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Polynuclear aromatic hydrocarbon retention indices on SE-54 stationary phase of the volatile components of a coal tar pitch

Relationships between chromatographic retention and thermal reactivity

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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 stationary phase SE-54 in both instances. The molecular weight and the retention indices of each identified compound are given. These values are compared with those determined on the stationary phase OV-1701. Relationships between information from the gas chromatography study and from the thermal reactivity of coal tar pitch components are discussed.

INTRODUCTION

Coal tar pitches are very complex mixtures of polynuclear aromatic hydrocarbons (PAHs) and heterocyclic compounds [1] and they behave as eutectic mixtures. Their chemical compositions, physical properties and structures are not known with any degree of certainty. However, it is obvious that their behaviour, reactivity and properties are governed by their composition, and it is generally accepted that the search for relationships between composition, properties and behaviour in the study of carbonaceous materials constitutes the key for a more rational use of these materials [2].

However, the study of their composition is very difficult. Sample fractionations and subsequent characterization of the fractions obtained may be an adequate approach [3–5]. Another possible approach is the characterization of the volatile fraction and the search for relationships between the composition and properties of the entire coal tar pitch. Whatever the approach used, the reproducibility of the fractionation or extraction experiment should always be taken into account. Our experience with coal tar pitch extractions has shown a reproducibility of experiments with some solvents [6], which hinders the correct qualitative and quantitative characterization of coal tar pitches.

Capillary gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) [7, 8] are two of the most powerful techniques for the study of mixtures of polynuclear aromatic compounds. In our efforts to study in depth the volatile fraction of a coal tar pitch, we have reported the retention indices of the possible components of this complex mixture [9] on OV-1701 stationary phase (86% methyl, 7% phenyl, 7% cyanopropyl). In this paper GC and GC–MS studies of the volatile

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fraction of the same coal tar pitch using SE-54 stationary phase (94% methyl, 5% phenyl, 1% vinyl) are reported. The retention indices and the masses of all the peaks obtained are given. These values are compared with those determined on OV-1701. Relationships between information from the GC study and the thermal reactivity of coal tar pitch components are discussed.

EXPERIMENTAL

The sample was the 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 have been described in detail elsewhere [6].

Retention times were determined with a Model 8320 gas chromatograph (Perkin-Elmer, Beaconsfield, UK) 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 SE-54 stationary phase 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 PAH retention indices (*I*) [10,11] were calculated as follows:

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

where n is the number of rings in the hydrocarbon standard that elutes prior to the substance being measured, t_r(compound) is the retention time of the analyte compound and $t_r(n)$ and $t_r(n+1)$ are the retention times of the PAH standard that elutes just before and after the analyte compound. 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 SE-54 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 [12]. 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 [13,14].

RESULTS AND DISCUSSION

Fig. 1 shows the chromatogram of the volatile fraction of Al coal tar pitch on SE-54 stationary phase. Table I gives the retention indices, the mass and the compound assigned to each peak in Fig. 1. The retention indices of some of the coal tar pitch components obtained on SE-54 are fairly close to those obtained on SE-52 for standard compounds [10,11].

In agreement with previous results [9], the fraction examined is composed basically of polynuclear aromatic *cata-* and *peri*-condensed hydrocarbons, and among the latter there are alternant and non-alternant systems[a], acenaphtene and fluorene and their benzo derivatives, some partially hydrogenated PAHs, benzo derivatives of quinoline, carbazole, dibenzo[*b,d*]thiophene and dibenzofuran, alkyl derivatives of all the above-mentioned compounds and PAHs supporting phenyl or naphthyl radicals.

Table II shows some components of the different families together with the differences in their retention indices on SE-54 (non-polar) and OV-1701 (moderately polar) stationary phases. The data on OV-1701 were taken from a previous paper [9]. For the comparison of some incompletely identified compounds such as methyl, phenyl or naphthyl derivatives, the first isomer eluted was taken into account. It was observed that the unsubstituted PAHs show the same elution order with both stationary phases, and in general they show a smaller retention index on SE-54 than on OV-1701 (with some exceptions). However, the latter stationary phase is able to separate benz[*a*]anthracene,

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[a] Alternant systems contain only six-membered rings; non-alternant systems have at least one five-membered ring.

