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CHARACTERIZATION OF THE PHENOLIC FRACTION OBTAINED FROM FOSSIL-FUEL MATERIALS BY MICROCOLUMN LIQUID CHROMATOGRAPHY AND ITS ANCILLARY TECHNIQUES

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SUMMARY

The phenolic fraction of two coal-derived liquids has been isolated prior to high-resolution liquid chromatography and spectral characterization. Over 70 high-molecular-weight compounds were separated, in each case, with a slurry-packed capillary column. Off-line mass spectrometry and on-line miniaturized fluorescence spectroscopy were used for peak characterization. Two- to five-ring structures, with a high degree of alkylation or heteroatomic features, are suggested.

INTRODUCTION

The analysis of coal-derived materials is a technologically important problem, since adequate knowledge of their composition can be crucial in the determination of fuel quality and combustibility, as well as their potential use as chemical feedstocks. Different chromatographic techniques have been employed to obtain important structural information on various fossil fuels.

The extraordinary complexity of fuel-related materials necessitates highly effective separation techniques. Due to its great resolving power, capillary gas chromatography (GC) has found numerous applications for these types of materials[1–7]. Its utilization has become limited, however, with the increasing emphasis placed on non-volatile fractions and more polar fossil fuel constituents (azaarenes, nitro- and amino-substituted polyaromatics, phenolics, etc.). Although sample derivatization for polar compounds somewhat extends the applications scope[3,8–10], this approach is not generally effective for the polyaromatics with a greater number of rings.

Conventional liquid chromatography (LC), an otherwise logical choice for the analysis of non-volatile and polar components, does not possess the necessary resolving power for complex mixtures. During recent years, microcolumn LC has been under development[11–13] to address the problems of complex non-volatile samples. This technique was applied successfully to neutral aromatics[14–16] and azaarenes[17]. The present communication extends the approach to the analysis of polycyclic phenols in coal-derived fluids. The slurry-packed LC capillary columns with efficiencies of over 100 000 theoretical plates have been applied here to the phenolic fraction of solvent-refined coal and a fuel oil blend.

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It has been commonly appreciated that even the high-resolution chromatographic techniques become more effective if the coal-derived samples are first fractionated into various compound classes, and each fraction is then subjected to an in-depth analysis. Several recently-developed fractionation schemes[18–21] support this perception. Furthermore, structural characterization of the sample components by mass spectrometry or fluorescence spectroscopy clearly benefits from sample fractionation.

EXPERIMENTAL

Solvent-refined coal, heavy distillate (SRC II, 850°F) and fuel oil blend 1701 were obtained from the Fossil Fuel Matrix Co. repository, administered by the Oak Ridge National Laboratory. The fuel oil blend was prefractionated according to the method of Later *et al.*[18]. Fraction A-4 of their scheme was used without further preparation. Initially, the SRC II sample was also separated by this method, but fraction A-4 was further separated from the hydroxylated nitrogen compounds according to Nishioka *et al.*[21].

The hydroxypolycyclic aromatic hydrocarbons (HPAH) and hydroxypolycyclic aromatic sulfur heterocycles (HPASH) obtained via this procedure were subjected to conventional reversed-phase chromatography, using a 5-μm, C_{18}, 25 cm $\times$ 4.6 mm I.D. packed column (Alltech, Deerfield, IL, U.S.A.). This step was useful in eliminating certain lower-molecular-weight species. The final samples were dissolved in methylene chloride (approximately 50 mg/ml).

A Varian Model 8500 syringe pump and a Schoeffel Model FS 970 fluorescence detector were used for the solvent delivery and detection, respectively. Detection was carried out at an excitation wavelength of 265 nm, and an emission cutoff filter of 318 nm was used to collect the fluorescence signal. Microcolumn chromatography was performed with a 200-μm fused-silica capillary column[22], slurry-packed with 5-μm ODS particles (Spherisorb, Hauppage, NY, U.S.A.). The efficiency of the 1.6 m long column was 140 000 theoretical plates. The fuel oil blend sample fraction was eluted in approximately 4 h, using a stepwise gradient, starting at acetonitrile–water (50:50) and ending with 100% acetonitrile. The SRC II sample was eluted in about 8 h with a much slower gradient, beginning at acetonitrile–water–acetic acid (69:30:1), and ending with acetonitrile–acetic acid (99:1). The sample introduction and stepwise gradient systems have been previously described[23].

