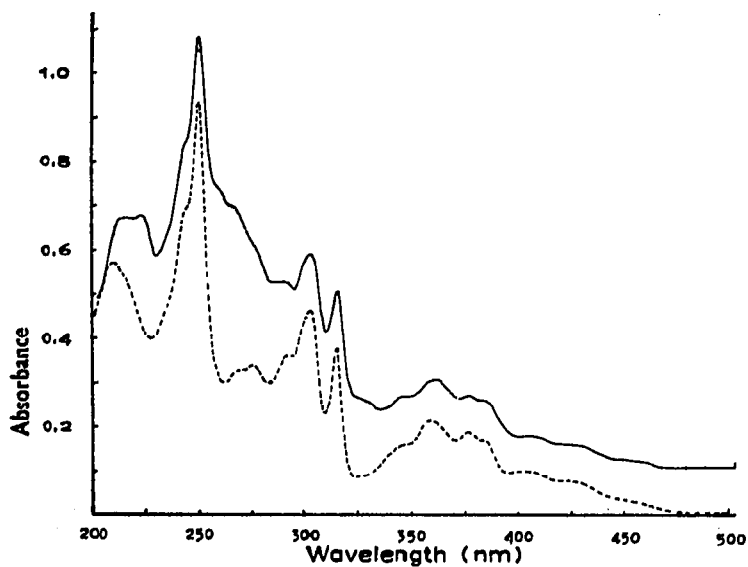
Fig. 11. (———) fraction 4, (– – – –) 2,3-o-phenylenepyrene.

Fig. 12. (———) fraction 5, (– – – –) 10,11-benzofluoranthene.

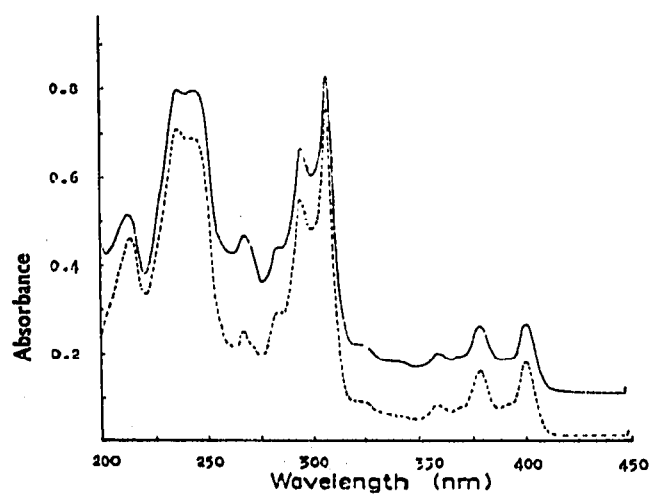

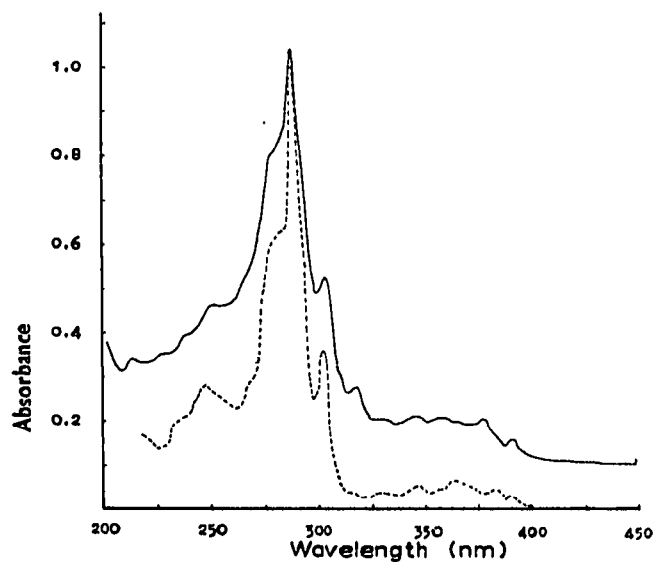Fig. 13. (———) fraction 6, (– – – –) 11,12-benzofluoranthene.

Fig. 14. (———) fraction 7, (– – – –) 3,4-benzotetraphene.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).

Fig. 15. Fraction 8.

