

# Aromatic Sulfur Compounds Other Than Condensed Thiophenes in Fossil Fuels: Enrichment and Identification

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A rapid and simple method has been established for the isolation of condensed thiophenes (PASH) and other types of aromatic sulfur compounds (S-PAC) based on ligand-exchange chromatography (LEC). This procedure has been applied to the aromatic fractions of a crude oil, a coal extract, and a hydrogenated coal liquid to obtain PASH and S-PAC fractions. Both fractions were examined by capillary column gas chromatography with flame ionization and flame photometric detection and by gas chromatography/mass spectrometry. A variety of previously unidentified S-PAC were found in these samples. Alkyl phenyl disulfides were the major S-PAC in the crude oil, and alkylphenylthiophene and propyl naphthyl sulfide were found in the coal extract, while alkyldihydrobenzothiophenes were isolated in the hydrogenated coal liquid. Structural characteristics of the identified S-PAC are discussed and compared with sample properties. The interaction of PASH and S-PAC with PdCl<sub>2</sub> in LEC used in this study was also discussed.

## Introduction

Sulfur is present in various forms in all fossil fuels. The organic sulfur compounds found in these materials have been categorized according to functionality: thiol, disulfide, sulfide, and thiophene. Condensed thiophenes (PASH) are generally the most abundant of aromatic sulfur compounds in various upgraded fossil fuels due to their resonance stabilities, and they have been extensively studied.<sup>1,2</sup> In addition to PASH, crude oils, and coals are thought to contain other types of aromatic sulfur compounds (S-PAC), such as thiols, sulfides, and disulfides.<sup>3-6</sup> However, S-PAC in these samples has never been fully identified. The relatively low abundances of these compounds make their analysis extremely difficult.

The isolation or enrichment of target compounds in selected fractions is an essential step for their unambiguous identification. Since the properties of aromatic sulfur compounds are very similar to those of aromatic hydrocarbons, finding such procedures is very difficult. During the investigation of various isolation methods for PASH, a new isolation method based on ligand-exchange chromatography (LEC) using PdCl<sub>2</sub> was found to be the most successful.<sup>7</sup> LEC has been used to identify compounds containing two- to six-ring PASH in coal-derived materials<sup>8</sup> and complex alkylated PASH mixtures in a catalytically cracked vacuum residue.<sup>9</sup>

LEC was first suggested for chromatography by Helfferich in 1961,<sup>10</sup> and the basic principles of LEC were

explained to some extent by him.<sup>11-13</sup> Recent advances were reviewed by Davankov and Semechkin,<sup>14</sup> and the most recent studies are cited in Takayanagi's paper.<sup>15</sup> Although a fundamental understanding of LEC is still incomplete, it offers a unique chromatographic selectivity that cannot be attained with conventional partition or adsorption chromatography.

A number of anions and neutral molecules that possess pairs of free electrons are capable of functioning as ligands because of their electron-donation properties.<sup>16</sup> Sulfides readily form ligands, as do amines, alcohols, and amino acids, and their LEC behavior has been studied.<sup>17-22</sup> These papers, however, deal mostly with alkyl sulfides and their chromatographic selectivities. Many complex-forming ions in the LEC are known, such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+,3+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Ag<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, and VO<sub>2</sub><sup>2+</sup>.<sup>14</sup> Recently, CuCl<sub>2</sub> and PdCl<sub>2</sub> were selected and studied for the isolation of aliphatic thioethers and simple sulfur heterocycles.<sup>23</sup>

In this study, an isolation method for S-PAC based on LEC using silica gel impregnated with PdCl<sub>2</sub> was established and applied to the analyses of a crude oil, a coal extract, and a hydrogenated coal liquid. The isolated fractions were analyzed by capillary column gas chromatography (GC) and gas chromatography/mass spectrom-

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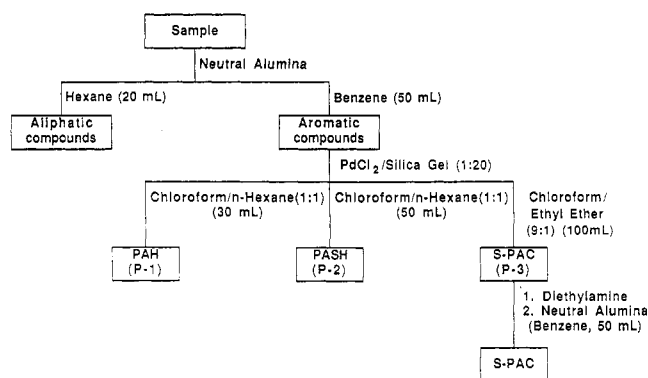


Figure 1. Fractionation and isolation scheme for aromatic sulfur compounds.

etry (GC/MS). For the first time, various kinds of new S-PAC in these samples were identified. Structural characteristics of the S-PAC were discussed and compared with sample properties. The interaction of PASH and S-PAC with  $\text{PdCl}_2$  in the LEC used in this study was also discussed.

