Capillary gas chromatographic and combined gas chromatography–mass spectrometric study of the volatile fraction of a coal tar pitch using OV-1701 stationary phase

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ABSTRACT

The components of the volatile fraction of a coal tar pitch were studied by capillary gas chromatography and combined gas chromatography–mass spectrometry using the OV-1701 stationary phase in both instances. The temperature-programmed retention indices and the molecular weight of each identified compound are given. It is shown that the volatile fraction of the coal tar pitch is composed of a group of homologous series of polycyclic aromatic compounds.

INTRODUCTION

The identification and determination of polycyclic aromatic compounds (PACs) is a fundamental task in the study of pitches, tars and other carbonaceous materials, not only for the optimization of production processes but also for their more satisfactory utilization. This area is also of interest from other points of view, such as environmental pollution and health, owing to the mutagenic and carcinogenic properties of some of these compounds. For these reasons many of analytical studies on PACs have been reported in recent years [1–4].

Coal tar is a by-product obtained in coal carbonization, and coal tar pitch is the primary distillation residue of coal tar. Coal tar pitches are complex mixtures of hundreds of PACs. Many of them (50–70% or more) are volatile substances. The boiling points of these compounds range from 218°C for naphthalene to 525°C for coronene. Unfortunately, most of the PACs present in a coal tar pitch are not available commercially. Some excellent gas chromatographic–mass spectrometric (GC–MS) studies on the composition of coal tars have been published [5–11], but coal tar pitch has not received much attention [12].

In this paper a capillary GC study of the components of the volatile fraction of a coal tar pitch using OV-1701 (86% methyl, 7% phenyl and 7% cyanopropyl) stationary phase is reported. To the best of our knowledge, this moderately polar stationary phase has not been used before in the study of these complex mixtures. The retention indices of all peaks obtained using temperature programming were determined. Also, a mass spectrometric study of the sample was carried out using the same capillary column and the same separation conditions as in the GC study, in order to identify as many components of this complicated mixture as possible.

EXPERIMENTAL

The sample was the extracted fraction of a coal tar pitch, obtained by extraction in an ultrasonic bath, using toluene as solvent. The characteristics of the coal tar pitch and the extraction procedure are described in detail in another paper [13].

Retention times were determined with a Model 8320 gas chromatograph (Perkin-Elmer, Beaconsfield, U.K.) with flame ionization detection (FID). Separation was carried out on a fused-silica capillary column (25 m × 0.22 mm I.D.) (Chrompack) coated with OV-1701 stationary phase (McReynolds polarity [14] $\approx$ 789) with hydrogen as the carrier gas at a flow-rate of 1.8 ml/min (measured at the working temperature). The splitting ratio was 1:120. The detector and injector temperatures were 300°C and the column temperature was programmed from 50 to 300°C at 4°C/min.

The retention indices were calculated using Van den Dool and Kratz's method [15]:

$$I = 100 \left[n + \frac{t_r(\text{compound}) - t_r(n)}{t_r(n + 1) - t_r(n)} \right]$$ (1)

where I is the retention index to be calculated, n is the number of rings in the hydrocarbon standard that elutes prior to the substance measured, $t_r(\text{compound})$ is the retention time of the analyte compound and $t_r(n)$ and $t_r(n + 1)$ are the retention times of the PAC standards that elutes just before and after the analyte compound, respectively. The standards used were naphthalene, phenanthrene, chrysene and picene. Some retention indices after picene were calculated from an extension of the chrysene–picene interval. The number of determinations was more than 10.

Mass spectral data were obtained with a Hewlett-Packard combined Model 5880A gas chromatograph–Model 5987A mass spectrometer. The same capillary column as used in GC coated with OV-1701 stationary phase was connected directly to the ion source. The instrument was calibrated with perfluorotributylamine and electron impact mass spectra were recorded at an ionization energy of 70 eV. Peaks in the mass spectra were identified through comparison with other spectra in the literature [16]. Further, for the identification of the compounds, previous knowledge of the chromatographic behaviour (on stationary phases of different polarity) of a large group of compounds belonging to the different families of compounds present in coal tar pitches was used [3,4]. Likewise, the chromatographic behaviour and GC–MS data of the same coal tar pitch extract as studied here on SE-54 stationary phase were also used to help in identification [17].

