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CHARACTERIZATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN BITUMEN,
HEAVY OIL FRACTIONS BOILING ABOVE 350°C BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY

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ABSTRACT

The separation and characterization of polynuclear aromatic hydrocarbons of five fractions of bitumen, heavy oils and synthetic fuels boiling above 350°C were performed using a combination of chromatographic techniques. The polynuclear aromatic hydrocarbon fractions were obtained by liquid-solid chromatography using the modified USBM-API 60 procedure. Prior to the high performance liquid chromatography and gas chromatography/mass spectrometry techniques, the fractions were subjected to an acid/base extraction procedure to remove polar material. In total, 97 polynuclear aromatic hydrocarbons were tentatively identified by correlation of their mass spectra and retention indices with those of 25 model polynuclear aromatic compounds.

INTRODUCTION

Detailed compositional information on the polynuclear aromatic hydrocarbons (PNA) in feedstocks, such as bitumens, heavy oils and their synthetic products is necessary in order to help develop an effective utilization technology for such feedstocks. The PNA have the potential to play a significant role in coke deposition in reactors during upgrading processes. Detailed study of the chemistry of PNA present in processing products from increasing processing severities could give insight into the role of PNA in the mechanism of coke formation.

The use of high performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) will lead to a better understanding of the composition of bitumen and heavy oils. Many papers dealing with the analysis of PNA mixtures by HPLC have been reported in the literature (1-6). However one drawback of the HPLC technique is that it provides very little information on the structure of PNA. This is why the use of GC/MS becomes essential. Glass capillary GC provides excellent reproducibility, high sensitivity and resolution. The technique has been successfully applied to the analysis of PNA in environmental samples and coal derived materials (7-11).

The method used for the separation of the deasphalted residues boiling above 350°C into hydrocarbon-type (saturates, mono-diaromatics, polynuclear aromatics and polar compounds) has been reported earlier from this laboratory (12). As the PNA compounds are the main subject of this study, the PNA fraction was used for further study by instrumental techniques. Each PNA fraction was subjected to an acid/base extraction procedure based on the method reported by Novotny et al. (10,13). Some fractionation steps reported by these authors were omitted since the PNA were already concentrated by the liquid chromatography separation. Several of the sample fractions were analysed for carbon (C), hydrogen (H), nitrogen (N) and sulphur (S). The neutral PNA fractions and a mixture of model PNA compounds were analysed by HPLC for ring-size distribution by a procedure reported earlier (1). In addition to the HPLC analysis, the PNA fractions were semi-quantitatively analysed by capillary GC and MS and individual peaks were tentatively identified by correlation of their mass spectra and retention indices with those of model compounds. The chromatographic results for the five samples are discussed.

EXPERIMENTAL

Samples

Five oil/bitumen samples listed in Table 1 were vacuum distilled up to 350°C (152°C/1 mm Hg) using a BFR Instrument Corporation spinning band still. The residues of the distillation were deasphalted with twenty volumes of n-pentane by occasional shaking for 24 hours at room temperature. The asphaltenes were first separated by filtration, and then extracted with n-pentane in a soxhlet extractor until the solvent was colourless. The asphaltenes were then dried and weighed. The n-pentane extracts were combined with the main n-pentane solubles and the solvent removed under slight vacuum.

Table 1 summarizes the distillation results as well as the malthe (n-pentane solubles) and asphaltene contents for each sample. The fractionation steps are shown in Fig. 1.

Reagents

Methylene chloride and n-hexane used for liquid chromatography were HPLC grade. Reagent A.C.S. grade n-pentane, benzene, methanol, ether, pyridine and hydrochloric acid were used. The model compounds listed in Table 2 were used without further purification.

Liquid chromatography

The deasphalted distillation residues boiling above 350°C were separated into compound-type fractions of saturates, monoaromatics, diaromatics, polynuclear aromatics and polar compounds on a dual-packed silica gel-alumina column (12). The polynuclear aromatic fractions were used for further analysis. The liquid chromatography procedure is illustrated in Fig. 1.

