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Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels

Douglas W. Later, Milton L. Lee,* Keith D. Bartle,[1] Robert C. Kong, and Daniel L. Vassilaros

Department of Chemistry, Brigham Young University, Provo, Utah 84602

A separation method is described for the identification of organic compounds in synthetic fuel products. Prefractionation of crude synfuel materials into discrete chemical classes was performed by adsorption column chromatography using small quantities of neutral aluminum oxide and silicic acid. Subsequent high-resolution separation of individual components was achieved by using *capillary* column gas *chromatography*, and specific compound types were determined by gas chromatographic retention data and combined gas chromatography–mass spectrometry. The principal chemical classes investigated in a solvent-refined coal liquid were aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polycyclic aromatk sulfur heterocycles, nitrogen polycyclic aromatic compounds, and hydroxyl polycyclic aromatic hydrocarbons. The nitrogen-containing aromatk compounds were further separated into secondary nitrogen polycyclic aromatk heterocycles, amino polycyclic aromatic hydrocarbons, and tertiary nitrogen polycyclic aromatic heterocycles to facilitate their identification.

Current emphasis on the development of alternate energy sources has stimulated production of synthetic fuels derived from oil shale, tar sands, and coal. Although technology for producing liquid and solid fuels from these feed stocks has been available since the early 1900s (1), the chemical characterization of these products has recently received increased attention. There are several reasons for determining specific compound types in synfuels. The identification and elimination of specific toxic and carcinogenic compounds would reduce the environmental and occupational health hazards associated with the production and combustion of these materials *(2–4)*. Certain heteroatom species are known to decrease the efficiency of catalytic processes and contribute to the instability of liquid fuels during storage (5, 6). Synthetic fuels are also a valuable source of chemical materials for the manufacture of pharmaceuticals, pesticides, herbicides, and dyes (3, 7).

Because of the complex nature of synthetic fuel materials, fractionation according to chemical class is usually required before identification of individual components can be achieved. Traditionally, separation schemes have been developed by using solvent partitioning methods and column chromatography. The organic analytical group at the National Bureau of Standards has isolated neutral oils, acids, and bases using a solvent extraction method with subsequent high-performance liquid chromatographic (HPLC) and gas chromatographic analysis to separate and identify individual organic compounds in synfuels (8). The analytical group at Oak Ridge National Laboratory has developed a fractionation scheme using an acid–base extraction followed by solid–liquid chromatography on Sephadex LH-20, silicic acid, and basic alumina (1, 9, 10). They reported the separation of aliphatic and aromatic hydrocarbons as well as nitrogen heterocyclic and polar aromatic compounds. Wilson et al. (11) used a similar solvent fractionation scheme to analyze coal liquefaction producta before and after hydrotreatment. They reported the occurrence of neutral polycyclic aromatic hydrocarbons and sulfur, oxygen, and nitrogen heterocyclic aromatic compounds. In another separation scheme developed for solvent-refined coal (12), nine fractions were isolated from silica gel on the basis of chemical functionality. Schiller and Mathiason (13) reported the development of a chromatographic procedure using neutral alumina to fractionate a wide variety of coal-derived solids and liquids for analysis by mass spectrometry and other spectral methods. The principal compound types investigated were saturated hydrocarbons, aromatic hydrocarbons, benzofurans, ethers, nitrogen compounds, and hydroxyl compounds. A combination of ion exchange, coordination, and adsorption chromatography was employed by Jewell et al. *(14)* for the separation of petroleum distillates. This method has also been used to separate coal-derived products into five fractions: acids, bases, neutral nitrogen compounds, saturated hydrocarbons, and aromatic hydrocarbons. This method is commonly known as the SARA technique and has been widely used.

Several problems exist with the previously described separation methods. First, most schemes are complicated, time-consuming, tedious, and require highly trained personnel to execute each step with precision and accuracy. *Long* periods of time are required for pretreatment, cleaning, preparation, and activation of resins and adsorbent packings. Many methods use expensive materials, and large volumes of high-purity solvents are necessary for each chromatographic or partitioning step. Solvent extraction and partitioning of polar types of compounds can cause formation of tars and stable emulsions (15) which contribute to the loss of components and inefficient separations. Finally, many separation schemes are hindered by incomplete chemical class separation and overlap of compound types into adjacent fractions. Improvement of existing separation technology is necessary if faster analysis and better evaluation of the numerous types of synfuel products are to be achieved.

In this paper, the development of a two-step separation method using neutral alumina and silicic acid adsorption chromatography is described. This procedure minimizes the problems previously discussed and is rapid, reproducible, economical, and efficient. Crude solid and liquid synfuel products *can* be fractionated into seven chemical classes by this method. This separation scheme *can* be completed in less than 6 h and uses less than 500 mL of solvent and approximately 12 g of adsorbent packing. The applicability of this fractionation method is demonstrated by the characterization of a solvent-refined coal (SRC) liquid heavy distillate.

EXPERIMENTAL SECTION

An SRC II heavy distillate sample (boiling point range 260–450 °C) from the Fort Lewis, WA, pilot plant (using West Virginia coal from the Pittsburgh seam) was provided by Pacific Northwest Laboratory for analysis. This material is of pilot plant origin and should not necessarily be considered representative of commercial scale production. A schematic diagram of the separation method is shown in Figure 1. First, neutral aluminum oxide (Brockman

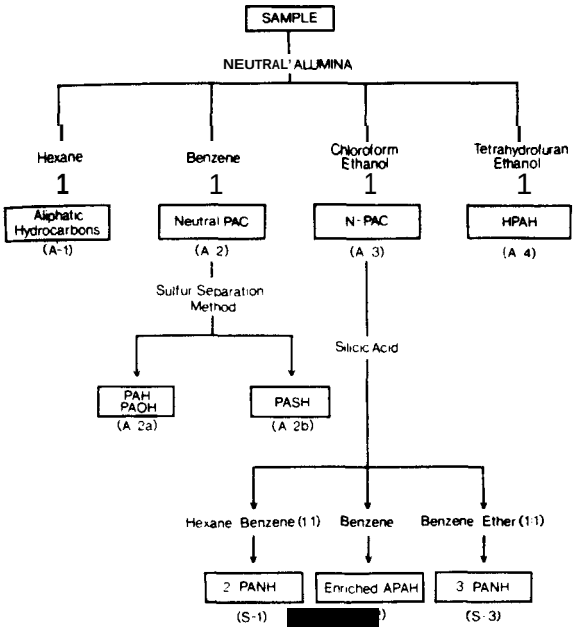

Figure 1. Chemical class separation scheme for synthetic fuel prod- & neutral polycyclic aromatic (PAC), nitrogen polycyclic aromatic compounds (N-PAC), hydroxyl polycyclic aromatic hydrocarbons (HPAH), polycyclic aromatic oxygen heterocycles (PAOH), polycyclic aromatic sulfur heterocycles (PASH), secondary nitrogen polycyclic aromatic heterocycles (2°-PANH), amino polycyclic aromatic hydrocarbons (APAH), and tertiary nitrogen polycyclic aromatic heterocycles (3°-PANH).