RESULTS AND DISCUSSION

Fig. 1 shows the chromatogram of the volatile fraction of the coal tar pitch, and Table I gives the retention index, the mass and the compound assigned to each peak in the chromatogram.

It can be seen that high peaks generally belong to one only compound and small peaks sometimes belong to more than one compound. The compounds with the highest concentrations in the mixture are the polycyclic aromatic hydrocarbons (PAHs). The following are present in this carbonaceous material: hydrocarbons with two and three aromatic rings (compounds 1, 39 and 40), hydrocarbons with four aromatic rings *peri-* (compounds 72 and 77) and *cata*-condensed (compounds 103$_b$, 109, 110, 111 and 112$_a$), five-ring systems also *peri-* (compounds 144, 145$_a$, 146, 149$_a$, 150 and 152) and *cata*-condensed (compounds 170$_a$, 174, 175$_b$, 176$_a$, 177, 178 and 180$_b$) and six-ring *peri*-condensed hydrocarbons (compounds 175$_a$, 179 and 181$_a$).

The *peri*-condensed hydrocarbons always elute before the *cata*-condensed hydrocarbons with the same number of rings, and even *peri*-condensed systems with n aromatic rings elute before other *cata*-condensed hydrocarbons with $n - 1$ aromatic rings (see compounds 104, 175$_a$ and 179). Among the *peri*-condensed hydrocarbons the non-alternant systems always elute before the alternant systems, *e.g.*, fluoranthene elutes before pyrene and benzofluoranthenes elute before benzopyrenes.

It can also be seen that *cata*-condensed hydrocarbons whose aromatic rings form a straight line are more retained than the corresponding standard (see retention indices of anthracene and naphthacene in relation to phenanthrene and chrysene, respectively). Taking into account this observation, compounds 180$_b$ may be either benzo[*a*]naphthacene or pentacene. On the other hand, *cata*-condensed hydrocarbons whose aromatic rings form a curved line are less retained and elute before the corresponding standard (*e.g.*, benzo[*c*]phenanthrene elutes before chrysene). For this reason, compounds 155$_c$, 158$_b$ and 170$_a$ could be identified as benzo derivatives of benzo[*c*]phenanthrene.

Acenaphthene, fluorene and some partially hydrogenated PAHs, such as 9,10-dihydro- and 1,2,3,4-tetrahydroanthracene (compounds 15, 22, 29 and 37), are also present in this mixture in considerable concentrations. In addition, other partially hydrogenated PAHs have been found in low concentrations. Hydrogenated PAHs always elute before the corresponding aromatic hydrocarbons.

Two different fluorene series have been found: on the one hand, 4*H*-cyclopenta[*def*]phenanthrene (compound 51) and its benzo derivatives 11*H*-benzo[*bc*]aceanthrylene, 4*H*-cyclopenta[*def*]chrysene and 4*H*-cyclopenta[*def*]triphenylene (compounds 125$_a$, 126$_a$ and 127$_a$) and on the other benzo[*a*]-, benzo[*b*]- and benzo[*c*]fluorene (compounds 85, 86$_a$ and 87) and some dibenzofluorenes (compounds 157$_a$ and 158$_a$). It should be noted that compound 51 and its benzo derivatives shows retention indices similar to those of the methyl derivatives of hydrocarbons with the same number of aromatic rings, whereas benzo- and dibenzofluorenes show retention indices similar to those of methyl derivatives of *peri*-condensed hydrocarbons with an additional aromatic ring but with the same molecular weight.