Acid-base fractionation

The benzene eluates containing the polynuclear aromatics were subjected to an acid-base extraction (10-13). The objective was to remove any polar organic compounds from the PNA fraction. The fractionation steps for the acid-base extraction are illustrated in Fig. 2. The PNA fraction was then dissolved in 25 mL n-hexane containing 4% methylene chloride. This solution was used for ring size separation by HPLC and for GC/MS analysis.

Elemental analysis

Elemental analysis (C, H, N, S) were performed on the oil/bitumen samples, malthenes, asphaltenes and the PNA fractions before and after acid-base extraction. In addition the polar fraction from the liquid chromatographic separation of each sample was also analysed (12).

High performance liquid chromatography

The silica - $R(NH_2)_2$ (10 μ m; 300 x 4.6 mm) column was supplied by ES Industries, Marlton, New Jersey. The HPLC system consisted of a Spectra-Physics Model 3500, a Schoeffel SF 770 UV spectroflow monitor with an 8 μ l cell. Chromatographic separations were performed on a 10 μ l sample solution using a 96% hexane: 4% CH_2Cl_2 mobile phase at a flow rate of 1.2 mL/min at 24°C. The PNA fractions of the five samples were diluted with the mobile phase in a ratio of 1 to 5. Initial concentrations before dilution were in the range of 3 to 8 mg/mL. A mixture of PNA model compounds was chromatographed under identical conditions to identify the ring-size classes. The following 16 PNA were used for that study: fluorene, phenanthrene, anthracene, 3-methylphenanthrene, 2-methylanthracene, 3-methylanthracene, fluoranthene, pyrene, 4-methylpyrene, 3-methylpyrene, 1-methylpyrene, benz(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(ghi)perylene. The retention indices are given in Table 2.

Gas chromatography and gas chromatography-mass spectrometry

Analyses of PNA fractions as well as model compounds were carried out using 15 m x 0.2 mm fused silica capillary column coated with SE-54. The gas chromatographic profiles were recorded with a Varian 3700 gas chromatograph with precisely controlled oven temperature programmed from 70°C to 275°C at 5°C/min. Carrier gas flow rate was 2 ml/min of N_2 . Data acquisition was accomplished with a Spectra-Physics SP 4000 integrator. Retention indices, Table 2, were calculated according to an equation described elsewhere (14). Retention indices obtained from the samples were compared with those of model compounds reported in the literature (14).

Mass spectral data were obtained with a Hewlett-Packard 5980A quadrupole combined GC/MS. Electron impact spectra were recorded at an ionization energy of 70 eV. The scanning rate of the spectrometer was 380 amu/s. Mass spectra were identified through comparison with library data.

RESULTS AND DISCUSSION

Distillation and deasphalting

A summary of the distillation and deasphalting results is presented in Table 1. As expected the data show that the samples with larger amounts of distillation residue (b.p. > 350°C) have lower maltheane/asphaltene ratio. For example Cold Lake vacuum with a distillation residue of 98.1 wt % have a ratio of 3.8, whereas Medicine River which is a light oil with 38.3 distillation residue had a ratio of 46.6.

Liquid chromatography

The results of the hydrocarbon type distribution of the five deasphalted distillation residues boiling above 350°C are presented in Table 3. The data indicate that an increase in the weight percent of distillation residue results in an increase in polynuclear aromatic as well as in polar compounds content, and at the same time a decrease in saturates content. Comparison of the PNA content for the Cold Lake bitumen (sample 1) with the hydrocracked Cold Lake (sample 4) shows that hydrocracking results in a decrease of PNA content. This observation is also true for the comparison of bitumen and heavy oils with a light oil like Medicine River (sample 5).

Elemental analysis data of the oil/bitumen samples, the corresponding PNA fractions before and after acid-base extraction and the polar fraction are presented in Table 4. The nitrogenous compounds were found in the polar fractions and asphaltenes. Comparison of the corresponding PNA fractions before and after acid-base extraction show very little difference.