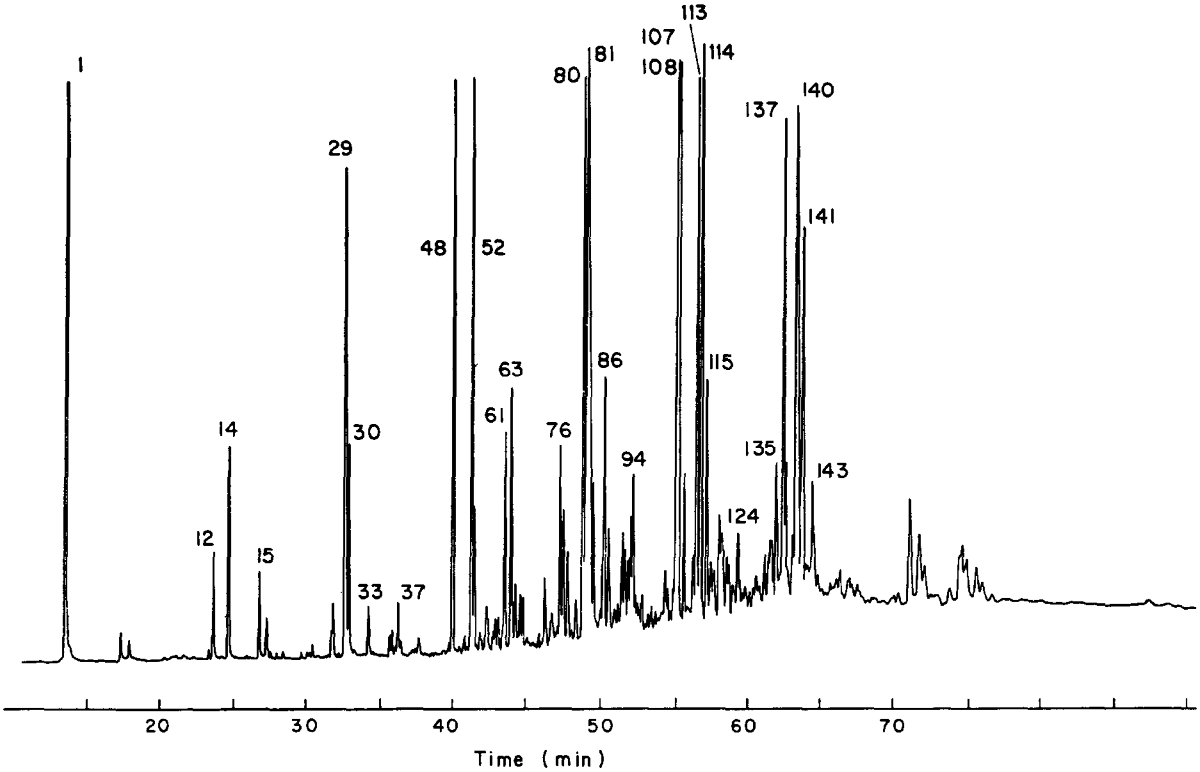

Fig. 1. Capillary gas chromatogram of the volatile fraction of a coal tar pitch on SE-54 stationary phase. For peaks, see Table I.

chrysene and triphenylene (see Fig. 2), like Poly-179 polyphenyl ether sulphone [15] and mixtures of BBBT liquid crystal and SE-52 silicone gum [16]. Acenaphthene, fluorene its benzo derivatives and partially hydrogenated PAHs elute in a similar order on both stationary phases, always before the corresponding hydrocarbons. However, they show higher retentions on SE-54 than on OV-1701, apart from some benzo derivatives of fluorene. The alkylated benzo derivatives elute in the same order on both stationary phases, but in all instances (except for the methyl derivatives of carbazole) their retention is higher on SE-54 than on OV-1701. Other groups of compounds such as phenyl and naphthyl derivatives are also more retained on SE-54 than on OV-1701.

