CO_2 was easy to remove from the fractions that were collected. The selectivity produced by varying the density of the supercritical fluid enabled the use of larger particle packings. The lower cost of these packings eliminated the need for extensive sample cleanup prior to analysis by SFF. In addition, this procedure may be used to fractionate thermally labile materials, since CO_2 has a very low critical temperature. Overall, it was found during this study that semipreparative SFF shows great potential for high-quality separations with easy solvent removal.

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Supercritical Fluid Fractionation and Detailed Characterization of the Sulfur Heterocycles in a Catalytically Cracked Petroleum Vacuum Residue

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The sulfur heterocycles in a catalytically cracked vacuum residue were isolated by use of a newly developed ligand exchange chromatographic procedure, and they were then fractionated according to the number of aromatic rings by using a supercritical fluid fractionation system with supercritical CO_2 as the fractionation solvent. Compounds in each fraction were identified by capillary column gas chromatography and gas chromatography/mass spectrometry. Characteristic mass spectral fragmentation patterns were used to confirm identifications, particularly for the alkyl-substituted compounds. The sulfur heterocycles in this sample were annellated on both sides of the thiophene ring and were highly alkylated; the most abundant compounds contained alkyl chains with three carbon atoms. Several four-ring compounds containing two sulfur heteroatoms were also detected. This example illustrates the effectiveness of supercritical fluid fractionation according to the number of aromatic rings for highly alkylated samples.

The petroleum industry has continually been troubled with various problems related to sulfur in petroleum, such as product odor and storage stability, corrosion of processing equipment, and pollution during usage. With regard to pollution, sulfur oxides produced during fossil fuel combustion are major contributors to air pollution (*1*) and can lead to acid rain damage to forests (*2*). For these reasons, hydrodesulfurization during refining is important. It is essential to identify the structures of sulfur compounds in crude oils and petroleum-derived products in order to more effectively optimize these desulfurization processes.

Desulfurization of heavy oils is more difficult than that of light oils. This is because highly aromatized polycyclic aromatic sulfur heterocycles (PASH) in heavy oils decrease the reactivity of desulfurization (*3-5*). These compounds are also known to poison catalysts used in catalytic desulfurization processes (*6*). High-molecular-weight sulfur compounds in high-boiling-point fractions and heavy residues are difficult to determine and have not yet been adequately characterized. This is primarily because they are highly alkylated and their identification in such complex mixtures is difficult, even when using high-resolution mass spectrometry.

The structures of sulfur compounds found in petroleum and the analytical methods for different types of sulfur compounds were reviewed by Drushel (*7*) and Dean et al. (*8*). Isolation or concentration of sulfur-rich fractions is essential for accomplishing the required detailed analysis. Although a totally nondiscriminating separation method for sulfur heterocycles has not been found, a new isolation method for compounds with two to six annellated rings, based on ligand exchange chromatography, was recently developed by us (*9*, *10*). Further subfractionation based on molecular weight or number of aromatic rings is necessary in order to further simplify complex PASH fractions for final characterization (*11*).

In this study, PASH in a catalytically cracked petroleum vacuum residue were isolated by ligand exchange chromatography, followed by ring-number separation using a new supercritical CO_2 fractionation system. The resultant PASH fractions were then analyzed using capillary column gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) in order to provide detailed structural information.

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Table I. Elemental Analysis of an FCC VR Crude and Its P-1 and P-2 Fractions

element	concentration, wt %		
	FCC VR crude	P-1	P-2
C	90.7	91.8	77.2
H	8.0	7.1	5.7
S	1.7	1.4	9.7
N	0.2	*a*	*a*

[a] Trace.

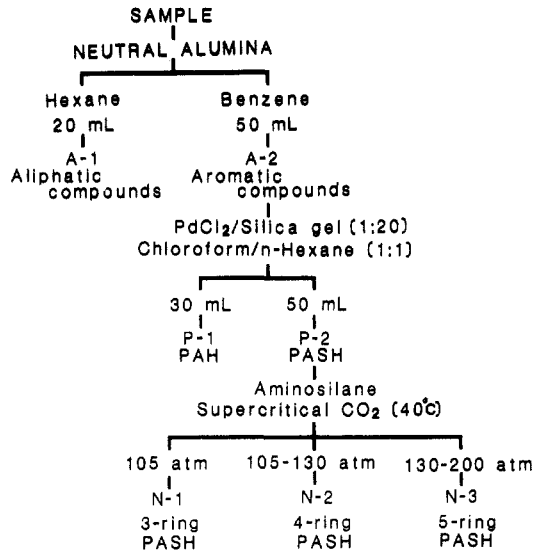

Figure 1. Isolation and fractionation scheme for sulfur heterocycles.