Fig. 16. (————) fraction 9, (— — — —) 1,2-benzanthracene.
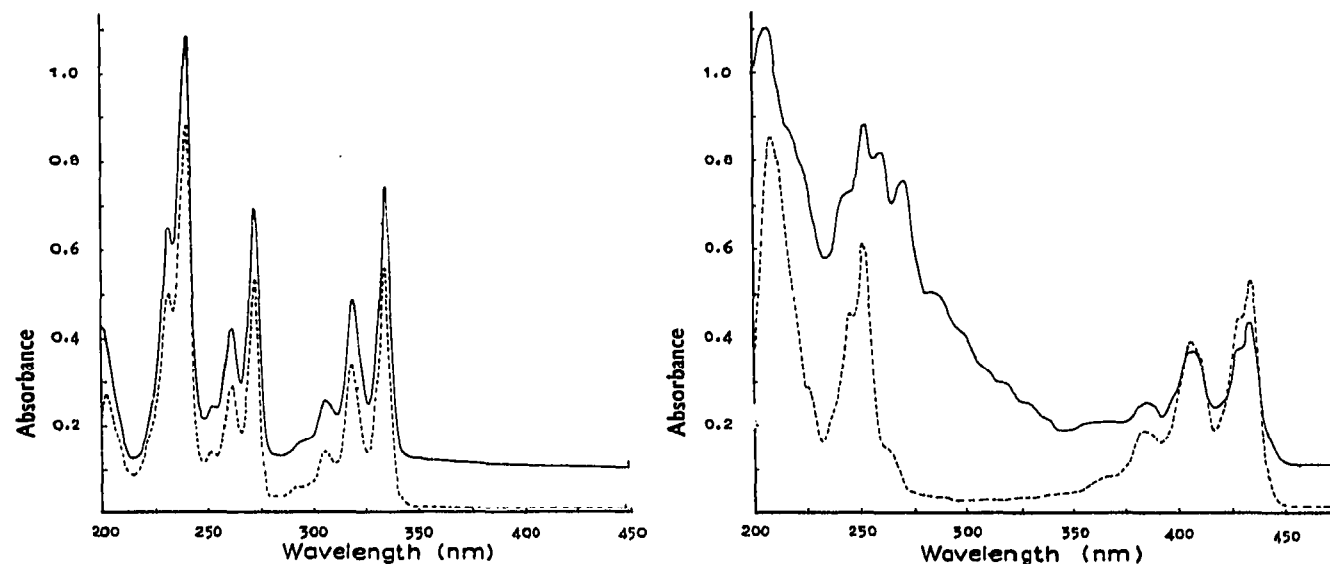
Fig. 17. (————) fraction 10, (— — — —) pyrene.

