PNL-5805
UC-90d

2F

Effects of Coal Rank on the Chemical Composition and Toxicological Activity of Coal Liquefaction Materials

C. W. Wright
D. D. Dauble

May 1986

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

PNL-5805

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

PNL-5805
UC-90d

EFFECTS OF COAL RANK ON THE CHEMICAL COMPOSITION AND TOXICOLOGICAL ACTIVITY OF COAL LIQUEFACTION MATERIALS

C. W. Wright
D. D. Dauble

May 1986

Prepared for
the U. S. Department of Energy
under Contract DE-AC06-76RLO-1830

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This report presents data from the chemical analysis and toxicological testing of coal liquefaction materials from the EDS and H-Coal processes operated using different ranks of coal. Samples of recycle solvent from the bottoms recycle mode of the EDS direct coal liquefaction process derived from bituminous, sub-bituminous, and lignite coals were analyzed. In addition, the H-Coal heavy fuel oils derived from bituminous and sub-bituminous coals were analyzed. Chemical methods of analysis included adsorption column chromatography, high-resolution gas chromatography, gas chromatography/mass spectrometry, and low-voltage probe-inlet mass spectrometry. The toxicological activity of selected samples was evaluated using the standard microbial mutagenicity assay, an initiation/promotion assay for mouse-skin tumorigenicity, and a static bioassy with Daphnia magna for aquatic toxicity of the water-soluble fractions.

CONTRIBUTORS

Chemical Separations

S. A. Barraclough
B. K. Hayden

Gas Chromatography

B. K. Hayden
C. W. Wright

Mass Spectrometry

E. K. Chess
C. W. Wright

Microbial Mutagenicity Assay

E. L. Lewis
D. L. Stewart

Initiation/Promotion Assay

D. D. Mahlum

Aquatic Toxicity Bioassay

D. D. Dauble
A. J. Scott
B. L. Thomas

ACKNOWLEDGEMENTS

These studies were supported by the U. S. Department of Energy, Office of Fossil Energy under Contract No. DE-AC06-76RLO-1830 with the Pacific Northwest Laboratory. The EDS recycle solvent samples derived from the bituminous and sub-bituminous coals were supplied by Exxon Research and Engineering Company. The Oak Ridge National Laboratory Repository supplied the H-Coal heavy fuel oil samples and the EDS recycle solvent derived from the Texas lignite. The authors thank B. W. Wilson and R. M. Bean for technical assistance in the preparation of this report.

EXECUTIVE SUMMARY

As part of an ongoing effort to define the potential health effects of advanced coal liquefaction technology, the effect of processing different ranks of coal has been evaluated with regards to the chemical composition and toxicological activity of the coal liquefaction materials produced. Coal liquefaction main stream products from two different processes were analyzed, namely, the EDS and H-Coal direct coal liquefaction processes. The EDS recycle solvents derived from the processing of bituminous Illinois No. 6 and sub-bituminous Wyoming (Wyodak) coals as well as Texas lignite in the bottoms recycle mode comprised one sample set. The H-Coal heavy fuel oils derived from the processing of Illinois No. 6 and Wyodak coals represented the second sample set.

The coal liquefaction materials studied were produced using somewhat different operating parameters dependent upon the rank of coal which was processed. Modifications in operating parameters required to optimize conversion for each of the pilot plants undoubtedly had some effects on the chemical composition and toxicological activity of each of the coal liquids studied. Because operating parameters were optimized as a function of the coal rank, however, these studies indicate the general differences in material composition and toxicology attributable to the use of differing feed coal ranks.

Chemical analyses were performed using the following methods: adsorption column chromatography, high-resolution gas chromatography, gas chromatography/mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological activity was determined using the standard histidine microbial mutagenicity assay, an initiation/promotion mouse skin tumorigenicity assay, and a static bioassay with the freshwater invertebrate *Daphnia magna.*

Results from the chemical class composition analyses indicated that both coal liquids produced from the bituminous coals contained higher concentrations of polycyclic aromatic hydrocarbons (PAH), nitrogen-containing polycyclic aromatic compounds (NPAC), and hydroxy-substituted PAH than did their corresponding sub-bituminous coal or lignite-derived liquids. The materials produced from the sub-bituminous coal or lignite contained a significantly higher aliphatic hydrocarbon content than those derived from the higher rank bituminous coal. Qualitatively, the individual components present in the chemical class fractions were similar amongst the products from the same direct coal liquefaction process, regardless of the rank of coal from which they were derived. The products derived from the Illinois No. 6 coal did, however, have a generally increased molecular weight distribution of approximately ten atomic mass units.

Toxicological testing of the materials from the two coal liquefaction processes derived from the various coals indicated a general trend of increased biological activity with increasing coal rank. The NPAC fractions from both the EDS recycle solvent and the H-Coal heavy fuel oil

derived from the Illinois No. 6 coal expressed significantly increased microbial mutagenicity as compared to their respective Wyodak and/or Texas Lignite-derived counterparts. Increased tumor initiating activity, as determined by total number of tumors per mouse, was noted to correlate with increased coal rank feed for the EDS recycle solvents; the greatest tumorigenicity was expressed by the recycle solvent derived from the Illinois No. 6 coal, while the least tumorigenicity was expressed by the recycle solvent derived from the Texas Lignite. The EDS recycle solvent derived from the bituminous coal also had a greater aquatic toxicity to D. magna than did the recycle solvents derived from the sub-bituminous coal or lignite.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AH = Aliphatic hydrocarbon(s)
amu = Atomic mass unit

cm =Centimeter

D. =Daphnia
°C =Degrees Celsius
°F =Degrees Farenheit
DOE =U.S. Department of Energy
DMSO =Dimethylsulfoxide

ECLP =EDS coal liquefaction pilot plant
eV =Electron volt(s)

FID =Flame ionization detector

g =Gram(s)
GC =Gas Chromatography
GC/MS =Gas Chromatography/mass spectrometry

HP =Hewlett-Packard
HRGC =High resolution gas chromatography
hydroxy-PAH =Hydroxy-substituted polycyclic aromatic hydrocarbon(s)

ID =Inner diameter
I/P =Initiation/promotion

L =Liter(s)
lb =Pound(s)
LC_{50} =Lethal concentration for 50% of the organisms
LVMS =Low-voltage probe-inlet mass spectrometry

m =meter(s)
MAF =Moisture and ash-free
MF =Moisture-free
mg =Milligram(s)
μg =Microgram(s)
min =Minute(s)
ml =Milliliter(s)
μl =Microliter(s)
mm =Millimeter(s)
μm =Micrometer(s)
MS =Mass spectrometry

ng =Nanogram(s)
ND =No data
No. =Number
NPAC =Nitrogen-containing polycyclic aromatic compound(s)

PA_1 =Aliphatic hydrocarbon(s) fraction
PA_2 =Hydroaromatic compound(s) fraction
PA_3 =Dihydro-PAH and <three-aromatic-ringed PAH fraction

PA_4	=>Three-aromatic-ringed PAH and some polar polycyclic aromatic compound(s) fraction
PAC	=Polycyclic aromatic compound(s)
PAH	=Polycyclic aromatic hydrocarbon(s)
PNL	=Pacific Northwest Laboratory
ppt	=Parts per thousand
psig	=Pounds per square inch
rev	=Revertant(s)
S.	=Salmonella
S9	=Metabolic enzyme system used in microbial mutagenicity assay
sec	=Second(s)
SRC	=Solvent refined coal
TA98	=Designation for strain of Salmonella typhimurium used in microbial mutagenicity assay
TC	=Total carbon
TIC	=Total ion current
V	=Volt(s)
VGO	=Vacuum gas oil
WSF	=Water soluble fraction(s)
Wt	=Weight
Wt %	=Weight percent

INTRODUCTION

Research and development of advanced direct coal liquefaction technology is being supported by the U. S. Department of Energy (DOE) as a means of utilizing domestic supplies of coal to produce petroleum-substitute fuels. As a component of this effort, the U. S. DOE has supported the chemical analysis and toxicological evaluation of coal liquefaction products to define the potential health effects and industrial hygiene concerns associated with coal liquefaction technology.

Feed coal rank is an important variable in direct coal liquefaction processes. Coals of different rank from different mines and seams are widely available across the U. S. The purpose of this document is to present and compare the results of the chemical and toxicological investigations performed with coal liquefaction materials derived from different coal ranks. Main stream products from two different coal liquefaction processes were studied. These products included the recycle solvent from the EDS coal liquefaction process (operated in the bottoms recycle mode) derived from bituminous, sub-bituminous, and lignite coals and the heavy fuel oil from the H-Coal process derived from bituminous and sub-bituminous coals. The pilot plant operating parameters were optimized for and were dependent upon the coal rank being processed. Therefore, these studies indicate the general differences in coal liquid composition and toxicology attributable to the use of differing feed coal ranks, eventhough somewhat different operating parameters were used during their processing. Coal liquefaction products derived from feed coals of the same rank but from different mines and seams were not compared in this study.

Chemical analyses were performed to determine the compositions of the materials produced from the various ranks of coal. Gross chemical compositional differences between the liquids produced from the different coal rank feeds were determined by fractionation using adsoprtion column chromatography. Fractions of aliphatic hydrocarbons (AH), polycyclic aromatic hydrocarbons (PAH), nitrogen-containing polycyclic aromatic compounds (NPAC), hydroxy-substituted PAH (hydroxy-PAH), and hydroaromatic compounds were among the chemical class fractions isolated from the EDS recycle solvents and H-Coal heavy fuel oils. Selected fractions were analyzed by high-resolution gas chromatography (HRGC), gas chromatography/mass spectrometry GC/MS, and/or low-voltage probe-inlet MS (LVMS) to determine the qualitative and quantitative composition of the individual constituents present in the fractions.

Toxicological response was determined using three biological endpoints. The microbial mutagenicity of selected chemical class fractions isolated from the three EDS bottoms recycle solvents and the two H-Coal heavy fuel oils was measured using the standard histidine reversion assay with Salmonella typhimurium, TA98. The EDS recycle solvents derived from the bituminous, sub-bituminous, and lignite coals were also evaluated for tumor-initiating activity using the initiation/promotion assay for mouse skin tumorigenicity. The ecotoxicity of water-soluble fractions (WSF) derived from the three EDS recycle solvents was evaluated using static bioassays with Daphnia magna. The toxicological properties of the coal liquids WSF mainly reflect the presence of highly soluble phenolic constituents (Dauble et al., 1982, 1983). In contrast, increased mutagenic and tumorigenic activity predominates in the NPAC, particularly the amino-substituted PAH, and the higher molecular weight PAH compounds, respectively (Wright et al., 1985). Thus, the three different toxicological studies were utilized to better identify the potential overall environmental hazard of the coal-derived materials.

ENGINEERING AND SAMPLES

EDS PROCESS

The EDS coal liquefaction pilot plant (ECLP) was designed to process 200 tons/day of dry coal. The plant was successfully operated on lignite, sub-bituminous, and bituminous coals to produce a full range of products and by-products. A simplified flow scheme of the EDS process is shown in Figure 1. A more detailed description of the process is given by Later et al. (1984). The samples provided for analysis were produced during bottoms recycle operation and represented the principle products of the process. During bottoms recycle operation, liquid vacuum bottoms were recycled to the slurry drier and mixed with the recycle solvent and feed coal (see Figure 1).

To compare the chemical composition and toxicological activity of coal liquefaction materials produced from the various ranks of coal, samples of the recycle solvent were provided from the bottoms recycle processing of Texas Lignite, Wyoming, and Illinois No. 6 coals. A summary of typical elemental analyses of Illinois No. 6 coal from the Monterey Mine, Wyoming coal from the Wyodak Mine, and Texas Lignite from the Martin Lake Mine is given in Table 1. The variation between the elemental analysis of coals from the same seam is given by the range of nine determinations for the Illinois No. 6 and Wyoming coals. The Illinois coal had a higher sulfur and nitrogen content and lower oxygen content than did the lower rank Wyodak coal and Texas lignite. The Texas lignite had a significantly lower carbon content than did the Illinois and Wyodak coals.

Operating parameters of the EDS Coal Liquefaction Pilot Plant (ECLP) were modified for each of the three coals, because each of the different coal ranks processed exhibited different liquefaction characteristics. A summary of reactant feedrates and reaction conditions for each of the coals studied is given in Table 2. Generally, increased residence time and operating temperatures were used with increasing coal rank.

H-COAL PROCESS

A simplified schematic diagram of the single-stage, catalytic H-Coal direct coal liquefaction process is shown in Figure 2. A description of this process was given by Wilson et al. (1985). Samples of the heavy oil were taken from the Catlettsburg, KY pilot plant during the processing of Illinois No. 6 and Wyodak coals in the syncrude mode. Nominal reactor temperature for the processing of the Illinois coal was 850°F, with the reactor operated at a pressure of approximately 3000 psig. Nominal reactor temperature for the processing of the Wyodak coal was 835°F, with

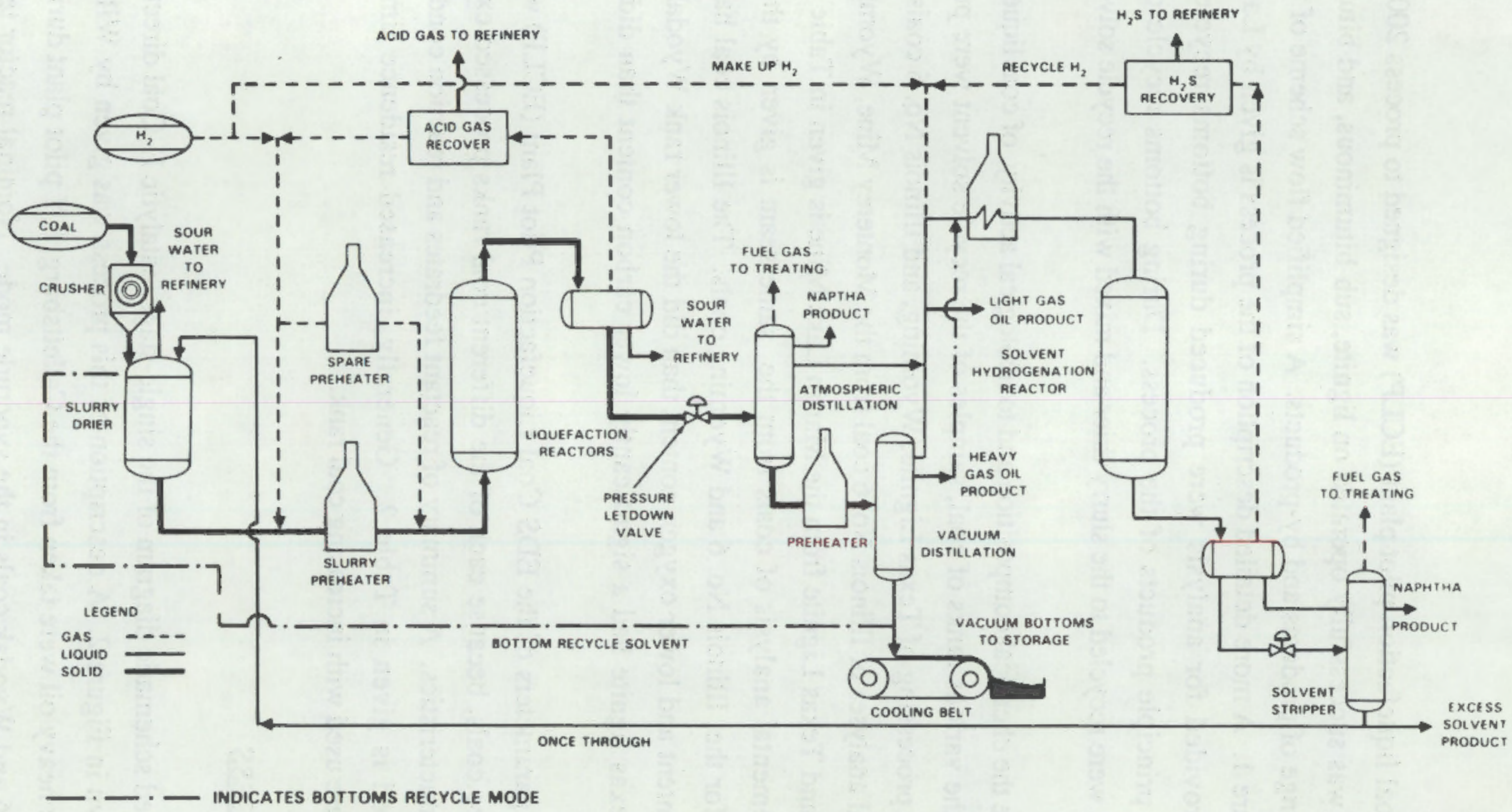

FIGURE 1. Simplified Flow Scheme of the EDS Direct Coal Liquefaction Process.