Other compounds detected in considerable amounts in this coal tar pitch contain sulphur. Taking dibenzo[*b,d*]thiophene (compound 38) as the starting point, two families have been detected: the family of phenanthro[4,5-*bcd*]thiophene (com-
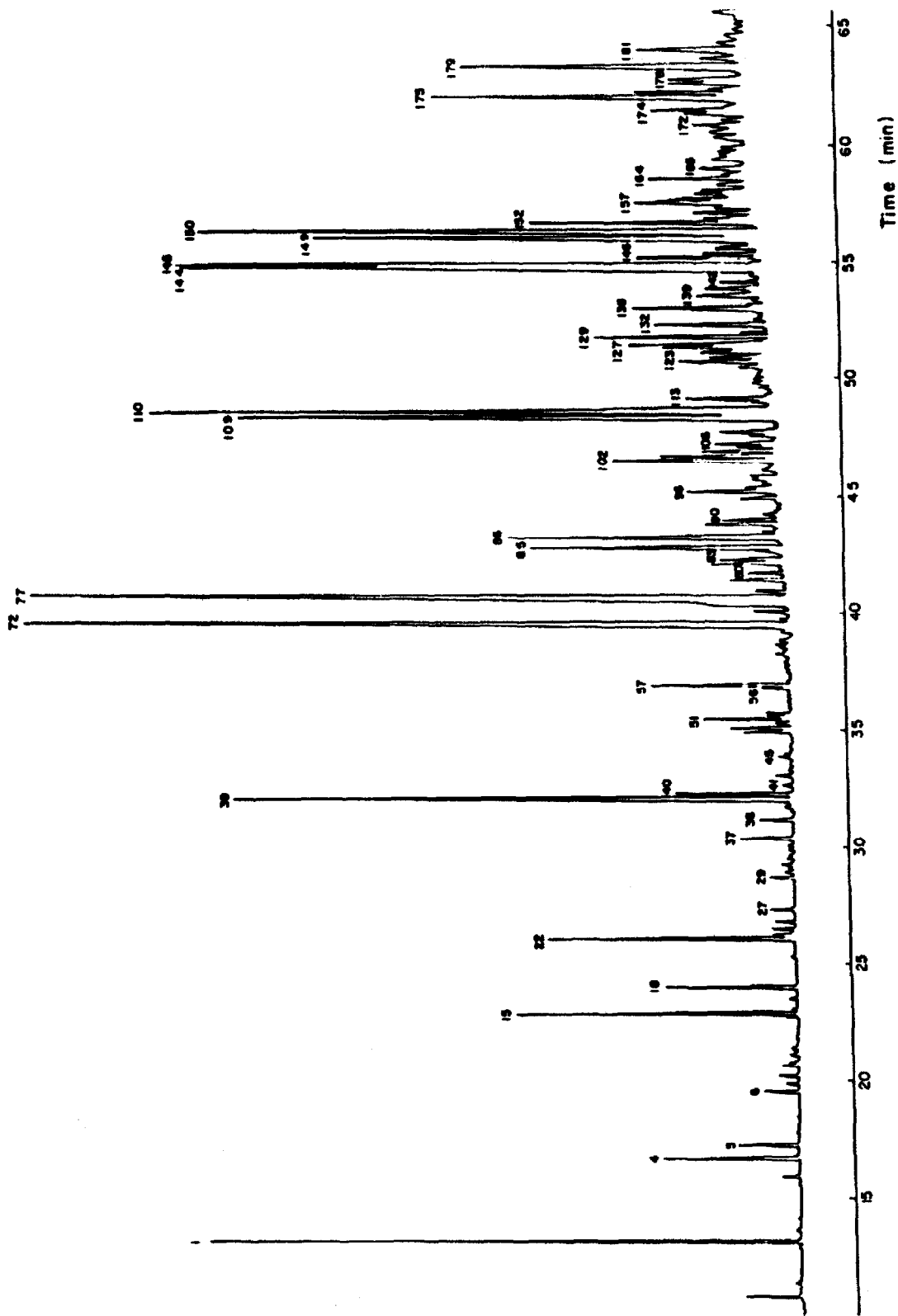
Fig. 1. Capillary gas chromatogram of the volatile fraction of a coal tar pitch on OV-1701 stationary phase. For peaks, see Table I.