Fig. 18. (————) fraction 11, (— — — —) perylene.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).
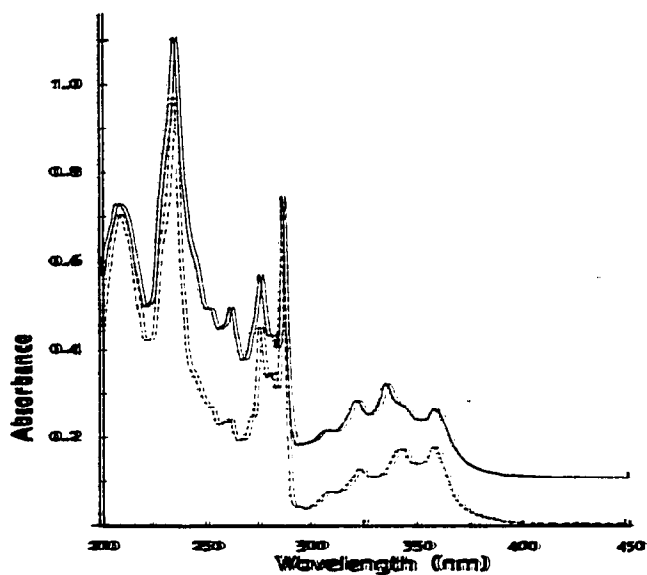
Fig. 19. (———) fraction 12, (— — — —) fluoranthene.
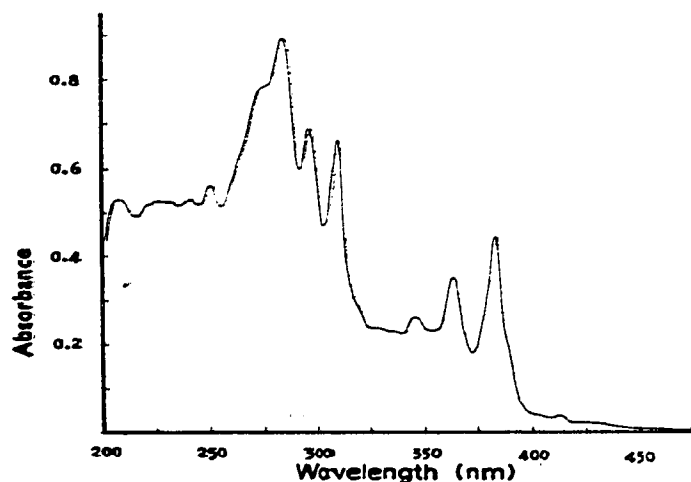
Fig. 20. Fraction 13.
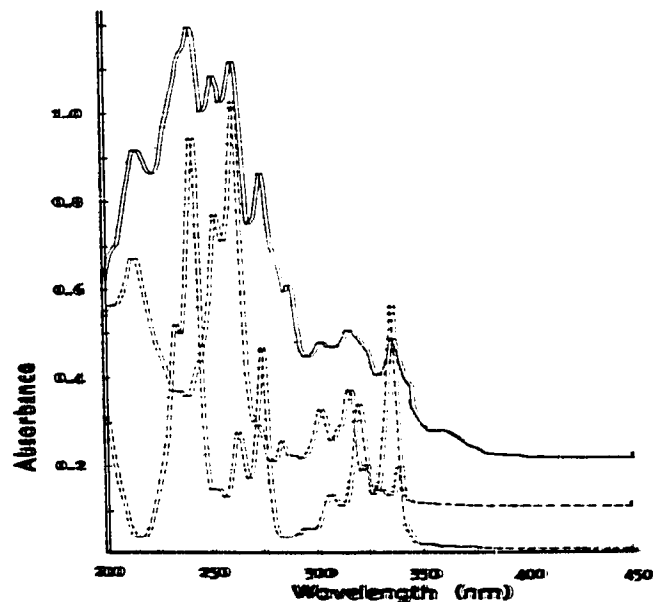
Fig. 21. (———) fraction 14, (upper — — — —) 1-methylpyrene, (lower ------) 2,3-benzofluorene.
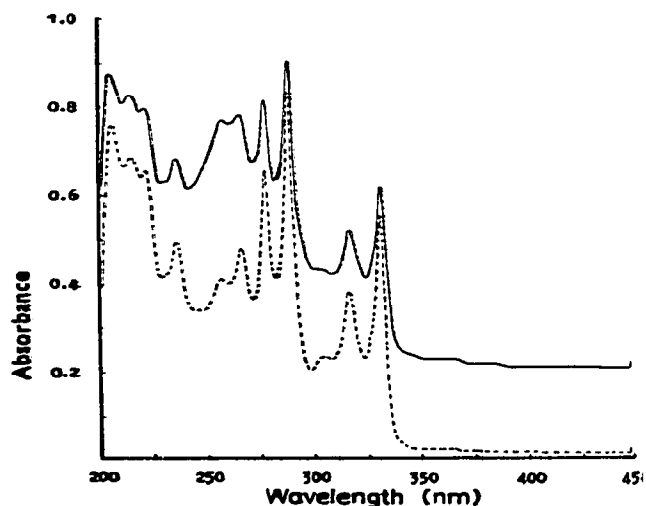
Fig. 22. (———) fraction 15, (— — — —) 1,2-benzopyrene.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).

Fig. 23. Fraction 16.

Fig. 24. Fraction 17.

Fig. 25. (———) fraction 19, (— — — —) 1,12-benzoperylene.

Fig. 26. Fraction 20.