### Experimental Section

Wilmington crude oil sealed in ampules under a nitrogen atmosphere and SRC-I process solvent were obtained from Battelle Pacific Northwest Laboratory, Fossil Fuel Repository. Elemental analysis and other physical-chemical data for the Wilmington crude oil have been reported earlier.<sup>3</sup> A PSOC-521 coal (Rock Springs No. 7, Sweetwater, WY) obtained from The Pennsylvania State University Coal Repository has been described.<sup>24</sup> A 25-g portion of PSOC-521 coal was extracted with 500 mL of benzene for 24 h in a Soxhlet apparatus before fractionation. Aromatic fractions were isolated as previously described<sup>25</sup> from 0.3 g of the Wilmington crude oil, 0.3 g of the SRC-I process solvent, or 0.6 g of the PSOC-521 benzene extract. These fractions containing PAH, PASH, and S-PAC were further analyzed in this study. Standard reference compounds (Aldrich Chemical Co., Milwaukee, WI) and spectrometric grade solvents (Fisher Scientific, Fair Lawn, NJ) were used without further purification.

The 5.0 g of material used for the LEC column was prepared as previously described<sup>7</sup> using silica gel impregnated with  $\text{PdCl}_2$ . The samples were eluted with chloroform/*n*-hexane (1:1), yielding fractions P-1 (30 mL) and P-2 (50 mL), and with chloroform/ethyl ether (9:1), yielding fraction P-3 (100 mL). The PAH were eluted in fraction P-1, the PASH were eluted in fraction P-2, and the S-PAC were eluted in fraction P-3. The P-3 fraction was reduced in volume to 0.5 mL by rotary evaporation, and 30  $\mu\text{L}$  of diethylamine were added. This fraction was once more cleaned by passing it through neutral alumina with 50 mL of benzene. A diagram of this isolation method is shown in Figure 1.

A Hewlett-Packard Model 5880 gas chromatograph equipped with flame ionization and flame photometric detectors (FID and FPD) was used for all gas chromatographic analyses. Sample injection was made in the splitless mode with hydrogen as a carrier gas at a linear velocity of 100  $\text{cm s}^{-1}$ . Semiquantitation was accomplished by FID peak areas of the resolved components using a response factor determined for a standard injection of dibenzothiophene. The capillary column was prepared by statically coating fused silica tubing (15 m  $\times$  0.20 mm i.d., Hewlett-Packard, Avondale, PA) with SE-54 (film thickness of 0.25  $\mu\text{m}$ ), cross-linking with 2,2'-azoisobutane,<sup>26</sup> and conditioning overnight at 280  $^\circ\text{C}$  under nitrogen gas flow. Mass spectral data were collected with a Hewlett-Packard 5970 mass spectrometer system operated in the electron-impact mode at 70 eV with the ion source and analyzer temperatures held at 250 and 280  $^\circ\text{C}$ , respectively, and the scan speed set at 300  $\text{amu s}^{-1}$ .

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Table I. Approximate Recoveries of Selected Sulfur-Containing Compounds by Ligand-Exchange Chromatography on Silica Gel Impregnated with  $\text{PdCl}_2$

compd	structure	recovery, wt %		
		P-1	P-2	P-3
hexyl sulfide	$(n\text{-C}_6\text{H}_{11})_2\text{S}$	0	30	30 <sup>a</sup>
2,2'-bithiophene		>95	<1	0
2-naphthalenethiol		0	0	b
phenyl sulfide		0	<5	>90
benzyl sulfide		0	<5	>90
phenyl disulfide		0	0	>95
2-phenyl-1,3-dithiane		0	0	5 <sup>a</sup>
thianthrene		0	0	20 <sup>a</sup>

<sup>a</sup> Other portion remained in the column. <sup>b</sup> Showed decomposition during analysis by GC.

Table II. Hückel  $\pi$ -Electron Density and Approximate Recoveries in Each Fraction of Thiophene Benzologs

compd	structure	Hückel $\pi$ -electron density <sup>a</sup>	recovery, wt %		
			P-1	P-2	P-3
bithiophene		(1.599) <sup>b</sup>	>95	<1	0
benzothiophene		1.663	50	20	0
dibenzothiophene		1.722	<1	70	20
benzo[b]naphtho[2,1-d]thiophene		1.697	<1	90	0

<sup>a</sup> Reference 30. <sup>b</sup> Value given for thiophene.