The oxygen benzo derivatives are more retained on SE-54 than on OV-1701. The benzo derivatives of dibenzo[*b*,*d*]thiophene show a similar retention and elution order on both stationary phases, and there is no general trend. The pyrrole and pyridine benzo derivatives are retained much more on OV-1701 than on SE-54, especially the pyrrole derivatives, which change their elution order. As shown in Figs. 1 and 2, the characterization of benzo derivatives of carbazole can be achieved much better on OV-1701 because on this stationary phase these compounds elute in a zone free from other compounds, whereas on SE-54 these compounds elute in the chrysene–methylchrysene range. For this reason, the quantification of these compounds in coal tar pitches using the non-polar stationary phase is much more difficult, if not impossible. It is concluded that although non-polar stationary phases such as SE-52 and SE-54 have often been used for the chromatographic study of PAHs in general, OV-1701 has advantages for the characterization of the volatile components of coal tar pitches.

The reactivity of a compound is governed by its ability to establish interactions with other molecules. In the chromatographic process the solute–stationary phase interactions also control solute retention. In a chromatographic run the stationary

TABLE I

PAH RETENTION INDICES (*I*) ON SE-54 STATIONARY PHASE AND MOLECULAR WEIGHTS OF THE COMPONENTS IDENTIFIED IN THE VOLATILE FRACTION OF A COAL TAR PITCH

Peak No. (Fig. 1)	I^{SE-54}	Molecular weight	Possible compound	Peak No. (Fig. 1)	I^{SE-54}	Molecular weight	Possible compound
1	200.00	128	Naphthalene	79	391.46	232	Tetrahydrochrysene or isomer
2	201.44	134	Benzo[*b*]thiophene	80	393.17	234	Benzo[*a*]naphtho[2,3-*d*]thiophene
3	210.17	129	Quinoline	81	396.46	228	Benz[*a*]anthracene
4	220.06	142	2-Methylnaphthalene	82a	400.00	228	Chrysene
5	223.06	142	1-Methylnaphthalene	82b		217	11*H*-Benzo[*a*]carbazole
6	235.51	154	Biphenyl	83a	401.28	228	Naphthacene
7	237.74	156	2-Ethylnaphthalene	83b		248	Methylbenzonaphthothiophene
8	239.81	156	Dimethylnaphthalene	84	404.38		
9	242.13	156	Dimethylnaphthalene	85a	405.34	242	Methylbenz[*a*]anthracene or isomer
10	243.01	156	Dimethylnaphthalene	85b		258	Tetramethylfluoranthene or isomer
11	248.85	168	Methylbiphenyl	86a	406.26	217	7*H*-Benzo[*c*]carbazole
12	253.15	154	Acenaphthene	86b		242	Methylbenz[*a*]anthracene or isomer
13	255.85	153	Naphtonitrile or azaacenaphthylene	86c		258	Tetramethylfluoranthene or isomer
14	258.53	168	Dibenzofuran	87a	407.54	217	5*H*-Benzo[*b*]carbazole
15	269.22	166	Fluorene	87b		243	Methylbenzophenanthridine or isomer
16	271.08	168	Methylacenaphthene	88a	411.20	219	Dimethylbenzo[*cd,f*]carbazole
17	271.91	168	Methylacenaphthene	88b		242	Methylchrysene or isomer
18	273.32	168	Methylacenaphthene	89	412.71	242	Methylchrysene or isomer
19	275.32	182	Methyldibenzofuran	90a	414.26	242	Methylbenz[*a*]anthracene or isomer
20	277.60	182	Methyldibenzofuran	90b		256	Dimethylbenz[*a*]anthracene or isomer
21	284.15	180	9,10-Dihydroanthracene	91a	415.66	242	Methylbenz[*a*]anthracene or isomer
22	286.22	180	9,10-Dihydrophenanthrene	91b		256	Dimethylbenz[*a*]anthracene or isomer
23	287.24	180	Methylfluorene	92a	417.16	240	11*H*-Benz[*bc*]aceanthrylene or isomer
24	288.31	180	Methylfluorene	92b		242	Methylbenz[*a*]anthracene or isomer
25	289.85	180	Methylfluorene	93a	418.55	240	4*H*-Cyclopenta[*def*]chrysene or isomer
26	293.48	180	Methylfluorene	93b		242	Methylbenz(a)anthracene or isomer
27	294.67	182	1,2,3,4-Tetrahydroanthracene	93c		254	Binaphthalene or isomer
28	295.24	184	Dibenzo[*b,d*]thiophene	94	419.67	240	4*H*-Cyclopenta[*def*]triphenylene or isomer
29	300.00	178	Phenanthrene	95a	420.56	256	Dimethylbenz[*a*]anthracene or isomer
30	301.05	178	Anthracene	95b		242	Methylbenz[*a*]anthracene or isomer
31	302.98	179	Acridine	96	421.56	254	Binaphthalene or isomer
32	307.03	179	Phenanthridine	97a	422.44	256	Dimethylbenz[*a*]anthracene or isomer
33	309.02	167	Carbazole	97b		242	Methylbenz[*a*]anthracene or isomer
34	317.68	192	Methylphenanthrene, -anthracene	98	423.92	254	Binaphthalene or isomer
35	318.53	192	Methylphenanthrene, -anthracene	99	425.67		
36	320.04	192	Methylphenanthrene, -anthracene	100	426.96		
37	321.05	190	4*H*-Cyclopenta[*def*]phenanthrene	101	428.36	254	Phenylphenanthrene or isomer
38	322.38	192	Methylphenanthrene, -anthracene	102	430.42		
39	325.81	192	Methylphenanthrene, -anthracene				