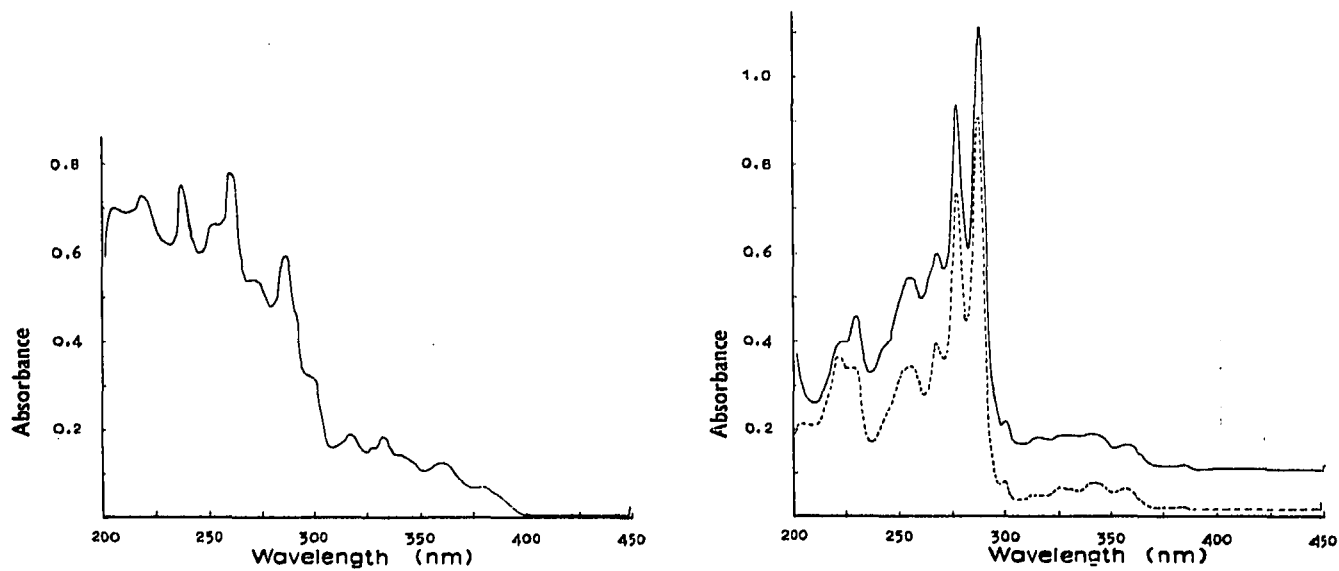Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).

Fig. 27. Fraction 21.
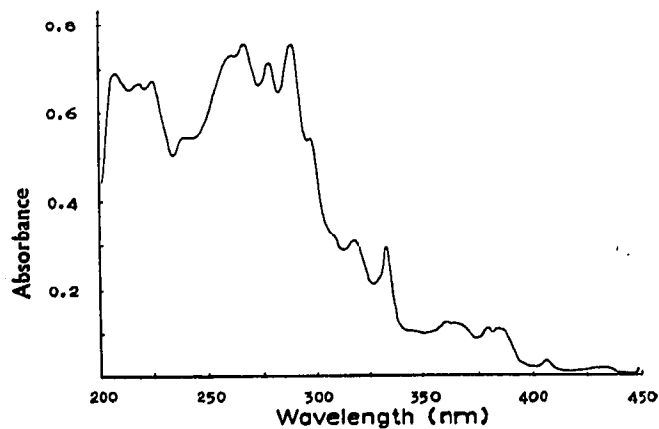
Fig. 28. Fraction 22.
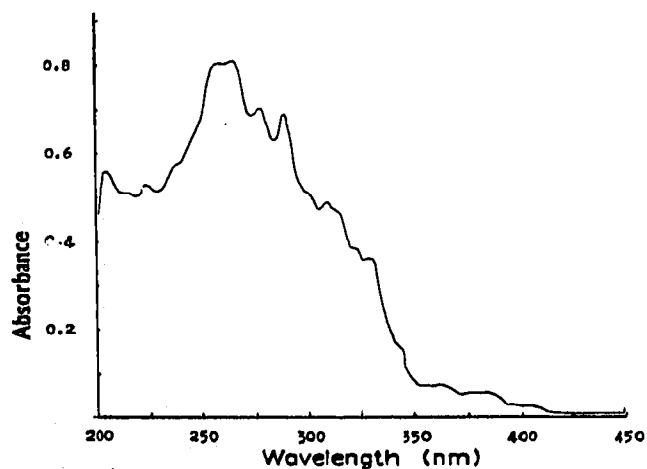
Fig. 29. Fraction 23.
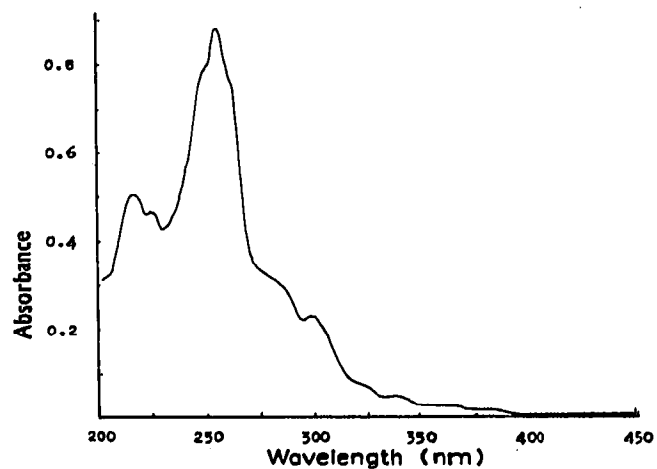
Fig. 30. Fraction 24.