High performance liquid chromatography

The neutral PNA fractions of all samples were analysed by normal phase HPLC using Chromegabond diamine stationary phase according to the procedure developed in our laboratory (1). Previous work has shown that the diamine bonded stationary phase separates PNA according to condensed ring number, regardless of alkyl substitution (15). The objective of that study was to determine the PNA ring size distribution e.g., 3-ring (phenanthrene/anthracene group), 4 ring (pyrene group) etc. prior to GC-MS analysis.

Figure 3 shows the chromatographic profile of the PNA concentrates for Cold Lake (A) and Boscan heavy oil (B). The chromatogram of a mixture of

16 PNA (C) consisting of 3 ring, 4 ring and > 4 ring is also shown in this figure. Retention indices of PNA were calculated using the method of Popl et al. (Table 2), (16). All samples give identical profiles with one large peak matching the retention time range of 3-ring class PNA. In addition all samples show tailing peaks attributed to 4-ring class PNA. This is more pronounced with samples 1, 2 and 3 (samples containing high distillation residue and PNA content) than the other two samples with low distillation residue and PNA content.

Gas chromatography - mass spectrometry

The five PNA fractions which have been submitted to acid-base fractionation were analysed by GC-MS. Initially, chromatographic resolution of a mixture of 25 PNA model compounds was examined by GC for determination of their retention indices (Table 2) under identical conditions used for the GC-MS analysis.

A typical gas chromatographic profile of the PNA fraction for sample 4 is shown in Fig. 14. The components tentatively identified by GM-MS for the five samples are listed in Table 5. The PNA in each sample were quantified based on the response of 2-methylanthracene using the peak area method for calibration and calculation. The semi-quantitative data, which are also included in Table 5, are given for most of the resolved peaks.

In total, 97 polynuclear aromatic components in bitumen, heavy oils and light oils (5 samples) were tentatively identified by their molecular weight and comparison of individual mass spectra and retention data with appropriate model compounds. The electron mass spectra of the PNA are distinctive and consist of an intense molecular ion M^+ and a lower intensity ions $(M-1)^+$. Although many fundamental structures have been assigned, it is understood that the position of alkyl substituents on PNA rings are difficult to identify. A lack of model compounds greatly reduced the number of positive identification.

As a result of high sulphur content in the PNA fractions (Table 4), many thiophenic compounds were identified in these fractions. Since naphthothiophenes were not found in any of the samples, we assumed that all the thiophenic compounds having molecular weight below 234 have a dibenzothiophenic structure.

Comparison of the two Cold Lake samples (sample 1 and 4) Table 5 shows that both samples have PNA molecular weight up to 252. Moreover most of the PNA present in the two mixtures are different. The results show that hydrocracking leads to less substituted rings. PNA, such as phenyl-2 naphthalene, fluoranthene, pyrene, benzo(a)fluorene, methylbenz(a)anthracene and benzo(e)pyrene were only found in sample 4. Comparison of the two light oils (sample 4 and 5) shows two differences. In the Medicine River sample, smaller molecular weight PNA are more abundant and in general more substituted.

CONCLUSION

The PNA content increased as the wt% of distillation residue above 350°C increased. Polynuclear aromatic hydrocarbons are more abundant in bitumens and heavy oils than in the synthetic crude derived from bitumen and Medicine River light oil. Nitrogenous material was not found in any of the PNA fractions obtained from the liquid chromatographic separations. The high sulphur content in the PNA fractions is associated to thiophenic compounds.

Although investigation of other crude oils and processed heavy oils remains to be carried out, this study has shown that a combination of liquid chromatography, HPLC and GC-MS permits a better understanding of the composition of the crude oil related products.

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CAPTIONS

- Figure 1 Scheme for separation and characterization
- Figure 2 Acid-base fractionation schematic
- Figure 3 Ring size distribution by HPLC on the silica- $\text{R}(\text{NH}_2)_2$ column with mobile phase of n-hexane-methylene chloride (96:4). (A) Cold Lake polynuclear aromatic fraction; (B) Boscan polynuclear aromatic fraction; (C) Mixture of model PNA, see Table 2 for key.
- Figure 4 Capillary gas chromatogram of the polynuclear aromatic fraction of sample 4; for key, see Table 5.