TABLE 1. Elemental Analysis Data for Selected Coals

	Coal Rank; Weight Percent Moisture Ash Free Coal		
Element	Illinois No. 6[a]	Wyoming (Wyodak)[a]	Texas Lignite
Carbon	69.40-70.82	66.16-67.30	55.35
Hydrogen	4.68- 4.91	4.76- 5.06	4.15
Nitrogen	1.08- 1.27	0.70- 0.93	0.92
Oxygen[b]	9.77-10.29	16.90-18.08	16.54
Sulfur	3.28- 3.49	1.10- 1.66	1.54

---

[a] Range of determinations of nine coal samples from the same mine
[b] By difference

TABLE 2. Summary of ECLP Operating Parameters Using Selected Coals

	Coal Rank		
	Illinois No. 6	Wyoming (Wyodak)	Texas Lignite
Reactant Feedrates			
Coal Feed Rate	137 tons/day	132 tons/day	130 tons/day
Solvent/MF[a] Coal	1.5 lb/lb	2.2 lb/lb	2.2 lb/lb
H_2/MF Coal	4.9 wt % MF coal	6.5 wt % MF coal	6.3 wt % MF coal
Bottoms/MF Coal	0.65 lb/lb	0.45 lb/lb	0.65 lb/lb
VGO[b]/MF Coal	0-0.3 lb/lb	0-0.1 lb/lb	ND[c]
Reaction Conditions			
Liquefaction Temperature	840°F	806°F	835°F
Liquefaction Pressure	2550 psig	2515 psig	2522 psig
Slurry Residence Time	92 minutes	85 minutes	79 minutes

---

[a] Moisture-free basis
[b] Vacuum gas oil
[c] No data

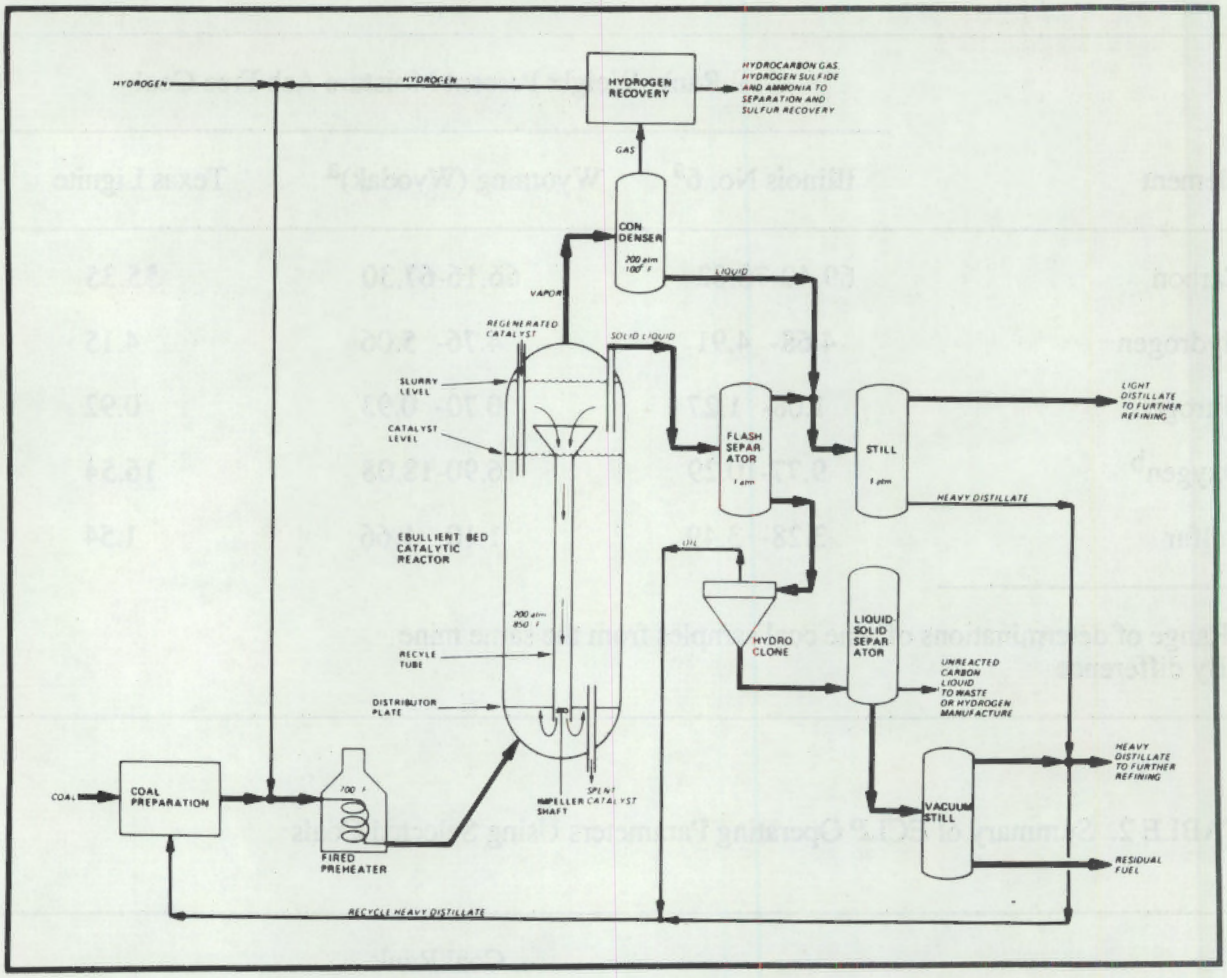

Figure 2. Simplified Schematic Diagram of the H-Coal Direct Coal Liquefaction Process. (Baughman, 1978)

---

the reactor also operated at a pressure of approximately 3000 psig. Catalyst replacement was between one and two lb/ton of feed coal for both runs.

SUMMARY

A summary of the samples analyzed, identified with their PNL numbers and a brief description, is given in Table 3. Identifying runs from the ECLP and the H-Coal Pilot Plant are also given.

TABLE 3. Coal Rank Samples Analyzed

Sample Number	Sample Description
5226-003	EDS Recycle Solvent, Bottoms Recycle Mode, ETP-13[a], Illinois No. 6 Coal
5226-107	EDS Recycle Solvent, Bottoms Recycle Mode, ETP-8[a], Wyoming (Wyodak) Coal
5226-108	EDS Recycle Solvent, Bottoms Recycle Mode, ETP-22[a], Texas Lignite
5226-118	H-Coal Heavy Fuel Oil, Illinois No. 6 Coal, Pilot Plant Run No. 8.
5226-119	H-Coal Heavy Fuel Oil, Wyodak Coal, Pilot Plant Run No. 10.

---

[a] Refers to ECLP identifying sample set

METHODS

CHEMICAL ANALYSIS

Adsorption Column Chromatography

Alumina. Samples were fractionated by chemical class according to the method described by Later et al. (1981) and Later and Lee (1983). Samples (approximately 100 mg) were sequentially eluted from standardized alumina (1.5% H_2O, Later et al., 1985) with 20 ml hexane, 50 ml benzene, 70 ml chloroform:ethanol (99:1), and 50 ml methanol. The chemical class fractions produced were AH, PAH, NPAC, and hydroxy-PAH. The weight percent contribution of each fraction was determined gravimetrically.

Picric-Acid-Coated Alumina. The hydroaromatic compounds were isolated from the coal liquids using a layered adsorption column of 15% picric-acid-coated alumina over alumina as described by Wozniak and Hites (1983). Samples were sequentially eluted with 10 ml hexane to obtain the AH (PA_1), 40 ml methylene chloride:hexane (3:97) to obtain the hydroaromatic compounds (PA_2), 30 ml methylene chloride:hexane (3:17) to obtain the dihydro-PAH and <three-aromatic-ringed PAH (PA_3), and 25 ml benzene to obtain the >three-aromatic-ringed PAH and some polar compounds (PA_4). The weight percent contribution of each fraction was determined gravimetrically.

High-Resolution Gas Chromatography (HRGC)

The fractions isolated from the coal liquefaction materials were analyzed by HRGC using a Hewlett-Packard (HP; Avondale, PA) 5880A gas chromatograph equipped with a 30-m x 0.25-mm-ID fused silica capillary column coated with 0.25-μm film thickness DB-5 (J & W Scientific, Rancho Cordova, CA). The oven was temperature-programmed to 300°C at 3°C/min after 2 min isothermal at 50°C. Splitless injection was used with helium as the carrier gas at 50 cm/sec linear velocity. The injection port and flame ionization detector were operated at 275 and 300°C, respectively. Components were identified by retention index (Lee et al., 1979; Vassilaros et al., 1982), absolute retention times of standard compounds, and/or GC/MS data. Selected components of the PAH and NPAC fractions were quantified according to the external standard calibration method outlined by Wilson et al. (1984) using 2-chloroanthracene as an internal standard. Response factors (amount/area) were calculated from standard compounds chromatographed at eight concentration levels, ranging over two orders of magnitude. The response factor of a closely eluting or similar compound was used to quantify components for which standards were not available. Fractions were analyzed at 10.0, 5.00, and 2.50 mg/ml concentrations with averaged results and standard deviations of the mean reported in parts per thousand (ppt) for each particular fraction.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed on an HP-5982A quadrupole mass spectrometer interfaced with an HP-5710 gas chromatograph equipped with a 15-m x 0.25-mm-ID DB-5 fused silica capillary coumn (J & W Scientific, Rancho Cordova, CA). Gas chromatographic conditions were similar to those previously described for the HRGC analyses, except that the oven was temperature-programmed at 8^{o}C/min. The MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units/sec (amu/sec).

Low-Voltage Probe-Inlet Mass Spectrometry (LVMS)

The chemical class fractions isolated from the coal liquefaction materials by alumina column chromatography were analyzed by LVMS using a Vacuum Gasifier (VG; Manchester, England) ZAB 2-F double-focusing MS operated in the electron impact mode with ionizing electron energies of 10-12 eV. Each sample (10 to 20 µg) was loaded into a glass capillary tube, which was then inserted into the source affixed to the end of a direct insertion probe. The probe was heated in a linear fashion from ambient to 250-280^{o}C while the MS scanned repeatedly throughout the desorption period. The MS was operated with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 sec/mass decade, a source temperature of 250^{o}C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. The intensities of each mass across the entire profile were summed, generating an average spectrum that was representative of the entire sample. Average spectra were composed primarily of signals representing molecular ions rather than fragments or doubly charged ions, due to the low ionization voltage.

TOXICOLOGICAL ASSAYS

Microbial Mutagenicity

Standard agar-plate mutagenicity assays were performed as described by Ames et al. (1975) using S. typhimurium, TA98 microbial tester strain with optimized levels of Aroclor-induced rat liver (S9) homogenate metabolic activation. Dimethylsulfoxide (DMSO) was used as the solvent. Revertant colonies per petri plate were counted electronically using a Biotran II automated colony counter. The specific mutagenic activity of the chemical class fractions isolated by alumina column chromatography are expressed as revertant colonies of S. typhimurium, TA98 per µg of test material (rev/µg), as estimated by linear regression analysis of dose-response data. The following criteria were used for selecting the best dose range for estimating a linear dose response: at least a four-point dose range; approximate doubling of response for doubled dose concentration; a correlation coefficient of 0.8 or greater; and an intercept on the response (ordinate) axis within 20% of the negative control for the day.

Initiation/Promotion (I/P)

The I/P mouse skin tumorigenicity assays were performed on the EDS recycle solvents as described by Mahlum (1983a) using female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age. The animals were housed five per cage on standard bedding material with food and water availabe ad libitum. Prior to administration of test materials, the animals were ear-tagged for unique identification, weighed, shaved, and assigned to a test groups, 30 animals per group. Each test material was diluted 1:1 with acetone or methylene chloride, and 50 µl of the diluted material was applied to the shaved backs of the mice (approximately 25 mg dose per mouse). Two weeks after initiation, 5-µg doses of phorbol myristate acetate (0.1 mg/ml acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regularly for tumor growth, and the number of tumors per animal was counted biweekly. The data are expressed as the total number of tumors per group of 30 mice, as the total number of tumors per mouse normalized to a groups of 30 mice, and as the percent incidence.

Aquatic Toxicity

Aquatic toxicity of the water-soluble fractions (WSF) derived from the EDS recycle solvents was determined by conducting static bioassays with the freshwater invertebrate D. magna. All tests were conducted at 20°C with a 16:8-hour, light:dark cycle. The test consisted of placing five first-instar D. magna in each of four 100-ml-capacity glass jars at six treatment levels, plus a control (4 x 7 test matrix, 20 organisms per treatment level).

The WSF were generated by adding 100 ml of each of the EDS recycle solvent materials listed in Table 3 to ten L of well water (1:100 ratio) in a 15-L-capacity glass carboy. The mixture was stirred at 90 rpm with a teflon-coated rod for 4 hours. After a one hour settling period, approximately eight L of the WSF were siphoned from the center of the carboy, chemically analyzed, and used for bioassays. Exposure solutions for testing were made by diluting the WSF with well water.

Total carbon (TC) of the WSF was determined by direct aqueous injection into a Beckman 915B carbon analyzer. Detailed chemical analysis of the WSF by GC was conducted to determine phenol composition according to methodology outlined by Dauble et al. (1982, 1983) Total phenols in selected test solutions were estimated by the direct photometric method (APHA 1980) at test initiation to check dilutions.

Three to five tests were conducted using the WSF from each of the EDS recycle solvents produced from the different coal types. The 48 hour LC_{50} (lethal concentration for 50% of the organisms) values were determined by the graphical method (APHA 1980). Toxicity thresholds were expressed as percent WSF and TC, based on dilution of measured stock solution.

RESULTS AND DISCUSSSION

CHEMICAL ANALYSIS

Chemical Class Composition

Table 4 presents the chemical class composition data, as determined by adsorption column chromatography using neutral alumina, for the coal liquids derived from the different ranks of coal. The products from the lower rank Wyodak coal and Texas lignite contained significantly higher concentrations of AH compared to the products from the higher rank coal (Illinois No. 6) for both the EDS recycle solvents and the H-Coal heavy fuel oils. Both coal liquids produced from Illinois No. 6 coal contained higher concentrations of PAH, NPAC, and hydroxy-PAH compared to their respective coal liquids produced from the Wyodak coal or Texas lignite.

Hydrogenated and partially hydrogenated PAH compounds were detected in both the AH and PAH fractions isolated from the EDS and H-Coal products derived from the different ranks of coal. Because of the presence of these hydrogenated components and the inadequate class separation of AH, hydroaromatics, and PAH on neutral alumina, a second adsorption column chromatographic separation was performed on these samples. The results of fractionation using picric-acid-coated alumina on alumina column chromatography are given in Table 5 for the EDS recycle solvents and H-Coal heavy fuel oils. Again, the coal liquids produced from the lower rank Wyodak coal or Texas lignite showed increased concentrations of AH compared to their higher rank Illinois No. 6 coal counterparts. The EDS recycle solvents derived from the Wyodak coal and Texas lignite also showed lower hydroaromatic (fraction PA_2) composition than did the recycle solvent produced from the Illinois No. 6 coal. Lower concentrations of PAH compounds of greater than three rings (fraction PA_4) were present in the coal liquids produced from the sub-bituminous coals or lignite as compared to the materials produced from the bituminous Illinois coal.

Aliphatic Hydrocarbon Fractions

Chromatograms of the AH fractions isolated from the EDS recycle solvents produced using different coal ranks are shown in Figure 3. Selected straight-chained AH are labeled with their number of carbon atoms. The major components in these fractions were AH with a high concentration of hydroaromatic components also present. Qualitatively, the components were similar to each other in the AH fractions isolated from the EDS recycle solvents produced from the various ranks of coal. Increased levels of the straight-chained AH were evident relative to the hydroaromatic species in the AH fractions isolated from the recycle solvents derived from the

TABLE 4. Chemical Class Composition of Process Materials Derived from Different Coal Ranks

Sample	Fraction Weight Percent				
	AH	PAH	NPAC	Hydroxy-PAH	Total
EDS Recycle Solvent					
5226-003 Illinois No. 6 Coal[a]	46	39	7.7	12	105
5226-107 Wyodak Coal[b]	61	22	3.6	8.7	95
5226-108 Texas Lignite[b]	61	25	3.8	7.0	97
H-Coal Heavy Fuel Oil					
5226-118 Illinois No. 6 Coal[c]	38	42	7.8	12	100
5226-119 Wyodak Coal[c]	61	31	5.1	5.8	103

[a] Average of four determinations
[b] Average of three determinations
[c] Average of two determinations

Wyoming coal and Texas lignite compared to the recycle solvent derived from the Illinois No. 6 coal.

Similar results were achieved for the AH fractions isolated from the H-Coal heavy fuel oils derived from the bituminous Illinois No. 6 and sub-bituminous Wyodak coals, as shown in Figure 4. Increased concentrations of straight-chained AH compounds were present relative to the hydroaromatic components in the AH fraction isolated from the heavy fuel oil derived from the Wyodak versus the Illinois No. 6 coal.

Polycyclic Aromatic Hydrocarbon (PAH) Fractions

The HRGC chromatograms from the analyses of the PAH fractions isolated from the EDS recycle solvents derived from the three different ranks of coal are shown in Figure 5; the PAH fraction derived from the Illinois No. 6 coal is on top; the Wyoming-coal-derived fraction is in

TABLE 5. Hydroaromatic Composition of Process Materials Derived from Different Coal Ranks

	Fraction Weight Percent[a]				
Sample	PA_1[b]	PA_2[c]	PA_3[d]	PA_4[e]	Total
EDS Recycle Solvent					
5226-003 Illinois No. 6 Coal[f]	23	40	13	17	93
5226-107 Wyoming (Wyodak) Coal	49	29	8.4	14	100
5226-108 Texas Lignite	51	32	9.4	12	104
H-Coal Heavy Fuel Oil					
5226-118 Illinois No. 6 Coal	21	39	12	29	101
5226-119 Wyodak Coal	50	36	8.8	16	101

[a] Average of two determinations, unless otherwise noted
[b] AH
[c] Hydroaromatic compounds
[d] Dihydro-PAH and <three-ringed PAH
[e] >Three-ringed PAH and some polar PAC
[f] Average of six determinations

the middle; the Texas-lignite-derived fraction is on the bottom. The peaks labeled in Figure 5 are identified in Table 6 with quantitative values given for selected components. Qualitatively, the components were similar in each of the PAH fractions isolated from the EDS recycle solvents from the bottoms recycle mode, regardless of the rank of coal processed. There were few differences in the chromatograms. Quantitatively, the PAH fraction isolated from the Illinois No. 6-derived recycle solvent tended to have increased concentrations of components containing five aromatic rings or greater compared to the other materials (although the difference was only significant between the former versus the Wyoming-coal-derived recycle solvent). A higher degree of alkylation was present in the recycle solvent derived from the Texas lignite versus the other two materials. This result was based on the ratio of the combined concentrations of the