EXPERIMENTAL SECTION

A catalytically cracked petroleum vacuum residue (FCC VR) was obtained from Exxon Research and Engineering Co., Linden, NJ. A 0.3-g sample was fractionated into chemical classes by column adsorption chromatography on neutral alumina (*12*). The PASH fraction (P-2, approximately 10 mg) was isolated from the second fraction (A-2, 0.2 g) by ligand exchange chromatography as previously described (*9*). Silica gel impregnated with $PdCl_2$, which was stored in an oven at 160 °C after activation at 200 °C, was used. The elemental analyses of the crude sample, the P-1 (polycyclic aromatic hydrocarbon) fraction, and the P-2 (PASH) fraction are given in Table I.

The supercritical fluid extraction/fractionation (SFF) system used in this study was recently reported by Campbell and Lee (*13*). About 5 mg of the P-2 fraction in 50 μL of methylene chloride was fractionated. The separation column was dry-packed with NH_2-Adsorbosil (30–70 μm, Applied Science, State College, PA). The oven temperature was raised to 40 °C and held there for the duration of the fractionation. The pressure of the CO_2 mobile phase was initially brought to 105 atm and held there until the first fraction (N-1) was eluted, whereupon it was raised at 1.5 atm min^{-1} to 130 atm. As soon as the second fraction (N-2) eluted, the pressure was again programmed at 8 atm min^{-1} to 200 atm and held there for about 10 min while the third fraction (N-3) eluted. The above fractionation scheme is summarized in Figure 1. Approximately 100 μL of diethylamine was added to each fraction before analysis by GC (*9*).

A Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector (FID) and flame photometric detector (FPD) was used for all gas chromatographic analyses in this study. Sample injection was made in the splitless mode, and hydrogen carrier gas was set at a linear velocity of 100 cm s^{-1}. The capillary column used in this study was prepared by statically coating fused silica capillary tubing (20 m × 0.3 mm i.d., Hewlett-Packard, Avondale, PA) with SE-54 (film thickness of 0.25 μm), cross-linking using azo-*t*-butane (*14*), and conditioning overnight at 300 °C under nitrogen gas flow. Semiquantitation of the PASH in the samples was accomplished by comparing FID areas of the resolved components with the average peak areas of a standard injection of dibenzothiophene and phenanthrene.

A Hewlett-Packard 5982A GC/MS system was used for obtaining mass spectral information on the isolated fractions and standard samples. The mass spectrometer was operated in the electron impact mode at 70 eV.

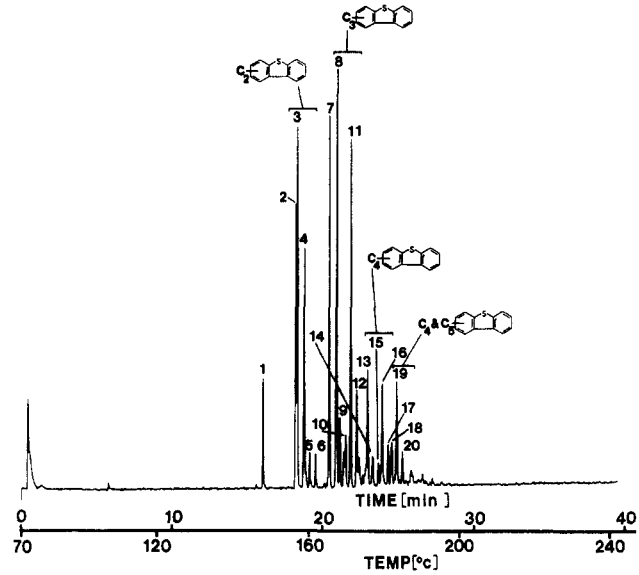

Figure 2. FPD gas chromatogram of the N-1 fraction of an FCC VR P-2 fraction. Conditions were as follows: 70–120 °C at 10 °C min^{-1} and 120–240 °C at 4 °C min^{-1} after an initial 2-min isothermal period; hydrogen carrier gas at a linear velocity of 100 cm s^{-1}. Peak assignments are listed in Table II.