Table 1 - Distillation and deasphalting results for the five oil samples

Sample	Initial weight (g)	Distillation residue > 350°C (g)	Distillation residue > 350°C wt %	Asphaltenes residue > 350°C wt %	Malthenes residue > 350°C wt %
1. Cold Lake	48.2	47.3	98.1	20.6	79.4
2. Boscan heavy oil	82.2	76.3	92.8	22.9	77.1
3. Athabasca	98.6	88.2	89.4	15.7	84.3
4. Cold Lake ^a	104.0	56.2	54.0	3.9	96.1
5. Medicine River	108.0	41.4	38.3	2.1	97.9

a Hydrocracked Cold Lake sample (100% pitch conversion)

Table 2 - Retention indices of model polynuclear aromatic hydrocarbons

Compound number	Molecular weight	Compound name	GC-FID	GC-FID	HPLC/UV
			retention index (I)	Literature ¹⁴	logI
1	166	fluorene	268.10	268.17	2.50
2	178	phenanthrene	300.00	300.00	3.00
3	178	anthracene	301.60	301.69	2.95
4	192	3-methylphenanthrene	319.32	319.46	3.05
5	192	2-methylanthracene	321.26	321.57	3.04
6	192	9-methylanthracene	328.90	329.13	3.00
7	206	3,6-dimethylphenanthrene	337.50	337.83	-
8	202	fluoranthene	345.13	344.01	3.39
9	202	pyrene	352.76	351.22	3.43
10	216	4-methylpyrene	370.61	369.54	3.49
11	216	Benzo(b)fluorene	370.61	369.39	-
12	216	Benzo(c)fluorene	370.61	-	-
13	216	3-methylpyrene	374.67	-	3.51
14	216	1-methylpyrene	374.67	373.55	3.50
15	228	Benzo(a)anthracene	399.02	398.50	4.00
16	228	triphenylene	400.00	400.00	-
17	228	chrysene	400.00	400.00	-
18	252	Benzo(k)fluoranthene	441.30	442.56	4.30
19	256	9,10-dimethylbenz(a)anthracene	445.65	-	-
20	252	Benzo(a)pyrene	451.45	453.44	4.28
21	252	perylene	454.35	456.22	-
22	278	o-phenylpyrene	488.22	-	-
23	278	dibenz(a,h)anthracene	491.12	495.45	4.95
24	278	picene	500.00	500.00	-
25	276	Benzo(ghi)perylene	501.00	501.32	>5

Table 3 - Hydrocarbon-type distribution of the deasphalted residues
>350°C (API procedure, wt %)

Sample	Distillation residue > 350°C wt %	Saturates	Mono- diaromatics	Polynuclear aromatics	Polar compounds
1. Cold Lake	98.1	20.8	23.5	19.2	36.5
2. Boscan heavy oil	92.8	17.9	24.8	19.8	37.5
3. Athabasca	89.4	24.0	24.2	14.5	37.3
4. Cold Lake ^a	54.0	38.8	31.8	10.6	18.8
5. Medicine River	38.3	55.7	22.7	7.2	14.4

^a Hydrocracked Cold Lake sample (100% pitch conversion)

Table 4 - Elemental analysis of the different fractions

Sample 1	Initial oil	Asphaltenes	Malthenes	PNA before extraction	PNA after extraction	Polar compounds
%C	82.77	78.57	83.56	81.78	81.59	77.55
%H	10.95	8.79	10.87	9.30	9.51	9.82
%N	0.57	0.70	0.00	0.00	0.00	0.87
%S	5.71	8.44	5.34	9.06	6.43	7.26
<u>Sample 2</u>						
%C	82.80	80.84	83.39	78.67	76.58	73.94
%H	10.95	7.97	11.29	9.44	9.95	9.64
%N	0.80	1.47	0.00	0.00	0.00	0.97
%S	5.45	6.24	5.34	8.14	8.13	7.12
<u>Sample 3</u>						
%C	82.49	74.85	83.22	80.86	80.89	80.84
%H	10.76	8.39	11.08	8.85	9.65	9.67
%N	0.42	0.96	0.00	0.00	0.00	0.91
%S	6.33	8.23	5.66	8.42	6.69	6.73
<u>Sample 4</u>						
%C	83.04	65.19	86.03	87.22	87.73	85.40
%H	12.75	4.83	10.60	7.00	6.56	7.51
%N	0.38	1.63	0.00	0.00	0.00	3.25
%S	3.84	3.51	3.48	5.49	5.68	3.87
<u>Sample 5</u>						
%C	83.20	70.80	85.07	85.29	84.55	82.92
%H	14.55	8.13	12.77	9.25	9.05	11.05
%N	0.28	0.52	0.00	0.00	0.00	0.99
%S	1.97	4.56	2.00	5.35	5.02	4.30