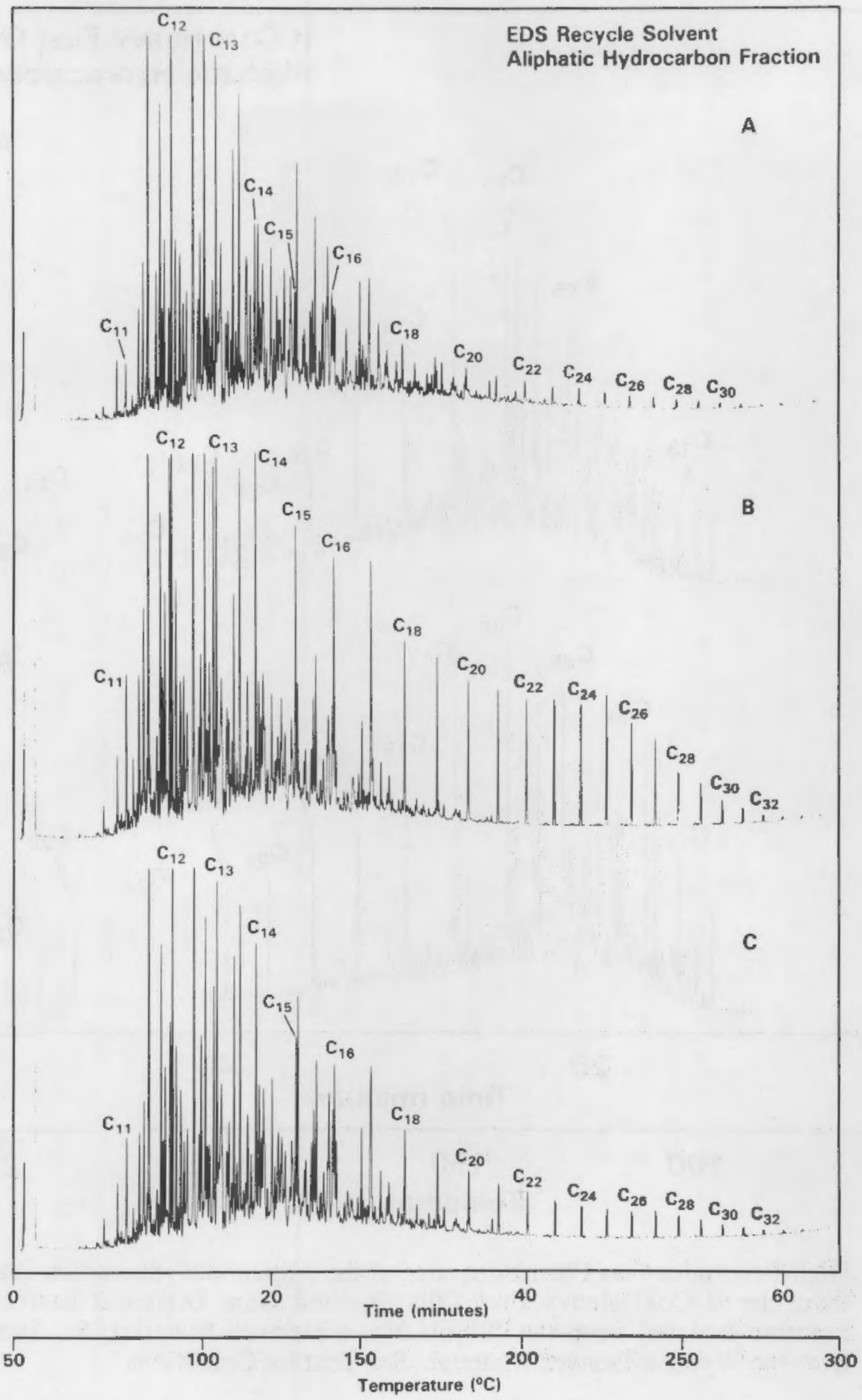

Figure 3. High-Resolution Gas Chromatograms of the Aliphatic Hydrocarbon Fractions Isolated From the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions.

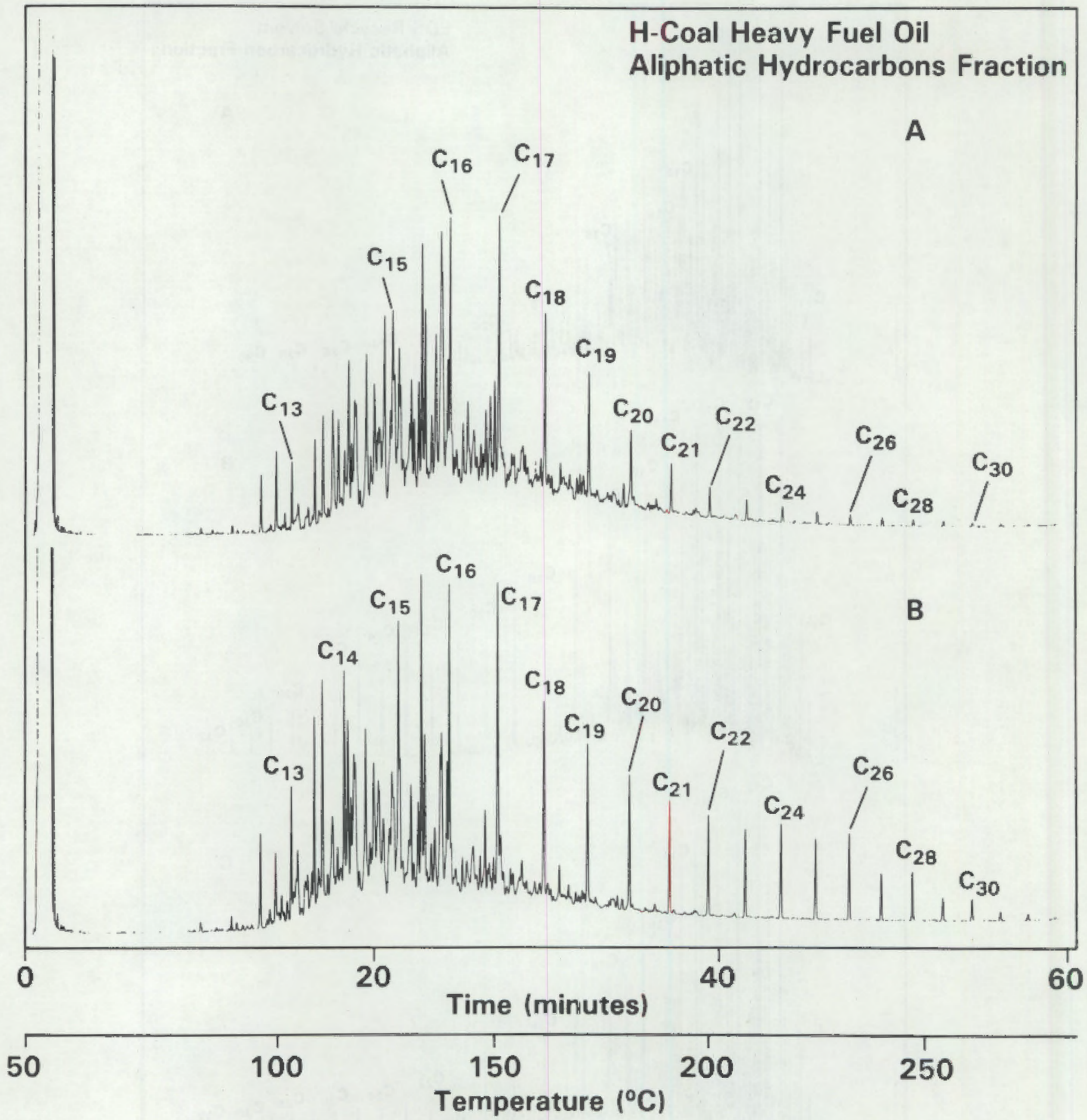

Figure 4. High-Resolution Gas Chromatograms of the Aliphatic Hydrocarbon Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyodak-Derived Material. See Text for Conditions.

---

methylphenanthrene isomers divided by the concentration of the parent phenanthrene; these ratios were 1.02, 0.75, and 0.74 for the EDS recycle solvents PAH fractions produced from the Texas Lignite, Wyodak coal, and Illinois No. 6 coal, respectively.

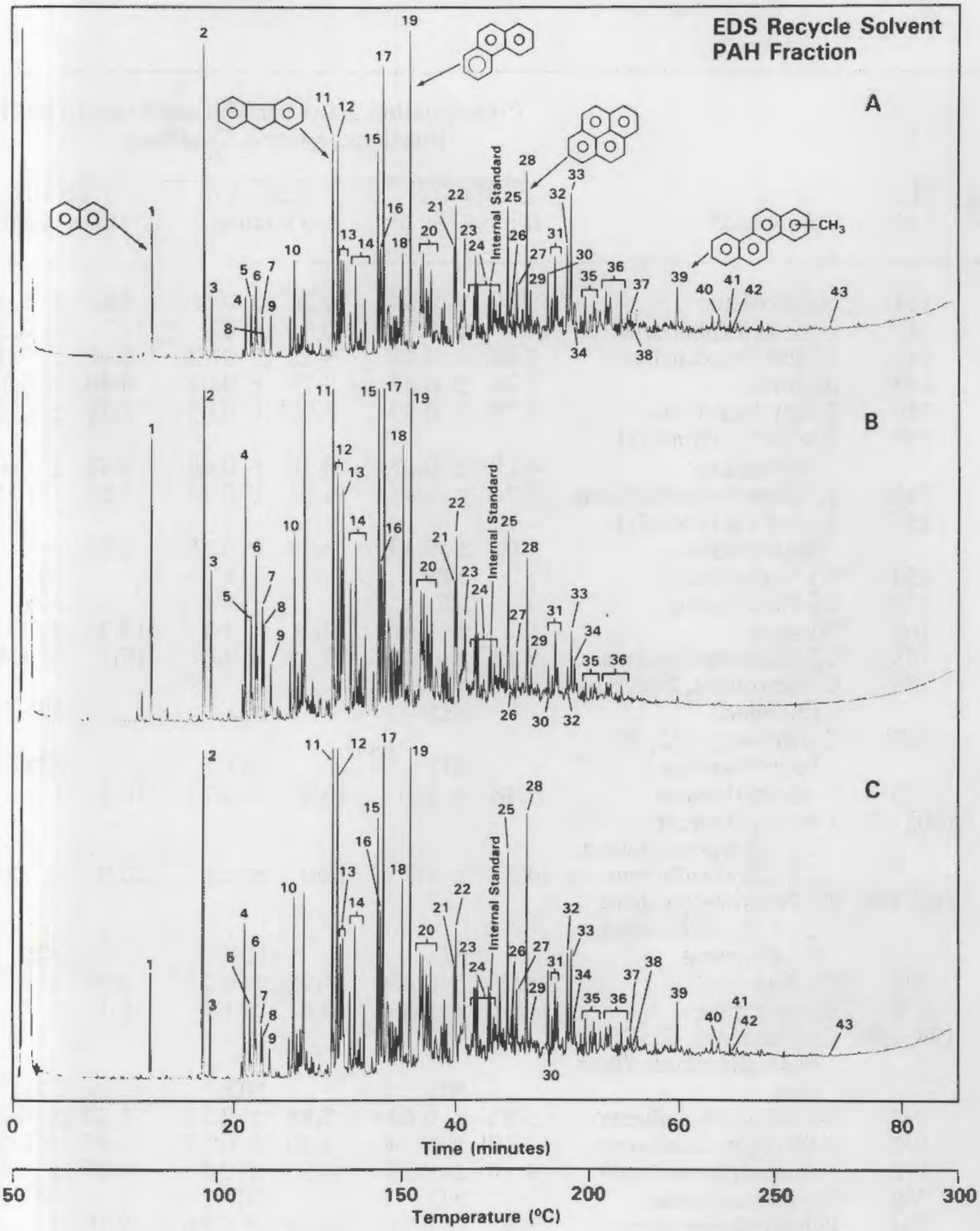

Figure 5. High-Resolution Gas Chromatograms of the PAH Fractions Isolated from the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions. Peaks Numbered Refer to Compounds Identified in Table 6.

TABLE 6. Concentration of Selected Components in the PAH Fractions Isolated from the EDS Recycle Solvents Derived from Different Ranks of Coal

Peak No.^{a}	Mol. Wt.	Compound^b	Concentration, Parts per Thousand (mg/g) PAH Fractions; Sample; Coal Rank		
			5226-003 Illinois No. 6	5226-107 Wyoming	5226-108 Texas Lignite
1	128	Naphthalene	5.69 ± 0.84	9.36 ± 0.06	3.84 ± 0.07
2	142	2-Methylnaphthalene	14.5 ± 2.0	20.5 ± 0.5	13.2 ± 0.33
3	142	1-Methylnaphthalene	2.68 ± 0.41	5.35 ± 0.13	2.45 ± 0.04
4	154	Biphenyl	3.04 ± 0.47	9.79 ± 0.01	6.40 ± 0.10
5	156	2-Ethylnaphthalene	2.73 ± 0.59	4.09 ± 0.09	2.79 ± 0.26
6	156	2,6- or 2,7-Dimethylnaphthalene	4.29 ± 0.92	8.26 ± 0.23	6.53 ± 0.19
7	156	1,7-Dimethylnaphthalene	1.78 ± 0.43	4.22 ± 0.18	2.05 ± 0.09
8	156	1,3- or 1,6-Dimethylnaphthalene	1.01 ± 0.43	3.79 ± 0.25	1.62 ± 0.14
9	156	C_2-Naphthalene	ND^c	ND	ND
10	170	C_3-Naphthalene	ND	ND	ND
11	166	Fluorene	10.2 ± 1.6	23.4 ± 1.1	16.7 ± 1.0
12	168	1,2-Dihydrophenalene	9.88 ± 1.55	9.22 ± 1.0	15.1 ± 1.4
13	168	C_1-Biphenyls, Dihydrofluorenes	ND	ND	ND
14	182	C_2-Biphenyls, C_1-Dihydrofluorenes	ND	ND	ND
15	180	2-Methylfluorene	7.48 ± 1.1	10.3 ± 0.7	10.4 ± 1.2
16	180, 182	1-Methylfluorene, C_1-Dihydrophenalene, C_1-Dihydrofluorene	14.5 ± 1.7	18.0 ± 1.2	20.9 ± 2.0
17	182, 180	C_1-Dihydrophenalene, C_1-Dihydrofluorene, C_1-Fluorene	ND	ND	ND
18	196	C_3-Biphenyl	3.26 ± 0.42	4.95 ± 0.28	3.88 ± 0.30
19	178	Phenanthrene	16.0 ± 1.8	26.8 ± 1.4	16.1 ± 0.9
20	194, 196	C_2-Fluorenes, C_2-Dihydrophenalenes/fluorenes	ND	ND	ND
21	192	3-Methylphenanthrene	5.53 ± 0.63	5.88 ± 0.21	4.92 ± 0.27
22	192	2-Methylphenanthrene	1.40 ± 0.14	8.30 ± 0.47	7.49 ± 0.58
23	192	1-Methylphenanthrene	4.86 ± 0.39	5.93 ± 0.56	4.06 ± 1.83
24	206	C_2-Phenanthrenes	ND	ND	ND
25	204	Dihydrofluoranthene	6.97 ± 0.91	6.71 ± 0.86	9.19 ± 0.28
26	202	Fluoranthene	1.09 ± 0.51	0.673 ± 0.568	1.54 ± 0.16
27	220	C_3-Phenanthrene	ND	ND	ND
28	202	Pyrene	7.64 ± 0.87	5.70 ± 0.19	10.6 ± 0.5
29	204	Dihydropyrene	ND	ND	ND
30	218	C_1-Dihydrofluroanthene/pyrene	ND	ND	ND
31	234	C_4-Phenanthrenes	ND	ND	ND

TABLE 6. (Continued)

			Concentration, Parts per Thousand (mg/g) PAH Fractions; Sample; Coal Rank		
Peak No.[a]	Mol. Wt.	Compound[b]	5226-003 Illinois No. 6	5226-107 Wyoming	5226-108 Texas Lignite
32	216	Benzo[b]fluorene, 2- or 4-Methylpyrene	4.34 ± 0.27	1.24 ± 0.04	4.61 ± 0.37
33	218	C_1-Phenylnaphthalene	6.35 ± 1.57	2.36 ± 0.12	4.29 ± 0.50
34	216	1-Methylpyrene	1.22 ± 1.44	1.75 ± 0.04	2.00 ± 0.51
35	234	Benzonaphthothiophenes	ND	ND	ND
36	232	C_2-Dihydrofluoranthenes/pyrenes	ND	ND	ND
37	228	Benz[a]anthracene	0.784 ± 0.129	0.154 ± 0.020	0.981 ± 0.074
38	228	Chrysene	0.453 ± 0.081	0.172[e]	0.250 ± 0.052
39	242	4- or 6-Methylchrysene	2.26 ± 0.21	0.406 ± 0.019	2.32 ± 0.06
40	252	Benzofluoranthenes[d]	0.610 ± 0.322	0.055 ± 0.006	0.556 ± 0.024
41	252	Benzo[e]pyrene	0.643 ± 0.119	ND	0.460 ± 0.115
42	252	Benzo[a]pyrene	0.114 ± 0.019	ND	0.064
43	276	Benzo[ghi]perylene	0.166 ± 0.025	ND	0.136 ± 0.002

---

[a] Refers to peaks labeled in Figure 5
[b] Tentative identifications based on GC/MS and retention information
[c] No data or none detected
[d] Composite of three isomers
[e] One determination only

Added insight into the composition of the PAH fractions isolated from the EDS recycle solvents derived from the three different ranks of coal is given by the LVMS spectra in Figure 6. The average molecular weight of the PAH fraction isolated from the bituminous-coal-derived EDS recycle solvent was higher than the average molecular weight for the same fraction isolated from the sub-bituminous or lignite-derived materials; 280 amu for the Illinois No. 6-derived PAH fraction versus 250 and 260 amu for the Wyodak coal and Texas lignite-derived PAH fractions, respectively. Despite the differences in the molecular weight ranges of the fractions, the overall composition of the fractions appeared to be similar with a few exceptions. Both the materials derived from the Wyodak coal and the Texas lignite had increased concentrations of components in the series including masses of 208, 222, and 262 amu in their respective PAH fractions. The recycle solvent derived from the Illinois No. 6 coal had increased concentrations of components in the series of mass 256 in its isolated PAH fraction as compared to the PAH fractions isolated from

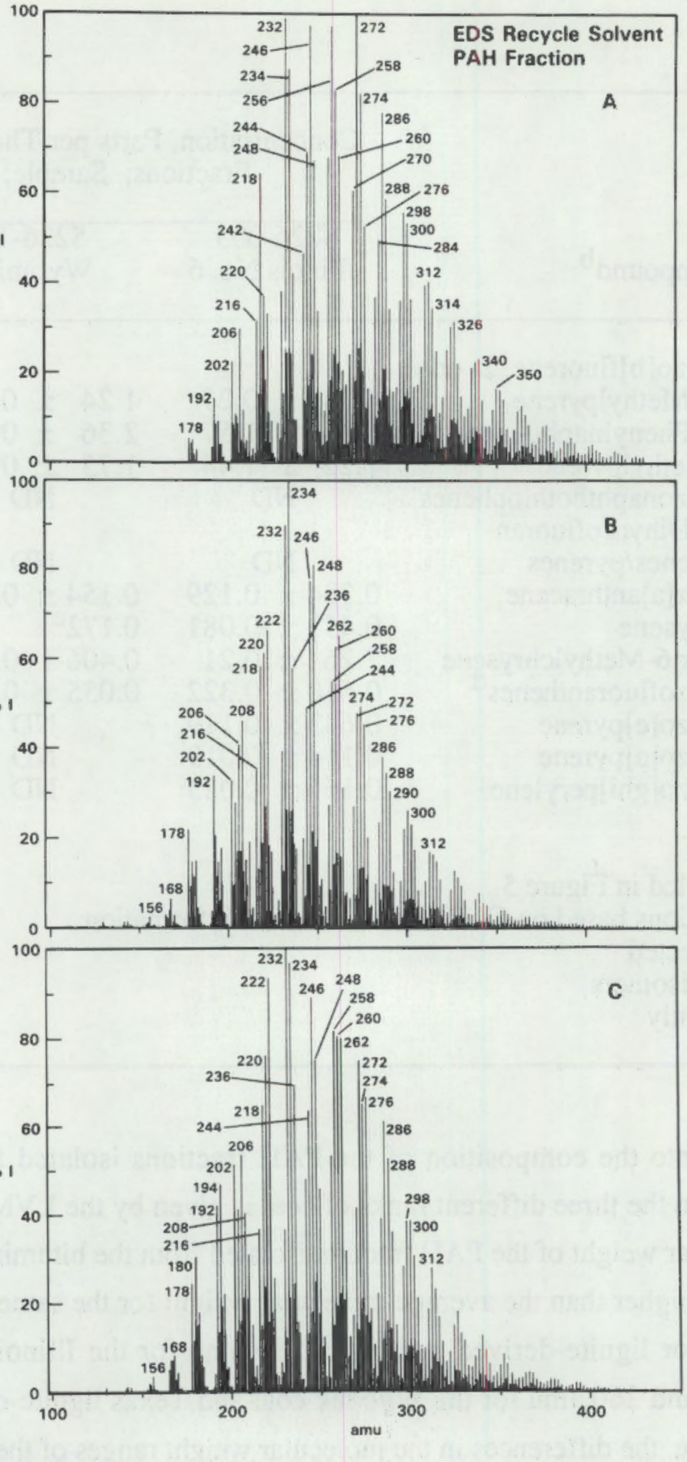

Figure 6. Low-Voltage Mass Spectra of the PAH Fractions Isolated from the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions. See Table A-1 in Appendix A for a Key to Mass Identifications.

the lower-rank-coal-derived materials. A key to possible structures which correspond to the masses labeled in Figure 6 is given in Table A-1 of Appendix A.