40	326.84	181	Methylcarbazole	103	431.68	254	Dihydrobenzofluoranthene or isomer
41	328.57	181	Methylcarbazole	103a		256	Dimethylchrysene or isomer
42	329.78	204	2-Phenylnaphthalene	104a	434.97	253	Dibenzophenanthridine or isomer
43	332.07			104b		256	Biquinoline
44	334.82			105	436.51	256	Biquinoline
45	336.17			106	437.41		
46	339.44			107a	440.92	252	Benzo[*j*]fluoranthene
47	341.63	204	Dihydropyrene or isomer	107b		254	Dihydrobenzofluoranthene or isomer
48	343.24	202	Fluoranthene	108a	441.63	252	Benzo[*b*]fluoranthene
49	345.73	203	Azafluoranthene, -pyrene	108b		254	Dihydrobenzofluoranthene or isomer
50	347.89	208	Phenanthro[4,5-*bcd*]thiophene	109a	444.43	252	Benzo[*k*]fluoranthene
51	348.68	203	Azafluoranthene, -pyrene	109b		268	Dibenzonaphthofuran or isomer
52	350.83	202	Pyrene	109c		254	Dihydrobenzofluoranthene or isomer
53a	351.66	218	Benzonaphthofuran	110a	445.61	256	Dimethylchrysene or isomer
53b		204	Benzacenaphthene or isomer	110b		253	Azabenzopyrene or isomer
54	352.60	204	Benzacenaphthene or isomer	111	446.28		
55	354.31	218	Benzonaphthofuran	112a	448.67	268	Dibenzonaphthofuran or isomer
56	356.50	218	Benzonaphthofuran	112b		258	Benzophenanthrothiophene
57	356.93	203	Benzo[*lmn*]phenanthridine	112c		253	Azabenzopyrene or isomer
58	359.77	218	Benzo[*kl*]xanthene	113a	450.75	252	Benzo[*e*]pyrene
59	360.61	216	Methylfluoranthene, -pyrene	113b		268	Dibenzonaphthofuran or isomer
60a	361.51	191	4*H*-Benzo[*def*]carbazole	114a	452.95	252	Benzo[*a*]pyrene
60b		203	Azafluoranthene, -pyrene	114b		268	Dibenzonaphthofuran or isomer
61	364.80	216	Benzo[*a*]fluorene	115a	455.59	252	Perylene
62	365.48	216	Methylfluoranthene, -pyrene	115b		268	Dibenzonaphthofuran or isomer
63	367.20	216	Benzo[*b*]fluorene	115c		266	Methylbenzofluoranthene or isomer
64	367.62	216	Benzo[*c*]fluorene or isomer	116a	457.84	266	Methylbenzofluoranthene or isomer
65a	368.61	218	Methylbenzacenaphthene or isomer	116b		253	Azabenzopyrene or isomer
65b		232	Methylbenzonaphthofuran or isomer	117a	459.33	241	4*H*-Naphtho[1,2,3,4-*def*]carbazole or isomer
66	370.22	216	Methylpyrene or isomer	117b		266	Methylbenzofluoranthene or isomer
67	371.72	216	Methylpyrene or isomer	118a	461.52	266	Dibenzofluorene or isomer
68	373.73	232	Methylbenzonaphthofuran or isomer	118b		278	Dihydroindenopyrene or isomer
69	376.32	232	Methylbenzonaphthofuran or isomer	119	462.33	266	Dibenzofluorene or isomer
70a	377.16	217	Methylazapyrene or isomer	120	462.92	266	Dibenzofluorene or isomer
70b		232	Methylbenzonaphthofuran or isomer	121a	465.39	266	Methylbenzopyrene or isomer
71	378.52	230	Methylbenzofluorene	121b		278	Dibenzo[*c,g*]phenanthrene or isomer
72	379.39			121c		282	Dimethyldibenzonaphthofuran or isomer
73	380.62	230	Dihydrochrysene or isomer	122	466.29	266	Methylbenzopyrene or isomer
74a	383.09	230	Dimethylfluoranthene, -pyrene	123	468.38	266	Methylbenzopyrene or isomer
74b		244	Trimethylfluoranthene, -pyrene	124a	470.53	264	11*H*-Cyclopenta[*ghi*]perylene or isomer
75	383.96	230	Dimethylfluoranthene, -pyrene	124b		266	Methylbenzopyrene or isomer
76	387.08	234	Benzo[*b*]naphtho[2,1-*d*]thiophene	124c		280	Dimethylbenzopyrene or isomer
77a	388.58	228	Benzo[*c*]phenanthrene	125	471.41	266	Methylbenzopyrene or isomer
77b		226	Benzo[*ghi*]fluoranthene	126a	473.15	266	Methylbenzopyrene or isomer
77c		246	Dimethylbenzonaphthofuran	126b		280	Dimethylbenzopyrene or isomer
78a	390.33	234	Benzo[*b*]naphtho[1,2-*d*]thiophene	127a	474.21	264	11*H*-Indeno[2,1,7-*cde*]pyrene or isomer
78b		229	Dibenzoquinoline or isomer	127b		280	Dimethylbenzopyrene or isomer