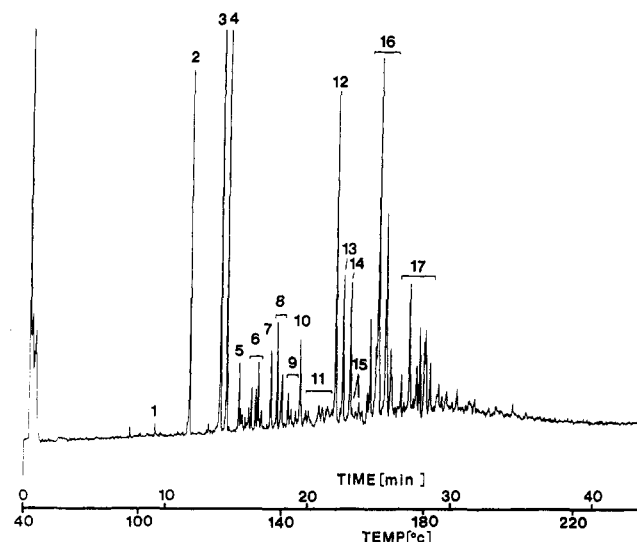
### Results and Discussion

Most of the PASH eluted as PASH/Pd complexes in the P-2 fraction.<sup>7</sup> Leaching of Pd complexes in the P-3 fraction from the stationary phase was even greater. In fact, when the P-3 fraction was concentrated, the S-PAC/Pd complexes precipitated. Because diethylamine is a stronger ligand than S-PAC and can replace S-PAC in the S-PAC/Pd complexes, the P-3 fraction was treated with diethylamine as previously described for the P-2 fractions.<sup>7</sup> To eliminate the diethylamine/Pd complexes and the trace amounts of nitrogen-containing compounds from the released S-PAC, this fraction was cleaned by passing it again through neutral alumina using a benzene eluent.

Table I lists the recoveries of selected model thiols, sulfides, and disulfides in the P-1 to P-3 fractions. More than 90% of the phenyl sulfide, benzyl sulfide, and phenyl disulfide were recovered in fraction P-3; however, only a low percentage of 2-naphthalenethiol was detected by using GC. It is known that thiols are difficult compounds to analyze.<sup>27,28</sup> Thiols readily converted to other compounds in the presence of air or during analysis by GC/MS. For example, only 10% of the 2-naphthalenethiol injected into the GC was recovered. Hexyl sulfide, 2-phenyl-1,3-dithiane, and thianthrene showed strong interaction with  $\text{PdCl}_2$ . They partially eluted in the P-3 fraction and partially remained on the column. Bithiophene did not show significant interaction with  $\text{PdCl}_2$ . These results suggest that the ligand exchange of sulfur compounds with  $\text{PdCl}_2$  depends upon their nucleophilicity.<sup>23,29</sup> Alkyl

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**Figure 2.** FPD gas chromatogram of the P-2 fraction of a Wilmington crude oil. Conditions: temperature program from 40 to 100 °C at 10 °C min<sup>-1</sup> and then from 100 to 265 °C at 4 °C min<sup>-1</sup> after an initial 2-min isothermal period; hydrogen carrier gas at a linear velocity of 100 cm s<sup>-1</sup>. Peak assignments are listed in Table IIIa.

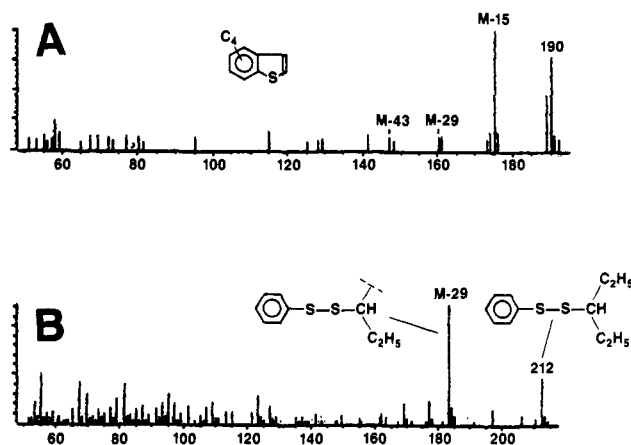
**Table III. Aromatic Sulfur Compounds Identified and Quantified in a Wilmington Crude Oil**