The composition of the PAH fractions isolated from the Illinois No. 6 and Wyodak-coal-derived H-Coal heavy fuel oils were both qualitatively and quantitatively similar (see Figure 7 and Table 7). There was a general trend of increased concentrations of low molecular weight compounds and decreased concentrations of higher molecular weight compounds in the PAH fraction derived from the lower rank, sub-bituminous Wyodak coal compared to the PAH fraction derived from the bituminous Illinois No. 6 coal.

The average molecular weights of the PAH fractions isolated from the H-Coal heavy fuel oils were both 240 amu. Little to no difference in the molecular weight ranges of these fractions were shown by the LVMS spectra of Figure 8. This result was in contrast to the results given above for the EDS recycle solvents derived from coals of similar rank. There was, however an increased concentration of compounds which were of the series including the masses of 208 and 222 amu in the PAH fraction of the heavy fuel oil derived from the Wyodak coal as compared to the Illinois No. 6 coal-derived material. This result was comparable to the results acheived for the EDS recycle solvents derived from similar coals. A key to possible structure identifications to those masses given in Figure 8 is given in Table A-1 of Appendix A.

Nitrogen-Containing Polycyclic Aromatic Compound NPAC Fractions

The major components of the NPAC fractions isolated from the EDS recycle solvents were carbazole and its alkylated derivatives, regardless of the rank of coal from which they were derived. HRGC chromatograms of the NPAC fractions isolated from the EDS recycle solvents from the processing of Illinois No. 6 and Wyoming coals and Texas lignite are shown in Figure 9 (top, middle, and bottom, respectively). Qualitatively, the components analyzed in each of these fractions were similar to each other. Increased concentrations of lower molecular weight components were evident in the NPAC fractions isolated from the lower rank Wyoming coal and Texas lignite-derived recycle solvents as compared to the Illinois No. 6 coal-derived recycle solvent, however.

The quantitative values are given in Table 8 for selected components in the NPAC fractions isolated from the EDS recycle solvents derived from the various ranks of coal. The highest concentrations of carbazole (a three-ringed compound) were found in the fractions derived from the Wyoming coal and the Texas Lignite. The highest concentration of benzo[c]carbazole (a four-ringed compound) was found in the fraction derived from the higher rank Illinois No. 6 coal.

The LVMS spectra of the NPAC fractions isolated from the EDS recycle solvents complement the HRGC data (see Figure 10). The molecular weight profile of the recycle solvent NPAC fraction derived from the Illinois No. 6 coal (top) was of a slightly higher molecular weight

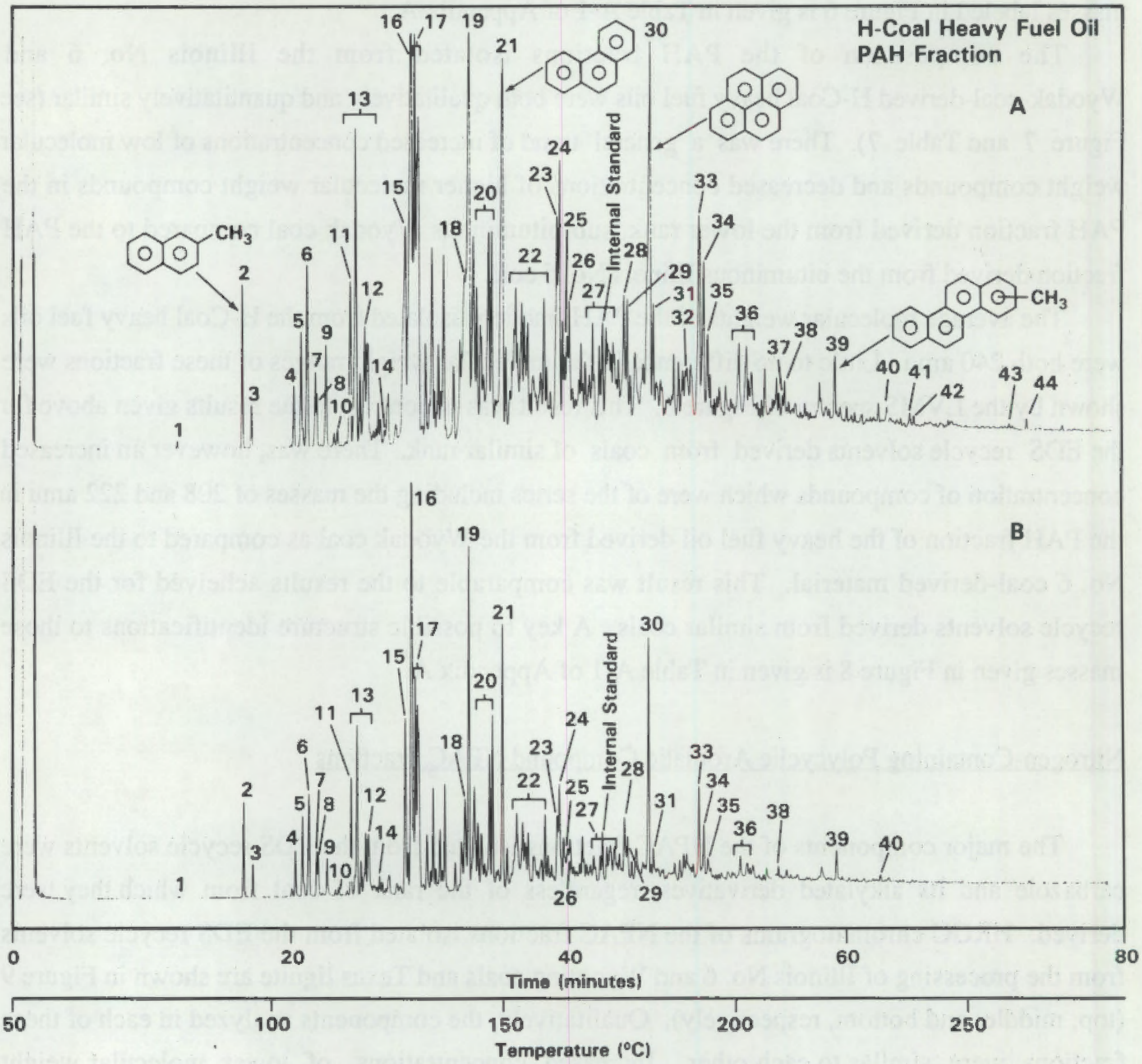

Figure 7. High-Resolution Gas Chromatograms of the PAH Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyodak-Derived Material. See Text for Conditions. Peaks Numbered Refer to Compounds Identified in Table 7.

---

range than either fractions of the EDS recycle solvents derived from the Wyoming coal (middle) or the Texas Lignite (bottom). The average molecular weight of the NPAC fractions were calculated to be 250, 240 and 240 amu for the EDS recycle solvents derived from the bituminous coal, sub-bituminous coal, and lignite. For a key to possible stucture identifications of the masses given in Figure 10, see Table A-2 in Appendix A.

TABLE 7. Concentrations of Selected Components in the PAH Fractions Isolated from the H- Coal Heavy Fuel Oils Derived from Different Ranks of Coal

			Concentration, Parts Per Thousand (mg/g) PAH Fractions; Sample; Coal Rank	
Peak No.[a]	Mol. Wt.	Compound[b]	5226-118 Illinois No. 6	5226-119 Wyodak
1	128	Naphthalene	0.251 ± 0.030	0.146 ± 0.051
2	142	2-Methylnaphthalene	5.10 ± 0.36	5.47 ± 1.40
3	142	1-Methylnaphthalene	1.26 ± 0.10	1.87 ± 0.49
4	154	Biphenyl	2.69 ± 0.20	3.44 ± 0.86
5	156	2-Ethylnaphthalene	5.75 ± 0.38	6.68 ± 1.69
6	156	2,6- or 2,7-Dimethylnaphthalene	9.97 ± 0.61	9.09 ± 2.28
7	156	1,7-Dimethylnaphthalene	3.17 ± 0.27	3.71 ± 1.22
8	156	1,3- or 1,6-Dimethylnaphthalene	1.69 ± 0.01	2.37 ± 0.50
9	156	1,4- or 2,3-Dimethylnaphthalene	ND[c]	ND
10	156	1,2-Dimethylnaphthalene	ND	ND
11	154	Acenaphthene	8.29 ± 0.46	8.76 ± 2.3
12	168	Dibenzofuran	7.84 ± 1.17	8.05 ± 1.63
13	170	C_3-Naphthalenes	ND	ND
14	170	2,3,6-Trimethylnaphthalene	ND	ND
15	166	Fluorene	20.7 ± 2.1	15.2 ± 1.8
16	168	1,2-Dihydrophenalene	47.8 ± 1.6	46.6 ± 0.5
17	168	Dihydrofluorenes[d]	55.6 ± 2.3	42.5 ± 0.9
18	180	2-Methylfluorene	ND	ND
19	180,182	1-Methylfluorene, C_1-Dihydrophenalene, C_1-Dihydrofluorene	ND	ND
20	182	C_1-Dihydrophenalene/fluorene	ND	ND
21	178	Phenanthrene	29.6 ± 0.8	19.7 ± 1.2
22	194, 196	C_2-Fluorenes, C_2-Dihydrophenalenes/fluorenes	ND	ND
23	192	3-Methylphenanthrene	7.81 ± 0.39	3.37 ± 0.17
24	192	2-Methylphenanthrene	11.3 ± 0.6	7.75 ± 0.39
25	192	4- or 9-Methylphenanthrene	3.31 ± 1.0	2.05 ± 0.27
26	192	1-Methylphenanthrene	6.38 ± 2.73	4.68 ± 0.11
27	206	C_2-Phenanthrenes	ND	ND
28	204	Dihydrofluoranthene	6.72 ± 0.78	6.44 ± 0.16
29	202	Fluoranthene	3.99 ± 0.36	3.40 ± 0.47
30	202	Pyrene	24.5 ± 5.5	19.3 ± 3.1
31	204	Dihydropyrene	ND	ND
32	216	Benzo[a]fluorene	ND	ND
33	216	Benzo[b]fluorene, 4- or 6-Methylchrysene	11.3 ± 0.5	6.50 ± 0.83
34	218	C_1-Phenylnaphthalene	6.63 ± 0.05	4.22 ± 0.46
35	216	1-Methylpyrene	3.66 ± 0.47	2.78 ± 0.21
36	230	C_1-Pyrenes/fluoranthenes	ND	ND
37	228	Benz[a]anthracene	ND	0.184 ± 0.032
38	228	Chrysene	0.304 ± 0.103	0.064 ± 0.001
39	242	4- or 6-Methylchrysene	1.78 ± 0.20	1.57 ± 0.21
40	252	Benzo[j or b]fluoranthene	0.333 ± 0.020	0.293 ± 0.039

TABLE 7. (Continued)

Peak No.[a]	Mol. Wt.	Compound[b]	Concentration, Parts Per Thousand (mg/g) PAH Fractions; Sample; Coal Rank 5226-118 Illinois No. 6	 5226-119 Wyodak
41	252	Benzo[e]pyrene	0.389 ± 0.118	0.224 ± 0.067
42	252	Benzo[a]pyrene	0.294 ± 0.057	0.116 ± 0.048
43	276	Indeno[1,2,3-cd]pyrene	0.096 ± 0.010	0.056 ± 0.011
44	276	Benzo[ghi]perylene	0.319 ± 0.049	0.313 ± 0.063

---

[a] Numbers refer to peaks labeled in Figure 7
[b] Tentative identifications based on GC/MS and retention information
[c] No data or none detected
[d] Composite of two peaks

The components were also similar to each other in the NPAC fractions isolated from the H-Coal heavy fuel oils derived from either the bituminous and sub-bituminous coals, as was the case with the EDS recycle solvents derived from different ranks of coal. The HRGC chromatograms of the H-Coal NPAC fractions are shown in Figure 11 with corresponding identifications and quantification of selected components given in Table 9. Carbazole and its alkylated species were the major components of both NPAC fractions. Increased concentrations of heavier molecular weight components were present in the fraction isolated from the material derived from the higher rank Illinois No. 6 coal as compared to the material derived from the lower rank Wyodak coal, as has been the case for majority of the chemical class fractions isolated.

The LVMS spectra showed a molecular weight shift of approximately 10 amu between the NPAC fractions isolated from the H-Coal heavy fuel oils derived from the two different ranks of coal, with the fraction isolated from the Illinois No. 6-derived material having increased concentrations of heavier molecular weight species and decreased concentrations of lower molecular weight species as compared to the fraction isolated from the Wyodak-derived material (see Figure 12). The average molecular weights of the NPAC fractions were 240 and 230 amu for the NPAC fractions isolated from the H-Coal heavy fuel oils derived from the Illinois No. 6 and Wyodak coals, respectively. Possible structures for the molecular ions in Figure 12 are given in Table A-2 of Appendix A.

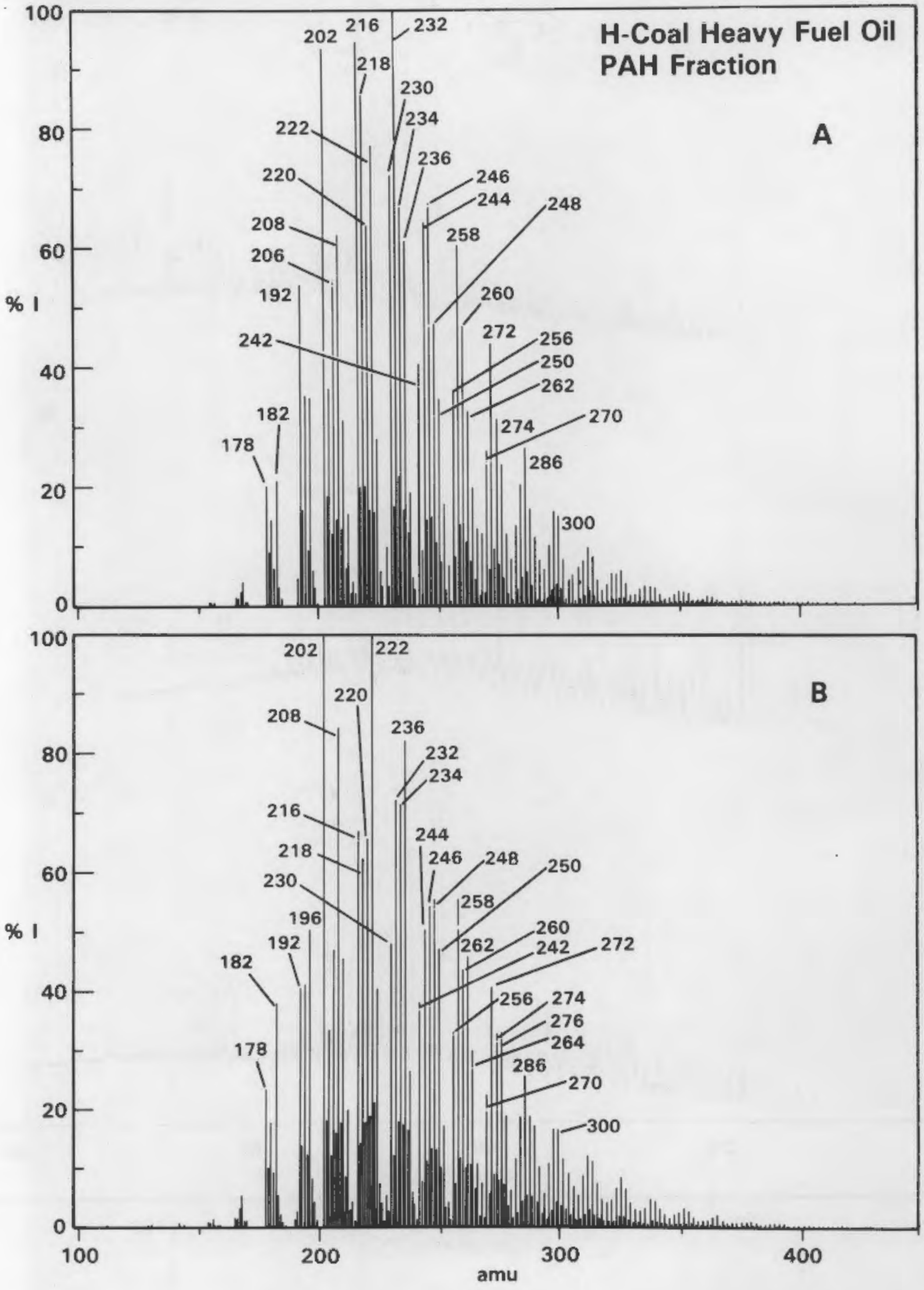

Figure 8. Low-Voltage Mass Spectra of the PAH Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming-Derived Material. See text for Conditions. See Table A-1 in Appendix A for a Key to Mass Identifications.