(Continued on p. 292)

TABLE I (*continued*)

Peak No. (Fig. 1)	I^{SE-54}	Molecular weight	Possible compound	Peak No. (Fig. 1)	I^{SE-54}	Molecular weight	Possible compound
128	476.15			135c		282	Dimethyldibenzonaphthofuran
129a	478.30	284	Dinaphthothiophene	135d		292	Methyldibenzophenanthrene, -anthracene
129b		280	Dimethylbenzopyrene or isomer	136a	492.60	276	Indenopyrene or isomer
129c		279	Dibenzophenanthridine or isomer	136b		272	Methylbenzophenanthrothiophene
130a	479.38	284	Dibenzonaphthothiophene	137a	493.39	278	Dibenz[*a,c*]anthracene
130b		280	Dimethylbenzopyrene or isomer	137b		292	Methyldibenzophenanthrene, -anthracene
131a	480.58	267	Dibenzocarbazole	137c		280	Dimethylbenzofluoranthene or isomer
131b		280	Dimethylbenzopyrene or isomer	138a	494.19	278	Dibenz[*a,h*]anthracene
131c		278	Dibenzo[*b,g*]phenanthrene or isomer	138b		294	Trimethylbenzofluoranthene or isomer
132a	483.25	278	Benzo[*g*]chrysene or isomer	138c		292	Dimethyldibenzophenanthrene, -anthracene
132b		284	Dinaphthothiophene	139a	496.65	278	Benzo[*b*]chrysene
132c		280	Dimethylbenzofluoranthene or isomer	139b		282	Dimethyldibenzonaphthofuran
133a	485.20	279	Dibenzoacridine or isomer	140a	500.00	278	Picene
133b		284	Dinaphthothiophene	140b		280	Dimethylbenzopyrene or isomer
134a	486.20	284	Dinaphthothiophene	140c		282	Dimethyldibenzonaphtofuran
134b		278	Benzo[*c*]chrysene or isomer	141	501.90	276	Benzo[*ghi*]perylene
134c		267	Dibenzocarbazole	142a	503.80	278	Benzo[*a*]naphthacene or pentacene
134d		280	Dimethylbenzofluoranthene or isomer	142b		282	Dimethyldibenzonaphthofuran
135a	488.81	278	Dibenz[*a,j*]anthracene	143a	506.49	276	Anthanthrene
135b		276	Indenopyrene or isomer	143b		290	Methyl derivative of indenopyrene or isomer