aliphatic hydrocarbons; A-2, neutral polycyclic aromatic compounds (PAC); A-3, nitrogen polycyclic aromatic compounds N-PAC); and A-4, hydroxy polycyclic aromatic hydrocarbons HPAH). [The acronyms used in this paper are assigned according to the format defined by Bartle et al. (16).] Approximately 0.1–0.3 g of crude sample was dissolved in a few milliliters of chloroform and adsorbed onto 3 g of neutral alumina. The solvent was removed from the alumina by vigorously stirring the mixture under a gentle stream of dry nitrogen gas. The alumina with sample was then packed on top of an 11-mm i.d. column which already contained 6 g of neutral alumina The sample was then eluted with the following chromatographic grade solvents: fraction A-1, 20 mL of hexane; fraction A-2, 50 mL of benzene; fraction A-3, 70 mL of chloroform (containing 0.75% ethanol preservative); fraction A-4, 50 mL of 10% ethanol in tetrahydrofuran (containing no inhibitors).

Polycyclic aromatic oxygen heterocycles (PAOH) and polycyclic aromatic sulfur heterocycles (PASH) are eluted with the polycyclic aromatic hydrocarbons (PAH) in fraction A-2. Because the PASH are in such low concentration in coal-derived materials, the alumina column procedure was scaled up (100 g of neutral alumina) and 10 g of coal liquid (preadsorbed onto 50 g of neutral alumina) was used to obtain a neutral PAC fraction. The PASH were then separated from the PAH and PAOH by a procedure previously reported by Willey et al. (17). Briefly, the PASH were oxidized with H_2O_2 to their corresponding sulfones, the sulfones were then separated from the other unoxidized neutral PAC on silica gel (fraction A-2a), reduced with $LiAlH_4$ to the original PASH and repurified on silica gel (fraction A-2b).

Several distinct classes of nitrogen heterocyclic compounds were present in the initial N-PAC, fraction A-3. Consequently, a method was developed to subfractionate the N-PAC into three additional classes of compounds using silicic acid adsorption chromatography. The alumina N-PAC fraction was adsorbed onto 1.5 g of silicic acid (Mallinckrodt No. 2847, 100-mesh powder, used as received from supplier) and the solvent removed by stirring the mixture under dry nitrogen gas. A 22-mm i.d. column was packed with a hexane slurry of 2 g of silicic acid. The silicic acid with the adsorbed sample was then packed on top of the 2-g column and eluted to give the following fractions and compound types: fraction S-1, secondary nitrogen polycyclic aromatic heterocycles (2°-PANH) with 50 mL of 1:1 (v:v) hexane:benzene; fraction S-2, enriched amino polycyclic aromatic hydrocarbons (APAH) with 30 mL of benzene; fraction S-3, tertiary nitrogen polycyclic aromatic heterocycles (3°-PANH) with 50 mL of 1:1 (v:v) benzene:anhydrous ethyl ether.

Each of the alumina and silicic acid fractions was concentrated to approximately 2 mL on a rotary evaporator, taken to dryness under nitrogen gas, weighed, and dissolved in an appropriate volume of benzene for capillary column gas chromatographic analysis. A Hewlett-Packard 5880 gas chromatograph equipped with a fused-silica capillary column (20 m × 0.30 mm i.d.) coated with SE52 methylphenylsilicone stationary phase (film thickness 0.25 μm) was used to obtain chromatograms of each fraction. The oven was held at 50 °C for 2 min during injection and then temperature programmed at 3 °C/min (alumina fractions) or 4 °C/min (PASH and silicic acid fractions) to a final temperature of 260 °C and held for 5 min. A flame ionization detector (FID) was generally used, but nitrogen and sulfur heterocycle fractions were also analyzed by using a nitrogen-selective detector (NPD) and a sulfur-selective detector (FPD). A Perkin-Elmer Sigma 2 gas chromatograph equipped with these detectors was used.

Identification of specific compounds was accomplished by using gas chromatographic retention data and combined gas chromatography–mass spectrometry (GC-MS). Gas chromatographic conditions were similiar to those already described. A Hewlett-Packard 5982A quadrupole mass spectrometer was operated in the electron impact mode (70 eV electron energy). Spectra were acquired and processed with a Hewlett-Packard 5934A data system.

Infrared spectrometry of the HPAH fraction was performed by evaporating the solvent from the sample and placing an aliquot between two salt plates. The sample was then analyzed by scanning from 4000 to 600 cm^{-1} on a Beckman ACCULAB 2 infrared spectrometer.

RESULTS AND DISCUSSION

The separation of oxygen and nitrogen heterocyclic compounds in petroleum products by adsorption chromatography on alumina has been extensively studied by Snyder and Buell (18). Similarly, Schiller (13.19) used alumina chromatography to develop a rapid, simple separation method for heterocyclic compounds in synthetic fuels. The alumina step reported in this paper is a modified version of the method developed by Schiller. It was found in this study that column chromatography on neutral alumina minimized sample loss due to irreversible adsorption, eluted a wide range of solutes rapidly, and provided reproducible class separation according to the functionality of the heteroatom present in the polycyclic aromatic structure.

Compounds which contain nitrogen heteroatoms of different functionality can be separated on silicic acid by varying the eluent polarity. Silicic acid has previously been used to separate indoles and carbazoles from other N-PAC in tobacco smoke (20) and synfuels (9). The silicic acid procedure reported in this paper was developed to complement the alumina method by providing an equally simple and rapid method for subsequent chemical class separation of the nitrogen-containing polycyclic aromatic compounds. Using a small quantity of adsorbent (2.5 g) reduces the contact time of the sample components with the silica structure and decreases degradation, artifact formation, and sample loss normally associated with chromatography on silica adsorbents.