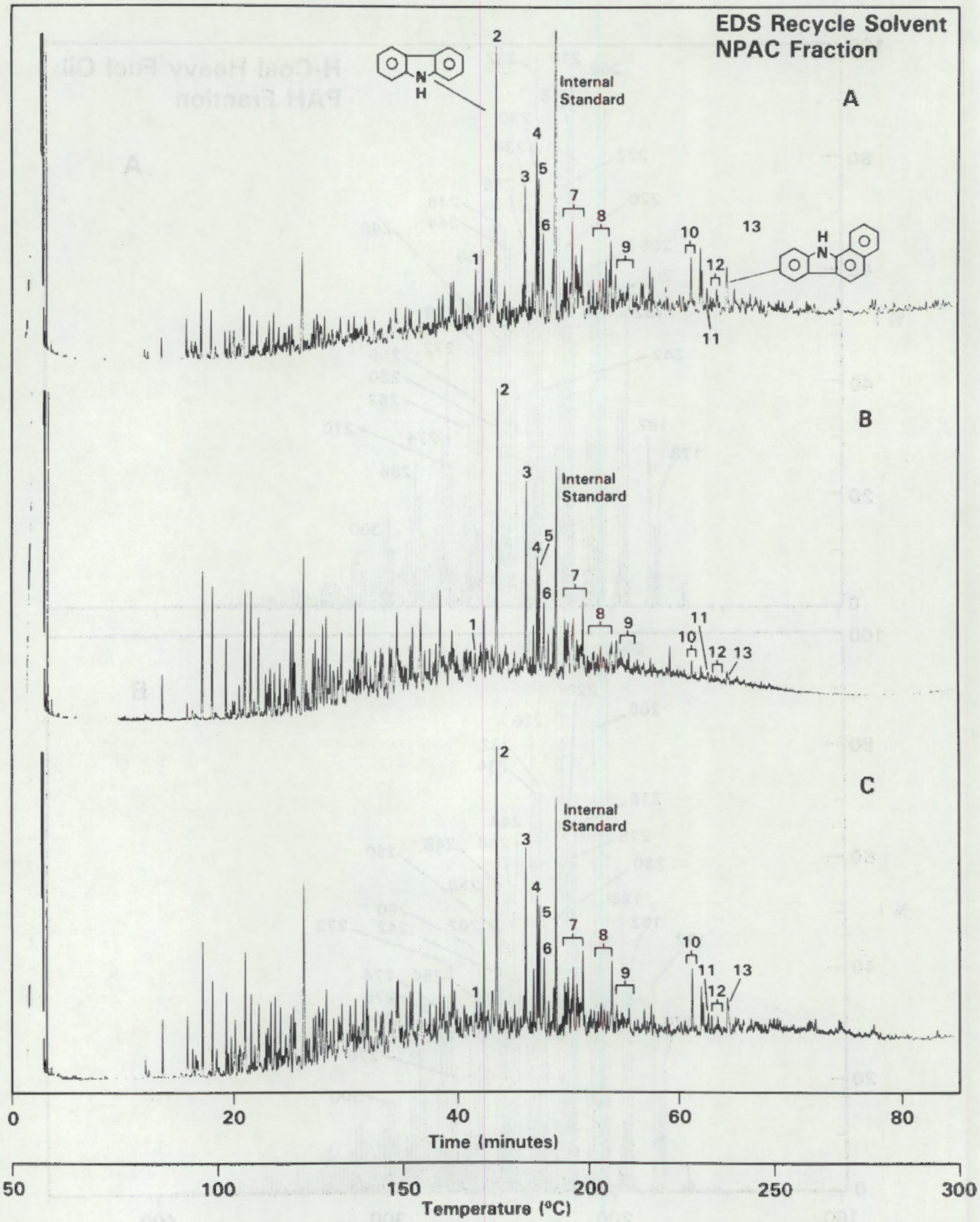

Figure 9. High-Resolution Gas Chromatograms of the NPAC Fractions Isolated from the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions. Peaks Numbered Refer to Compounds Identified in Table 8.

TABLE 8. Concentrations of Selected Components in the NPAC Fractions Isolated from the EDS Recycle Solvents Derived from Different Coal Ranks

			Concentration, Parts per Thousand (mg/g) NPAC Fractions; Sample; Coal Rank		
Peak No.[a]	Mol. Wt.	Compound[b]	5226-003 Illinois No. 6	5226-107 Wyoming	5226-108 Texas Lignite
1	210	C_6-Indole	ND[c]	ND	ND
2	167	Carbazole	5.94 ± 0.94	7.65 ± 0.04	7.56 ± 0.15
3	181	1-Methylcarbazole	2.27 ± 0.38	4.64 ± 0.19	3.50 ± 0.13
4	181	3-Methylcarbazole	3.80 ± 0.25	3.09 ± 0.12	3.19 ± 0.21
5	181	2-Methylcarbazole	2.74 ± 0.21	2.43 ± 0.16	2.65 ± 0.32
6	181	4-Methylcarbazole	2.92 ± 0.37	1.83 ± 0.65	1.90 ± 0.367
7	195	C_2-Carbazoles	ND	ND	ND
8	209	C_3-Carbazoles	ND	ND	ND
9	223	C_4-Carbazoles	ND	ND	ND
10	221	C_3-Azaphenanthrenes	ND	ND	ND
11	217	Benzo[a]carbazole	0.900 ± 0.190	ND	0.474 ± 0.317
12	235	C_4-Azaphenanthrenes	ND	ND	ND
13	217	Benzo[c]carbazole	2.46 ± 0.51	0.408[d]	1.18 ± 1.13

---

[a] Numbers refer to peaks labeled in Figure 9
[b] Tentative identification based on GC/MS and retention information
[c] No data or none detected
[d] One determination only

Hydroxy-PAH Fractions

The LVMS spectra from the analyses of the hydroxy-PAH fractions isolated from the EDS recycle solvents from the bottoms recycle mode of operation using different ranks of coal are shown in Figure 13. The profiles of the recycle solvents hydroxy-PAH fractions were quite similar to each other regardless of the coal which was processed, indicating similar components were present in the hydroxy-PAH fractions of the EDS material derived from the processing of Illinois No. 6 and Wyoming coals as well as the Texas lignite. The molecular weight range of the hydroxy-PAH fraction isolated from the recycle solvent derived from the bituminous coal was approximately 10 amu higher than those isolated from the recycle solvents derived from the sub-bituminous coal or the lignite. The average molecular weights of the hydroxy-PAH fractions were 250, 240, and 240 amu, respectively, for the fractions isolated from the Illinois No. 6 coal, the Wyoming (Wyodak) coal, and the Texas lignite-derived materials. These results

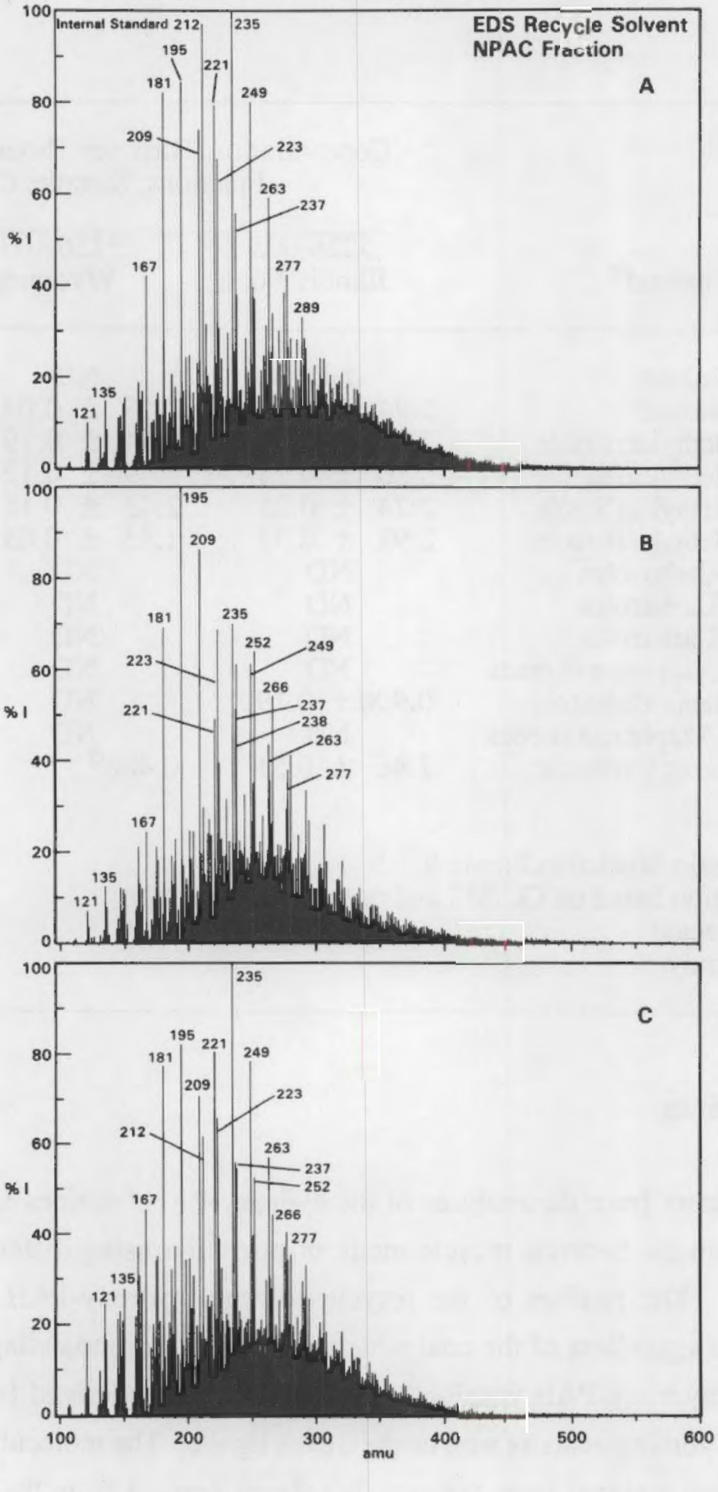

Figure 10. Low-Voltage Mass Spectra of the NPAC Fractions Isolated from the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions. See Table A-2 in Appendix A for a Key to Mass Identifications.

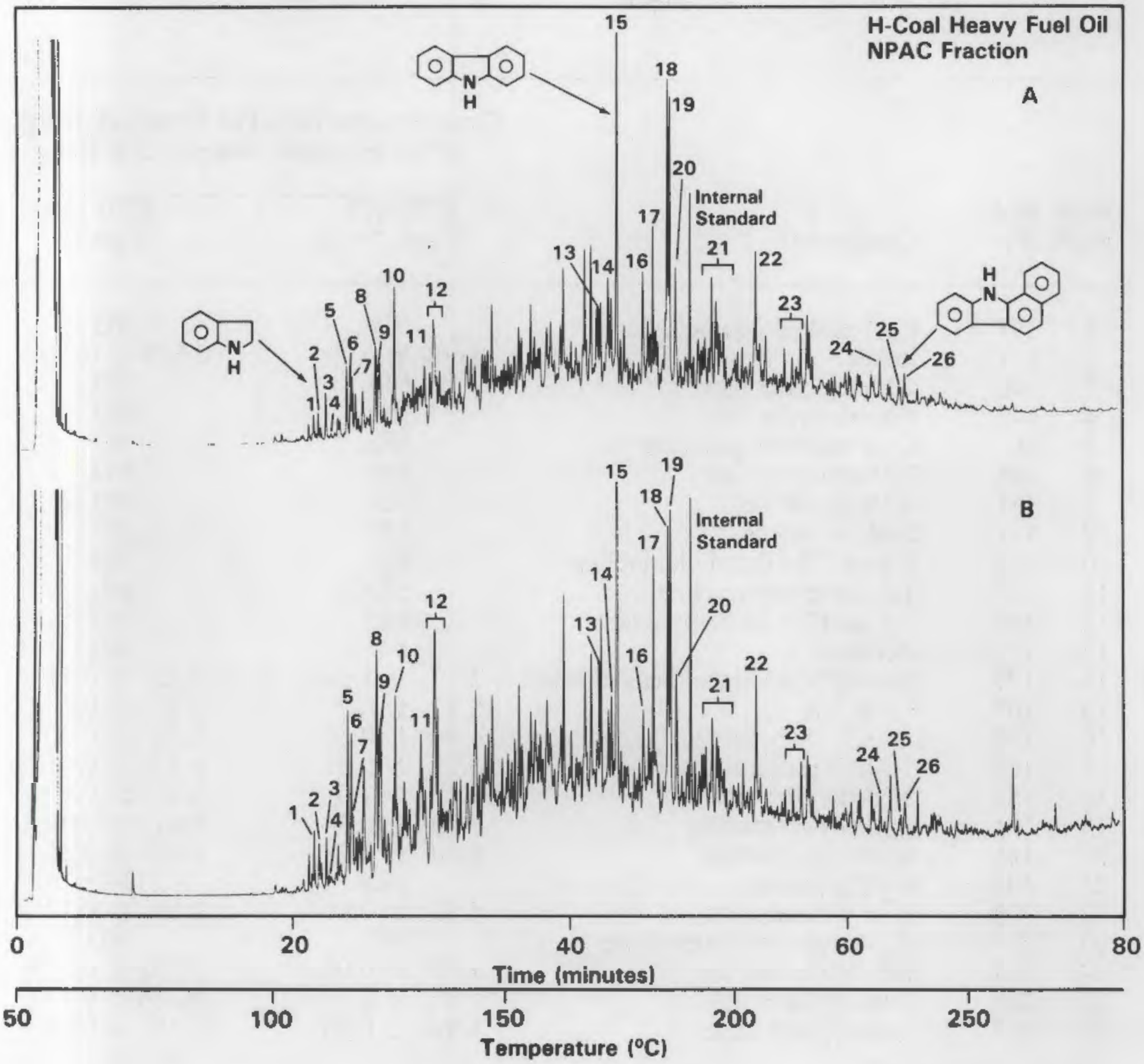

Figure 11. High-Resolution Gas Chromatograms of the NPAC Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyodak-Derived Material. See Text for Conditions. Peaks Numbered Refer to Compounds Identified in Table 9.

---

were consitent with the majority of the LVMS results which indicated that the material derived from the bituminous coal was of a generally higher molecular weight range than the materials derived from the lower rank sub-bituminous coal or lignite. For a key to possible structure identifications of the masses given in Figure 13, see Table A-3 in Appendix A.

TABLE 9. Concentrations of Selected Components in the NPAC Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Coal Ranks

			Concentration, Parts Per Thousand (mg/g) NPAC Fractions; Sample; Coal Rank	
Peak No.[a]	Mol. Wt.	Compound[b]	5226-118 Illinois No. 6	5226-119 Wyodak
1	147	C_1-Tetrahydroquinoline	ND[c]	ND
2	117	Indole	0.669 ± 0.097	0.810 ± 0.028
3	143	2-Methylquinoline	ND	ND
4	143	8-Methylquinoline	ND	ND
5	161	C_2-Tetrahydroquinoline	ND	ND
6	143	7-Methylquinoline	ND	ND
8	131	3-Methylindole	ND	ND
9	131	2-Methylindole	ND	ND
10	157	2,6- or 2,7-Dimethylquinoline	ND	ND
11	157	1,2-Dimethylquinoline	ND	ND
12	145	2,3- and 2,5-Dimethylindole	ND	ND
13	179	Acridine	ND	ND
14	179	Benzo[f]quinoline, Phenanthridine	2.32 ± 1.34	1.15 ± 0.11
15	167	Carbazole	15.3 ± 0.7	13.2 ± 0.6
16	193	2- or 3-Methylbenzo[f]quinoline	4.46 ± 0.59	2.53 ± 0.30
17	181	1-Methylcarbazole	3.99 ± 0.87	4.17 ± 0.51
18	181	3-Methylcarbazole	11.1 ± 1.0	5.57 ± 0.29
19	181	2-Methylcarbazole	8.20 ± 0.54	5.21 ± 0.35
20	181	4-Methylcarbazole	4.20 ± 0.21	2.75 ± 0.36
21	195	C_2-Carbazoles	ND	ND
22	203	1- or 4-Azapyrene	4.93 ± 0.46	2.86 ± 0.12
23	217	C_1-Azapyrene/fluoranthene	ND	ND
24	217	Benzo[a]carbazole	1.69 ± 0.04	0.892 ± 0.076
25	217	Benzo[b]carbazole	1.36 ± 0.10	0.286 ± 0.173
26	217	Benzo[c]carbazole	1.94 ± 0.09	1.19 ± 0.21

---

[a] Numbers refer to peaks labeled in Figure 11
[b] Tentative identifications based on GC/MS and retention information
[c] No data or none detected

The hydroxy-PAH fraction isolated from the H-Coal heavy fuel oil derived from the Illinois No. 6 coal also showed an increased molecular weight range than did the material derived from the Wyodak coal when analyzed by LVMS (see Figure 14). The average molecular weights of the heavy fuel oils were calculated to be 240 and 230 amu for the bituminous-derived and sub-bituminous-derived hydroxy-PAH fractions, respectively. Table A-3 in Appendix A gives a key to possible structure identifications of the masses shown in Figure 14.