The fluorescence spectra from the resolved chromatographic peaks were obtained with an on-line photodiode array fluorescence detector constructed in this laboratory[24,25]. Its excitation wavelength was set at 280 nm. Mass spectral data from the manually trapped peaks were obtained on a Hewlett-Packard Model 5980A mass spectrometer equipped with a direct insertion probe inlet. Electron-impact ionization was employed. Data were acquired and stored using a Finnigan MAT Incos Nova 3 data system.

All solvents were analytical grade (Fisher Scientific, Pittsburgh, PA, U.S.A.). Water was distilled and deionized in-house. The solvents were filtered through a 0.2-μm PTFE filter prior to use.

RESULTS AND DISCUSSION

The literature reports on phenolic compounds are scarce and limited mostly to one-ring molecules. Capillary GC and conventional LC techniques have been used to adequately resolve halogenated and alkyl-substituted phenols in water and waste water[26–28]. Hurtubise and co-workers[29,30] investigated the retention characteristics of phenols, cresols, and naphthols in both normal- and reversed-phase high-performance liquid chromatographic (HPLC) systems. Ogan and Katz[31] have separated nineteen alkyl phenols by reversed-phase LC employing fluorescence and UV detection. They report that within an isomeric series of alkylated phenols, a polymethylated compound will elute before a singly alkylated isomer, *i.e.*, trimethyl phenols before the propyl phenols. In addition to retention characteristics, Ogan and Katz[31] studied the effect of alkyl substitution on the fluorescence spectra of phenols. They found

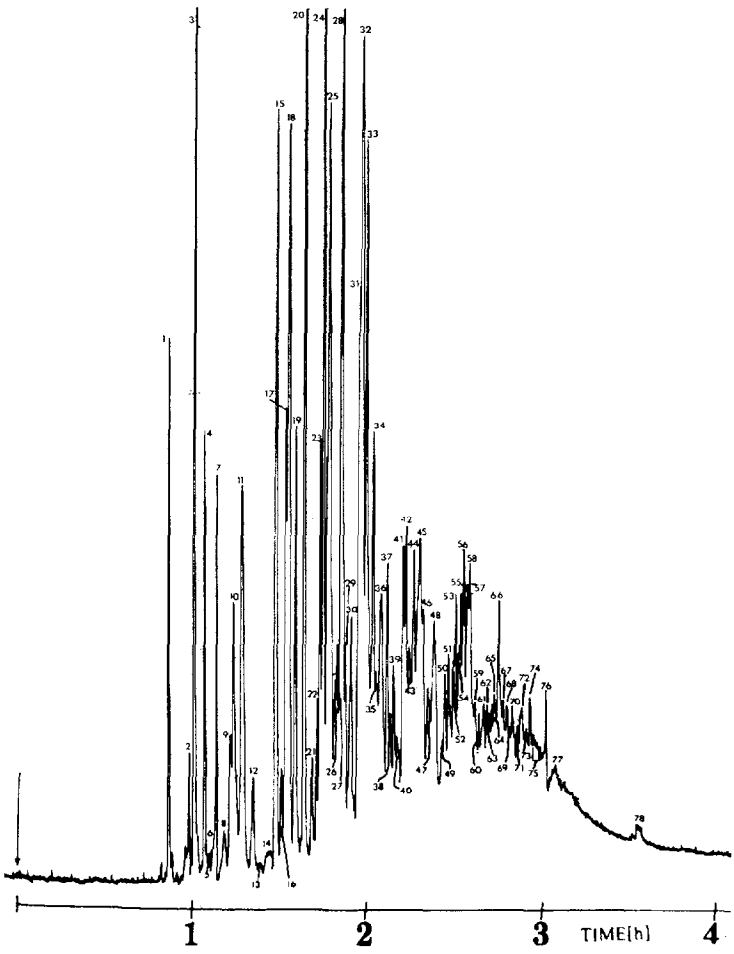


Fig. 1. Chromatographic profile of the phenolic fraction isolated from fuel oil blend 1701. Conditions as described in the text.