TABLE II

DIFFERENCES IN THE PAH RETENTION INDICES OF SOME COMPOUNDS OF SEVERAL FAMILIES ON SE-54 AND OV-1701 STATIONARY PHASES

Compound	$I^{\text{SE-54}} - I^{\text{OV-1701}}$	Compound	$I^{\text{SE-54}} - I^{\text{OV-1701}}$
Anthracene	+0.3	Dimethylnaphthalene	+1.8
Fluoranthene	−1.0	Methylacenaphthene	+3.4
Pyrene	−0.4	Methyldibenzofuran	+3.4
Benzo[*c*]phenanthrene	0.0	Methylfluorene	+4.0
Benzo[*ghi*]fluoranthene	−1.1	Methylphenanthrene, -anthracene	+1.9
Benzo[*a*]anthracene	−1.4	Methylcarbazole	−14.9
Triphenylene	+0.3	Methyl 4*H*-cyclopenta[*def*]phenanthrene	+7.0
Naphthacene	−1.1	Methylfluoranthene, -pyrene	+2.3
Benzo[*j*]fluoranthene	−2.4	Methylbenzonaphthofuran	+3.0
Benzo[*b*]fluoranthene	−2.7	Dimethylbenzonaphthofuran	+4.7
Benzo[*k*]fluoranthene	−2.5	Methylbenz[*a*]anthracene	+1.9
Benzo[*e*]pyrene	−2.5	Biphenyl	+3.0
Benzo[*a*]pyrene	−2.0	2-Phenylnaphthalene	+2.1
Perylene	−2.5	Binaphthalene	+3.5
Dibenz[*a,j*]anthracene	−3.2	Phenylphenanthrene	+5.5
Dibenz[*a,c*]anthracene	−1.4	Benzo[*b*]thiophene	−0.2
Dibenz[*a,h*]anthracene	−1.9	Dibenzo[*b,d*]thiophene	+0.4
Benzo[*ghi*]perylene	−0.6	Phenanthro[4,5-*bcd*]thiophene	+0.1
Benzo[*a*]naphthacene	−1.0	Benzonaphtho[2,1-*d*]thiophene	−0.4
Anthanthrene	+1.7	Benzonaphtho[1,2-*d*]thiophene	−0.3
Acenaphthene	+2.6	Benzonaphtho[2,3-*d*]thiophene	−1.3
Fluorene	+2.5	Benzophenanthrothiophene	+0.3
9,10-Dihydroanthracene	+2.6	Dibenzofuran	+1.9
9,10-Dihydrophenanthrene	+3.7	Benzonaphthofuran	+1.2
1,2,3,4-Tetrahydroanthracene	+4.1	Benzo[*kl*]xanthene	+1.8
4*H*-Cyclopenta[*def*]phenanthrene	+1.5	Quinoline	−3.3
Benzo[*a*]fluorene	+0.5	Azafluoranthene	−3.7
Benzo[*b*]fluorene	−0.0	Dibenzoquinoline	−1.2
Benzo[*c*]fluorene	−0.6	Carbazole	−19.2
11*H*-Benz[*bc*]aceanthrylene	−0.9	4*H*-Benzo[*def*]carbazole	−18.5
4*H*-Cyclopenta[*def*]chrysene	−1.1	11*H*-Benzo[*a*]carbazole	−22.9
4*H*-Cyclopent[*def*]triphenylene	−1.0	7*H*-Benzo[*c*]carbazole	−20.0
2-Methylnaphthalene	+2.2	5*H*-Benzo[*b*]carbazole	−24.0
1-Methylnaphthalene	+2.2	4*H*-Naphtho[1,2,3,4-*def*]carbazole	−18.7
2-Ethylnaphthalene	+5.6	Dibenzocarbazole	−15.6