Ultraviolet spectra of purified TLC fractions and corresponding standard PAH (when available).
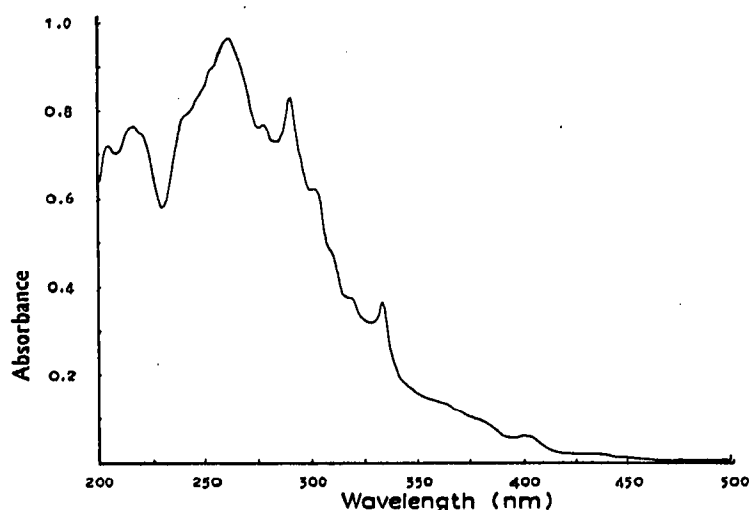