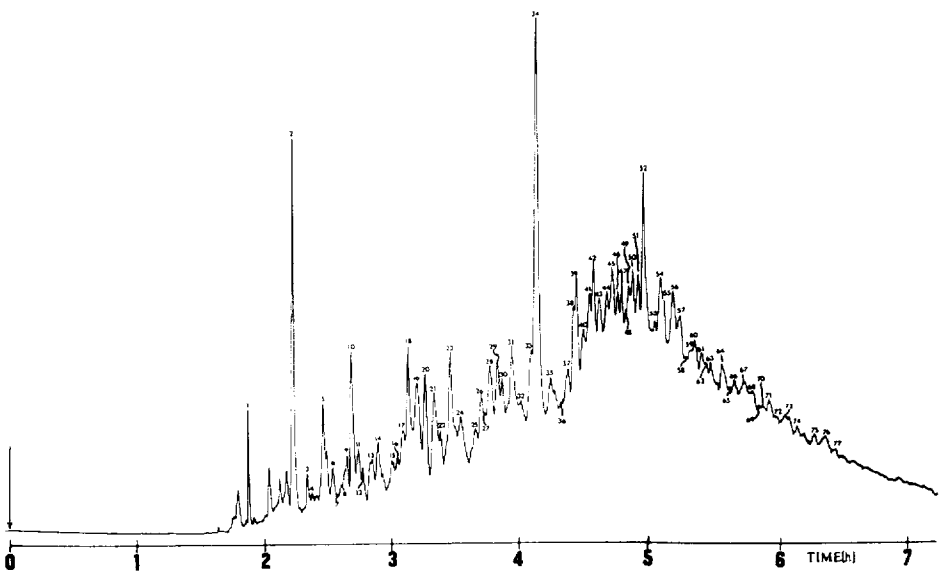


Fig. 2. Separation of the phenolic fraction isolated from SRC II (HPAH). Conditions as described in the text.

only very subtle shifts in wavelength and no influence on the fluorescence intensity with respect to the alkyl chain length.

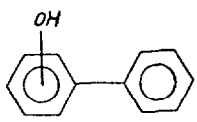
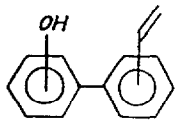
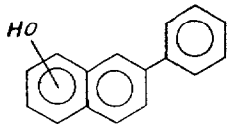
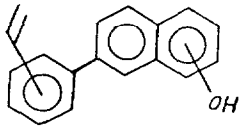
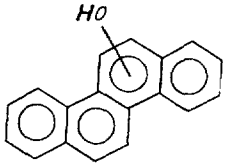
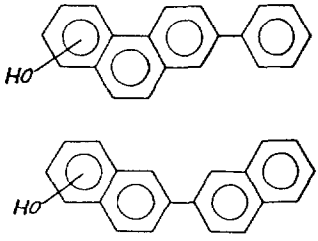
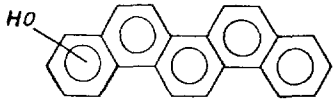
Examples in the literature on the analysis of phenolic compounds in fossil fuels are very limited due to the complexity and polarity of large phenolic molecules. Schabron *et al.*[32] identified phenol and several alkylphenols in a coal recycle solvent and provided fluorescence data for some substituted phenols and naphthols. Parees and Kamzelski[6] analyzed an SRC I distillate and found alkylated phenols and naphthols in the hydroxy aromatic subfraction. More recently, Lee and co-workers[21,33] have analyzed the hydroxylated thiophenic and hydroxylated nitrogen heterocycles in coal-derived liquids. With the use of capillary GC and GC–mass-spectrometry (MS), they identified compounds as large as 2-(2-hydroxy phenyl)-4-phenylthiophene (mol.wt. 252), and hydroxyazapyrenes and/or hydroxyazafluoranthenes (mol.wt. 219).

A previous report from our laboratory[16] has dealt with the high-efficiency separation of the phenolic fraction from fuel oil blend on a C_8 reversed-phase microcolumn. However, the emphasis of that report was on sample "fingerprinting" rather than on a more complete characterization. Consequently, structural characterization has been the subject of this report.

Initially, chromatographic conditions had to be optimized to provide the necessary degree of resolution. Once the phenolic fractions from the fuel oil blend and SRC II were adequately resolved chromatographically (Figs. 1 and 2, respectively), their mass spectral characterization was approached in the manner successful with that previously described for the neutral[14,15] and nitrogen-containing[17] polycyclics. Table I illustrates the different monohydroxylated structural types that we feel are most likely to fit the mass spectral and fluorescence data, which are detailed in Tables II and III. The constituents can be conveniently listed by a set of symbols denoting

TABLE I

REPRESENTATIVE PARENT MOLECULES

Number of rings	*Molecular type**		
	BO	*CO*	*VCO*
2			
3			
4			
5			

* B and C refer to "molecular compactness", with C being less compact than B. O represents the hydroxy functional group. V indicates a vinyl derivative.

number of rings, molecular compactness, extent of alkyl substitution, degree of saturation in a side chain, and number of hydroxy groups.