Table 5 - Components identified in five polynuclear aromatic hydrocarbon fractions of bitumen and heavy oils

Peak number	Molecular weight	Possible compound types	R.I.	Samples				
				concentration ppm				
				1	2	3	4	5
1	180	9-Methylfluorene	273.53		0.30		2.53	119.80
2	184	Dibenzothiophene	294.79			-	-	
3	178	Phenanthrene	300.00		1.55	10.16	84.29	81.30
4	178	Anthracene	301.62	-			16.30	
5	194	Ethylfluorene ^a	304.03			-		
6	194	Dimethylfluorene	306.61		0.49	-	-	-
7	194	Dimethylfluorene	308.06		1.68		52.61	44.85
8	194	Dimethylfluorene	309.70	-	2.82	2.47	-	54.08
9	194	Dimethylfluorene	313.71		0.53		-	-
10	198	Methyldibenzothiophene	315.69	-	0.49		-	-
11	198	Methyldibenzothiophene	318.27	-	1.23	-		
12	192	2-methylphenanthrene	319.25	-	6.52	9.59	119.67	-
13	192	2-methylanthracene	321.77	1.24	0.55	-	22.92	105.96
14	192	1-methylanthracene	323.30	-		-		92.98
15	192	1-methylphenanthrene	323.71	-	5.42	14.21	54.72	77.29
16	208	Ethylmethylfluorene ^b	324.72		10.54	-		
17	208	Ethylmethylfluorene ^b	326.37		0.28			-
18	208	Trimethylfluorene	327.34	0.31	1.01	-	-	-
19	212	Ethyldibenzothiophene ^a	329.35		0.34			-
20	208	Trimethylfluorene	331.29		1.08	-		-
21	204	Phenyl-2 naphthalene	332.25				36.73	
22	212	Ethyldibenzothiophene ^a	332.90	0.42	2.96			40.50
23	212	Dimethyldibenzothiophene	334.90			1.91		
24	208	Trimethylfluorene	334.35		1.07		-	-
25	212	Dimethyldibenzothiophene	334.90	-	5.72	-		-
26	206	3,6-dimethylphenanthrene	337.90			-	50.43	
27	212	Dimethyldibenzothiophene	338.38	0.76	11.19			-
28	206	2,7- dimethylphenanthrene	339.80	1.23	-	3.44	-	79.59