Fig. 31. Fraction 26.
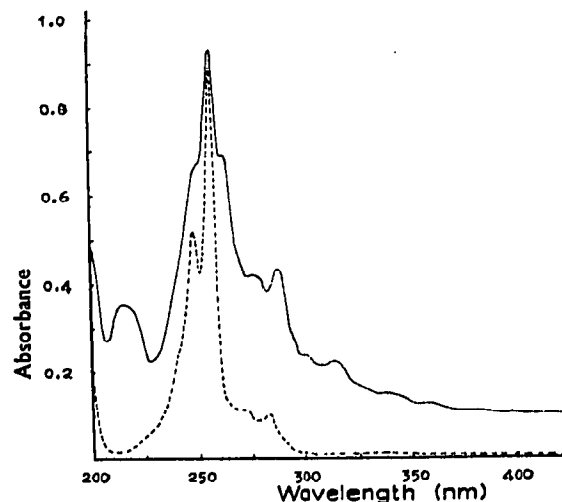
Fig. 32. (————) fraction 27, (– – – –) triphenylene.
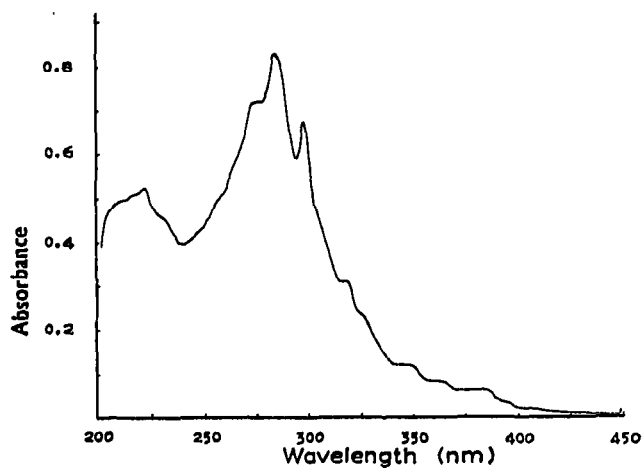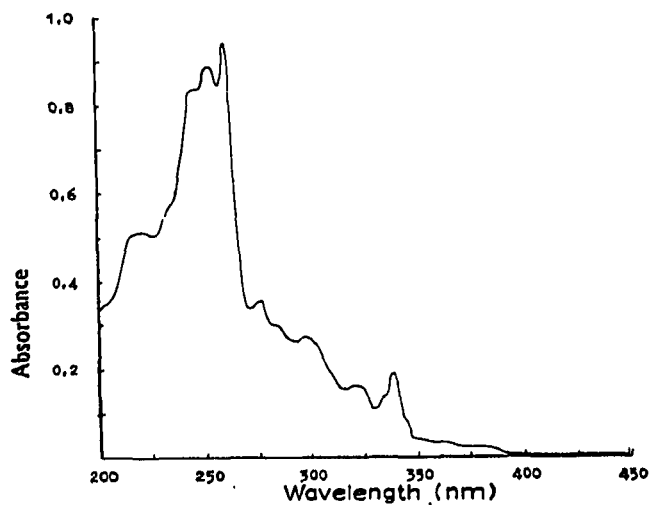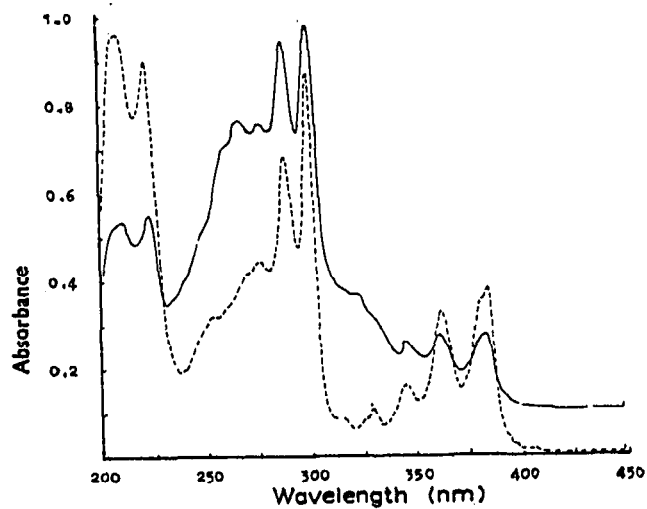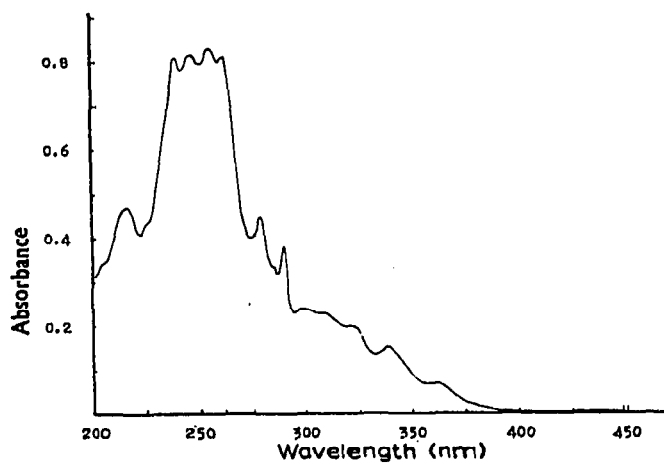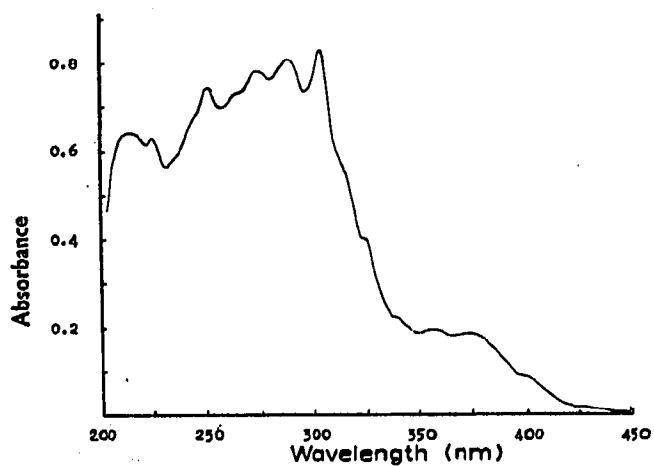
Fraction 4. The lower edge of this spot showed a blue fluorescence and therefore the lower part of fraction 4, called 4' (Fig. 1), was run separately in the last chromatographic step. From the spectra it seems that this component may be anthanthrene, but this was confirmed only by comparing R_F values and fluorescent colors.

Fraction 7. A 3,4-benzotetraphene standard was not available and therefore R_F values could not be compared. The standard UV spectrum is taken from reference 20.

Fraction 13. The mass spectrum of this fraction shows the presence of PAH having a mol. wt. of 302. However, we do not know any PAH of mol. wt. 302 for which the absorption spectrum corresponds to that of fraction 13. It is considered that at least two such PAH are present. R_F values and fluorescent colors indicate that dibenzo[a,e]pyrene, but not the other dibenzopyrenes, may be present.