Table II lists the mass spectral data obtained from the individual microcolumn LC peaks collected from the fuel oil blend. In addition, fluorescence emission data and the most likely molecular type are included in this table. In this series, no phenolic compounds were actually found before peak 17 or after peak 76. Two interesting findings were made regarding this fraction that differ from the preliminary results previously reported in the profiling work done in this laboratory[16]: (1) two families of hydroxyvinyl derivatives are suggested (2VCO and 3VCO); and (2) the common all-condensed ring systems, *i.e.*, hydroxyanthracenes, hydroxychrysenes, etc., are not observed. Instead, less compact molecules displaying a relatively large amount of alkyl substitution are evident.

TABLE II

STRUCTURAL DATA FOR FUEL OIL BLEND (Fig. 1)

The underlined values are the wavelength of maximum intensity in the emission spectrum of the solute.

Peak	*Mol.wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
18	170	2CO	–	346,355,361,374
24	184	2CO	C1	342,356
25	184	2CO	C1	–
26	184	2CO	C1	–
27	196	2VCO	–	–
28	196	2VCO	–	331,338
	198	2CO	C2	
29	196	2VCO	–	–
	198	2CO	C2	–
30	196	2VCO	–	–
31	196	2VCO	–	–
	198	2CO	C2	
32	196	2VCO	–	–
	198	2CO	C2	
33	196	2VCO	–	
	198	2CO	C2	347,355,363
	220	3CO	–	
34	196	2VCO	–	–
	198	2CO	C2	
35	198	2CO	C2	–
36	198	2CO	C2	–
	210	2VCO	C1	
	220	3CO	–	
37	198	2CO	C2	–
	210	2VCO	C1	
	220	3CO	–	
38	210	2VCO	C1	–
39	210	2VCO	C1	–
	220	3CO	–	
40	210	2VCO	C1	–
	212	2CO	C3	
	220	3CO	–	
41	210	2VCO	C1	338,343
	212	2CO	C3	
42	210	2VCO	C1	
	212	2CO	C3	338,343
	234	3CO	C1	
43	210	2VCO	C1	
	212	2CO	C3	–
	234	3CO	C1	
44	212	2CO	C3	
	224	2VCO	C2	–
	234	3CO	C1	
45	212	2CO	C3	
	224	2VCO	C2	392,334
	234	3CO	C1	
46	212	2CO	C3	392,335
	234	3CO	C1	

TABLE II (*continued*)

Peak	*Mol.wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
47	224	2VCO	C2	–
	234	3CO	C1	
48	224	2VCO	C2	–
	234	3CO	C1	
49	224	2VCO	C2	
	226	2CO	C4	–
	234	3CO	C1	
50	224	2VCO	C2	–
	226	2CO	C4	
51	224	2VCO	C2	
	226	2CO	C4	
	238	2VCO	C3	–
	248	3CO	C2	
52	234	3CO	C1	–
	248	3CO	C2	
53	224	2VCO	C2	–
	226	2CO	C4	
54	226	2CO	C4	–
	238	2VCO	C3	
55	226	2CO	C4	
	238	2VCO	C3	359,385,403
	248	3CO	C2	
56	238	2VCO	C3	347,385,403
	248	3CO	C2	
57	226	2CO	C4	
	238	2VCO	C3	–
	248	3CO	C2	
	260	3VCO	C1	
58	238	2VCO	C3	
	248	3CO	C2	–
	260	3VCO	C1	
59	238	2VCO	C3	
	240	2CO	C5	–
	248	3CO	C2	
60	238	2VCO	C3	
	240	2CO	C5	
	248	3CO	C2	–
	252	2VCO	C4	
	260	3VCO	C1	
	262	3CO	C3	
61	238	2VCO	C3	
	240	2CO	C5	
	252	2VCO	C4	–
	260	3VCO	C1	
62	262	3CO	C3	–
64	240	2CO	C5	
	252	2VCO	C4	–
	262	3CO	C3	

(Continued on p. 398)

TABLE II (*continued*)

Peak	*Mol.wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
65	240	2CO	C5	
	252	2VCO	C4	–
	262	3CO	C3	
	274	3VCO	C2	
66	252	2VCO	C4	325,331,338,347
	274	3VCO	C2	338,389,394,403
67	252	2VCO	C4	–
	262	3CO	C3	
68	252	2VCO	C4	376,383,389,412
72	266	2VCO	C5	371,388,399,410
	276	3CO	C4	
73	270	4CO	–	321,339,359