RESULTS AND DISCUSSION

The elemental analysis data (Table I) support the isolation of the PASH from other aromatic compounds using the ligand exchange chromatographic procedure. FPD chromatograms of the three PASH fractions (N-1 to N-3) fractionated by SFF with CO_2 are shown in Figures 2–4, respectively. Although FPD chromatograms are shown in order to clearly distinguish PASH and residual polycyclic aromatic hydrocarbons (PAH) in the PASH (P-2) fraction, these low amounts of PAH did not interfere with the GC/MS analysis. The compounds identified, their molecular masses, and their approximate concentrations are listed in Table II. It was found previously that Pd in the $PdCl_2$/PASH complexes, which eluted from the ligand exchange chromatographic column, catalyzed desulfurization in the column or injection port of the gas chromatograph if the sulfur atom in the compounds analyzed was not in an interior ring of the molecule (*9*). Therefore, diethylamine-treated P-2 fractions were analyzed by gas chromatography. The gas chromatograms of the diethylamine-treated and nontreated FCC VR P-2 fractions were compared. Since both chromatograms were exactly the same, PASH with fusion on only one side of the thiophene ring were not present in this sample.

A chemically bonded aminosilane stationary phase has become popular in liquid chromatography for the separation of PAH according to the number of aromatic rings (*15*). Recently, this aminosilane phase was similarly applied to the ring-number separation of PAH using SFF (*13*). However, the application of this SFF technique to highly alkylated samples had not been investigated until this study. The ring-number separation of alkylated PASH by SFF on the aminosilane phase was very effective as is shown in Figures 2–4. The C_4- and C_5-benzonaphthothiophenes were collected in the second fraction (N-2), while the C_1- and C_2-chrysenothiophenes, which have lower molecular masses, were collected in the third fraction (N-3) according to the number of aromatic rings. Gas chromatographic retention temperatures were

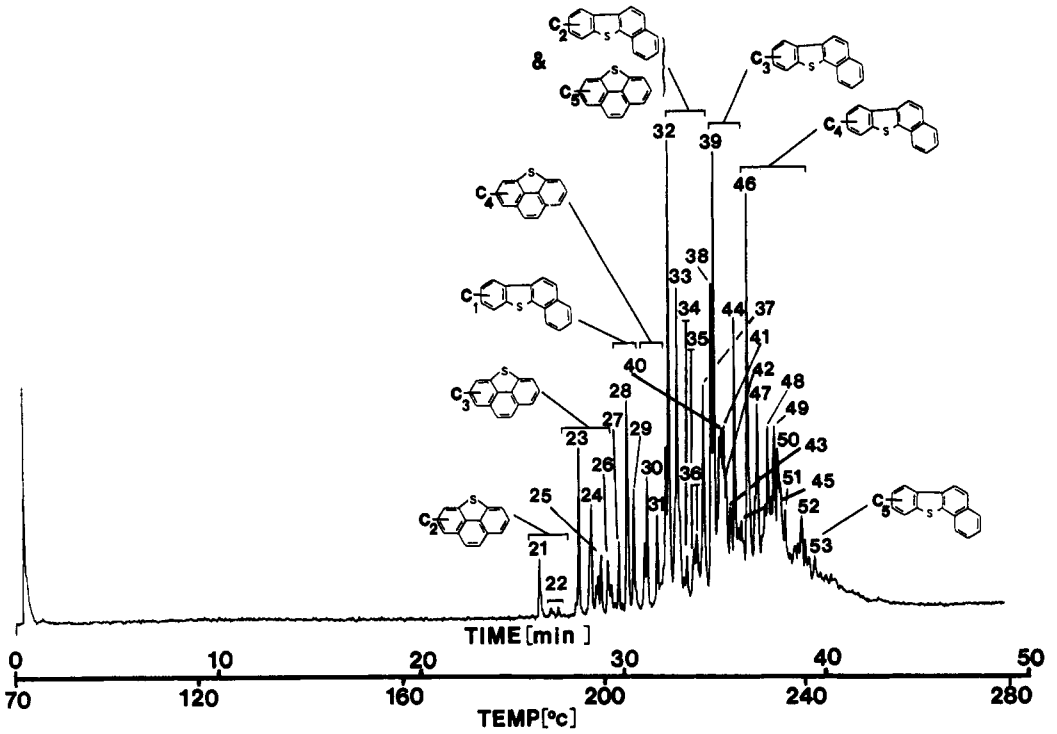

Figure 3. FPD gas chromatogram of the N-2 fraction of an FCC VR P-2 fraction. Conditions were as follows: 70–120 °C at 10 °C min^{-1} and 120–280 °C at 4 °C min^{-1} after an initial 2-min isothermal period; hydrogen carrier gas at a linear velocity of 100 cm s^{-1}. Peak assignments are listed in Table II.