Numerous compounds are present in each chemical class, even after extensive prefractionation, and further high-resolution separation is required prior to the identification of specific components. The application of capillary column GC-MS to resolve and determine compounds in complex mixtures of PAC has been well established (21). This simple alumina–silica fractionation scheme combined with capillary column GC-MS provides a rapid, effective, and reproducible method for the detailed chemical characterization of synthetic fuels. Additionally, this two–step separation method can easily be scaled up to produce larger quantities of sample which is

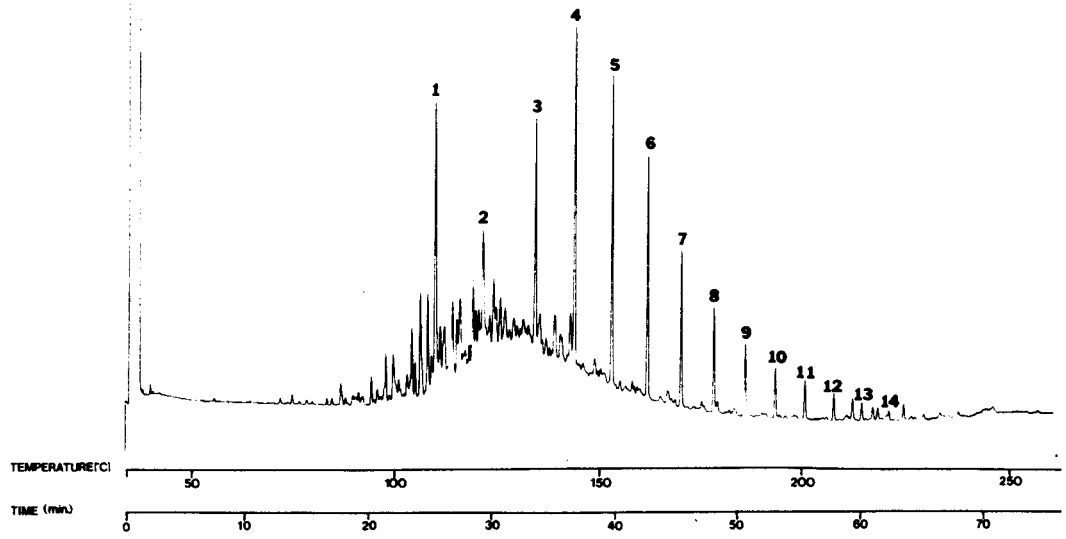

Figure 2. Capillary column gas chromatogram of aliphatic hydrocarbon fraction A-1. Peak numbers refer to compounds listed in Table III. Con were 20 m × 0.30 mm fused-silica capillary column coated with SE-52, temperature programmed from 40 °C to 250 °C at 3 °C/min.

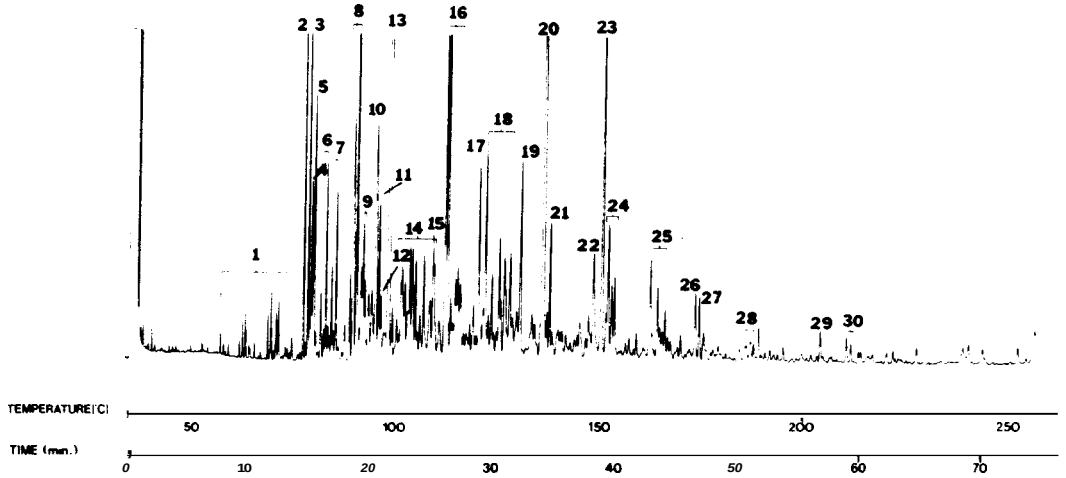

Figure 3. Capillary column gas chromatogram of PAH fraction A-2. Peak numbers refer *to* compounds listed in Table III. Conditions in Figure 2.

sometimes required for the concentration of trace components and for bioassay to determine mutagenicity or carcinogenicity.

The quantitative data obtained by *using* this procedure are presented in Tables I and II. A total recovery of greater than 90% was obtained by this method for the separation of an SRC II heavy distillate into chemical classes. A chromatogram of *each* of the fractions is shown in Figures 2–9. Tables III–V list the compound types identified in each fraction.

Aliphatic **Hydrocarbons.** Due to the nonpolar nature of the aliphatic hydrocarbons, this class of compounds elutes immediately from alumina with hexane. The gas chromatographic retention time of standard octadecane, *n*-C_{18}, was used to determine *n*-C_{18} in the aliphatic fraction. Mass spectral data supplemented the identification of *n*-C_{18} and were used to determine the other constituents in the homologous series of straight-chain hydrocarbons. The nonlinearity of the base line in the *n*-C_{18}–*n*-C_{20} region (see Figure 2) is caused by the numerous unresolved components (related olefins and branched isomers of the straight-chain parent hydrocarbons). The relatively low concentration of the aliphatic hydrocarbons in *this* coal liquid illustrates the highly aromatic nature of this product. The structural features of saturates in *coal* liquids are similar to those of some petroleums and both can be

Table I. Weight Percent of Neutral Alumina Fractior from an SRC II Heavy Distillate Coal Liquid

fraction	compound type	fraction[a] w
A-1	aliphatic hydrocarbons	5.5
A-2	neutral PAC	56.6
A-3	N-PAC	*20.0*
A-4	HPAH	14.0
total		96.1

[a] Average values for three different assays of SRC II heavy distillate.