Peak 18 features a strong *m/z* 170, while *m/z* values of 184, 198, 212, etc. are seen in subsequent fractions. Thus, *m/z* 170 seems to be the parent of a homologous series of hydroxy derivatives of an aromatic compound with mol.wt. 154. Of the three obvious possibilities (biphenyl, vinylnaphthalene, acenaphthene), the most highly probable parent structure is biphenyl. This assignment would be impossible based solely upon the mass spectral data; however, such data in conjunction with the fluorescence emission data provide fairly conclusive evidence for the biphenyl structure. The emission wavelength of maximum intensity, from peak 18, is 355 nm, which matches exactly with the emission maximum of 4-phenylphenol[32], indicating the biphenyl skeleton as opposed to a condensed ring system. Along with the hydroxy biphenyls, symbolized as 2CO, appears a second series (*m/z* 196, 210, 224, etc.), whose members exhibit chromatographic retention roughly the same as the 2CO compounds, indicating similar structural features. Thus, of the few structural types possible, we assign to this series the designation 2VCO, indicating hydroxyvinylbiphenyls, that is, hydroxy biphenyls with one site of unsaturation in a side chain.

Following this line of thought, the next expected series of compounds would have an aromatic ring fused to one of the molecular types already seen. Fusion of one aromatic ring to another increases the molecular weight of the parent by 50 mass units. Thus, the molecular types 3CO (mol.wt. 220) and 3VCO (mol.wt. 246) should elute at the end of the 2CO and 2CVO series (with some overlap). Both these families are seen in the expected parts of the chromatogram. Similarly, 4CO (mol.wt. 270) is seen at the end of the chromatogram (fraction 73).

Table III summarizes the molecular weights, structural assignments, and fluorescence data for the SRC II phenolic fraction. Structural assignments for this sample are approached as described for the fuel oil blend. Here, no phenolic compounds were found before peak 18. Structural data for this sample indicate mono- and dihydroxy derivatives of smaller, "less compact" molecules, rather than the hydroxy derivatives of the neutral PAC elucidated earlier. The smaller systems are postulated using an argument based on continuity; that is, it is reasonable that a compound with mol.wt. 342 be assigned to the already well represented 4BO family (with seven

TABLE III

STRUCTURAL DATA FOR SRC II (Fig. 2)

Peak	*Mol. wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
18	270	4CO	–	368,378,390,412
19	270	4CO	–	388,405
20	270	4CO	–	388,408
22	270	4CO	–	388,397
23	270	4CO	–	342,358,371
	272	4BO	C2	
25	258	4BO	C1	426,435
	260	4BO2	–	
26	260	4BO2	–	–
	272	4BO	C2	
27	260	4BO2	–	397,409,415
	272	4BO	C2	
28	258	4BO	C1	
	260	4BO2	–	452,464
	272	4BO	C2	
30	284	4CO	C1	390,403,411
31	260	4BO2	–	
	272	4BO	C2	
	274	4BO2	C1	361,381,402
	284	4CO	C1	
32	294	5CO	–	347,364,379
34	284	4CO	C1	364,381
35	272	4BO	C2	
	274	4BO2	C1	
	284	4CO	C1	391,411
	308	5CO	C1	
36	284	4CO	C1	–
37	294	5CO	–	393,412
38	274	4BO2	C1	–
	294	5CO	–	
39	284	4CO	C1	
	294	5CO	–	349,367,396,418
	308	5CO	C1	
40	272	4BO	C2	
	274	4BO2	C1	
	294	5CO	–	364,384,417
	298	4CO	C2	
	308	5CO	C1	
42	274	4BO2	C1	360,379,397,419
	298	4CO	C2	
	310	5CO2	–	
43	272	4BO	C2	
	298	4CO	C2	360,385
	308	5CO	C1	
44	298	4CO	C2	345,359,375,400
	308	5CO	C1	
45	298	4CO	C2	352,369,393,411
	308	5CO	C1	

(Continued on p. 400)

TABLE III (*continued*)