peak no.	molecular ion	proposed compd or isomer	concn, <sup>a</sup> μg/g
<b>(a) Polycyclic Aromatic Thiophenes</b>			
1	148	C <sub>1</sub> -benzothiophene	1
2	162	C <sub>2</sub> -benzothiophene	50
3	176	C <sub>3</sub> -benzothiophene	100
4	176	C <sub>3</sub> -benzothiophene	90
5	176	C <sub>3</sub> -benzothiophene	10
6	190	C <sub>4</sub> -benzothiophene	<i>b</i>
7	190	C <sub>4</sub> -benzothiophene	20
8	190, 204	C <sub>4</sub> - and C <sub>5</sub> -benzothiophene	<i>b</i>
9	204	C <sub>5</sub> -benzothiophene	<i>b</i>
10	184	dibenzothiophene	20
11	218	C <sub>6</sub> -benzothiophene	<i>b</i>
12	198	4-methyldibenzothiophene	50
13	198	2- and 3-methyldibenzothiophene	30
14	198	1-methyldibenzothiophene	30
15	232	C <sub>7</sub> -benzothiophene	<i>b</i>
16	212	C <sub>2</sub> -dibenzothiophene	<i>b</i>
17	226	C <sub>3</sub> -dibenzothiophene	<i>b</i>
<b>(b) Aromatic Disulfides</b>			
1	172	unknown	3
2	156	methyl phenyl disulfide	1
3	170	ethyl phenyl disulfide	3
4	184	propyl phenyl disulfide	9
5	198	butyl phenyl disulfide	3
6	212	pentyl phenyl disulfide	3
7	226, 212	hexyl and pentyl phenyl disulfide	2
8	212	pentyl phenyl disulfide	40
9	212	pentyl phenyl disulfide	10
10	252	C <sub>2</sub> -cyclohexyl phenyl disulfide	10
11	266	C <sub>3</sub> -cyclohexyl phenyl disulfide	4

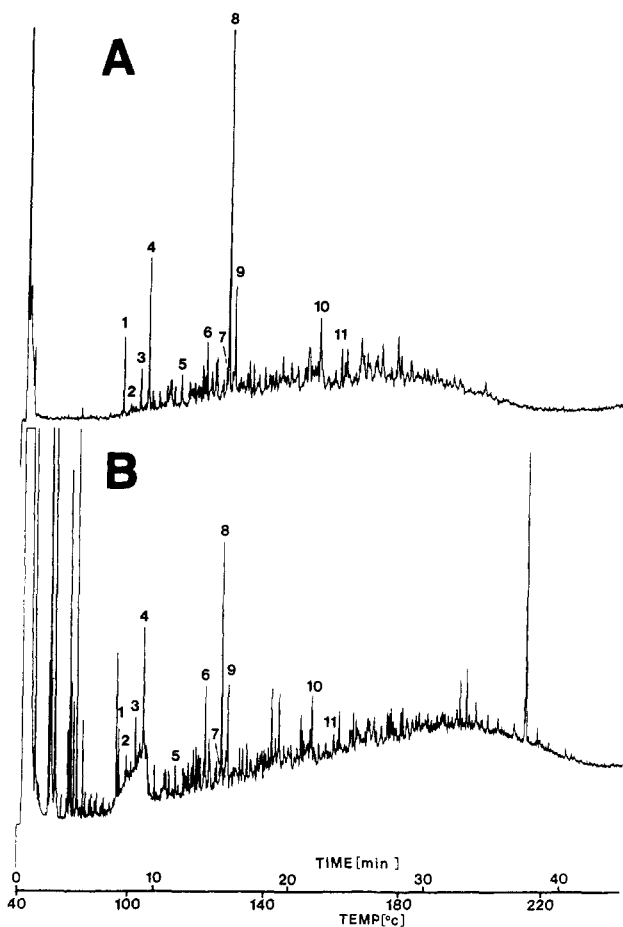
<sup>a</sup> Approximate concentration in μg/g of original material.

<sup>b</sup> These compounds were detected but not quantified.

sulfides and cyclic sulfides with aromatic rings are the most nucleophilic, followed by phenyl sulfides and phenyl disulfides, all of which elute in the P-3 fraction. Table II lists Hückel  $\pi$ -electron densities of selected thiophene benzologs.<sup>30</sup> The elution behavior of these PASH is



**Figure 3.** Mass spectra of (A) peak 7 in Figure 2 and (B) peak 8 in Figure 4.



**Figure 4.** Gas chromatograms of the P-3 fraction of a Wilmington crude oil using (A) FPD and (B) FID. Conditions are as in Figure 2. Peak assignments are listed in Table IIIb.

coincident with their  $\pi$ -electron densities. Elemental balances of the P-1 and P-2 fractions were checked earlier for a petroleum-derived product.<sup>9</sup> Because S-PAC were minor constituents, elemental analyses of the P-3 fraction of fossil fuels were not performed. In the present work, the efficiency of LEC method is demonstrated by GC-(FPD) and GC/MS in the analyses of three different natural samples.