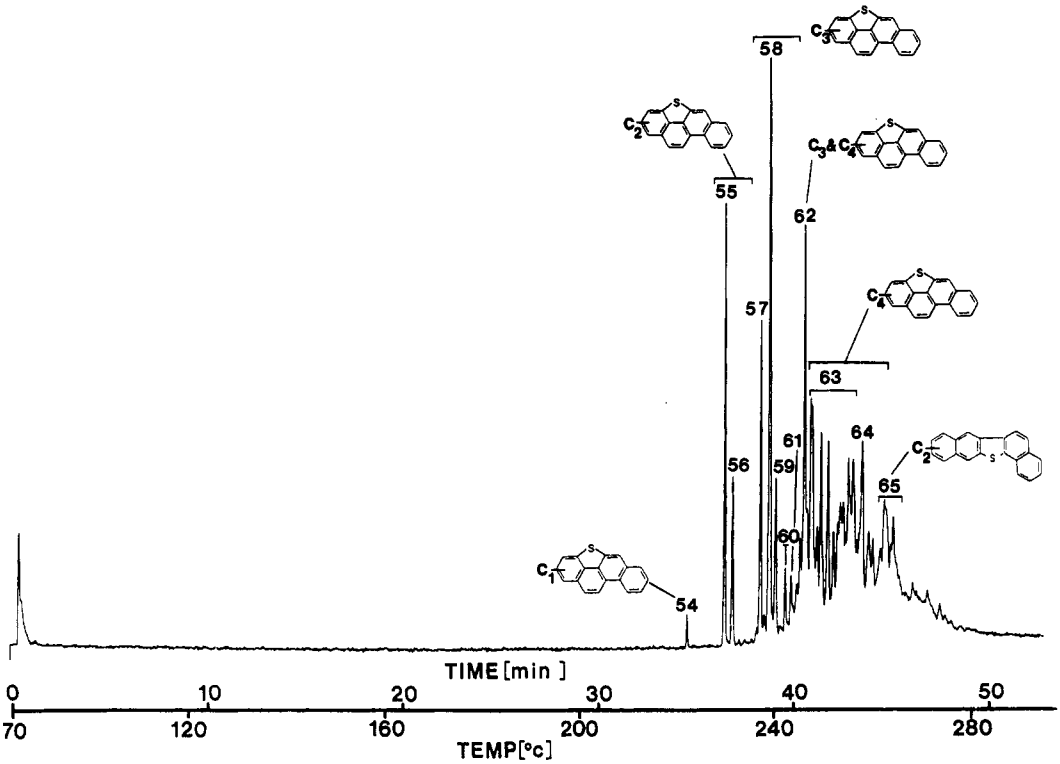

Figure 4. FPD gas chromatogram of the N-3 fraction of an FCC VR P-2 fraction. Conditions are as in Figure 2. Peak assignments are listed in Table II.

higher for the former than for the latter. This ring-size separation was essential for the detailed analysis of such highly alkylated compounds.

Representative mass spectra for several of the PASH identified are shown in Figure 5. Although the molecular ion (M^+) is generally the most abundant ion in PAH mass spectra, methyl-substituted PAH show strong $(M - 1)^+$ ions because of the stability of the tropylium ion (*16*, *17*). Furthermore, $(M - 15)^+$ ions are also observed for the alkylated PAH; the $(M - 15)^+$ ion of ethylnaphthalene is more abundant than the M^+ ion (*17*). Similarly, these mass spectral fragmentation patterns are expected for the PASH.

Figure 5A shows a mass spectrum of a C_1-chrysenothiophene. The absence of the $(M - 15)^+$ ion and the high abundance of the $(M - 1)^+$ ion are characteristic of the formation of the tropylium ion. The mass spectrum of a C_3-chrysenothiophene (Figure 5B) illustrates a typical spectrum of a compound with higher alkylation than methyl substitution. In this case, one observes a strong $(M - 15)^+$ ion and an $(M - 29)^+$ ion. The mass spectra of alkylated compounds