Peak	*Mol. wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
46	286	4BO	C3	
	288	4BO2	C2	–
	298	4CO	C2	
	310	5CO2	–	
47	298	4CO	C2	347,360,378,392,415
	308	5CO	C1	and
	310	5CO2	–	399,417
49	286	4BO	C3	
	288	4BO2	C2	
	298	4CO	C2	–
	308	5CO	C1	
	310	5CO2	–	
	322	5CO	C2	
50	286	4BO	C3	
	288	4BO2	C2	
	298	4CO	C2	359,404
	308	5CO	C1	
	310	5CO2	–	
	322	5CO	C2	
51	288	4BO2	C2	
	300	4BO	C4	–
	310	5CO2	–	
	324	5CO2	C1	
52	288	4BO2	C2	
	300	4BO	C4	
	308	5CO	C1	358,408
	312	4CO	C3	
	322	5CO	C2	
	324	5CO2	C1	
53	302	4BO2	C3	
	308	5CO	C1	
	312	4CO	C3	402,421
	322	5CO	C2	
	324	5CO2	C1	
54	300	4BO	C4	
	302	4BO2	C3	
	312	4CO	C3	378,399,411,423
	322	5CO	C2	
	324	5CO2	C1	
55	298	4CO	C2	
	300	4BO	C4	
	312	4CO	C3	–
	322	5CO	C2	
	324	5CO2	C1	
56	300	4BO	C4	
	312	4CO	C3	
	314	4BO	C5	349,376,400
	322	5CO	C2	
	324	5CO2	C1	

TABLE III (*continued*)

Peak	*Mol. wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
	326	4CO	C4	
57	300	4BO	C4	
	312	4CO	C3	
	314	4BO	C5	355,368,389
	322	5CO	C2	
	324	5CO2	C1	
	336	5CO	C3	
58	300	4BO	C4	
	302	4BO2	C3	–
	322	5CO	C2	
	324	5CO2	C1	
59	300	4BO	C4	
	302	4BO2	C2	
	314	4BO	C5	–
	322	5CO	C2	
	324	5CO2	C1	
	336	5CO	C3	
60	300	4BO	C4	
	302	4BO2	C2	
	314	4BO	C5	
	324	5CO2	C1	359,383,400
	326	4CO	C4	
	336	5CO	C3	
	338	5CO2	C2	
61	302	4BO2	C2	
	324	5CO2	C1	411,423
	326	4CO	C4	
62	322	5CO	C2	348,409
	328	4BO	C6	
63	322	5CO	C2	
	324	5CO2	C1	418,447
	326	4CO	C4	
64	324	5CO2	C1	
	326	4CO	C4	
	328	4BO	C6	409,417,423
	336	5CO	C3	
	338	5CO2	C2	
65	314	4BO	C5	
	322	5CO	C2	
	326	4CO	C4	–
	328	4BO	C6	
	338	5CO2	C2	
66	314	4BO	C5	
	316	4BO2	C4	
	324	5CO2	C1	410,423,429
	326	4CO	C4	
	328	4BO	C6	
	338	5CO2	C2	
67	314	4BO	C5	

(Continued on p. 402)

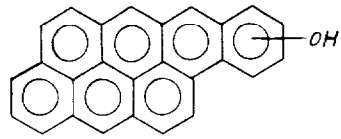
TABLE III (*continued*)

Peak	*Mol. wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
	316	4BO2	C4	
	326	4CO	C4	337,353,409
	328	4BO	C6	
	338	5CO2	C2	
68	314	4BO	C5	
	316	4BO2	C4	
	326	4CO	C4	
	336	5CO	C3	348,408
	338	5CO2	C2	
	340	4CO	C5	
	350	5CO	C4	
69	314	4BO	C5	
	326	4CO	C4	
	328	4BO	C6	421,439
	336	5CO	C3	
	338	5CO2	C2	
	340	4CO	C5	
70	326	4CO	C4	
	328	4BO	C6	
	336	5CO	C3	–
	338	5CO2	C2	
	340	4CO	C5	
71	328	4BO	C6	
	338	5CO2	C2	395,411,437
	340	4CO	C5	
	352	5CO2	C3	
72	316	4BO2	C4	
	328	4BO	C6	–
	338	5CO2	C2	
73	316	4BO2	C4	
	328	4BO	C6	
	338	5CO2	C2	354,403
	342	4BO	C7	
	350	5CO	C4	
	354	4CO	C6	
74	328	4BO	C6	
	336	5CO	C3	
	338	5CO2	C2	408,419
	340	4CO	C5	
	352	5CO2	C3	
75	316	4BO2	C4	
	328	4BO	C6	412
	340	4CO	C5	
	342	4BO	C7	
76	338	5CO2	C2	
	340	4CO	C5	
	342	4BO	C7	355,379,391
	350	5CO	C4	
	354	4CO	C6	
77	326	4CO	C4	