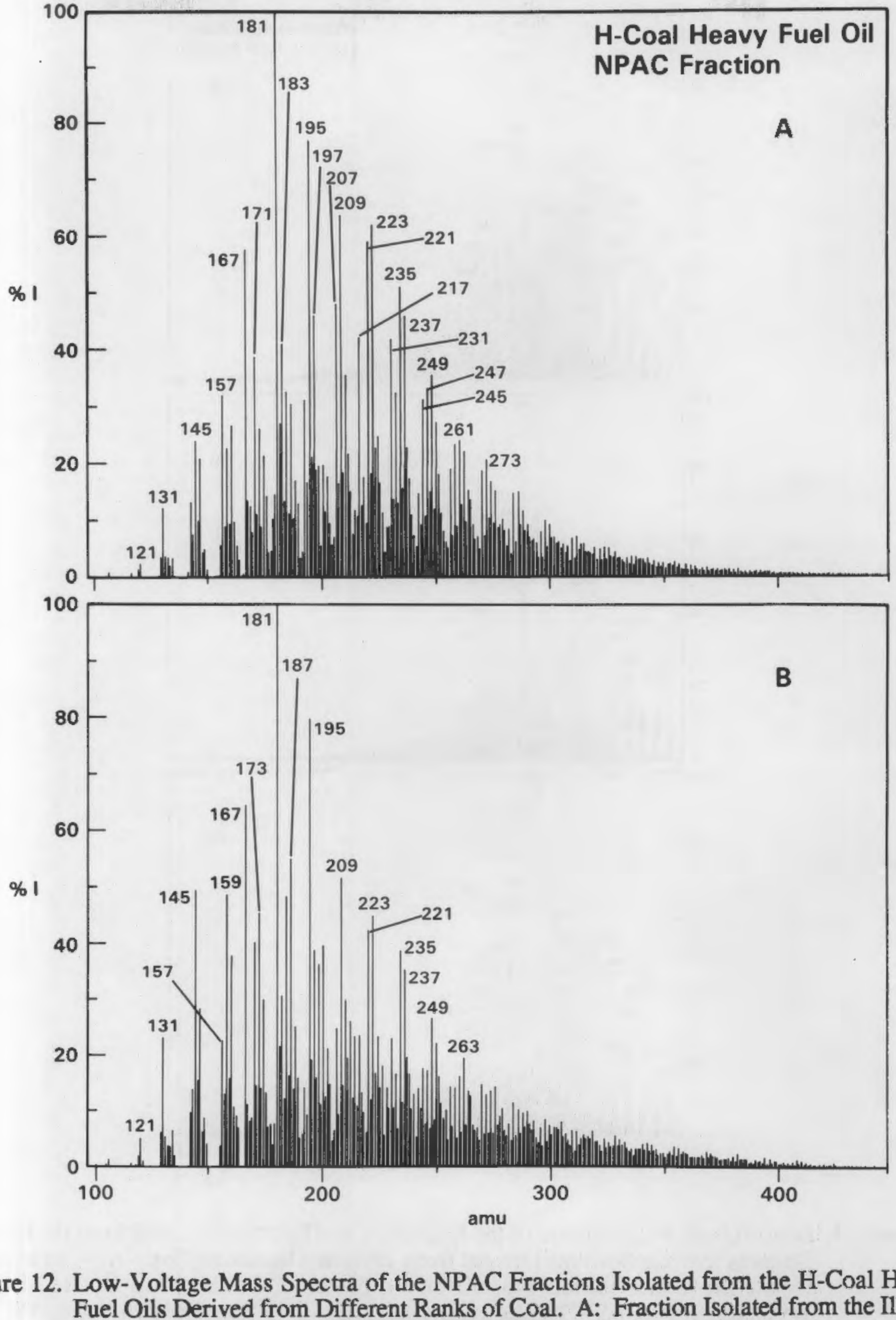

Figure 12. Low-Voltage Mass Spectra of the NPAC Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6 -Derived Material; C: Fraction Isolated from the Wyodak-Derived Material. See Text for Conditions. See Table A-2 in Appendix A for a Key to Mass Identifications.

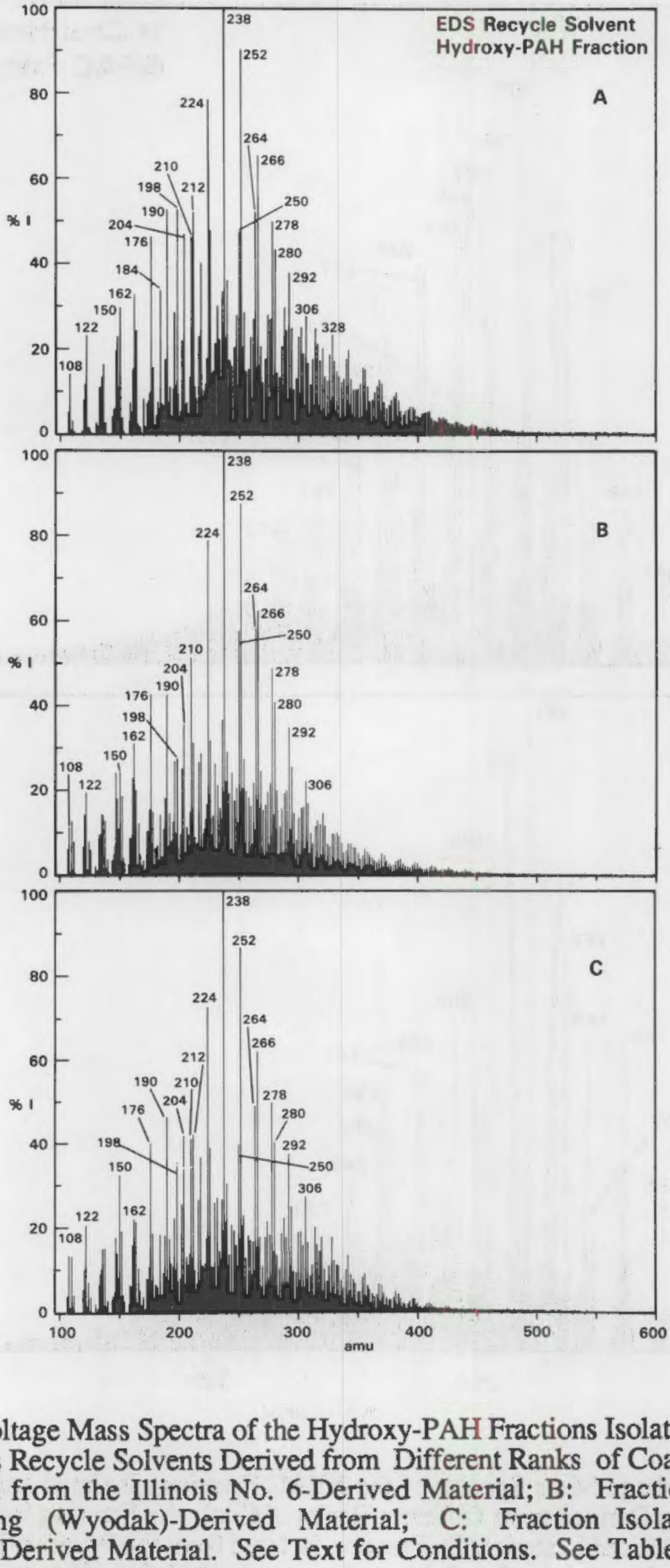

Figure 13. Low-Voltage Mass Spectra of the Hydroxy-PAH Fractions Isolated from the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. A: Fraction Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyoming (Wyodak)-Derived Material; C: Fraction Isolated from the Texas Lignite-Derived Material. See Text for Conditions. See Table A-3 in Appendix A for a Key to Mass Identifications.

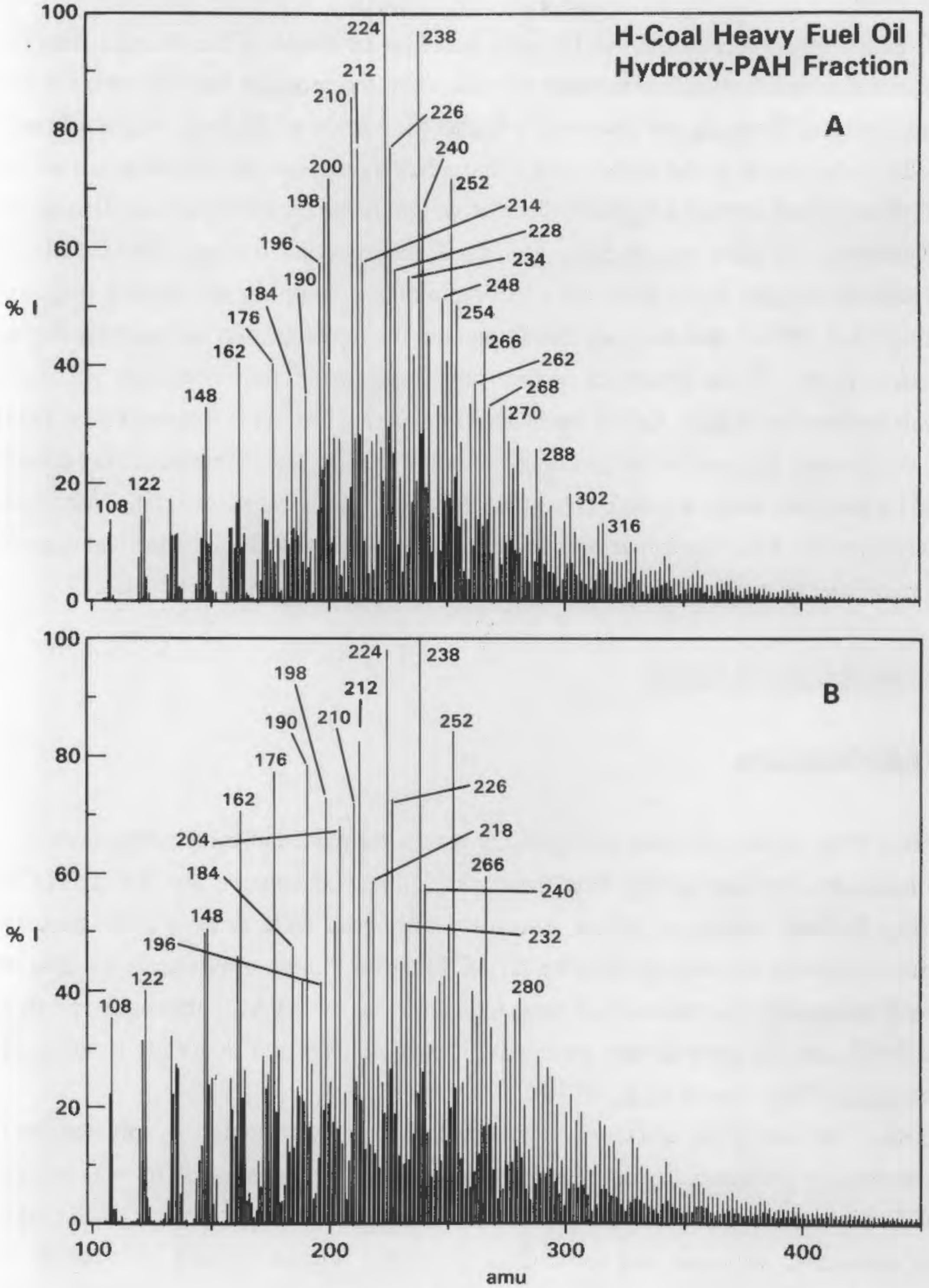

Figure 14. Low-Voltage Mass Spectra of the Hydroxy-PAH Fractions Isolated from the H-Coal Heavy Fuel Oils Derived from Different Ranks of Coal. A: Fractions Isolated from the Illinois No. 6-Derived Material; B: Fraction Isolated from the Wyodak-Derived Material. See Text of Conditions. See Table A-3 in Appendix A for a Key to Mass Identifications.

Summary

The following observations can be made based on the results of the chemical analyses of the coal liquids derived from different ranks of coal: first, the products derived from the lower rank Wyodak coal and Texas lignite contained a higher proportion of aliphatic hydrocarbons than did the products derived from the higher rank Illinois No. 6 coal; second, the materials derived from the bituminous coal were of a higher molecular weight range (generally about 10 amu) than their sub-bituminous or lignite counterparts; and, third, the materials derived from the Illinois No. 6 coal contained higher concentrations of components containing condensed ring structures, including PAH, NPAC, and hydroxy-PAH, than did the materials derived from the Wyodak coal or Texas Lignite. These observations are consistent with the structures of the organic materials in these coal ranks. Of the feeds used in these studies, the bituminous coal had the most highly condensed, aromatic structure, and the lignite had the least amount of ring condensation. Figure 15 presents some average structures for the various ranks of coal. The coal liquids produced from the sub-bituminous coal and lignite showed many similar chemical characteristics, which may have been a function of the mines from which the materials originated.

TOXICOLOGICAL TESTING

Microbial Mutagenicity

Table 10 gives the microbial mutagenicity results for the chemical class fractions isolated by alumina column chromatography from the three EDS recycle solvents and the two H-Coal heavy fuels oils. In those materials where mutagenic responses were detected, the majority of the mutagenic response was expressed in the NPAC fractions. These results are consistent with other microbial mutagenicity results which have indicated that the NPAC compounds, particularly the amino-PAH, are the determinant mutagens in coal liquefaction materials (Later et al., 1983; Wilson et al., 1980; Guerin et al., 1980).

Little to no mutagenic activity was detected in the EDS recycle solvents derived from the Wyodak coal or the Texas lignite. However, significant mutagenic activity was detected in the NPAC fraction of the EDS recycle solvent derived from the Illinois No. 6 coal. Significantly greater mutagenic response was detected in the NPAC fraction isolated from the H-Coal heavy fuel oil derived from the Illinois No. 6 coal compared to the same fraction isolated from the H-Coal heavy fuel oil derived from the Wyodak coal. These results indicated that an increased microbial mutagenic activity was detected in the materials derived from the higher rank versus the lower rank coals. Chemical analyses results showed that the Illinois No. 6 coal produced

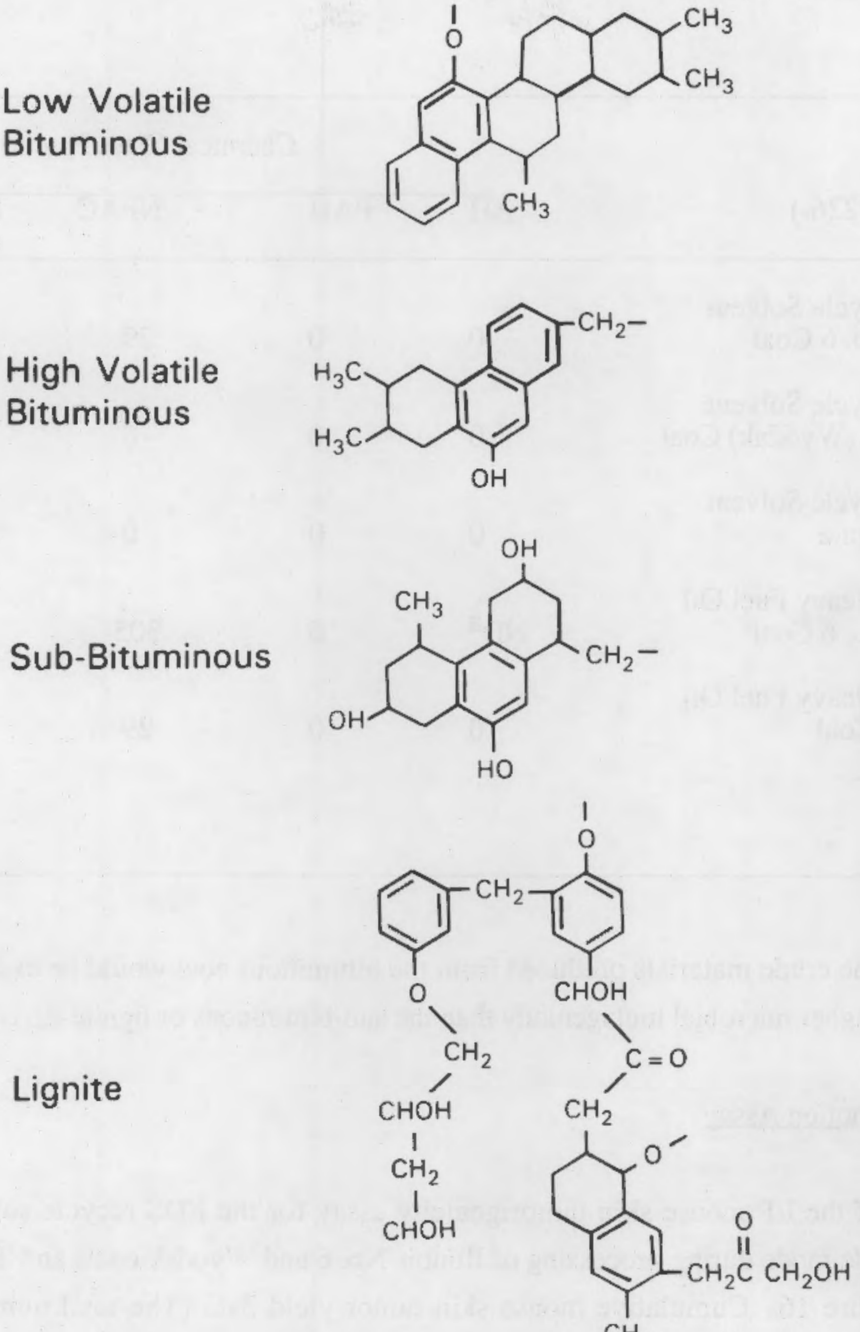

Figure 15. Average Structures for Different Ranks of Coal. (Wender et al., 1975)

---

materials with higher NPAC compositions than did either the Wyodak coal or the Texas lignite. The microbial mutagenicity results indicated that the NPAC fractions isolated from the Illinois No. 6 coal expressed increased activity as compared to the lower rank coals. These two results

TABLE 10. Microbial Mutagenicity Results (revertants/µg) of Coal Liquefaction Materials Derived from Different Coal Types

Sample (5226-)	Chemical Class Fraction AH	 PAH	 NPAC	 Hydroxy-PAH
003, EDS Recycle Solvent Illinois No. 6 Coal	0	0	29	0
107, EDS Recycle Solvent Wyoming (Wyodak) Coal	0	0	0	0
108, EDS Recycle Solvent Texas Lignite	0	0	0	0
118, H-Coal Heavy Fuel Oil Illinois No. 6 Coal	ND[a]	0	305	3
119, H-Coal Heavy Fuel Oil Wyodak Coal	0	0	29	0

[a]No data

indicate that the crude materials produced from the bituminous coal would be expected to have a significantly higher microbial mutagenicity than the sub-bituminous or lignite-derived materials.