TABLE I

RETENTION INDICES (I) ON OV-1701 STATIONARY PHASE AND MOLECULAR WEIGHTS OF THE COMPONENTS IDENTIFIED IN THE VOLATILE FRACTION OF A COAL TAR PITCH

Peak No.	$I^{OV-1701}$	Molecular weight	Possible compound
1	200.00	128	Naphthalene
2	201.66	134	Benzo[b]thiophene
3	213.46	129	Quinoline
4	217.87	142	2-Methylnaphthalene
5	220.81	142	1-Methylnaphthalene
6	232.50	154	Biphenyl
7	234.22	156	2-Ethylnaphthalene
8	236.22	156	Dimethylnaphthalene
9	238.34	156	Dimethylnaphthalene
10	238.93	156	Dimethylnaphthalene
11	241.01	156	Dimethylnaphthalene
12	242.53	156	Dimethylnaphthalene
13	244.99	156	Dimethylnaphthalene
14	249.89	168	Methylbiphenyl
15	250.59	154	Acenaphthene
16	251.54	170	Trimethylnaphthalene
17	253.62	168	Methylbiphenyl
18	256.56	168	Dibenzofuran
19	259.90	170	Trimethylnaphthalene
20	262.30	170	Trimethylnaphthalene
21	263.56	153	Naphthonitrile or azaacenaphthylene
22	266.72	166	Fluorene
23	267.78	168	Methylacenaphthene
24	268.49	168	Methylacenaphthene
25	269.90	168	Methylacenaphthene
26	271.53	182	Methyldibenzofuran
27	274.59	182	Methyldibenzofuran
28	275.42	198	
29	281.56	180	9,10-Dihydroanthracene
30$_a$	282.55	180	9,10-Dihydrophenanthrene
30$_b$	282.55	196	Dimethyldibenzofuran
31$_a$	283.49	180	9-Methylfluorene
31$_b$	283.49	196	Dimethyldibenzofuran
32	284.38	180	Methylfluorene
33	285.75	180	Methylfluorene
34	286.63	180	Methylfluorene
35	287.74	196	Dimethyldibenzofuran
36	288.81	196	Dimethyldibenzofuran
37	290.56	182	1,2,3,4-Tetrahydroanthracene
38	294.83	184	Dibenzo[b,d]thiophene
39	300.00	178	Phenanthrene
40	300.72	178	Anthracene
41	302.96	179	Benzoquinoline
42	305.32	179	Benzoquinoline
43	306.79	204	1-Phenylnaphthalene
44	307.32		
45	308.43	179	Benzoquinoline
47	313.48		
48	316.78	192	Methylphenanthrene, -anthracene
49	317.56	192	Methylphenanthrene, -anthracene