This LEC method was applied to a Wilmington crude oil. Figure 2 shows the FPD chromatogram of the P-2

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Table IV. Aromatic Sulfur Compounds Identified and Quantified in a PSOC-521 Coal Extract and an SRC-I Process Solvent

peak no.	molecular ion	proposed compd or isomer	concn, <sup>a</sup> $\mu\text{g/g}$			
			PSOC-521		SRC-I	
			P-2	P-3	P-2	P-3
1	136	dihydrobenzothiophene				20
2	148	C <sub>1</sub> -benzothiophene	0.02		20	
3	150	C <sub>1</sub> -dihydrobenzothiophene				b
4	162	C <sub>2</sub> -benzothiophene	b	0.04	b	
5	164	C <sub>2</sub> -dihydrobenzothiophene				b
5*	164	C <sub>2</sub> -dihydrobenzothiophene				70
6	176	C <sub>3</sub> -benzothiophene	b	b	b	
7	178	C <sub>3</sub> -dihydrobenzothiophene				b
8	190	C <sub>4</sub> -benzothiophene	b			
9	202	C <sub>3</sub> -phenylthiophene		0.03		
10	216	C <sub>4</sub> -phenylthiophene		0.01		
11	202	propyl naphthyl sulfide		0.02		
12	188	tetrahydrodibenzothiophene			10	
13	184	dibenzothiophene	0.04	0.01	11000	20
14	198	4-methyldibenzothiophene	0.05	0.03	2200	20
15	198	2- and 3-methyldibenzothiophene	b	b	2700	380
16	198	1-methyldibenzothiophene	b	b	30	
17	212	C <sub>2</sub> -dibenzothiophene		b	b	b
18	212	C <sub>2</sub> -dibenzothiophene		0.02	50	b
19	208	phenanthro[4,5- <i>bcd</i> ]thiophene			80	
20	222	C <sub>1</sub> -phenanthro[4,5- <i>bcd</i> ]thiophene			40	
21	222	C <sub>1</sub> -phenanthro[4,5- <i>bcd</i> ]thiophene			30	

<sup>a</sup> Approximate concentration in  $\mu\text{g/g}$  of original material. <sup>b</sup> These compounds were detected but not quantified.

fraction of this crude oil. Compounds were identified by comparison with previous work<sup>2</sup> and by GC/MS. The identified compounds, their molecular masses, and their approximate concentrations are listed in Table IIIa. Alkylated benzothiophenes and dibenzothiophenes were the major thiophenic compounds in this sample, and even two C<sub>7</sub>-benzothiophenes were detected. The mass spectra of the alkylated compounds in this sample showed extended chain alkylation instead of multimethyl substitution because of the presence of M - 15, M - 29, and M - 43 peaks (Figure 3A).

Figure 4 shows the FPD and FID chromatograms of the P-3 fraction of the Wilmington crude oil. Some remaining diethylamine/Pd complexes were observed in the FID chromatogram. Comparison of these chromatograms verifies that aromatic sulfur compounds were isolated in the P-3 fraction. These compounds were also identified by GC/MS. The identified compounds, their molecular masses, and their approximate concentrations are listed in Table IIIb. Sulfides were not detected at significant levels, and only alkyl phenyl disulfides were present as major S-PAC components.

Figure 3B shows the mass spectrum of peak 8 as an example. Aromatic sulfur compounds with a molecular mass of 212 are probably C<sub>2</sub>-dibenzothiophenes and pentyl phenyl disulfides. Retention times of C<sub>2</sub>-dibenzothiophenes are quite large compared with that of peak 8. Disulfides are difficult to identify from the mass fragment patterns, because, in general, they easily rearrange under the mass spectrometry operating conditions used in this study.<sup>31</sup> This peak, however, can be tentatively identified as isopentyl phenyl disulfide because of the absence of a M - 1 peak and the observation of very weak M - 15 peaks and very strong M - 29 peaks.