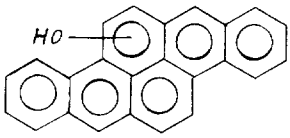
TABLE III (*continued*)

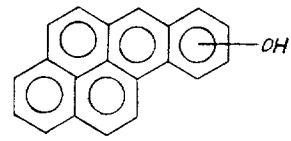
Peak	*Mol. wt.*	*Molecular type*	*Substitution*	*Fluorescence maxima (nm)*
	328	4BO	C6	
	330	4BO2	C5	
	338	5CO2	C2	378
	342	4BO	C7	
	352	5CO2	C3	
	354	4CO	C6	

carbon substitution), although 342 daltons is also the molecular weight of the structure:



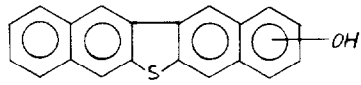
It was not, however, assigned to the 7BO family because there was no evidence for its predecessors in that family, *i.e.*:





In contrast, all the alkyl derivatives that would precede the postulated compound, starting with the C_1 derivative (mol.wt. 258), are seen throughout the sample. Consequently, all remaining structural assignments (Table III) may be rationalized in this manner.

Previous GC studies indicate that hydroxylated sulfur heterocyclic compounds may be expected in this fraction[21]; however, these are not among our proposed structures for the following reasons: (1) the largest hydroxylated thiophenic compounds found in SRC II to date[33] are below the molecular-weight range investigated in this study; and, (2) any hydroxylated thiophenic compounds that could be postulated from the data (the smallest of which is shown below) do not appear as a homologous series, or in any other recognizable pattern.



Based on preliminary mass-spectroscopic evidence, many higher m/z values could be interpreted as hydroxylated thiophenes. However, a more general view of data, as discussed above, makes assignments of this nature less likely. It is difficult to propose a seven-ring hydroxylated thiophenic structure when the five- or six-ring homologues are not seen or fit into the middle of another homologous series. Isotopic analysis of the mass spectral data would allow the distinction between a thiophenic

and a phenolic compound. These are, however, difficult to assess from such small samples due to the unfavorable signal-to-noise ratio.

Definitive statements based upon fluorescence data are difficult to make, but some distinctions and generalizations appear feasible. The first four peaks assigned as phenols (peaks 18–20 and 22) are all placed in the 4CO family, but the emission maximum of peak 22 is significantly higher than that of the other three. Extrapolation of the fluorescence data reported by Schabron *et al.*[29,32] leads to the conclusion that, as the ring systems become more condensed, their fluorescent emission maxima will be shifted to a somewhat higher wavelength, while the chromatographic retention in the reversed-phase system should also increase. Therefore, it seems possible to assign the binaphthyl structure of the 4CO family to peaks 18–20 (λ_{max} = 388–390 nm), while peak 22 appears to be a phenylphenanthrene type molecule (λ_{max} = 397 nm). The position of a hydroxy group will determine the elution order of the three compounds within the binaphthyl group, as shown by Schabron *et al.*[29]. The fluorescence data presented here bear out the extension of these earlier observations to larger molecules, *i.e.*, more condensed systems (4BO as opposed to 4CO) will have fluorescent maxima at higher wavelengths and should display less distinct spectral features. This is illustrated in Figs. 3 and 4.