Initiation/Promotion Assay

Results of the I/P mouse skin tumorigenicity assay for the EDS recycle solvents from the bottoms recycle mode during processing of Illinois No. 6 and Wyodak coals and Texas lignite are shown in Figure 16. Cumulative mouse skin-tumor yield data (The total number of tumors, nomalized to a population of 30 mice) indicated a general trend of increasing tumor initiating activity with increasing rank of coal processed. The 25-mg dose of the recycle solvent from the Illinois No. 6 coal produced a mean number of tumors per mouse of 1.0, while the recycle solvents from the Wyodak coal and the Texas lignite produced mean number of tumors per mouse of 0.7 and 0.5, respectively. The percent tumor incidence was also higher for the Illinois No. 6 coal as compared to the Wyodak coal or the Texas lignite.

The results of increasing tumor initiating activity with increasing rank of coal was consistent with the chemical analyses results that showed the EDS recycle solvent from the Illinois No. 6 coal had increased PAH content, decreased AH content, and an increased molecular weight

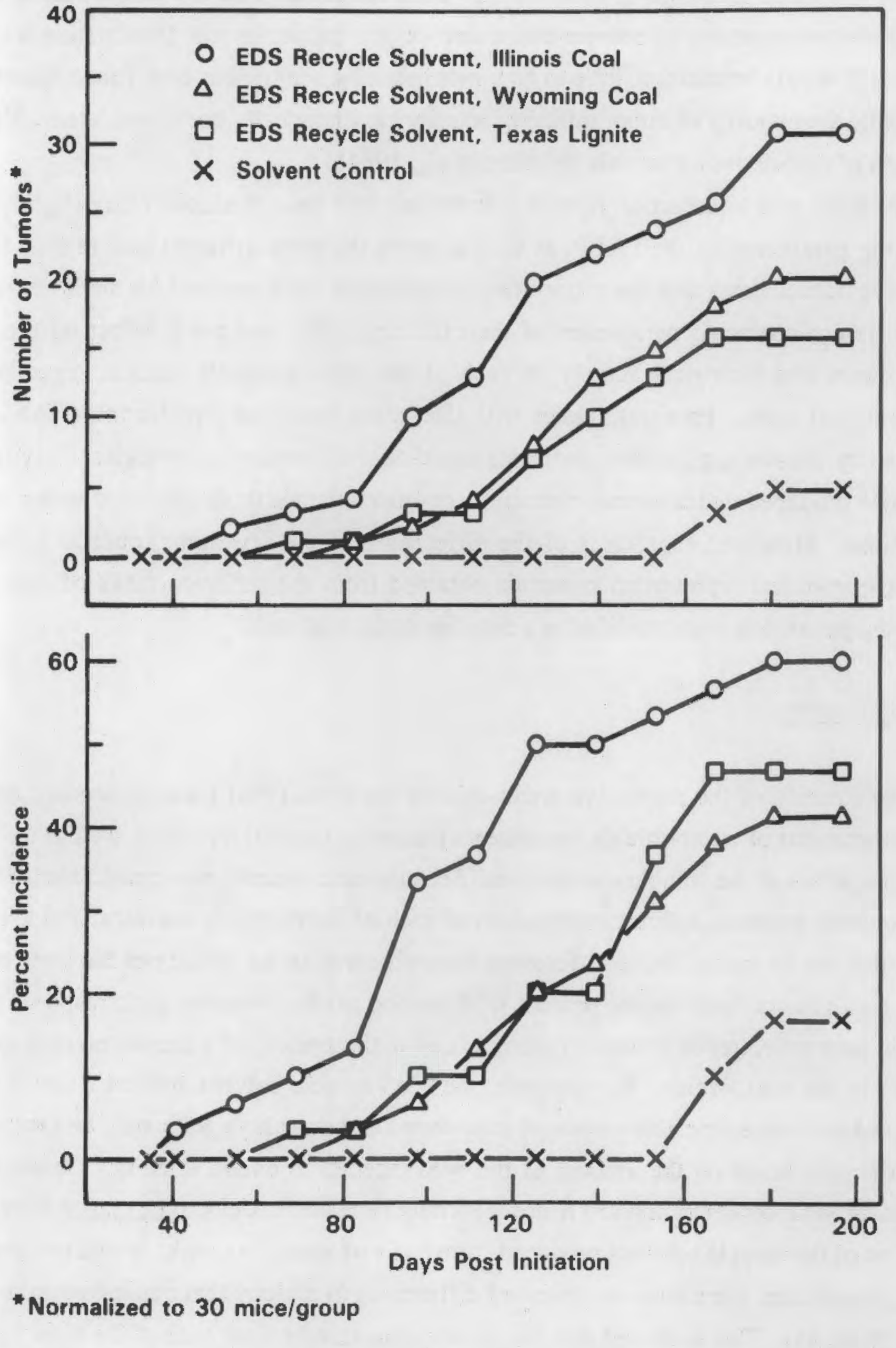

Figure 16. Initiation/Promotion Mouse Skin Tumorigenicity Results for the EDS Bottoms Recycle Solvents Derived from Different Ranks of Coal. Top: Total Number of Tumors per Mouse Data Normalized to Groups of 30 Mice. Bottom: Percent Incidence.

distribution as compared to the recycle solvents derived from the Wyoming coal and the Texas lignite. Increased tumorigenic potential has been correlated with increased boiling point and increased concentrations of heavier-molecular-weight species in coal liquefaction materials by Mahlum (1983b). In addition, little to no tumor initiating activity has been found associated with AH, while the majority of tumor initiating activity has historically been associated with the PAH fractions of coal-derived materials (Mahlum et al., 1984).

The EDS coal liquefaction recycle solvents studied were produced using slightly different operating parameters of the ECLP, as well as using the three different coal ranks. In general, shorter residence times and lower operating temperatures were required for the lower rank coals. The different operating parameters of the ECLP probably had some effect on the chemical composition and biological activity of each of the three materials studied, regardless of the different coal ranks. Previous studies with integrated two-stage liquefaction (ITSL) materials reported by Wilson et al. (1984) indicated significant differences in biological activity between materials produced under normal operating conditions versus those produced under off-normal conditions. However, regardless of the differences in the operating conditions, the recycle solvents produced represented materials obtained from the different ranks of coal since the operating parameters were modified as a function of the coal rank.

Aquatic Toxicity

The toxicity of the respective water-soluble fractions (WSF) was dependent both on the relative amounts of water-soluble constituents present in the coal liquids as well as the collective toxic properties of the soluble constituents. Because each material was treated identically in this experimental protocol, a direct comparison of each of the materials chemical and toxicological properties can be made. Some differences were observed in the toxicity of the three WSF when LC_{50} results were based on the percent WSF needed to elicit an acute toxic response (see Table 11). In each case, trends in toxicity were related to the amount of water-extractable consituents present in the coal liquids. For example, the EDS recycle solvent derived from Texas lignite contained the least extractable carbon of those tested and was also significantly less toxic when the endpoint was based on the amount of the WSF needed to obtain toxicity. General trends of increasing WSF concentration and hence, generally increased toxicity to D. magna were noted as a function of the recycle solvents produced from coals of increasing rank. Based on concentration of TC in solution, there were no observed differences in toxicity that could be attributed to coal type (Table 11). This indicated that the soluble constituents from each of the three EDS recycle solvents were similar in toxicity. Previous studies with coal liquids of similar characteristics have also indicated a causal relationship between toxicity of parent material and presence of water-soluble components (Dauble et al., 1983; Later, 1985; Wright et al., 1985).

TABLE 11. Solubility, Inherent Toxicity and Acute Hazard to Daphnia magna of EDS Recycle Solvents (Bottoms Recycle Mode) Derived from Three Different Coals

Coal Rank	mg/L TC	48-Hour LC_{50}[a] mg/L TC	48-Hour LC_{50}[a] % WSF	N
Illinois No. 6	123 ± 41	6.4 ± 1.8	5.8 ± 2.5	5
Wyoming (Wyodak)	89 ± 12	6.7 ± 0.7	7.7 ± 1.7	3
Texas Lignite	58 ± 11	6.7 ± 1.1	13.1 ± 2.6[b]	4

[a] Values expressed as mean ± standard deviation of the mean
[b] Significantly different at $\alpha = 0.05$

The phenol composition of the WSF derived from the three EDS recycle solvents were compared since previous studies have shown that phenols usually comprised up to 90 percent of water-soluble chemical components in full-boiling-range coal liquids (Dauble et al., 1982, 1983). Other chemical constituents present in the WSF of coal liquids are the nitrogen bases, saturated hydrocarbons, aromatic hydrocarbons, and carboxylic acids (Wright et al., 1985, Thomas, 1984). The concentrations of these water-soluble components are generally significantly less than the phenols. For example, the total concentration of selected phenols in the WSF of a solvent refined coal (SRC) II product was 266 mg/ml; the total concentrations of selected nitrogen bases, saturated hydrocarbons, aromatic hydrocarbons, and carboxylic acids in the same WSF were 20 mg/ml, 0.18 µg/ml, 6.2 µg/ml, and 120 µg/ml, respectively (Thomas, 1984). The concentrations of the nitrogen bases, saturated and aromatic hydrocarbons, and carboxylic acids in the WSF of the EDS recycle solvents derived from the various ranks of coal were not determined based on these results.

Although the three EDS recycle solvents from the different ranks of coal differed in their water solubility, they showed similar overall composition of phenols to each other (see Table 12). Alkyl-substituted phenols of two to three carbon chain length were the major soluble components of each of the EDS materials, comprising from 69-77 percent of the total phenols for each of the three WSF. The amount of total carbon accounted for by the selected phenols in each WSF was directly related to coal rank. The lower concentration of water-soluble constituents and phenols from the relatively higher oxygen-containing lignite may be an effect of process conditions, or an effect of the type of oxygen linkages present in the original matrix (see Figure 15). It has been noted that sub-bituminous coals contain more oxygen ether linkages and that lignite contains more

TABLE 12. Concentrations (mg/L) of Phenols in Water-Soluble Fractions Derived from EDS Recycle Solvents Produced in the Bottoms Recycle Mode

	Coal Rank		
Compound	Illinois No. 6	Wyoming(Wyodak)	Texas Lignite
Phenol	1.00	0.36	0.46
Cresols	8.51	5.58	2.62
C_2-Phenols	42.40	34.81	12.77
C_3-Phenols	45.10	25.30	16.54
C_4-Phenols	13.26	7.37	5.05
C_5-Phenols	9.98	6.89	6.95
Indanols	9.01	4.51	3.56
C_1-Indanols	3.86	2.57	1.89
Total Phenols	131.12	87.39	49.84
%TC Accounted for by Phenols	85.8	81.2	68.3

oxygen ester linkages (Kwang E. Chung, Rockwell International, Thousand Oaks, CA, personal communication). Under process conditions, ether linkages may be expected to produce phenols, whereas ester linkages may not. Relative amounts of phenol and cresol in these WSF were substantially lower than were observed for similarly-derived WSF from the EDS recycle solvent material from the once-through recycle mode, and for other coal liquids with similar solubility characteristics, but produced under different operational conditions (Dauble et al., 1983; Later et al., 1985; Wright et al., 1985).

These studies indicated that feed coal selection may affect the toxicity of a material spilled into an aquatic environment. Observed differences with respect to the three EDS materials tested can be largely attributed to differences in relative amounts of extractable phenols present rather than the chemical composition of the WSF. The amount of material that went into solution, rather than the kinds of material in solution, dictated toxicity in this case. Potential differences in acute toxicity among the EDS recycle solvents derived from the different ranks of coal may be partly attributable to process conditions which were optimized for the specific characteristics of each of the coals.

REFERENCES

Ames, B. N., J. McCann, and E. Yamasaki. 1975. Methods for detecting carcinogens and mutagens with the Salmonella/mammalian-microsome mutagenicity test. Mutat. Res. 35: 247-364.

APHA (American Public Health Association). 1980. Standard Methods for the Examination of Water and Waste Water. 15th Edition. APHA-AWWA-WPCF, Washington, D. C.

Baughman, G. L. 1978. Synthetic Fuels Data Handbook, pp. 238-242. Cameron Engineers, Inc., Denver, CO.

Dauble, D. D., A. J. Scott, B. L. Thomas, and R. W. Hanf., Jr. 1983. Exotoxicity of Materials from Integrated Two-Stage Liquefaction and Exxon Donor Solvent Processes. PNL-4675, Pacific Northwest Laboratory, Richland, WA, NTIS, Springfield, VA.

Dauble, D. D., W. E. Fallon, R. H. Gray and R. M. Bean. 1982. Effects of coal liquid water-soluble fractions on growth and survival of four aquatic organisms. Arch. Environ. Contam. Toxicol. **11**: 553-560.

Later, D. W., B. W. Wilson, and M. L. Lee. 1985. Standardization of Alumina and Silica Adsorbents Used for Chemical Class Separations of Polycyclic Aromatic Compounds. Anal. Chem. 57: 2979-2984.

Later, D. W. 1985. Two-Stage Coal Liquefaction Process Materials from the Wilsonville Facility Operated in the Nonintegrated and Integrated Modes: Chemical Analyses and Biological Testing. PNL-5215, Pacific Northwest Laboratory, Richland, WA, NTIS, Springfild, VA.

Later, D. W., R. A. Pelroy, and B. W. Wilson. 1984. Chemical Analysis and Biological Testing of Materials from the EDS Coal Liquefaction Process: A Status Report. PNL-4960, Pacific Northwest Laboratory, Richland, WA, NTIS, Springfield, VA.

Later, D. W. and M. L. Lee. 1983. Chromatographic methods for the chemical and biological characterization of polycyclic aromatic compounds in synfuel materials, pp. 44-73. In: Advanced Techniqued in Synthetic Fuels Analysis, C. W. Wright, W. C. Weimer, and W. D. Felix (eds.). CONF-81160, NTIS, Springfield, VA.

Later, D. W., M. L. Lee, K. D. Bartle, R. C. Kong, and D. L. Vassilaros. 1981. Chemical class separation and characterization of organic compounds in synthetic fuels. Anal. Chem. **53**: 1612-1620.

Lee, M. L., D. L. Vassilaros, C. M. White, and M. Novotny. 1979. Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. Anal. Chem. **51**: 768-774.

Mahlum, D. D. 1983a. Initiation/promotion studies with coal-derived liquids. J. Appl. Toxicol. **3**: 31-34.

Mahlum, D. D. 1983b. Skin tumor initiation activity of coal liquids with different boiling-point ranges. J. Appl. Toxicol. 3: 31-34.

Mahlum, D. D., C. W. Wright, E. K. Chess, and B. W. Wilson. 1984. Fractionation of skin tumor initiating activity in coal liquids. Cancer Res. **44**: 5176-5181.

Thomas, B. L. 1984. Determination of Oil/Water and Octanol/Water Distribution Coefficients from Aqueous Solutions from Four Fossil Fuels. PNL-5002, Pacific Northwerst Laboratory, Richland, WA. NTIS, Springfield, VA.

Ullrich, D. O. and R. E. Millemann. 1983. Survival, respiration, and food assimilation of Daphnia magna exposed to petroleum and coal-derived oils at three temperatures. Can., J. Fish. Aquat. Sci. **40**: 17-26.

Vassilaros, D. L., R. C. Kong, D. W. Later, and M. L. Lee. 1982. Linear retention index system for polycyclic aromatic compounds: Critical evaluation and additional indices. J. Chromatogr. **252**: 1-20.

Wender, et al. 1975. ACS Div. Fuel Preprint. **20.**

Wilson, B. W., D. W. Later, C. W. Wright, and D. L. Stewart. 1985. Chemical Analysis and Mutational Assay of Distilled Oils from the H-Coal Direct Liquefaction Process: A Status Report. PNL-5288, Pacific Northwest Laboratory, Richland, WA, NTIS, Springfield, VA.

Wilson, B. W., R. A. Pelroy, D. D. Mahlum, M. E. Frazier, D. W. Later, and C. W. Wright. 1984. Comparative Chemical Composition and Biological Activity of Single- and Two-Stage Coal Liquefaction Process Streams. FUEL 63: 46-55.

Wright, C. W., D. W. Later, D.D. Dauble, and B. W. Wilson. 1985. Fractionally Distilled SRC-I, SRC-II, EDS, H-Coal and ITSL Direct Coal Liquefaction Process Materials: A Comparative Summary of Chemical Analysis and Biological Testing. PNL-5528, Pacific Northwest Laboratory, Richland, WA, NTIS, Springfield, VA.

Wozniak, T. J. and R. A. Hites. 1983. Separation of hydroaromatic compounds in synfuels by picric acid columns. Anal. Chem. 55: 1791-1796.

APPENDIX A: KEY TO MASS IDENTIFICATIONS OF LVMS SPECTRA

TABLE A-1. Key to Low-Voltage Mass Spectra of PAH Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Benzene	78	92	106	120	134	148	162	176	190	204	218	232
Indene	116	130	144	158	172	186	200	214	228	242	256	270
Indane	118	132	146	160	174	188	202	216	230	244	258	272
Naphthalene	128	142	156	170	184	198	212	226	240	254	268	282
Acenaphthalene	152	166	180	194	208	222	236	250	264	278	292	306
Biphenyl/ Acenaphthene	154	168	182	196	210	224	238	252	266	280	294	308
Fluorene/Phenalene	166	180	194	208	222	236	250	264	278	292	306	320
Phenanthrene	178	192	206	220	234	248	262	276	290	304	318	332
Cyclopenta[def]phenanthrene	190	204	218	232	246	260	274	288	302	316	330	344
Pyrene/Fluoranthene	202	216	230	244	258	272	286	300	314	328	342	356
Phenylnaphthalene	204	218	232	246	260	274	288	302	316	330	344	358
Benzofluorene	216	230	244	258	272	286	300	314	328	342	356	370
Cyclopenta[cd]pyrene/Benzo[ghi]fluoranthene	226	240	254	268	282	296	310	324	338	352	366	380
Chrysene/Benzo[a]anthracene	228	242	256	270	284	298	312	326	340	354	368	382
Cyclopentachrysenes/Benzo[a]anthracenes	240	254	268	282	296	310	324	338	352	366	380	394
Phenylfluorene	242	256	270	284	298	312	326	340	354	368	382	396
Benzopyrenes/ Benzofluoranthenes	252	266	280	294	308	322	336	350	364	37B	392	406
Binaphthyls	254	268	282	296	310	324	338	352	366	380	394	408
Cyclopentabenzopyrenes	264	278	292	306	320	334	348	362	376	390	404	418
Dibenzofluorenes	266	280	294	308	322	336	350	364	378	392	406	420
Indenopyrenes/ Cyclopentachrysenes	276	290	304	318	332	346	360	374	388	402	416	430
Dibenzanthracenes/Phenanthrenes	278	292	306	320	334	348	362	376	390	404	418	432

---

[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures. Furthermore, several of the mass assignments can be attributed directly to hydroaromatic species of the PAH. Increments of two mass units for dihydro-PAH species, four mass units for tetrahydro-PAH species, etc. can be used to provide a key for the hydroaromatic compounds.