Table II. Weight Percent of Silicic Acid Subtractions from an SRC II Heavy Distillate Coal Liquid

fraction	compound type	wt % of N-PAC	wt % o heavy distillat
S-1	2°-PANH	59.6	11.9
S-2	enriched APAH	8.5	1.7
S-3	3°-PANH	14.9	3.0
total		83.0	16.6

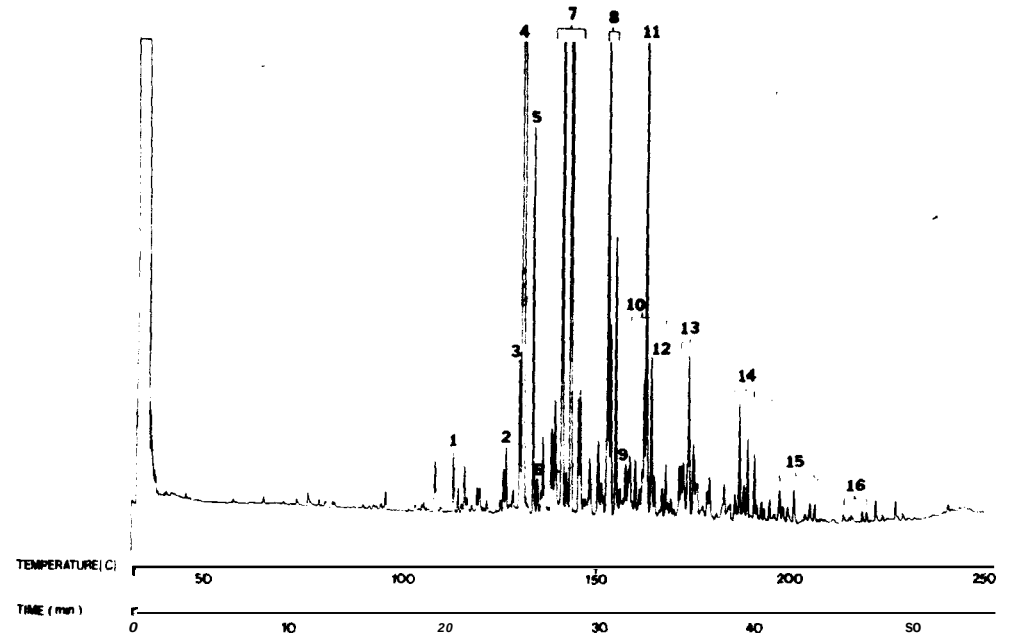

Figure 4. Capillary column gas chromatogram of PASH fraction A-2b. Peak numbers refer to compounds listed in Table IV. Conditions were 20 m × 0.30 mm fused-sib capillary column coated with SE-52, temperature programmed from 40 °C to 250 °C at 4 °C/min.

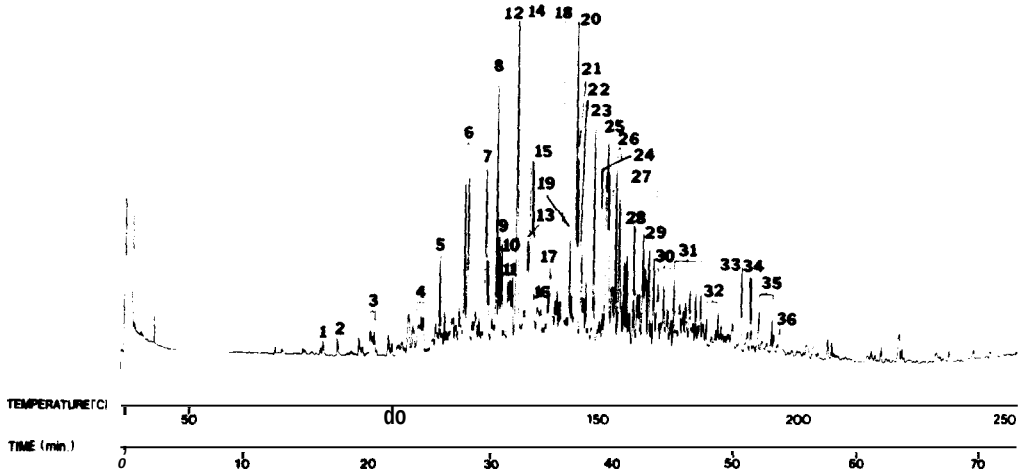

Figure 5. Capillary column gas chromatogram of N-PAC fraction A-3. Peak numbers refer to compounds listed in Table III. Conditions were as in Figure 2.

PAC fraction eluted from the alumina column. Benzene was chosen over toluene as the eluent because it is a slightly more polar solvent and reduced the overlap of the polycyclic furans PAOH) into the chloroform fraction. The PAH (see Figure) are the *chemical* class of highest concentration in this SRC I heavy distillate and generally are major constituents in most oal-derived fuel products. The literature in this area is too xtensive *to* cover here but has recently been reviewed (23, 1). The high degree of alkylation in this PAH fraction is of articular interest. A rough correlation between degree of kylation of PAH structures in energy-related materials and utagenicity has been reported by Griest and co-workers (25). xtensive alkylation ia observed in all fractions of this SRC liquid, and in some instances the alkylated species are more undant than the parent PAC.

Although the PASH, Figure 4, comprise less than 1% of e total heavy distillate, the detailed characterization of the lfur-containing compounds in synthetic fuel products is portant in light of recent evidence that specific sulfur terocycles have been shown to possess significant mutagenic tivity (26, 27). Furthermore, the removal of sulfur from fuels desirable *to* prevent the formation of noxious sulfur gases uring combustion and to prevent catalyst poisoning in *coal* conversion reactors. The identification of specific sulfur-containing species in synthetic fuels can provide insights into better methods of sulfur removal.

N-PAC. The elution of the N-PAC from neutral alumina with chloroform could be visually observed by the migration of a dark band down the column. Analysis by gas chromatography *using* a nitrogen-selective NPD verified that essentially *all* of the components in this fraction were nitrogen-containing compounds. Figure 5 is an FID chromatogram of the N-PAC fraction.

Primary (APAH), secondary (2°-PANH), and tertiary (3°-PANH) nitrogen heterocycles (*see* Figures 6–8) *occur* collectively in the alumina N-PAC fraction. Additional chemical class separation was essential for three reasons. First, the difficulty of identifying individual constituents in this fraction was increased by the fact that more than one compound eluted from the *capillary* column at the same time. For example, tetrahydrocarbazole coeluted with two benzoquinoline isomers. This was also the case with many of the alkylated carbazoles, alkylated benzoquinolines, and three-ring APAH. Second, different concentration levels between chemical classes obscured groups of compounds which *are* important to the overall chemical behavior of the sample.