TABLE I *(continued)*

Peak No.	$I^{OV-1701}$	Molecular weight	Possible compound
50	318.67	192	Methylphenanthrene, -anthracene
51	319.53	190	4*H*-Cyclopenta[*def*]phenanthrene
52	320.49	192	Methylphenanthrene, -anthracene
53	321.24	192	Methylphenanthrene, -anthracene
54	323.07		
55	324.64		
56	327.63	204	2-Phenylnaphthalene
57	328.19	167	Carbazole
58ₐ	328.72	206	Dimethylphenanthrene, -anthracene
58ᵦ	328.72	193	Methylbenzoquinoline or isomer
59	330.06	206	Dimethylphenanthrene, -anthracene
60	330.75	206	Dimethylphenanthrene, -anthracene
61	331.39	206	Dimethylphenanthrene, -anthracene
62	332.57	206	Dimethylphenanthrene, -anthracene
63	333.58	206	Dimethylphenanthrene, -anthracene
64ₐ	334.65	206	Dimethylphenanthrene, -anthracene
64ᵦ	334.65	204	Methyl 4*H*-cyclopenta[*def*]phenanthrene
65	335.49	206	Dimethylphenanthrene, -anthracene
66ₐ	337.03	206	Dimethylphenanthrene, -anthracene
66ᵦ	337.03	204	Dihydropyrene or isomer
67	338.29	204	Dihydropyrene or isomer
68	338.92	204	Benzacenaphthene or isomer
69	339.68	181	Methylcarbazole
70	340.54		
71	342.52		
72	344.20	202	Fluoranthene
73	345.60	181	Methylcarbazole
74	347.77	208	Phenanthro[4,5-*bcd*]thiophene
75	349.40	203	Azafluoranthene, -pyrene
76	350.43	218	Benzonaphthofuran
77	351.21	202	Pyrene
78	353.13	218	Benzonaphthofuran
79	356.09	218	Benzonaphthofuran
80	357.99	218	Benzo[*kl*]xanthene
81	359.53	220	Trimethylphenanthrene, -anthracene
82ₐ	360.64	216	Methylfluoranthene
82ᵦ	360.64	203	Azafluoranthene, -pyrene
83	361.58	203	Azafluoranthene, -pyrene
84	363.45	216	Methylfluoranthene, -pyrene
85	364.26	216	Benzo[*a*]fluorene
86ₐ	367.22	216	Benzo[*b*]fluorene
86ᵦ	367.22	232	Methylbenzonaphthofuran or isomer
87	368.23	216	Benzo[*c*]fluorene or isomer
88	368.90	232	Methylbenzonaphthofuran or isomer
89	370.62	232	Methylbenzonaphthofuran or isomer
90	371.70	216	Methylpyrene
91	373.41	232	Methylbenzonaphthofuran or isomer
92	374.44	232	Methylbenzonaphthofuran or isomer
93ₐ	375.41	217	Azabenzofluorene
93ᵦ	375.41	230	Dimethylfluoranthene, -pyrene
94	377.51	230	Dimethylfluoranthene, -pyrene
95	379.47	230	Dihydrochrysene or isomer