Thiols are generally not stable in air or at high temperatures and tend to form disulfides by a coupling reaction.<sup>27,28,32,33</sup> Alkyl phenyl disulfides identified in this

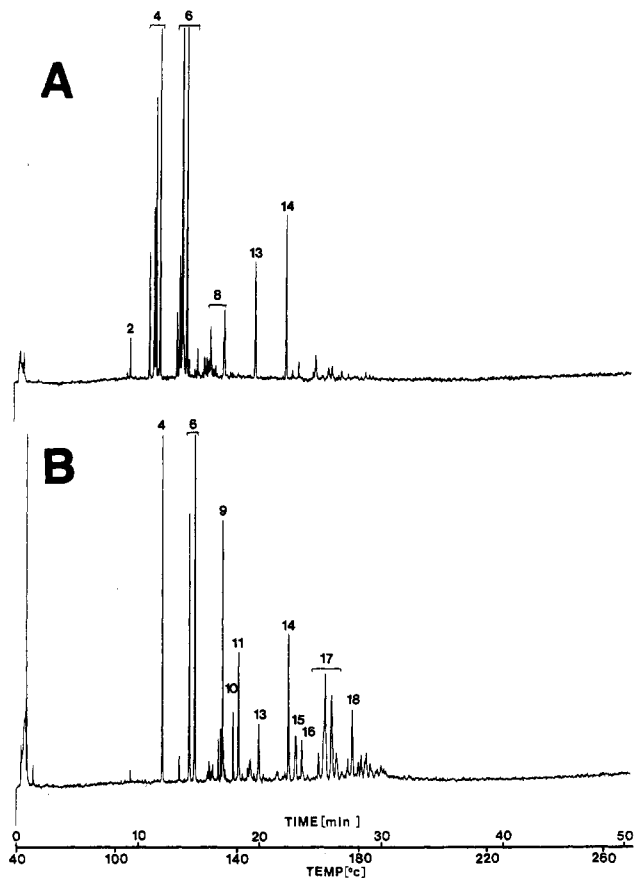


Figure 5. FPD gas chromatograms of (A) P-2 and (B) P-3 fractions of a PSOC-521 extract. Conditions are as in Figure 2. Peak assignments are listed in Table IV.

sample were presumably derived from benzenethiol and alkanethiols (eq 1).

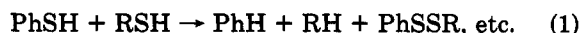
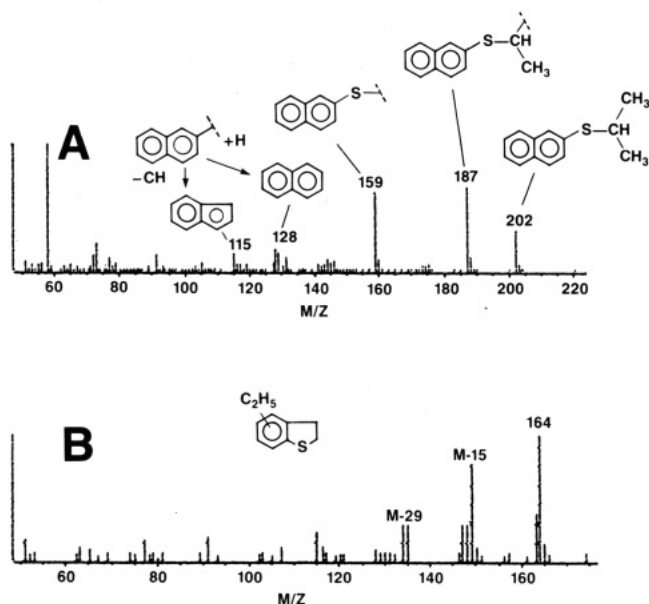


Figure 5 shows FPD chromatograms of the P-2 and the P-3 fractions of the PSOC-521 extract. The identified compounds, their molecular masses, and their approximate

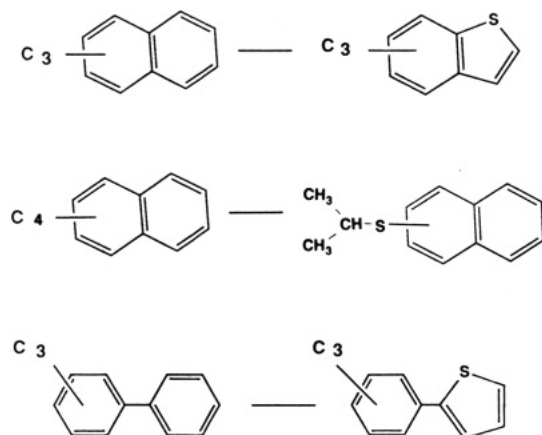
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**Figure 6.** Mass spectra of (A) peak 11 in Figure 5 and (B) peak 5\* in Figure 9.