Table III. Compounds Identified in the Alumina Chromatographic Fractions of an SRC II Heavy Distillate Coal Liquid

peak no.	mol wt	compound	peak no.	mol wt	compound
		Aliphatic Hydrocarbon Fraction A-1 (Figure 2)			
1	226	*n*-C_{16}	8	324	*n*-C_{23}
2	240	*n*-C_{17}	9	338	*n*-C_{24}
3	254	*n*-C_{18}	10	352	*n*-C_{25}
4	268	*n*-C_{19}	11	366	*n*-C_{26}
5	282	*n*-C_{20}	12	380	*n*-C_{27}
6	296	*n*-C_{21}	13	394	*n*-C_{28}
7	310	*n*-C_{22}	14	408	*n*-C_{29}
		PAC Fraction A-2 (Figure 3)			
1	142	C_1-naphthalene	14	196	**C_3-biphenyl/C_1-dibenzothiophene**
	156	C_2-naphthalene	15	204	1-phenylnaphthalene
	170	C_3-naphthalene	16	192	C_1-phenanthrene
	154	biphenyl	17	204	2-phenylnaphthalene
	154	acenaphthene	18	206	C_2-phenanthrene
	168	dibenzofuran	19	202	fluoranthene
2	166	fluorene	20	202	**pyrene**
3	168	C_1-biphenyl/C_1-acenaphthene	21		not identified
4	168	C_1-biphenyl/C_1-acenaphthene	22	216	benzo[*a*]fluorene
5	184/180	C_4-naphthalene/C_2-fluorene	23	216	benzo[*b*]fluorene
6	182	C_1-dibenzofuran	24	216	**C_1-pyrene/C_1-fluoranthene**
7	182	C_2-biphenyl	25	230	**C_2-pyrene/C_2-fluoranthene**
8	1801182	C_1-fluorene/C_1-biphenyl	26	228	benz[*a*]anthracene
9	1981194	C_5-naphthalene/C_1-fluorene	21	228	chrysene
10	184	dibenzothiophene	28	242	C_1-benz[*a*]anthracene/C_1-chrysene
11	182	tetrahydrophenanthrene	29	252	benzofluoranthene
12	196	C_3-biphenyl	30	252	benzopyrene
13	178	phenanthrene			
		N-PAC Fraction A-3 (Figure 5)			
1	131	C_1-indole	19	193/207	**C_1-benzoquinoline/C_2-benzoquinoline**
2	157	C_2-quinoline	20	181	C_1-carbazole
3	145	C_2-indole	21	193	C_1-benzoquinoline
4	159	C_3-indole	22	207	C_2-benzoquinoline
5	198	C_2-diphenyl ether	23	195	C_2-carbazole
6	185	C_3-quinoline	24	207	C_2-benzoquinoline
7	183	tetrahydrobenzoquinoline	25	195	C_2-carbazole
8	178	phenanthrene	26	195	C_2-carbazole
9	179	benzoquinoline	27	209	C_3-carbazole
10	179	benzoquinoline	25	203	azafluoranthene
11	197	C_3-tetrahydrobenzoquinoline	29	203	azapyrene
12	171/179	**tetrahydrocarbazole/benzoquinoline**	30	223	C_4-carbazole
13	197	**C_1-tetrahydrobenzoquinoline**	31	2171237	C_1-azapyrene/C_1-azafluoranthene/C_5-carbazole
14	167	carbazole	32	231	**C_2-azapyrene/C_2-azafluoranthene**
15	**193**	C_1-benzoquinoline	**33**	**221**	tetrahydrobenzocarbazole
16	185	C_2-tetrahydrocarbazole	34	229	naphthoquinoline
17	193	C_1-benzoquinoline	35	217	benzocarbazole
18	181/193	**C_1-carbazole/C_1-benzoquinoline**	36	**231**	C_1-benzocarbazole
		HPAH Fraction A-4 (Figure 9)			
1	148	C_2-indanol	17	198	C_2-hydroxybiphenyl
2	170	hydroxybiphenyl	18	182	hydroxyfluorene
3	162	C_3-indanol	19	182	hydroxyfluorene
4	184	C_2-hydroxybiphenyl	20	198	C_2-hydroxybiphenyl
5	184	C_2-hydroxybiphenyl	21	152	hydroxyfluorene
6	176	C_3-indanol	22	198	C_2-hydroxybiphenyl
7	198	C_2-hydroxybiphenyl	23	2261196	C_4-hydroxybiphenyl/C_2-hydroxyfluorene
8	170	hydroxybiphenyl	24	212	C_3-hydroxybiphenyl
9	170	hydroxybiphenyl	25	212/196	C_3-hydroxybiphenyl/C_2-hydroxyfluorene
10	190	**C_4-indanol**	26	220	naphthylphenol
11	212	C_3-hydroxybiphenyl	27	2261210	**C_4-hydroxybiphenyl/C_2-hydroxyfluorene**
12	184/204	C_2-hydroxybiphenyl/C_5-indanol	28	234	C_1-naphthylphenol
13	184	C_1-hydroxybiphenyl	29	2401224	**C_5-hydroxybiphenyl/C_3-hydroxyfluorene**
14	184	C_2-hydroxybiphenyl	30	220	naphthylphenol
15	212	C_3-hydroxybiphenyl	31	220	naphthylphenol
16	182	**hydroxyfluorene**	32	**234**	C_1-naphthylphenol

Although the *APAH* were lower in concentration than either the secondary or tertiary PANH (see Table 11), it has been suggested that the *APAH* are largely responsible for the biological activity of synfuel products (*9*, *28*). Third, detailed assignment of structure was complicated by the presence of anthracenes have molecular weights of 193 amu and all fragment similarly by mass spectrometry making exact structural identification nearly impossible. Therefore, it was necessary to separate the nitrogen-containing compounds into subfractions.