TABLE I *(continued)*

Peak No.	$I^{OV-1701}$	Molecular weight	Possible compound
96$_a$	380.01	191	4*H*-Benzo[*def*]carbazole
96$_b$	380.01	230	Dimethylfluoranthene, -pyrene
97	381.21	230	Dimethylfluoranthene, -pyrene
98$_a$	382.36	230	Dimethylfluoranthene, -pyrene
98$_b$	382.36	246	Dimethylbenzonaphthofuran or isomer
99$_a$	383.11	230	Dimethylfluoranthene, -pyrene
99$_b$	383.11	246	Dimethylbenzonaphthofuran
100$_a$	384.65	230	Dimethylfluoranthene, -pyrene
100$_b$	384.65	246	Dimethylbenzonaphthofuran
101	385.31	246	Dimethylbenzonaphthofuran
102	387.46	234	Benzo[*b*]naphtho[2,1-*d*]thiophene
103$_a$	388.58	232	Tetrahydrochrysene or isomer
103$_b$	388.58	228	Benzo[*c*]phenanthrene
104	389.64	226	Benzo[*ghi*]fluoranthene or isomer
105	390.65	234	Benzo[*b*]naphtho[1,2-*d*]thiophene
106	391.52	229	Dibenzoquinoline or isomer
107	393.60	244	Trimethylfluoranthene, -pyrene
108	394.49	234	Benzo[*a*]naphtho[2,3-*d*]thiophene
109	397.91	228	Benz[*a*]anthracene
110	400.00	228	Chrysene
111	400.33	228	Triphenylene
112$_a$	402.35	228	Naphthacene
112$_b$	402.35	248	Methylbenzo[*b*]naphthothiophene
113$_a$	403.44	242	Methylbenz[*a*]anthracene or isomer
113$_b$	403.44	248	Methylbenzo[*b*]naphthothiophene
114$_a$	407.39	248	Methylbenzonaphthothiophene
114$_b$	407.39	258	Tetramethylfluoranthene or isomer
115	408.73	242	Methylbenz[*a*]anthracene or isomer
116$_a$	409.68	248	Methylbenzonaphthothiophene or isomer
116$_b$	409.68	258	Tetramethylfluoranthene or isomer
117	410.49	242	Methylchrysene or isomer
118$_a$	411.48	241	Methylazabenzo[*ghi*]fluoranthene or isomer
118$_b$	411.48	258	Tetramethylfluoranthene or isomer
119$_a$	412.27	242	Methylchrysene or isomer
119$_b$	412.27	248	Methylbenzonaphthothiophene
120	412.73	242	Methylbenz[*a*]anthracene or isomer
121	413.58	256	Dimethylbenz[*a*]anthracene or isomer
122	414.48	242	Methylbenz[*a*]anthracene or isomer
123	415.35	242	Methylbenz[*a*]anthracene or isomer
124	416.68	242	Methylbenz[*a*]anthracene or isomer
125$_a$	418.02	240	11*H*-Benz[*bc*]aceanthrylene or isomer
125$_b$	418.02	254	Binaphthalene or isomer
126$_a$	419.66	240	4*H*-Cyclopenta[*def*]chrysene or isomer
126$_b$	419.66	254	Binaphthalene or isomer
127$_a$	420.68	240	4*H*-Cyclopenta[*def*]triphenylene or isomer
127$_b$	420.68	256	Dimethylbenz[*a*]anthracene or isomer
128	421.67	254	Phenylphenanthrene or isomer
129	422.92	217	11*H*-Benzo[*a*]carbazole
130	423.94	254	Phenylphenanthrene or isomer
131	425.50	254	Dihydrobenzofluoranthene or isomer
132	426.28	217	7*H*-Benzo[*c*]carbazole
133	428.17	254	Dihydrobenzofluoranthene or isomer

TABLE I *(continued)*

Peak No.	$I^{OV-1701}$	Molecular weight	Possible compound
134$_a$	429.18	241	Methylazabenzo[*ghi*]fluoranthene or isomer
134$_b$	429.18	256	Dimethylchrysene
135	430.69		
136	431.52	217	5*H*-Benzo[*b*]carbazole
137$_a$	432.43	241	Methylazabenzo[*ghi*]fluoranthene or isomer
137$_b$	432.43	256	Dimethylchrysene
137$_c$	432.43	268	Dibenzonaphthofuran or isomer
138	433.62	256	Dimethylchrysene or isomer
139$_a$	435.64	256	Dimethylchrysene or isomer
139$_b$	435.64	268	Dibenzonaphthofuran or isomer
140$_a$	436.32	256	Dimethylchrysene or isomer
140$_b$	436.32	268	Dibenzonaphthofuran or isomer
141$_a$	437.60	219	Dimethylbenzo[*c,d,f*]carbazole
141$_b$	437.60	231	Methylbenzocarbazole
142$_a$	439.45	254	Dihydrobenzofluoranthene or isomer
142$_b$	439.45	268	Dibenzonaphthofuran or isomer
143	442.25	268	Dibenzonaphthofuran or isomer
144	443.36	252	Benzo[*j*]fluoranthene
145$_a$	444.29	252	Benzo[*b*]fluoranthene
145$_b$	444.29	268	Dibenzonaphthofuran
146	446.96	252	Benzo[*k*]fluoranthene
147$_a$	448.40	268	Dibenzonaphthofuran
147$_b$	448.40	258	Benzophenanthrothiophene
148$_a$	450.08	254	Dihydrobenzopyrene or isomer
148$_b$	450.08	258	Benzophenanthrothiophene
148$_c$	450.08	268	Dibenzonaphthofuran
149$_a$	452.90	252	Benzo[*e*]pyrene
149$_b$	452.90	268	Dibenzonaphthofuran or isomer
150	454.96	252	Benzo[*a*]pyrene
151	455.58	253	Azabenzopyrene
152	458.04	252	Perylene
153	459.31	266	Methylbenzofluoranthene or isomer
154$_a$	460.67	266	Methylbenzofluoranthene or isomer
154$_b$	460.67	272	Methylbenzophenanthrothiophene
155$_a$	461.41	266	Methylbenzofluoranthene or isomer
155$_b$	461.41	253	Azabenzopyrene or isomer
155$_c$	461.41	278	Dibenzophenanthrene
156$_a$	462.59	253	Azabenzopyrene or isomer
156$_b$	462.59	266	Methylbenzofluoranthene or isomer
157$_a$	463.47	266	Dibenzofluorene or isomer
157$_b$	463.47	282	Methyldibenzonaphthofuran
158$_a$	464.23	266	Dibenzofluorene or isomer
158$_b$	464.23	278	Dibenzophenanthrene, -anthracene
159$_a$	465.24	266	Methylbenzofluoranthene or isomer
159$_b$	465.24	282	Dimethyldibenzonaphthofuran
160	466.01	266	Methylbenzopyrene or isomer
161$_a$	467.13	266	Methylbenzopyrene or isomer
161$_b$	467.13	282	Dimethyldibenzonaphthofuran
162	467.86	266	Methylbenzopyrene or isomer
163$_a$	469.66	266	Methylbenzopyrene or isomer
163$_b$	469.66	282	Dimethyldibenzonaphthofuran
164$_a$	471.50	264	11*H*-Cyclopenta[*ghi*]perylene