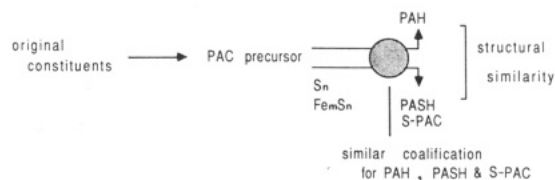
**Figure 7.** Structural similarities of major aromatic hydrocarbons and major aromatic sulfur compounds in a PSOC-521 coal extract.

concentrations are listed in Table IV. C<sub>2</sub>- and C<sub>3</sub>-benzothiophenes were major components in the P-2 fraction. Some alkylated PASH eluted in the P-3 fraction, because  $\pi$ -electron-rich sulfur compounds exhibit strong interactions with PdCl<sub>2</sub>. C<sub>3</sub>- and C<sub>4</sub>-phenylthiophenes were also identified in the P-3 fraction. If a phenyl group is attached to a thiophene, the  $\pi$ -electron density of the sulfur is high, and this type of compound may elute in the P-3 fraction.

Very interestingly, peak 11 in the P-3 fraction is most probably isopropyl naphthyl sulfide. In the mass spectrum (Figure 6A), each mass fragment can be interpreted as shown. This seems to be the first observation of sulfur-linked hydrocarbons in coal. Diaryl sulfides might be contained in higher rank coals.

Low-molecular-weight neutral compounds in the PSOC-521 coal extract were recently extensively identified by using GC/MS.<sup>34</sup> One of the major neutral aromatic hydrocarbon groups was C<sub>2</sub>- to C<sub>4</sub>-naphthalenes and C<sub>3</sub>- and C<sub>4</sub>-biphenyls. Structural similarities between these abundant aromatic hydrocarbons and the abundant aromatic sulfur compounds in this coal extract were observed (Figure 7). Major aromatic sulfur compounds were ob-

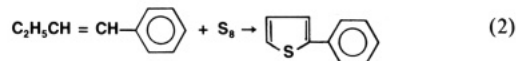
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**Figure 8.** Proposed coalification for aromatic sulfur compounds in coal.

tained by the replacement of a carbon in alkylnaphthalenes or alkydbiphenyls by a sulfur.<sup>8</sup>

Although very little is known about the origin of organosulfur compounds, two plausible origins exist for the occurrence of these compounds in coal.<sup>35</sup> One origin is the organosulfur constituents of the original plant debris, and the other is the products from reactions between elemental sulfur (S<sub>n</sub>) or Fe<sub>m</sub>S<sub>n</sub> compounds such as pyrite and hydrocarbons. Interaction between the pyritic sulfur and the organic matrix during carbonization has been discussed and reviewed.<sup>36-40</sup> Reactions between elemental sulfur and simple hydrocarbons such as toluene and ethylbenzene have also been studied.<sup>41,42</sup> These results demonstrate the possible origin of aromatic sulfur compounds from reactions with S<sub>n</sub> or Fe<sub>m</sub>S<sub>n</sub>. 2,4-Diphenylthiophene, analogous to alkyphenylthiophenes identified in this study, was produced by the mild reaction of ethylbenzene and elemental sulfur in air and water at 130 °C for 72 h.<sup>42</sup> Also, phenylthiophene can be synthesized from unsaturated alkylbenzene and elemental sulfur above 170 °C (eq 2).<sup>43</sup>



Our observation of structural similarities between hydrocarbons and sulfur compounds can be interpreted in the following way to explain the origin of aromatic sulfur compounds. PAH precursors derived from plant debris during diagenesis reacted with S<sub>n</sub> or Fe<sub>m</sub>S<sub>n</sub>. These sulfur compounds then followed the same coalification path as PAH (see Figure 8). On the basis of the results of analyses of various types of polycyclic aromatic compounds in coal-derived materials,<sup>44</sup> the possibilities of similar reactions occurring during diagenesis, despite the presence of heteroatoms, was proposed.

Although S-PAC seem to be minor constituents in upgraded samples such as coal liquids and petroleum-derived materials, they are present in substantial quantity in hydrogenated materials such as SRC-I products. Figure 9 shows FPD chromatograms of these isolated fractions of SRC-I process solvent. The identified compounds, their molecular masses, and their approximate concentrations are listed in Table IV. Cyclic sulfides, C<sub>1</sub>- to C<sub>3</sub>-dihydrobenzothiophenes, present as major compounds in the P-3 fraction, eluted in the P-3 fraction. Although the retentions of alkylbenzothiophenes are identical with those of alkyldihydrobenzothiophenes in GC, the alkyldihydrobenzothiophenes were isolated and identified in this study, some of which have been previously identified in crude