phase is the same for all components of the sample to be chromatographed. For this reason, the difference in the retentions of the several compounds in a mixture on two stationary phases of different polarity could be related to the reactivity of the compounds.

In carbonaceous mixtures, such as coal tar pitches, thermal reactivity is the factor controlling their behaviour in the pyrolysis process, and for this reason it has been studied experimentally for many polynuclear aromatic compounds [17]. Although it is very difficult to establish a reactivity scale among the different polynuclear aromatic compounds, it is generally accepted, on an experimental basis, that among the unsubstituted PAHs the most thermally reactive are those having an anthracene configuration; the alkyl-substituted PAHs are more reactive than the unsubstituted PAHs, the effect being more

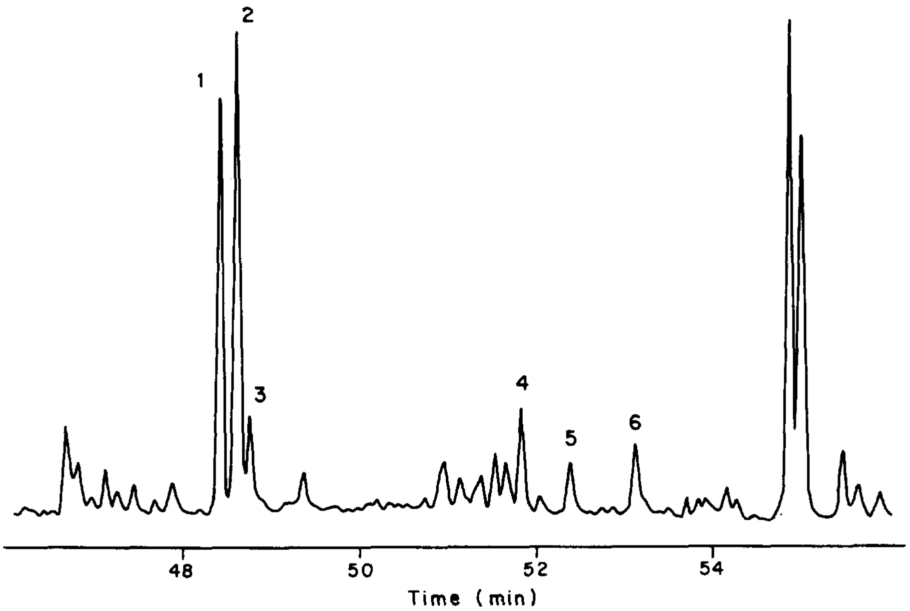

Fig. 2. Extension of a part of the capillary gas chromatogram of the volatile fraction of the coal tar pitch on OV-1701 stationary phase. Peaks: 1 = Benzo[*a*]anthracene; 2 = chrysene; 3 = triphenylene; 4 = 11*H*-benzo[*a*]carbazole; 5 = 7*H*-benzo[*c*]carbazole; 6 = 5*H*-benzo[*b*]carbazole.

pronounced the greater the number and length of the alkyl groups. Further, some workers [18] have identified as thermally reactive compounds 1-phenylnaphthalene and 9,10-dihydroanthracene and aromatics which have methylene bridges, such as 1,2-diphenylethane. However, the thermal stability of aromatics such as dibenzofuran [19] and dibenzo[*b,d*]thiophene [19,20] is thought to be high, and quinoline, isoquinoline and carbazole are considered to be very stable compounds [19].