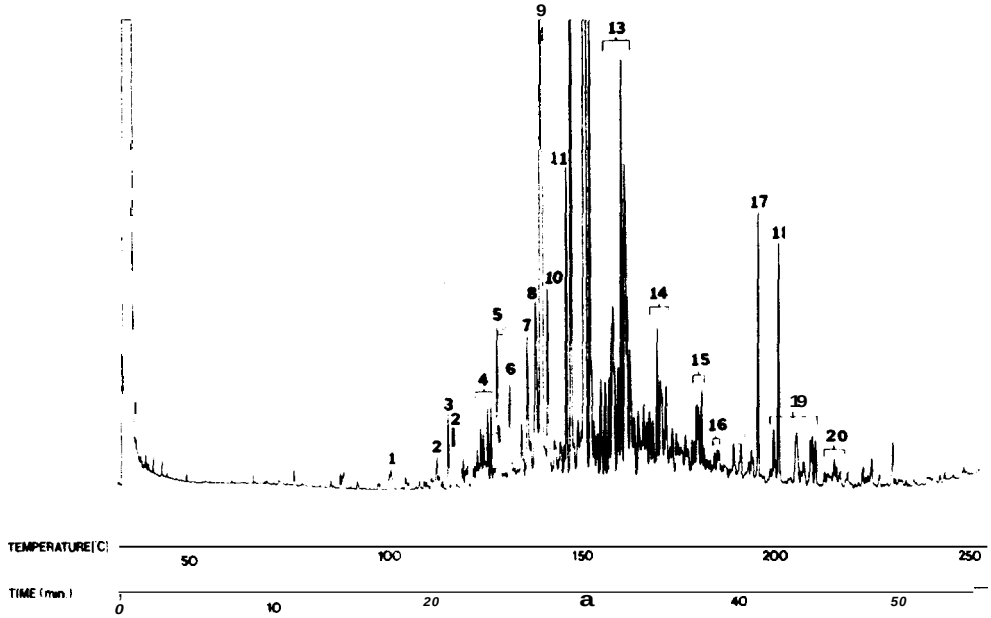

Figure 6. Capillary column gas chromatogram of 2°-PANH fraction S-1. Peak numbers refer to compounds listed in Table V. Conditions were as in Figure 4.

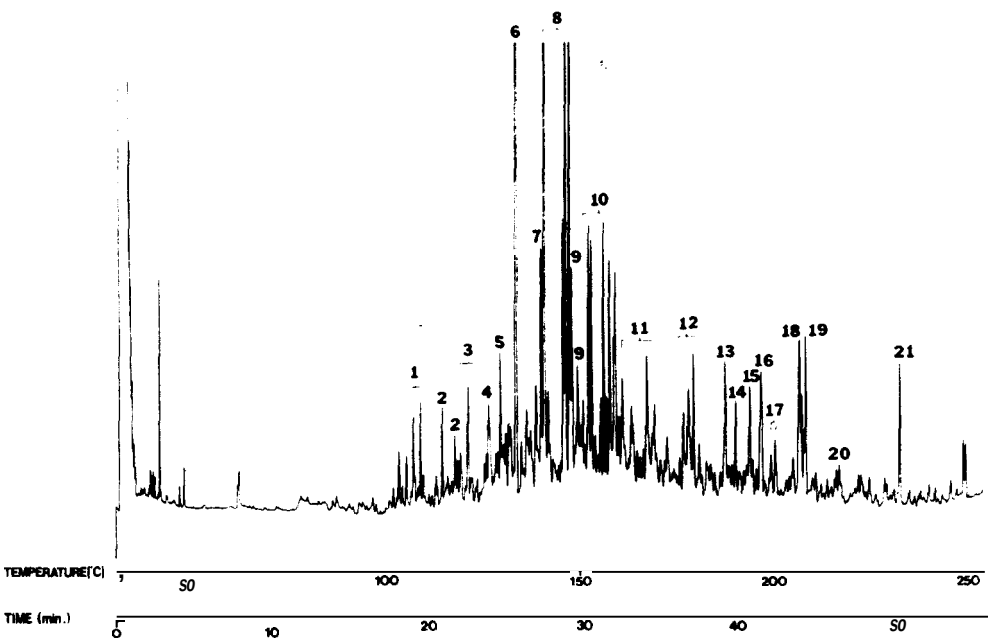

Figure 7. Capillary column gas chromatogram of *enriched* APAH fraction 52. Peak numbers refer to compounds listed in Table V. Conditions were as in Figure 4.

Table IV. Compounds Identified in the PASH Subfraction A-2b (Figure 4) of an SRC II Heavy Distillate *Coal* Liquid

peak no.	mol wt	compound	peak no.	mol wt	compound
1	166	fluorene	9	202	fluoranthene
2	180	C_1-fluorene	10	226	C_3-dibenzothiophene
3	188	tetrahydrodibenzothiophene	11	208	phenanthro[4,5-*bcd*]thiophene
4	184	dibenzothiophene	12	202	pyrene
5	178	phenanthrene	13	222	C_1-phenantho[4,5-*bcd*]thiophene
6	178	anthracene	14	234	benzonaphthothiophene
7	198	C_1-dibenzothiophene	15	248	C_1-benzonaphthothiophene
8	212	C_2-dibenzothiophene	16	262	C_2-benzonaphthothiophene

aration and identification of several pyridines and anilines; a number of two- and three-ring N-PAC have also been identified in synthetic fuel products (*7*, *13*, *19*, *29–33*). Relatively fewer studies have been reported on the isolation and determination of compounds containing a larger number of rings. The one- and two-ring N-PAC systems are of general interest because they are present in higher concentration levels, are more volatile, some are commercially useful, and a few are biologically active. However, it is believed that isomers of increasing ring number generally display a higher degree of mutagenicity and carcinogenicity. For example, carbazole is noncarcinogenic, benzo[*a*]carbazole is moderately