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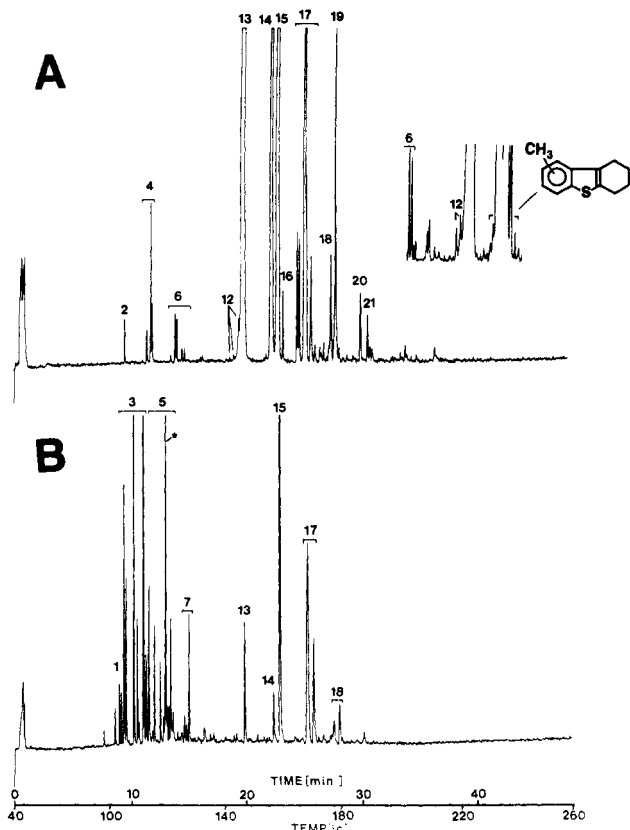
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**Figure 9.** FPD gas chromatograms of (A) P-2 and (B) P-3 fractions of an SRC-I process solvent. Conditions are as in Figure 2. Peak assignments are listed in Table IV.

oils,<sup>45-49</sup> shale oils,<sup>48,49</sup> and coal liquids.<sup>48,49</sup> Figure 6B shows one example of a mass spectrum for C<sub>2</sub>-dihydrobenzothiophenes. Alkylthiocranenes can be thought of as isomers of alkylidihydrobenzothiophenes; however, they were identified here as alkylidihydrobenzothiophenes on the basis of their molecular masses and the fragment patterns of the alkyl substituents.

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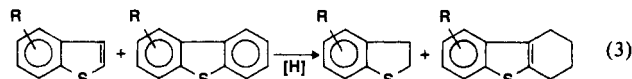
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Whereas benzologs of dihydrobenzothiophene were not present in significant concentration in this sample, three isomers of tetrahydrodibenzothiophene and methyltetrahydrodibenzothiophenes were detected in the P-2 fraction (see Figure 9A). These compounds were apparently produced by hydrogenation in the SRC-I process.<sup>50</sup>



One of the main purposes in this area is to discover detailed information about fossil fuel structures by identifying different types of sulfur compounds. Since sulfur is easily recognizable by using a sulfur-selective GC detector and <sup>34</sup>S in MS, etc., after enrichment of sulfur compounds, sulfur acts as a tracer in complex mixtures. LEC has great potential for the isolation and separation of sulfur compounds with different  $\pi$ -electron densities, because each sulfur functional group has different electronic properties. It is expected that the LEC used in this study will become increasingly popular for isolation and separation of sulfur compounds now that the nucleophilic interaction of sulfur compounds with PdCl<sub>2</sub> has been better characterized and understood.

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**Registry No.** Hexyl sulfide, 6294-31-1; 2,2'-bithiophene, 492-97-7; 2-naphthalenethiol, 91-60-1; phenyl sulfide, 139-66-2; benzyl sulfide, 538-74-9; phenyl disulfide, 882-33-7; 2-phenyl-1,3-dithiane, 5425-44-5; thianthrene, 92-85-3; bithiophene, 56902-08-0; benzothiophene, 95-15-8; dibenzothiophene, 132-65-0; benzo[*b*]naphtho[2,1-*d*]thiophene, 239-35-0; 4-methylidibenzothiophene, 7372-88-5; 2-methylidibenzothiophene, 20928-02-3; 3-methylidibenzothiophene, 16587-52-3; 1-methylidibenzothiophene, 31317-07-4; methyl phenyl disulfide, 14173-25-2; ethyl phenyl disulfide, 4032-81-9; propyl phenyl disulfide, 20126-55-0; butyl phenyl disulfide, 20129-23-1; pentyl phenyl disulfide, 21230-15-9; hexyl phenyl disulfide, 112549-16-3; dihydrobenzothiophene, 71001-77-9; propyl naphthyl sulfide, 13310-92-4; tetrahydrodibenzothiophene, 16587-33-0.

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