TABLE A-2. Key to Low-Voltage Mass Spectra of NPAC Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Pyridine	79	93	107	121	135	149	163	177	191	205	219	233
Indole	117	131	145	159	173	187	201	215	229	243	257	271
Quinoline/Isoquinoline	129	143	157	171	185	199	213	227	241	255	269	283
Azaacenaphthalene	153	167	181	195	209	223	237	251	265	279	293	307
Azaacenaphthene/ Azabiphenyls	155	169	183	197	211	225	239	253	267	281	295	309
Carbazole	167	181	195	209	223	237	251	265	279	293	307	321
Benzoquinolines	179	193	207	221	235	249	263	277	291	305	319	333
Benzo[def]carbazole	191	205	219	233	247	261	275	289	303	317	331	345
Azapyrene/Azafluoranthene	203	217	231	245	259	273	287	301	315	329	343	357
Azaphenylnaphthalene	205	219	233	247	261	275	289	303	317	331	345	359
Benzocarbazoles	217	231	245	259	273	287	301	315	329	343	357	371
Azabenzo[ghi]-fluoranthene/ Azacyclopentapyrene	227	241	255	269	283	297	311	325	339	353	367	381
Azachrysenes/Azabenzanthracenes	229	243	257	271	285	299	313	327	341	355	369	383
Azacyclopentachrysene	241	255	269	283	297	311	325	339	353	367	381	395
Azabenzopyrenes/ Azabenzofluoranthenes	253	267	281	295	309	323	337	351	365	379	393	407
Azabinaphthyls	255	269	283	297	311	325	339	353	367	381	395	409
Azacyclopentabenzopyrenes	265	279	293	307	321	335	349	363	377	391	405	419
Dibenzocarbazoles	267	281	295	309	323	337	351	365	379	395	407	421
Azaindenopyrenes	277	291	305	319	333	347	361	375	389	403	417	431

---

[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures. Only pyrrolic and pyridinic NPAC have been considered. Hydro-substituted NPAC were also present in most A_3 fractions and appropriate masses can be determined by addition of two mass units to the parent PAH molecular weight for dihydro-substitution, four mass units for tetrahydro-substitution, etc.

TABLE A-3. Key to Low-Voltage Mass Spectra of Hydroxy-PAH Fractions. Nominal Masses for Alkylated Homologous Series.

Compound[a]	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Phenol	94	108	122	136	150	164	178	192	206	220	234	248
Indenols	132	146	160	174	188	202	216	230	244	258	272	286
Indanols	134	148	162	176	190	204	218	232	246	260	274	288
Naphthols	144	158	172	186	200	214	228	242	256	270	284	298
Acenaphthylenols	168	182	196	210	224	238	252	266	280	294	308	322
Hydroxybiphenyls/ Acenaphthenols	170	184	198	212	226	240	254	268	282	296	310	324
Hydroxyfluorenes	182	196	210	224	238	252	266	280	294	308	322	336
Hydroxyphenanthrenes/Anthracenes	194	208	222	236	250	264	278	292	306	320	334	348
Hydroxycyclopentaphenanthrenes	206	220	234	248	262	276	290	304	318	332	346	360
Hydroxypyrenes/ Fluoranthenes	218	232	246	260	274	288	302	316	330	344	358	372
Hydroxyphenylnaphthalenes	220	234	248	262	276	290	304	318	332	346	360	374
Hydroxybenzofluorenes	232	246	260	274	288	302	316	330	344	358	372	386
Hydroxyindenopyrenes	242	256	270	284	298	312	326	340	354	368	382	396
Hydroxychrysenes/ Benzanthracenes	244	258	272	286	300	314	328	342	356	370	384	398
Hydroxycyclopentachrysenes	256	270	284	298	312	326	340	354	368	382	396	410
Hydroxyphenylfluorenes	258	272	286	300	314	328	342	356	370	384	398	412
Hydroxybenzopyrenes/Benzofluoranthenes	268	282	296	310	324	338	352	366	380	394	408	422
Hydroxybinaphthyls	270	284	298	312	326	340	354	368	382	396	410	424
Hydroxycyclopentabenzopyrenes	280	294	308	322	336	350	364	378	392	406	420	434
Hydroxydibenzofluorenes	282	296	310	324	338	352	366	380	394	408	422	436
Hydroxyindenopyrenes	292	306	320	334	348	362	376	390	404	418	432	446
Hydroxybenzochrysenes	294	308	322	336	350	364	378	392	406	420	434	448

---

[a] In most cases, only selected isomers are given. The MS data merely provide assistance in determining isomer groups, rather than identifying precise molecular structures.

DISTRIBUTION

Offsite

E. L. Alpen
Lawrence Berkeley Laboratory
University of California
Building 90, Room 2056
No. 1 Cyclotron Road
Berkeley, CA 94720

L. D. Attaway
1005 A Street
Suite 405
San Rafael, CA 94901

N. F. Barr
ER-73, GTN
U. S. Department of Energy
Washington, DC 20545

J. Batchelor
FE-43, GTN
U. S. Department of Energy
Washington, DC 20545

H. L. Bergman
University of Wyoming
Laramie, WY 82071

R. W. Biles
Exxon Corporation
Research and Environmental Health
Division
Medical Department
P. O. Box 235
East Millstone, NJ 08873

V. P. Bond
Brookhaven National Laboratory
Upton, Long Island, NY 11973

R. G. Boykin
Catalytic, Inc.
P. O. Drawer 239
Wilsonville, AL 35186

A. Brink
SASOL Technology (Proprietary), Ltd.
57 Commissioner Street
P. O. Box 5486
Johannesburg 2000
Republic of South Africa

P. H. Buhl (2)
FE-34, GTN
U. S. Department of Energy
Washington, DC 20545

H. H. Bulkowski
Catalytic, Inc.
Centre Square West
1500 Market Street
Philadelphia, PA 19102

F. P. Burke
Conoco Coal Development Co.
4000 Brownsville Road
Library, PA 15129

J. A. Carroll, Capt., USA
Medical Bioengineering R&D Laboratory
Ft. Detrick, MD 21701

C. E. Carter, Deputy Scientific Director
National Institute of Environmental
Health Sciences
P. O. Box 12233
Research Triangle Park, NC 27709

C. T. Chen
OSHA
U. S. Department of Labor
200 Constitution Avenue NW
Washington, DC 20210

P. Cho
ER-73, GTN
U. S. Department of Energy
Washington, DC 20545

A. G. Comolli
Hydrocarbon Research, Inc.
P. O. Box 6047
Laurenceville, NJ 08648

K. E. Cowser
The Maxima Corporation
107 Union Valley Road
Oak Ridge, TN 37830

DOE Public Document Room (2)
Attn: Mr. R. A. Evans
Room G-298, Federal Building
P. O. Box E
Oak Ridge, TN 37830

DOE Public Reading Room (2)
Room G-208
Oak Ridge Federal Building
Oak Ridge, TN 37830

DOE Public Reading Room (2)
Room GA-142
Forrestal Building
1000 Independence Avenue SW
Washington, DC 20585

DOE Public Reading Room, FOI (2)
Room IE-180, Forrestal Building
1000 Independence Avenue SW
Washington, DC 20585

DOE Technical Information Center (30)

J. V. Dorrigan
ER-75, GTN
U. S. Department of Energy
Washington, DC 20545

B. Z. Drozdowicz
Air Products and Chemicals, Inc.
P. O. Box 538
Allentown, PA 18105

H. Drucker
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

C. Drummond
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

A. P. Duhamel (2)
ER-74, GTN
U. S. Department of Energy
Washington, DC 20545

M. J. Eaman
Concord Scientific Corporation
220 Laurier Avenue West
4th Floor
Ottawa, Ontario, K1P-5Z9
Canada

H. Enoch
Kentucky Department of Energy
P. O. Box 11888
Lexington, KY 40578

J. L. Epler
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

J. P. Fillo
Environmental Research and
Technology, Inc.
601 Grant Street
Porter Building, 10th Floor
Pittsburgh, PA 15219

L. Fradkin
572 Terrace Avenue, Apt. 2
Cincinnati, OH 45220

M. R. J. Fry
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

R. Fry
FE-40, GTN
U. S. Department of Energy
Washington, DC 20545

K. Frye
FE-40, GTN
U. S. Department of Energy
Washington, DC 20545

A. A. Galli
U. S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

M. Gatti
Ente Natzionale per l'Energia
Elettrica
G. B. Martini 3
00100 Rome
Italy

C. W. Gehrs
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

H. Gerstenkorn
Ruhrkohle Oel und Gas GMBH
Geiwitzer Platz 3
4250 Bottropp
Federal Republic of Germany

J. M. Giddings
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

G. F. Goethel
Veba Oel Ag
Postfach 45
4660 Gelsenkirchen-Buer
Federal Republic of Germany

L. Goldberg
Chemical Industrial Institute of
Toxicology
2109 Nancy Ann Drive
Raleigh, NC 27607

G. Goldstein
ER-74, GTN
U. S. Department of Energy
Washington, DC 20545

J. R.Gough
Catalytic, Inc.
P. O. Box 239
Wilsonville, AL 35186

J. Gray
Ashland Synthetic Fuels, Inc.
P. O. Box 391
Ashland, KY 41101

M. D. Gray
NCB (Coal Products), Ltd.
Coal House, Lyon Road
Harrow, HA1 2EX
England

M. Green
The Lummus Company
1515 Broad Street
Bloomfield, NJ 07003

R. A. Griesemer
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

M. R. Guerin
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37380

R. M. Hamilton
FE-43, GTN
U. S. Department of Energy
Washington, DC 20545

L. Headley
Morgantown Energy Technology Center
Morgantown, WV 26505

R. Henderson
Lovelace Inhalation Toxicology
Research Institute
P. O. Box 5890
Albuquerque, NM 87115

R. Hill
Ashland Synthetic Fuels, Inc.
P. O. Box 391
Ashland, KY 41101

C. H. Hobbs
Lovelace Inhalation Toxicology
Research Institute
P. O. Box 5890
Albuquerque, NM 87115

J. M. Holland
The Upjohn Company
Kalamazoo, MI 49001

H. L. Hollister
PE-20, FORR
U. S. Department of Energy
Washington, DC 20585

G. R. Holt
ARCO Coal Company
1860 North Lincoln Street
P. O. Box 5300
Denver, CO 80217

H. Hosang
VEBA OEL AG
Postfach 45
4660 Gelsenkirchen-Buer
Federal Republic of Germany

W. Hubis
4031 South Magnolia Way
Denver, CO 80237

E. L. Huffman
Southern Company Services, Inc.
P. O. Box 2625
Birmingham, AL 35202

S. Ikeda
Japan Coal Liquefaction Development
Co., Ltd.
Rm. 1115, Shuwa Kioi-Cho TBR Bldg.
No. 7, Kojimachi 5-chome,
Chiyoda-Ku, Tokyo 102
Japan

T. W. Johnson
Southern Company Services, Inc.
c/o Catalytic, Inc.
P. O. Drawer 239
Wilsonville, AL 35186

W. S. Jones
FE-43, GTN
U. S. Department of Energy
Washington, DC 20545

J. S. Kane, Deputy Director
Office of Energy Research
ER-2, FORSTL
U. S. Department of Energy
Washington, DC 20585

C. M. Kelly
Air Products and Chemicals, Inc.
Corporate Research and Development
P. O. Box 538
Allentown, PA 18001

S. C. Lewis
Exxon Corporation
Research and Environmental
Health Division
Medical Department
P. O. Box 235
East Millston, NJ 08873

A. W. Maki
Exxon Corporation
Research and Environmental
Health Division
P. O. Box 235
East Millstone, NJ 08873

M. J. Massey
Environmental Research and
Technology, Inc.
696 Virginia Road
Concord, MA 01742

H. McCammon
ER-75, GTN
U. S. Department of Energy
Washington, DC 20545

R. O. McClellan
Lovelace Inhalation Toxicology
Research Institute
P. O. Box 5890
Albuquerque, NM 87115

R. E. McKee
Exxon Corporation
Research and Environmental
Health Division
P. O. Box 235
East Millstone, NJ 08873

P. M. Mehrle
Columbia National Fisheries
Research Laboratory
Route 1
Columbia, MO 65201

M. L. Mendelsohn
Lawrence Livermore Laboratory
University of California
P. O. Box 808
Livermore, CA 94550

J. A. Meyer
Chevron Research Company
P. O. Box 1627
Richmond, CA 94802

L. Miller
FE-42, GTN
U. S. Department of Energy
Washington, DC 20545

M. L. Minthorn
ER-72, GTN
U. S. Department of Energy
Washington, DC 20545

E. C. Moroni
FE-43, GTN
U. S. Department of Energy
Washington, DC 20545

S. C. Morris
Brookhaven National Laboratory
Building 475
Upton, NY 11973

N. B. Munro
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37831

David Gray
The Mitre Corp.
1820 Dolly Madison Blvd.
McLean, VA 22102

J. Norwood
International Coal Refining Co.
P. O. Box 2752
Allentown, PA 18001

M. Parmenter
Kerr-McGee Corporation
Kerr-McGee Center
Packaging and Labeling Dept.
Oklahoma City, OK 73125

R. M. Perhac
Electric Power Research Institute
P. O. Box 10412
Palo Alto, CA 93404

W. Piver
National Institute of Environmental
Health Sciences
P. O. Box 12233
Research Triangle Park, NC 27709

J. D. Potts
Cities Service Resarch and
Development Co.
Box 3908
Tulsa, OK 74102

C. A. Reilly
ER-72, GTN
U. S. Department of Energy
Washington, DC 20545

H. Retcofsky
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

D. E. Rhodes
Kerr-McGee Corporation
P. O. Box 035
Crescent, OK 73028

W. J. Rhodes (2)
Industrial Environmental
Research Laboratory
MD-61, US EPA
Research Triangle Park, NC 27711

C. R. Richmond
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

J. S. Robertson
ER-73, GTN
U. S. Department of Energy
Washington, DC 20545

T. C. Ruppel
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

R. Santore
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

M. Schulman
ER-70, GTN
U. S. Department of Energy
Washington, DC 20545

A. G. Sharkey
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

A. Shepard
American Petroleum Institute
2101 L Street, NW
Washington, DC 20037

D. A. Smith
ER-72, GTN
U. S. Department of Energy
Washington, DC 20545

V. G. Stamoudis
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

R. J. Stern
PE-25, FORSTL
U. S. Department of Energy
Washington, DC 20585

J. Stetter
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

J. A. Strasser
Atlantic Coal Institute
P. O. Box 1133
Sydney, Nova Scotia
Canada BIP 6J7

G. Styles
Southern Company Services, Inc.
P. O. Box 2625
Birmingham, AL 35202

R. F. Sullivan
Chevron Resarch Company
P. O. Box 1627
Richmond, CA 94802

J. W. Thiessen, Deputy Associate
Director
Office of Health and Environmental
Research
ER-71, GTN
U. S. Department of Energy
Washington, DC 20545

G. G. Thurlow
National Coal Board
Coal Research Establishment
Stoke Orchard
Cheltenham, Glos. GL52 4RZ
England

R. V. Trense
Exxon Corporation
Environmental Affairs Programs
Exxon Resarch and Engineering Co.
P. O. Box 101
Florham Park, NH 07932

A. W. Trivelpiece, Director (3)
Office of Energy Research
ER-1, FORSTL
U. S. Department of Energy
Washington, DC 20585

A. Uzzell
Chevron Research Co.
P. O. Box 7141
San Francisco, CA 94120-7141

G. K. Vick
Exxon Research and Engineering Co.
Route 22 East
Annandale, NJ 08801

W. Wallace
National Institute for Occupational
Safety and Health
Room 117
944 Chestnut Ridge Road
Morgantown, WV 26504

P. Walsh
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

P. Wambach
PE-241, GTN
U. S. Department of Energy
Washington, DC 20585

W. H. Weber
EPRI
c/o Catalytic, Inc.
P. O. Drawer 239
Wilsonville, AL 35186

K. Wilzbach
Argonne National Laboratory
9800 South Cass Avenue
Argonne, IL 60439

F. J. Wobber
U. S. Department of Energy
14 Goshen Ct.
Gaithersburg, MD 20879

R. W. Wood
ER-74, GTN
U. S. Department of Energy
Washington, DC 20545

A. F. Yen
International Coal Refining Co.
P. O. Box 2752
Allentown, PA 18001

ONSITE

DOE Richland Operations Office

K. W. Bracken

Pacific Northwest Laboratory (57)

R. L. Aaberg
W. J. Bair
R. M. Bean
D. A. Cataldo
D. B. Cearlock
E. K. Chess
D. D. Dauble
D. W. Dragnich
M. E. Frazier
R. H. Gray (10)
P. L. Hackett
D. R. Kalkwarf
B. J. Kelman
D. D. Mahlum
S. Marks
R. P. Marshall
P. J. Mellinger
R. A. Miller
J. E. Morris
O. R. Moss
T. L. Page
J. F. Park
R. A. Pelroy
R. W. Perkins
H. A. Ragan
R. A. Renne
R. G. Riley
L. B. Sasser
R. P. Schneider
M. R. Sikov
D. S. Sklarew
L. G. Smith
D. L. Springer
J. A. Strand
D. L. Stewart
T. A. Toste
W. C. Weimer
R. E. Wildung
B. W. Wilson
C. W. Wright
Bilogy Publications Office
Technical Information (5)
Publishing Coordination (2)