Fraction 14. According to the position of this spot (Fig. 3), the fraction consists essentially of PAH isomers of mol. wt. 216. Well-known coal-tar constituents (21) of this molecular weight are the three methylpyrenes and the three benzofluorenes. 3,4-Benzofluorene shows absorption peaks at 230 and 310 nm and hence it cannot be a major component of this fraction. 1,2-Benzofluorene has an R_F value of 0.52 in the second direction and can thus be excluded. However, the presence of methylpyrenes and 2,3-benzofluorene does not explain the fluorescent color of the fraction because these all show violet fluorescence on the thin-layer plate. Provided that the methylfluoranthenes have fluorescent colors and absorption spectra similar to fluoranthene, the fluorescent color in fraction 14 may be explained by the presence of methylfluoranthenes. This may also explain the absorption peaks at 290 and 360 nm. Unfortunately, methylfluoranthene standards were not available.

Fraction 17. According to the absorption spectrum (22), the component having mol. wt. 218 in this fraction may be benzo[b]naphtho[2,3-d]furan which is a known coal-tar constituent (21). A standard was not available.

Fraction 20. Fractions 20 and 14 have the absorption peaks at 290 and 360 nm

TABLE II

MASS SPECTROMETRIC DATA OF FRACTIONS AND STANDARDS

Fraction No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]
1			3,4-Benzo-pyrene
	252	1000	1000
	126	218	222
	253	208	237
	250	176	202
	125	153	152
	113	108	88
	112	77	60
	124	72	63
	251	65	64
	248	48	47
2			3,4-Benzo-fluoranthene
	252	1000	1000
	253	234	238
	126	199	196
	250	195	190
	125	128	131
	113	70	68
	112	58	56
	251	57	56
	124	55	54
	248	51	49
3			Chrysene
	228	1000	1000
	226	219	213
	229	185	177
	114	109	135
	113	106	135
	227	82	81
	101	67	74
	224	54	52
	225	44	52
	112	44	55
4			2,3-o-Phenyl-enepyrene
	276	1000	1000
	266	367	
	252	247	
	277	227	261
	138	227	277
	274	163	186
	265	147	
	137	145	186
	275	98	103
	125	92	61
	278	90	
	267	76	
	263	73	
	250	67	
	136	65	75
	124	63	55
	$131\frac{1}{2}$	61	
	$138\frac{1}{2}$	59	
	133	59	
	$132\frac{1}{2}$	59	
	253	57	
	272	53	47
5			10,11-Benzo-fluoranthene
	252	1000	1000
	253	233	234
	250	221	229
	126	164	178
	125	140	159
	251	64	65
	113	62	73
	124	56	64
	112	54	58
	266	53	
	248	53	55
6			11,12-Benzo-fluoranthene
	252	1000	1000
	126	261	234
	253	236	208
	250	169	169
	125	147	156
	113	96	96
	112	81	70
	266	70	
	124	67	57
	251	60	49
	248	52	44
7			Pentacyclic PAH
	278	1000	1000
	279	285	238
	139	195	165
	276	175	189
	138	140	95
	125	80	52
	137	75	56
	274	60	59
	277	47	53
	$139\frac{1}{2}$	50	47
8			
	230	1000	
	215	400	
	229	354	
	202	323	
	228	310	

TABLE II (continued)

Fraction No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]
	101	308	
	231	200	
	114	200	
	113	185	
	226	169	
9			1,2-Benzanthracene
	228	1000	1000
	226	245	225
	229	219	213
	114	181	191
	242	173	
	113	164	146
	101	105	75
	112	84	58
	227	68	64
	100	68	
	224	65	53
	225	55	49
10			Pyrene
	202	1000	1000
	101	246	275
	203	190	193
	200	190	193
	100	166	193
	201	156	164
	88	62	74
	100½	53	59
	234	51	
	87	44	57
	101½	39	
	199	36	41
11			Perylene
	252	1000	1000
	253	258	235
	250	250	235
	126	250	219
	125	194	191
	254	153	
	239	109	
	113	105	51
	282	94	
	124	90	72
	266	88	
	251	79	66
	284	70	
	248	65	59
	112	56	·50
12			Fluoranthene
	202	1000	1000
	101	232	235
	200	196	162
	100	188	149
	203	183	167
	201	129	116
	88	113	111
	87	77	66
	100½	63	43
	101½	39	41
13			
	302	1000	
	303	256	
	300	221	
	151	193	
	290	179	
	289	118	
	304	92	
	298	79	
	318	77	
	301	75	
14			1-Methylpyrene
	216	1000	1000
	215	658	414
	217	186	171
	213	186	119
	94½	183	167
	218	154	
	107½	141	86
	108	138	131
	189	135	74
	228	114	
	106½	111	84
	214	109	78
	107	68	
14			2,3-Benzofluorene
			1000
			771
			190
			174
			106
			200
			174
			93
			79
			74
15			1,2-Benzopyrene
	252	1000	1000
	250	208	253
	253	203	233
	126	169	196