TABLE I *(continued)*

Peak No.	$I^{OV-1701}$	Molecular weight	Possible compound
164ᵦ	471.50	266	Methylbenzopyrene
165	474.94	280	Dimethylbenzopyrene or isomer
166ₐ	478.01	241	4H-Naphtho[1,2,3,4-def]carbazole or isomer
166ᵦ	478.01	280	Dimethylbenzofluoranthene or isomer
167	481.40		
168ₐ	483.22	284	Dibenzonaphthothiophene
168ᵦ	483.22	280	Dimethylbenzofluoranthene or isomer
169ₐ	484.45	280	Dimethylbenzofluoranthene
169ᵦ	484.45	296	Trimethyldibenzonaphthofuran
170ₐ	488.36	278	Dibenzophenanthrene
170ᵦ	488.36	280	Dimethylbenzopyrene or isomer
171	489.49		
172ₐ	490.76	284	Dibenzonaphthothiophene
172ᵦ	490.76	279	Dibenzophenanthridine or isomer
172ᵨ	490.76	294	Trimethylbenzofluoranthene or isomer
173	491.37		
174	492.08	278	Dibenz[a,j]anthracene or isomer
175ₐ	494.80	276	Indenopyrene or isomer
175ᵦ	494.80	278	Dibenzo[a,c]anthracene
176ₐ	496.15	278	Dibenzo[a,h]anthracene
176ᵦ	496.15	267	
177	498.96	278	Benzo[b]chrysene or isomer
178	500.00	278	Picene
179	502.47	276	Benzo[ghi]perylene
180ₐ	504.80	290	Methyl derivative of indenopyrene or isomer
180ᵦ	504.80	278	Benzo[a]naphthacene or pentacene
181ₐ		276	Anthanthrene
181ᵦ		290	Methyl derivative of indenopyrene or isomer

pound 74, detected for the first time in 1977 in tars [18]) and their benzo derivatives (compounds 147ᵦ and 148ᵦ), and the family of benzo and dibenzo derivatives of dibenzo[b,d]thiophene (compounds 102, 105, 108, 168ₐ and 172ₐ). The significant concentration of benzo derivatives of benzo[b,d]thiophene in this complex mixture should be noted. All these compounds with *n* aromatic rings are retained on the stationary phase in an order similar to that of hydrocarbons which have $n + 1$ aromatic rings and a similar geometrical shape.