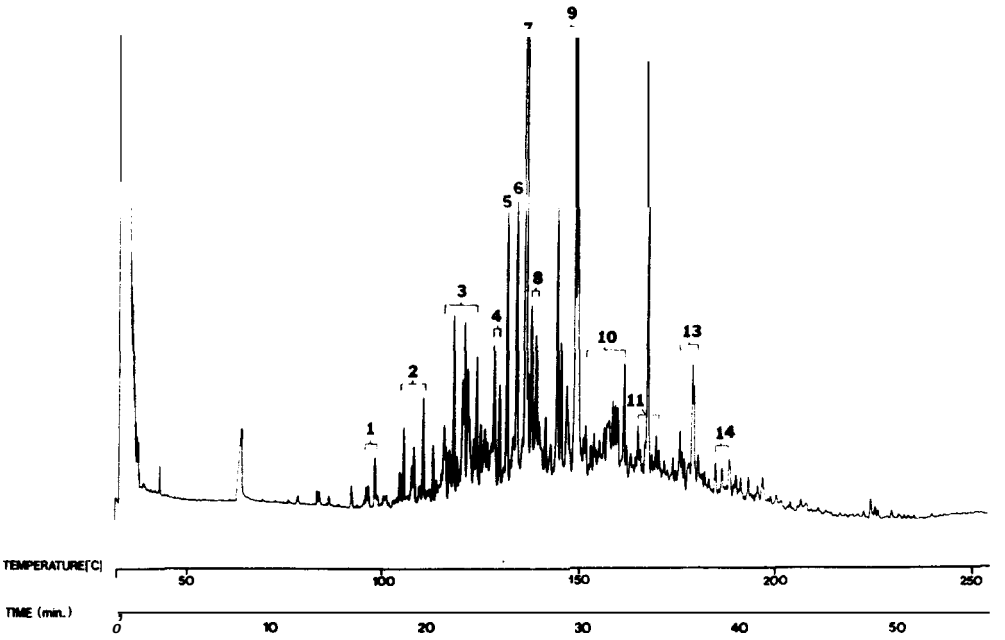

Figure 8. Capillary column gas chromatogram of 3°-PANH fraction S-3. Peak numbers refer to compounds listed in Table V. Conditions were as in Figure 4.

Table V. N-PAC Compounds Identified in the Silicic Acid Subfraction of an SRC II Heavy Distillate Coal Liquid

peak no.	mol wt	compound	peak no.	mol wt	compound
		2°-PANH Fraction S-1 (Figure 6)			
1	145	C_2-indole	11	167	carbazole isomer
2	159	C_3-indole	12	181	C_1-carbazole
3	184	C_1-diphenyl ether	13	195	C_2-carbazole
4	173	C_4-indole	14	209	C_3-carbazole
5	198	C_2-diphenyl ether	15	223	C_4-carbazole
6	178	phenanthrene	16	237	C_5-carbazole
7	171	tetrahydrocarbazole	17	217	benzocarbazole
8	212	C_3-diphenyl ether	18	217	benzocarbazole
9	167	carbazole	19	231	C_1-benzocarbazole
10	167	carbazole isomer	20	245	C_2-benzocarbazole
		Enriched APAH Fraction S-2 (Figure 7)			
1	143	naphthylamine	11	221/207	C_3-benzoquinoline/C_1-aminophenanthrene
2	169	aminobiphenyl	12	235	C_4-benzoquinoline
3	183	C_1-aminobiphenyl	13	233	tetrahydronaphthoquinoline
4	197	C_2-aminobiphenyl	14	217	aminopyrene/aminofluoranthene
5	181	aminofluorene	15	233	tetrahydronaphthoquinoline
6	179	benzo[*h*]quinoline[a]	16	229	naphthoquinoline (possibly benz[c]acridine[a])
7	167	carbazole	17	231	C_1-aminopyrene/C_1-aminofluoranthene
8	193	C_1-benzoquinoline	18	229	naphthoquinoline (possibly benz[*a*]acridine[a])
9	193	aminophenanthrene/aminoanthracene	19	230	benzanthrone
10	207	C_2-benzoquinoline	20	244	C_1-benzanthrone
			21		phthalate ester
		3"-PANH Fraction S-2 (Figure 8)			
1	157	C_2-quinoline	8	197	C_1-tetrahydroquinoline
2	171	C_3-quinoline	9	193	C_1-benzoquinoline
3	185/158/183	C_4-quinoline/unidentified peaks	10	2071203	C_2-benzquinoline/azafluoranthene
4	199	C_5-quinoline	11	221	C_3-benzoquinoline
5	183	tetrahydroquinoline	12	203	azapyrene
6	179	acridine[a]	13	217	C_1-azapyrene/C_1-azafluoranthene
7	179	phenanthridine[a]/benzo[*f*]quinoline[a]	14	229	naphthoquinoline

[a] Possible structures assigned by retention data comparisons with standard compounds.

carcinogenic, and dibenzo[*c*,*g*]carbazole is a potent carinogen (*34*). Therefore, it is important to isolate and identify the

mostly of two-, three-, and four-ring N-PAC. However, work has been done with standard N-PAC of up to five rinp (di-

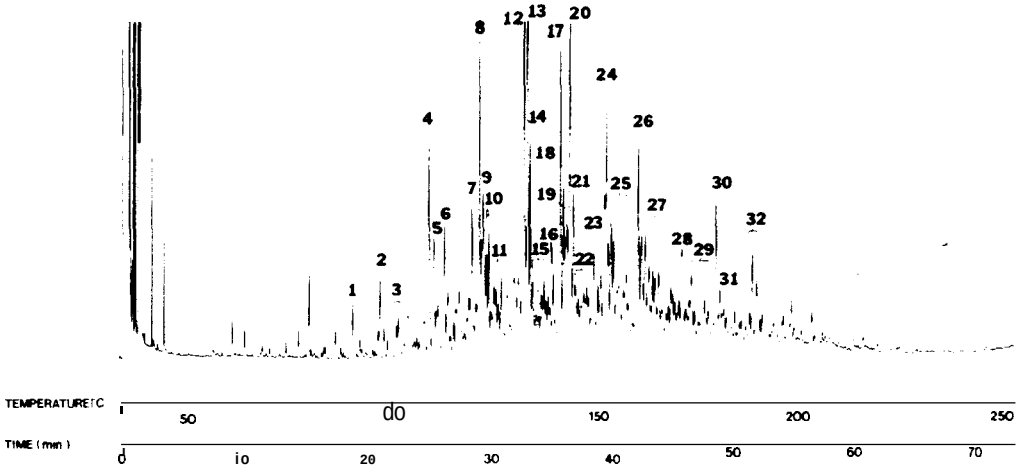

Figure 9. Capillary column gas chromatogram of HPAH fraction A-4. Peak numbers refer to compounds listed in Table III. Conditions were as in Figure 2.

The enriched APAH fraction, Figure 7, is of particular interest. Wilson et al. (28) initially suggested the presence of two-, three-, and four-ring primary aromatic amines in a similar SRC II heavy distillate. The results presented in this paper confirm the presence of these APAH and also report the Occurrence of several alkylated species of the parent AF'AH. The APAH were not completely separated from the 3°-PANH. Preliminary data suggest that the tertiary nitrogen heterocycles overlapping into the APAH fraction are either alkylated or angular-structured species where the lone pair of electrons on the nitrogen heteroatom is shielded. Therefore, some of the 3°-PANH and the APAH have similar retention characteristics. Many of the 3°-PANH that eluted in this fraction were more than twice as concentrated as the APAH and frequently obscured their presence. Thus, in addition to the retention and GC/MS data used, a derivatization method has been used (*35*) to ensure positive identification of the APAH listed in Table V. Although there was overlap between these two classes of N-PAC compounds in this fraction, the APAH were sufficiently enriched to verify their presence.