TABLE II (*continued*)

Fraction No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]	Fraction No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]
	125	162	204		275	110	121
	113	87	98		282	101	
	251	72	74		298	100	
	124	72	78		253	98	
	112	59	69		281	97	
	248	54	57		123	83	86
16					230	76	
	278	1000			126	76	
	290	485			272	73	
	280	359			215	73	
	276	348			124	71	68
	279	344			136	68	105
	289	333		20			
	292	307			216	1000	
	265	296			232	947	
	138	274			215	937	
	266	267			230	532	
17					231	468	
	218	1000			202	277	
	232	575			246	251	
	189	575			213	245	
	216	223			229	194	
	204	221			217	191	
	219	174		21			
	202	157			302	1000	
	192	157			316	294	
	94½	153			303	276	
	231	121			151	258	
19			*1,12-Benzo-perylene*		300	244	
	276	1000	1000		150	171	
	278	833			290	142	
	266	567			304	124	
	265	400			289	124	
	280	394			298	95	
	279	306		22			
	277	283	261		266	1000	
	138	278	292		263	255	
	274	222	206		267	242	
	263	222			265	235	
	268	189			131½	146	
	137	161	241		264	137	
	264	152			133	116	
	292	151			268	103	
	267	148			239	99	
	139	144			132	99	
	125	131	125	23			
	131½	126			266	1000	
	228	119			252	774	
	252	118			265	396	
	133	114			251	234	
	132½	114			263	211	
	239	112			267	208	
					250	196	

TABLE II (continued)

Frac-tion No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]	Frac-tion No.	Mass number m/e	MS intensities of fractions[a]	MS intensities of corresponding standard PAH[b]
	126	196		27			Triphenylene
	284	192			242	1110	
	133	166			228	1000	1000
24					230	538	
	246	1000			226	405	272
	232	448			215	392	
	245	395			229	386	214
	231	323			239	297	
	256	314			113	263	181
	258	305			241	259	
	115	269			243	253	
	242	265			114	234	123
	202	251			216	177	
	272	229			244	175	
26					227	172	128
	266	1000			101	172	58
	265	324			240	146	
	267	265			107½	138	
	270	245			119½	132	
	263	216			224	113	63
	282	163			121	109	
	280	153			112	104	79
	133	141			231	103	
	131½	139			225	91	55
	264	114					

[a] Usually only for the ten most intense MS-peaks.
[b] When standard PAH was available.

in common, and hence methylfluoranthenes may be present in fraction 20. Presence of methylpyrenes and benzofluorenes is excluded by R_F values.

Fraction 22. From mass spectra and spot positions it seems that fractions 22, 23 and 26 are PAH having mol. wt. 266. None of them seems to be 1,2:6,7-dibenzofluorene or 2',1':1,2-naphthofluorene, the two PAH having mol. wt. 266 reported by LANG AND EIGEN[21] as coal-tar constituents. However, the absorption spectrum of fraction 22 is rather similar to that of 1,2-benzopyrene, so the component of fraction 22 having mol. wt. 266 may be a methyl-1,2-benzopyrene. A standard was not available.

Fraction 27. From the spot position, it is considered that the component of this fraction having mol. wt. 228 is a tetracyclic PAH. Among the five possible cata-annelated tetracyclic PAH, naphthacene and 3,4-benzophenanthrene are excluded by their absorption spectra and R_F values. Chrysene and 1,2-benzanthracene were identified in fractions 3 and 9, respectively. Thus only triphenylene remains.

Mass spectrometry

The background disturbance of mass spectra was reduced by careful distillation of the solvents and by running the thin-layer plates with the second system solvent mixture before application. In this way, background disturbance became significant

only in the case of the minor component fractions, and it was rather easily compensated for by subtracting the peak heights in question from the mass spectra of the reference samples.

In Table II, mass spectra of fractions and standards are compared. From the spectra of the unknown fractions the 10 strongest peaks are reported, and for the other fractions enough peaks are reported to cover the 10 strongest peaks of the corresponding standard spectrum.

From mass spectra of PAH standards having mol. wt. 216 it appeared that the relative intensity of the M-1 peak was strongly affected by the position of methylene and methyl groups in the molecules. Mass spectrometry may afford a method of determining the orientation of alkyl substituents in nanogram quantities of PAH.

In the case of fraction 7, 3,4-benzotetraphene standard was not available and therefore comparison is made with the spectrum of the isomer 1,2:5,6-dibenzanthracene.

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