From a careful study of Table II, it can be concluded, with some exceptions, that the compounds more retained on SE-54 than on OV-1701 are in general those considered to be more reactive in thermal processes, whereas the compounds more retained on OV-1701 than on SE-54 stationary phase are in general those considered to be more thermally stable.

It is known that solute–non-polar stationary phase interactions are governed basically by dispersive interactions expressed by the molar refraction or molecular polarizability of each solute [21–23]. In addition, it is generally accepted that in solute–polar stationary phase interactions, in addition to the dispersive interactions there are also others that take place due to the polarity [24,25]. From what has been said, it might be considered that the thermal reactivity of polynuclear aromatic compounds is more closely related to the molecular polarizability than to the polarity of the compound.

Studies directed towards the search for relationships between the concentration of some families of compounds in the volatile fraction of several pitches and their thermal behaviour are in progress.

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REFERENCES

1 M. Zander, *Fuel*, 66 (1987) 1536.
2 M. H. Wagner, H. Jäger, J. Letizia and G. Wilhelmi, *Fuel*, 67 (1988) 792.
3 G.-P. Blümer, H. W. Kleffner, W. Lücke and M. Zander, *Fuel*, 59 (1980) 600.
4 W. Boenigk, M. W. Haenel and M. Zander, *Fuel*, 69 (1990) 1226.

5 K. D. Bartle, *Rev. Pure Appl. Chem.*, 22 (1972) 79.

6 M. D. Guillén, J. Blanco, J. S. Canga and C. G. Blanco, *Energy Fuels*, 5 (1991) 188.

7 A. Bjorseth (Editor), *Handbook of Polycyclic Aromatic Hydrocarbons*, Marcel Dekker, New York, Basle, 1983.

8 A. Bjorseth and T. Randall (Editors), *Handbook of Polycyclic Aromatic Hydrocarbons*, Vol. 2, Marcel Dekker, New York, Basle, 1985.

9 C. G. Blanco, J. Blanco, P. Bernad and M. D. Guillén, *J. Chromatogr.*, 539 (1991) 157.

10 M. L. Lee, D. L. Vassilaros, C. M. White and M. V. Novotny, *Anal. Chem.*, 51 (1979) 768.

11 M. L. Lee, M. V. Novotny, K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, New York, London, Toronto, 1981.

12 S. R. Heller and G. W. A. Milne, *EPA NIH Mass Spectral Data Base*, National Technical Information Service, US Department of Commerce, Washington, DC, 1978.

13 C. G. Blanco, J. Blanco, J. Bermejo and M. D. Guillén, *J. Chromatogr.*, 465 (1989) 378.

14 M. D. Guillén, J. Blanco, J. Bermejo and C. G. Blanco, *J. High Resolut. Chromatogr.*, 12 (1989) 552.

15 H. Borwitzky and G. Schomburg, *J. Chromatogr.*, 170 (1979) 99.

16 R. J. Laub, W. L. Roberts and C. A. Smith, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1980) 355.

17 E. Fitzer, H. Mueller and W. Schaefer, in P. L. Walker, Jr. (Editor), *Chemistry and Physics of Carbon*, Vol. 7, Marcel Dekker, New York, 1971, p. 287.

18 A. G. Sharkey, J. L. Schultz and R. A. Frieder, *Carbon*, 4 (1966) 365.

19 J. J. Madison and R. M. Roberts, *Ind. Eng. Chem.*, 50 (1958) 237.

20 G.-P. Blümer and M. Zander, *DGMK Compendium, Suppl. to Erdöl Kohle Erdgas Petrochem.*, (1977/78) 235.

21 J. Bermejo and M. D. Guillén, *Chromatographia*, 17 (1983) 664.

22 J. Bermejo and M. D. Guillén, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 191.

23 J. Bermejo and M. D. Guillén, *Int. J. Environ. Anal. Chem.*, 23 (1985) 77.

24 J. Bermejo and M. D. Guillén, *J. Chromatogr.*, 318 (1985) 187.

25 J. Bermejo and M. D. Guillén, *Anal. Chem.*, 59 (1987) 94.