In addition to the compounds mentioned above, pyridine and pyrrole derivatives are also present in this mixture. Pyrrole derivatives begin with carbazole (compound 57) and compounds corresponding to its *peri-* and *cata-*condensed series (compounds 96ₐ and 166ₐ, and 129, 132 and 136, respectively) have been found. It is interesting that all these compounds are much more retained on OV-1701 than hydrocarbons or sulphur derivatives with the same geometrical shape. All of them elute among other compounds which have a higher molecular weight and a higher boiling point (*e.g.*, boiling point of carbazole, compound 57, 355°C; boiling point of 4H-cyclopenta[def]phenanthrene, compound 51, 358°C; and boiling point of 2-phenylnaphthalene, compound 56, 359.8°C). This can be attributed to the fact that

the pyrrole derivatives are able to establish hydrogen bonds with the stationary phase. For this reason, they are more retained than the other compounds. Further, the considerable concentration of carbazole and its *cata*-condensed benzo derivatives in the mixture should be pointed out; the elution order of these latter compounds could be first 11*H*-benzo[*a*]carbazole (boiling point 450°C), then 7*H*-benzo[*c*]carbazole (boiling point 452°C) and 5*H*-benzo[*b*]carbazole (boiling point 455°C), if this sequence agrees with the sequence of increasing boiling points.

The group of pyridine derivatives has a very large number of members but all of them at very low concentrations. All these compounds (compounds 3, 41, 42, 45, 75, 82$_b$, 83, 93$_a$, 106, 151, 155$_b$, 156$_a$ and 172$_b$) elute near to the corresponding hydrocarbons. The chromatographic behaviour of this family of compounds has been previously studied using stationary phases of different polarity [3,19].

Another interesting group to be detected are oxygenated compounds. The first, dibenzofuran (compound 18), is followed by its benzo and dibenzo derivatives (compounds 76, 78, 79, 139$_b$, 140$_b$, 142$_b$, 143, 145$_b$, 147$_a$ and 148$_c$), but the *peri*-condensed series previously found for dibenzo[*b,d*]thiophene and carbazole have not been detected. Compound 80 has been identified as benzo[*k*]xanthene. According to Lang and Eigen [20], the boiling point of this latter compound is 400°C. However, the boiling points of benzo[*b*]naphtho[2,1-*d*]furan and benzo[*b*]naphtho[2,3-*d*]furan are 387.7 and 394.5°C, respectively.

In addition to all the above-mentioned types of compounds, their methyl derivatives have also been detected. The concentration of monomethyl derivatives is always lower than those of the unmethylated compounds but higher than those of the di- or trimethyl derivatives.

Phenyl and naphthyl derivatives of hydrocarbons (compounds 6, 43, 56, 125$_b$, 130, 131, etc.) and other compound types in very small proportions have also been detected. These small peaks are more difficult to identify because they generally belong to more than one compound.

All components found in the volatile fraction of coal tar pitch are also present in coal tar, as expected, but the concentrations of most of the compounds are very different. Likewise, most of these compounds are not available commercially and their physico-chemical properties are unknown, but they are present in many carbonaceous and environmental samples.

The volatile fraction of the coal tar pitch covers wide ranges of boiling points (from 218 to *ca*. 525°C) and molecular weights (from *ca*. 128 to 300). Most of the compounds contained in this fraction belong only to the different families mentioned before, and compounds with other special functional groups have not been detected. Because of this, it could be concluded that the involatile fraction of this coal tar pitch is formed by the components of the different series mentioned before with higher molecular weights.

In the light of this, it might be worthwhile looking for relationships between the qualitative and/or quantitative composition of the volatile fraction of coal tar pitches, obtained through a chromatographic study, and the properties and behaviour of the whole coal tar pitches.

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