3	178	Phenanthrene	300.00		1.55	10.16	84.29	81.30
4	178	Anthracene	301.62	-			16.30	
5	194	Ethylfluorene ^a	304.03			-		
6	194	Dimethylfluorene	306.61		0.49	-	-	-
7	194	Dimethylfluorene	308.06		1.68		52.61	44.85
8	194	Dimethylfluorene	309.70	-	2.82	2.47	-	54.08
9	194	Dimethylfluorene	313.71		0.53		-	-
10	198	Methyldibenzothiophene	315.69	-	0.49		-	-
11	198	Methyldibenzothiophene	318.27	-	1.23	-		
12	192	2-methylphenanthrene	319.25	-	6.52	9.59	119.67	-
13	192	2-methylanthracene	321.77	1.24	0.55	-	22.92	105.96
14	192	1-methylanthracene	323.30	-		-		92.98
15	192	1-methylphenanthrene	323.71	-	5.42	14.21	54.72	77.29
16	208	Ethylmethylfluorene ^b	324.72		10.54	-		
17	208	Ethylmethylfluorene ^b	326.37		0.28			-
18	208	Trimethylfluorene	327.34	0.31	1.01	-	-	-
19	212	Ethyldibenzothiophene ^a	329.35		0.34			-
20	208	Trimethylfluorene	331.29		1.08	-		-
21	204	Phenyl-2 naphthalene	332.25				36.73	
22	212	Ethyldibenzothiophene ^a	332.90	0.42	2.96			40.50
23	212	Dimethyldibenzothiophene	334.90			1.91		
24	208	Trimethylfluorene	334.35		1.07		-	-
25	212	Dimethyldibenzothiophene	334.90	-	5.72	-		-
26	206	3,6-dimethylphenanthrene	337.90			-	50.43	
27	212	Dimethyldibenzothiophene	338.38	0.76	11.19			-
28	206	2,7- dimethylphenanthrene	339.80	1.23	-	3.44	-	79.59
29	206	Dimethylphenanthrene ^c	340.13			-		76.06
30	212	Dimethyldibenzothiophene	340.93			-		
31	206	Dimethylphenanthrene ^c	341.90		13.23	-		48.71
32	206	Dimethylphenanthrene ^c	342.36		4.08	9.46	35.47	
33	206	Dimethylphenanthrene ^c	343.78	-	6.64	11.04		13.50
34	206	Dimethylphenanthrene ^c	344.35	0.95	5.27			-
35	222	Diethylfluorene	344.88			-		

Table 5 - Cont'd

Peak number	Molecular weight	Possible compound types	R.I.	Samples				
				concentration ppm				
				1	2	3	4	5
36	202	Fluoranthene	345.00				65.13	
37	222	Diethylfluorene ^d	345.82	1.17	1.93	-		
38	206	1,8-dimethylphenanthrene	346.90	0.73				
39	206	Dimethylphenanthrene ^c	347.57		-	-		
40	222	Diethylfluorene ^d	349.29			-		
41	206	Dimethylphenanthrene ^c	349.51		1.62			
42	208	Trimethylfluorene	349.51				54.28	
43	226	Ethylmethyldibenzothiophene	349.67	-		-		21.51
44	202	Pyrene	350.23			-	232.74	
45	206	Dimethylantracene	352.42	1.00	1.63			
46	226	Ethylmethyldibenzothiophene ^b	354.03	3.77	9.75	3.80	61.66	18.59
47	220	Ethylmethylphenanthrene ^{b,c}	356.49			-		-
48	226	Trimethyldibenzothiophene	357.09	3.36	10.64	-	23.62	
49	226	Trimethyldibenzothiophene	358.10	-	-			
50	220	Ethylmethylphenanthrene ^{b,c}	359.02		-	7.63	22.36	-
51	226	Trimethyldibenzothiophene	359.70	-				
52	220	9-methyl-10-ethylphenanthrene	360.16	5.27	2.92	11.97		26.82
53	218	Methylphenylnaphthalene	360.48				-	
54	220	Trimethylphenanthrene ^c	362.58	2.20	12.02	-		
55	220	Trimethylphenanthrene ^c	365.00	1.02	-	-	-	
56	216	Benzo(a)fluorene	365.64				56.92	
57	220	Trimethylphenanthrene ^c	366.34	1.71	-			
58	240	Diethyldibenzothiophene ^d	366.90		-	-		
59	220	Trimethylphenanthrene ^c	368.50	1.71	-	-		32.40
60	240	Diethyldibenzothiophene ^d	369.44	-		-		
61	216	4-methylpyrene	370.64			12.53	176.93	
62	220	Trimethylphenanthrene ^c	371.13		10.52			
63	218	Methylphenylnaphthalene	371.61				93.48	
64	240	Ethyl dimethyldibenzothiophene ^e	371.84	11.41	-	-		