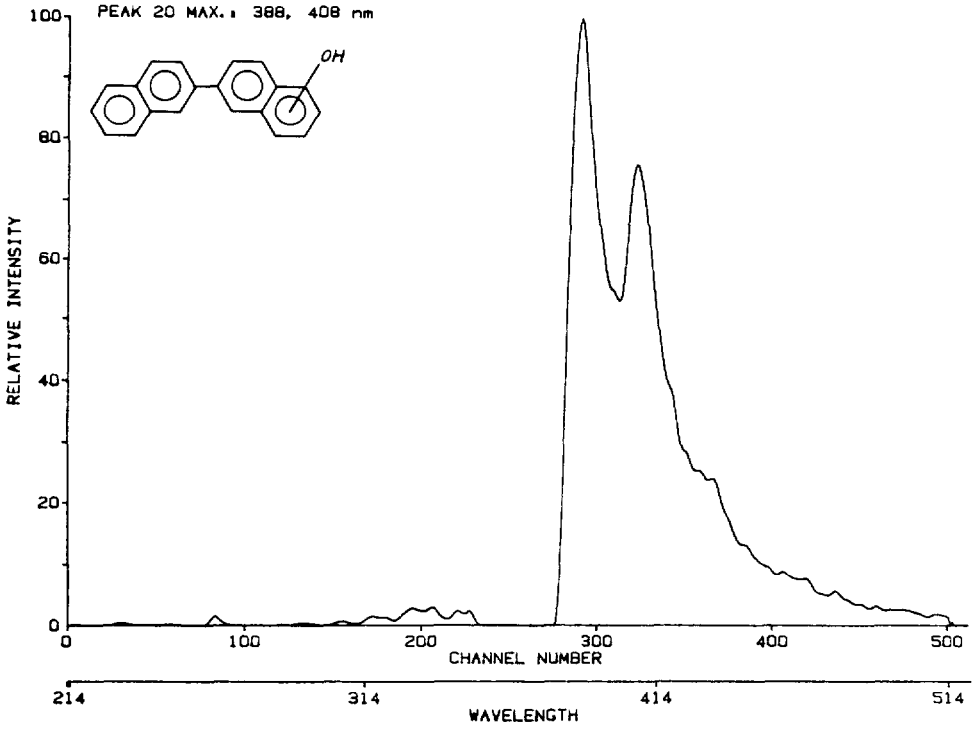


Fig. 3. Fluorescence emission spectrum of peak 20 separated from SRC II. 4CO binaphthyl structure is suggested.

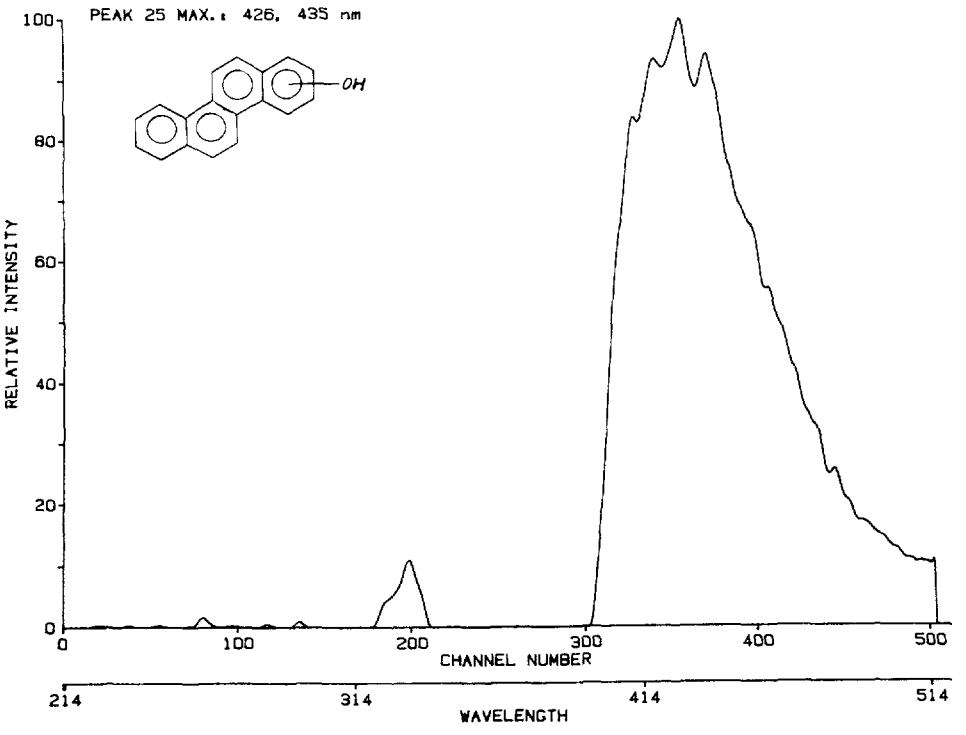


Fig. 4. Fluorescence emission spectrum of peak 25 separated from SRC II. 4BO or 4BO2 structural types are suggested.

As seen in this study and the previous investigations[14–17], separation and characterization of the heavy components in fossil fuels are analytically challenging. While microcolumn LC provides separation efficiencies that are an order of magnitude greater than those in conventional LC, further improvements in resolution are still desirable. MS remains the principal identification technique in this area. Fluorescence data are of some use as complementary information to mass spectra. However, the unavailability of high-molecular-weight reference compounds remains the greatest obstacle to more exact structural assignments at present.

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