Table II. Sulfur Heterocycles Identified and Quantified in an FCC VR

peak no.	molecular ion[a]	proposed identification	concn,[b] μg/g
1	198	2- and/or 3-methyldibenzothiophene	30
2	212, 204	C_2-dibenzothiophene, unknown	80
3	204, 212	unknown, C_2-dibenzothiophene	100
4	204, 212	unknown, C_2-dibenzothiophene	70
5	204, 212	unknown, C_2-dibenzothiophene	10
6	204, 212, 226	unknown, C_2-dibenzothiophene, C_3-dibenzothiophene	10
7	226, 212	C_3-dibenzothiophene, C_2-dibenzothiophene	100
8	226, 212	C_3-dibenzothiophene, C_2-dibenzothiophene	140
9	226	C_3-dibenzothiophene	20
10	226	C_3-dibenzothiophene	20
11	226	C_3-dibenzothiophene	90
12	226, 240	C_3-dibenzothiophene, C_4-dibenzothiophene	20
13	240, 226	C_4-dibenzothiophene, C_3-dibenzothiophene	30
14	240, 226	C_4-dibenzothiophene, C_3-dibenzothiophene	30
15	240	C_4-dibenzothiophene	30
16	240	C_4-dibenzothiophene	20
17	240, 254	C_4-dibenzothiophene, C_5-dibenzothiophene	10
18	240, 254	C_4-dibenzothiophene, C_5-dibenzothiophene	10
19	240, 254	C_4-dibenzothiophene, C_5-dibenzothiophene	20
20	240, 254	C_4-dibenzothiophene, C_5-dibenzothiophene	10
21	236	C_2-phenanthrothiophene	30
22	236	C_2-phenanthrothiophene	2
23	250, 236	C_3-phenanthrothiophene, C_2-phenanthrothiophene	50
24	250	C_3-phenanthrothiophene	40
25	250	C_3-phenanthrothiophene	20
26	250, 264	C_3-phenanthrothiophene, C_4-phenanthrothiophene	20
27	248, 264	C_1-naphthobenzothiophene, C_4-phenanthrothiophene	20
28	248, 264	C_1-naphthobenzothiophene, C_4-phenanthrothiophene	60
29	248, 264	C_1-naphthobenzothiophene, C_4-phenanthrothiophene	40
30	264	C_4-phenanthrothiophene	40
31	264, 278	C_4-phenanthrothiophene, C_5-phenanthrothiophene	20
32	262, 278	C_2-naphthobenzothiophene, C_5-phenanthrothiophene	150
33	262	C_2-naphthobenzothiophene	100
34	262, 278, 276, 282, 292	C_2-naphthobenzothiophene, C_5-phenanthrothiophene, C_3-naphthobenzothiophene, C_3-bis(benzothiophene), C_6-phenanthrothiophene	10
35	262, 276, 282	C_2-naphthobenzothiophene, C_3-naphthobenzothiophane, C_3-bis(benzothiophene)	10
36	262, 278, 282, 292	C_2-naphthobenzothiophene, C_5-phenanthrothiophene, C_3-bis(benzothiophene), C_6-phenanthrothiophene	20
37	276, 282	C_3-naphthobenzothiophene, C_3-bis(benzothiophene)	70
38	276	C_3-naphthobenzothiophene	100
39	276	C_3-naphthobenzothiophene	150
40	276	C_3-naphthobenzothiophene	50
41	276	C_3-naphthobenzothiophene	50
42	276	C_3-naphthobenzothiophene	30
43	276, 290	C_3-naphthobenzothiophene, C_4-naphthobenzothiophene	20
44	276, 290	C_3-naphthobenzothiophene, C_4-naphthobenzothiophene	80
45	290, 276, 296	C_4-naphthobenzothiophene, C_3-naphthobenzothiophene, C_4-bis(benzothiophene)	30
46	290, 276	C_4-naphthobenzothiophene, C_3-naphthobenzothiophene	130
47	290, 276	C_4-naphthobenzothiophene, C_3-naphthobenzothiophene	60
48	290	C_4-naphthobenzothiophene	50
49	290	C_4-naphthobenzothiophene	50
50	290	C_4-naphthobenzothiophene	50
51	290	C_4-naphthobenzothiophene	20
52	290	C_4-naphthobenzothiophene	20
53	304, 290	C_5-naphthobenzothiophene, C_4-naphthobenzothiophene	10
54	272	C_1-chrysenothiophene	10
55	286	C_2-chrysenothiophene	200
56	286	C_2-chrysenothiophene	90
57	300	C_3-chrysenothiophene	130
58	300	C_3-chrysenothiophene	240
59	300	C_3-chrysenothiophene	80
60	300	C_3-chrysenothiophene	30
61	300	C_3-chrysenothiophene	20
62	300, 314	C_3-chrysenothiophene, C_4-chrysenothiophene	180
63	314, 300	C_4-chrysenothiophene, C_3-chrysenothiophene	
64	314	C_4-chrysenothiophene	110
65	312	C_2-dinaphthothiophene	