42	208	Trimethylfluorene	349.51				54.28	
43	226	Ethylmethyldibenzothiophene	349.67	-				21.51
44	202	Pyrene	350.23				232.74	
45	206	Dimethylantracene	352.42	1.00	1.63			
46	226	Ethylmethyldibenzothiophene ^b	354.03	3.77	9.75	3.80	61.66	18.59
47	220	Ethylmethylphenanthrene ^{b,c}	356.49					-
48	226	Trimethyldibenzothiophene	357.09	3.36	10.64		23.62	
49	226	Trimethyldibenzothiophene	358.10	-	-			
50	220	Ethylmethylphenanthrene ^{b,c}	359.02			7.63	22.36	-
51	226	Trimethyldibenzothiophene	359.70	-				
52	220	9-methyl-10-ethylphenanthrene	360.16	5.27	2.92	11.97		26.82
53	218	Methylphenylnaphthalene	360.48					-
54	220	Trimethylphenanthrene ^c	362.58	2.20	12.02			
55	220	Trimethylphenanthrene ^c	365.00	1.02	-			-
56	216	Benzo(a)fluorene	365.64				56.92	
57	220	Trimethylphenanthrene ^c	366.34	1.71	-			
58	240	Diethyldibenzothiophene ^d	366.90					
59	220	Trimethylphenanthrene ^c	368.50	1.71	-			32.40
60	240	Diethyldibenzothiophene ^d	369.44	-				
61	216	4-methylpyrene	370.64			12.53	176.93	
62	220	Trimethylphenanthrene ^c	371.13		10.52			
63	218	Methylphenylnaphthalene	371.61				93.48	
64	240	Ethyl dimethyldibenzothiophene ^e	371.84	11.41	-			
65	218	Methylphenylnaphthalene	373.22				89.76	
66	216	1-methylpyrene	373.22		5.06			
67	220	Trimethylphenanthrene ^c	374.43	-				
68	240	Tetramethyldibenzothiophene	375.40	0.79		3.31		
69	216	Methylpyrene	376.37	0.54				
70	240	Tetramethyldibenzothiophene	377.40	1.68	4.40			
71	234	Tetramethylphenanthrene ^{c,d}	377.80			2.27		
72	232	Dimethylphenylnaphthalene	379.19				18.16	
73	240	Tetramethyldibenzothiophene	379.93	-	2.68			

Peak number	Molecular weight	Possible compound types	R.I.	Samples concentration ppm				
				1	2	3	4	5
74	234	Ethyldimethylphenanthrene ^c	377.80		1.61		-	
75	234	3-ethyl-9,10-dimethylphenanthrene	381.80	0.91	7.66		-	
76	234	Ethyldimethylphenanthrene ^{c,e}	383.22	-	-			
77	230	1-ethylpyrene	384.19			-	49.04	
78	234	Tetramethylphenanthrene ^c	386.14			4.39		
79	230	2,7-dimethylpyrene	386.29			-	62.36	
80	234	Benzo(b)naphtho(2,1d)thiophene	389.35		3.11	3.32	106.92	
81	234	Benzonaphthothiophene	392.74	3.57	3.16		-	
82	250	Diethyldimethylfluorene ^f	396.29		1.65			
83	230	Dimethylpyrene	396.58	2.27				
84	244	Trimethylpyrene	399.35				56.06	
85	250	Diethyldimethylfluorene ^f	399.85		1.42			
86	248	Methylbenzonaphthothiophene	403.20		3.64		45.42	
87	248	Methylbenzonaphthothiophene	407.04	2.68			51.26	
88	248	Methylbenzonaphthothiophene	413.73	-				
89	242	Methylbenz(a)anthracene	419.62				86.27	
90	262	Dimethylbenzonaphthothiophene	427.18	-				
91	256	Dimethylethylbenz(a)anthracene ^e	435.82				-	
92	276	Ethylmethylbenzonaphthothiophene ^b	443.18	-				
93	258	Tetramethylpyrene	444.82				-	
94	276	Ethylmethylbenzonaphthothiophene ^b	446.43	-				
95	252	Benzo(e)pyrene	447.80				-	
96	290	Dimethylethylbenzonaphthothiophene ^e	453.84	-				
97	290	Dimethylethylbenzonaphthothiophene ^e	457.81	-				

a) May also be dimethyl

b) may also be trimethyl

c) May also be anthracene

d) May also be ethyldimethyl

e) May also be tetramethyl

f) May also be ethyltetramethyl