HPAH. The hydroxyl PAH (see Figure 9) were eluted last from neutral alumina with 10% ethanol in tetrahydrofuran. Many HPAH have been shown to be present in synthetic fuel products and several methods have been developed for their isolation and determination (*8*, *29*, *30*, *36*). The major acidic compounds found in synfuels are phenol and the alkylphenols. Also, HPAH such as hydroxybiphenyls, indanols, naphthols, acenaphthenols, and hydroxyfluorenes have been reported to occur in these matrices *(29).*

Infrared spectrometry of the HPAH fraction showed the strong presence of hydroxyl functional groups and indicated that there was little if any carbonyl oxygen. This observation agrees well with others who have reported the absence of carbonyl group in coal liquefaction products (*29*). The major components identified by GC-MS in this fraction were indanols, hydroxybiphenyls, hydroxyfluorenes, and naphthylphenols. Low levels of naphthols were also detected. As with the Other fractions of this coal liquid, a high alkyl content was observed.

The Projected increase in use of synthetic fuels produced from coal, shale, and tar sands to meet growing energy demands has created a need for faster and more reliable methods of analysis of products and byproducts from these processes. The methodology presented in this paper and applied to the analysis of a representative solvent-refined coal liquid has been shown to be a rapid, effective, and reproducible means to a complete chemical analysis of these materials. Although not discussed, this separation method has been applied to the analysis of other SRC II products, coal tar, SRC recycle solvents, and SRC I process materials. In each case, the compounds in these materials were successfully separated according to chemical functionality as described for the SRC II heavy distillate.

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LITERATURE CITED

(1) Rubin, I. B.; Guerin, M. R.; Hardigree, A. A.; Epler, J. L. *Eviron. Res.* 1976. *12*, 358–365
(2) Sexton, R. J. *Arch Environ. Health* 1980, *1*, 208–231.
(3) Dong, M.; Schmeltz, I., LaVoie, E.; Hoffmann, D. In "Carcinogenesis, vol. 3: Polynuclear Aromatic Hydrocarbons"; Jones. P. W.. Fruedenthal, R. I., Eds.; Raven Press: New York, 1978; pp 98–108.
(4) Koppenhal, D. W.; Manahan, S. E. *Environ. Scl. Technol.* 1976. TO, 1104–1107.
(5) Drushel, H. V.; Sommers, A. L. *Anal. chem.* 1966, *3*, 19–28.
(6) Hartung, G. K.; Jewell, D. M. *Anal. Chim. Acta* 1902, *26*, 514–547.
(7) White. C. M.; Schweighardt, F. K.; Schultz, J. L. *Fuel Process. Technol.* 1978, *1*, 209–215.
(8) Hertz. H. S.; Brown, J. M.; Chesler, S. N.; Guenther, F. R.; Hilpert, L. W.; May, W. E.; Parris, R. M.; Wise, S. A. *Anal. Chem.* 1980, *52*, 1650–1657.
(9) Ho, C.-H.; clerk. B. R.; Guerin, M. R.; Ma, C. Y.; Rao, T. K. *Prepr. Pep.. Am. Chem. Soc., Div. Fuel Chem.* 1979, 24 (1). 281–291.
(10) Jones. A. R.: Guerin. M. R.: Clark. B. R. *Anal. Chem.* 1977. *49*, 1766–1771.
(11) Wilson, B. W.: Peterson, M. R.; Petroy, R. A.; Cresto, J. T. *Fuel* 1981, *60*, 289–294.
(12) Farcasiu, M. *Fuel* 1977, *56* (1), 9–14.
(13) Schiller, J. E.; Mathiason, D. R. *Anal. chem.* 1977. *49*. 1225–1228.
(14) Jewell, D. M.; Weber, J. H.; Bunger, J. W.: Plancher, H.; Latham, D. R. *Anal. Chem.* 1972. 44. 1391–1395.
(15) Clark, B. R.; Ho, C. H.; Jones, A. R. *Adv. chem. Ser.* 1978, *No. 170*, 282–294.
(16) Bartle, K. D.; Lee, M. L.; Wise, S. A. *chem. Soc. Rev.* 1911. *35*, 113–158.
(17) Willey, C.; Iwao, M.; Castle, R. N.; Lee, M. L. *AMI. Chem.* 1981, *53*, 400-407.
(18) Snyder. L. R.; Buell, B. E. *Anal. Chem.* 1968, *40*, 1295–1302.
(19) Schiller, J. E. *AMI. Chem.* 1977. 49. 2292–2294.
(20) Snook, M. E.; Arrendale, R. F.; Higman, H. C.; Chortyk, *O.* T. *Anal. chem.* 1978, *50*, 88–90.
(21) Lee. M. L.; Wright, B. W. *J. Chromatogr. Scl.* 1980, *18*, 345–357.
(22) White, C. M.; Shultz, J. L.; Sharkey, A. G *Nature (London)* 1977. *268*, 620–623.
(23) Guerin, M. R. In "Polycyclic Hydrocarbons and Cancer"; Gelboin, H. V.. Ts'O, P. *O.* P., Eds.; Academic Press: New York, 1978; Part I.
(24) White, C. M. In "Handbook of Polycyclic Aromatic Hydrocarbons"; Bjørseth, A., Ed.; Marcel Dekker: New York, in press.
(25) Griest, W. H.; Tomkins, B. A.; Epler, J. L.; Rao, T. K. In "Polynuclear Aromatic Hydrocarbons"; Jones. P. W., Leber, P.. Eds.; *Ann* Arbor Science Publishers: Ann *Arbor*, MI. 1979; pp 395–409.
(26) Karcher, W.; Nelen R.; Depaus, R.; van Elk, J. In "Proceedings of 5th International Symposium on Polynuclear Aromatic Hydrocarbons"; Battelle Columbus Laboratories: Columbus, OH, 1980.
(27) Petroy, R. A.. Pacific Northwest Laboratory. Richland, WA. 1981, unpublished work.
(28) Wilson, B. W.; Petroy, R. A.; Cresto, J. T. *Mutat. Res.* 1980, *79*, 193–202.