[a] Molecular ions are listed in order of decreasing abundance. [b] Approximate concentration in μg/g of original material.

in this sample reflect extended chain alkylation instead of multi-methyl substitution. Figure 5C is a composite mass spectrum of two coeluting compounds, a C_3-benzonaphthothiophene and a C_3-substituted four-ring compound containing two thiophene rings. Although a C_7-dibenzothiophene has the same molecular mass as the latter compound, it is not expected to be in the four-ring fraction. Since the thiophene compounds found in this sample are annellated on more than one side,

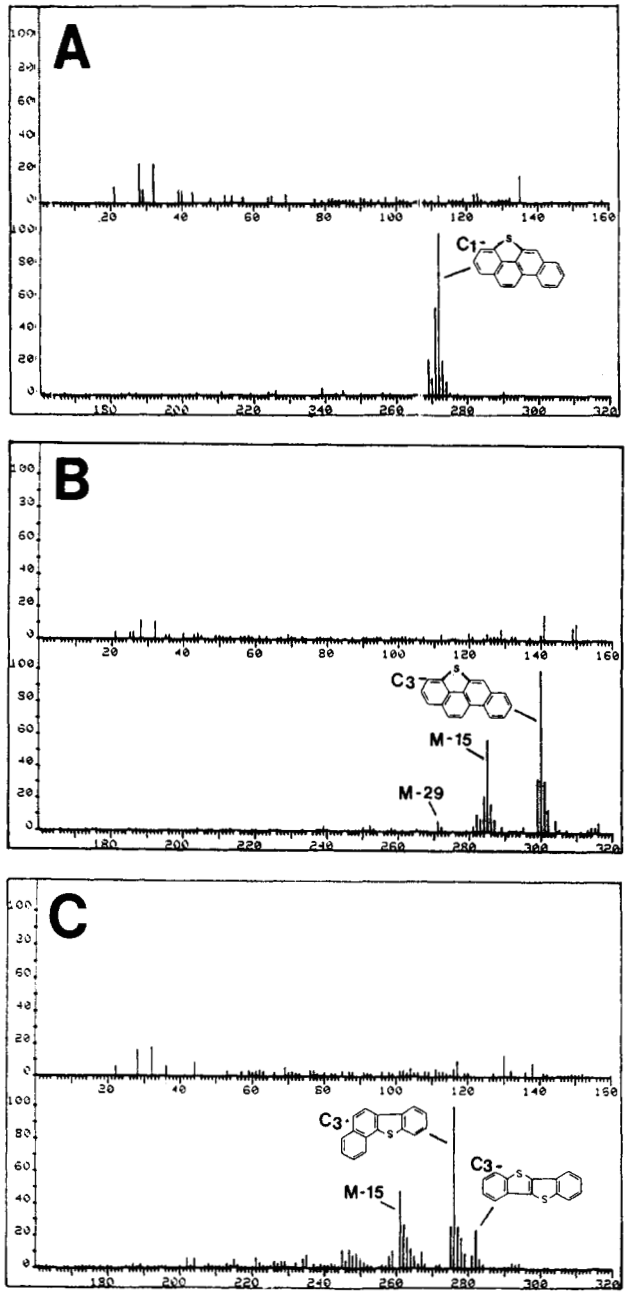

Figure 5. Mass spectra of peak 54 (A), peak 58 (B), and peak 37 (C).

compounds with two thiophene rings must have at least four rings total. Lower molecular weight compounds containing two thiophene rings were not detected. Compounds such as these were previously proposed (*3*, *18*, *19*).

In conclusion, the structural characteristics of the PASH in this FCC VR are summarized as follows:

(1) The empirical formula of the P-2 fraction determined by elemental analysis is $C_{21}H_{19}S$ and is consistent with the average structure, C_3-chrysenothiophene ($C_{21}H_{17}S$), as determined by GC/MS.

(2) PASH with fusion on only one side of the thiophene ring were not found. Since this type of PASH is easily desulfurized by a catalyst (*3*, *10*), it is believed that they were removed in the catalytic cracking process.

(3) The PASH in this sample were highly alkylated, and the average degree of alkylation was three carbons.

(4) Linear chain alkylation was predominant over multimethyl substitution.

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