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Chemical Analysis and Biological Testing of Materials from the EDS Coal Liquefaction Process: A Status Report

D. W. Later
R. A. Pelroy
B. W. Wilson

May 1984

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

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FOREWORD

This document reports the results from chemical and biological analyses of process materials collected during the operation of the EDS pilot plant in Baytown, TX. In particular, mutagenicity and carcinogenicity assays, integrated with chromatographic and mass spectrometric methods, were employed to achieve a detailed, comparative chemical and biological assessment of several representative EDS process materials. The EDS coal liquefaction process, developed and operated by Exxon Research and Engineering Company, received major support and funding from a number of organizations, including the U.S. Department of Energy, Office of Fossil Energy.

To provide perspectives, the results obtained for the EDS process materials are frequently compared with those from tests of other direct coal liquefaction materials from the solvent refined coal (SRC) I and II processes. The studies presented in this status report were carried out by investigators in the Department of Biology and Chemistry at Pacific Northwest Laboratory. Individual contributors are listed below.

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LIST OF ABBREVIATIONS

A_1 = aliphatic hydrocarbon alumina column fraction
A_2 = neutral PAH alumina column fraction
A_3 = N-PAC alumina column fraction
A_4 = hydroxy-PAH alumina column fraction
amino-PAH = amino-polycyclic aromatic hydrocarbon(s)
amu = atomic mass unit

bp = boiling point

cm^{-1} = reciprocal centimeters (wave numbers); used for Infrared spectrophotometry

°F = degrees Fahrenheit
DNA = deoxyribonucleic acid
DOE = U.S. Department of Energy

ECD = electron capture detector
ECLP = EDS Coal Liquefaction Pilot Plant

FID = flame ionization detector

g = grams
GC = gas chromatography
GC/MS = gas chromatography/mass spectrometry

HD = heavy distillate
HPLC = high performance liquid chromatography

I/P = Initiation/promotion (mouse skin tumorigenicity assay)
IR = Infrared spectrophotometry
ITSL = integrated two stage liquefaction

m = meter
μg = micrograms
ml = milliliters
μl = microliters
mm = millimeter
MS = mass spectrometry
m/z = mass to charge ratio

N-PAC = nitrogen-containing polycyclic aromatic compounds

PAC = polycyclic aromatic compound(s)
PAH = polycyclic aromatic hydrocarbon(s)
PASH = polycyclic aromatic sulfur heterocycle(s)
PMA = phorbol myristate acetate
PNL = Pacific Northwest Laboratory
ppm = parts per million
ppt = parts per thousand
PS = process solvent

rev/μg	= revertant colonies detected per microgram of test material in microbial mutagenicity assay
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
TA100	= designation for strain of Salmonella typhimurium used in microbial mutagenicity assay
TSL	= two stage liquefaction
UV	= Ultraviolet spectrophotometry
VGO	= vacuum gas oil

EXECUTIVE SUMMARY

Representative process materials were obtained from the EDS pilot plant for chemical and biological analyses. Unlike the solvent refined coal (SRC) processes, the EDS process configuration included an "in-stream" hydrogenation unit. Samples were collected during both the "once-through" and "bottoms recycle" process solvent (PS) production modes. Furthermore, a set of samples was obtained by fractionally distilling a 60/40 blend of raw naphtha and PS. Distillate cuts were obtained for every 50°F increment from 150 to 800°F; the 800°+F cut contained the distillation bottoms. These materials were characterized for biological activity and chemical composition using a microbial mutagenicity assay and chromatographic and mass spectrometric analytical techniques.

The two highest boiling distillation cuts, as well as PS obtained from the bottoms recycle mode operation, were tested for initiation of mouse skin tumorigenicity. All three materials were active; the crude 800°+F cut was substantially more potent than the crude bottoms recycle PS or 750-800°F distillate cut.

Results from chemical analyses showed the EDS materials, in general, to be more highly alkylated and have higher hydroaromatic content than analogous SRC II materials (no "in-line" process hydrogenation) used for comparison. Concentrations of nitrogen-containing polycyclic aromatic compounds (N-PAC) were relatively lower in the EDS materials and were primarily pyrrolic-type compounds such as carbazole, benzocarbazole and alkylated homologues. The reduced N-PAC levels included lower amino-polycyclic aromatic hydrocarbon (amino-PAH) concentrations, and generally a concomitant reduction in microbial mutagenic activity against *Salmonella typhimurium*, TA98.

The PS materials from the once-through production mode were generally of lower average molecular weight, higher aliphatic content, and lower N-PAC content than those from the bottoms recycle mode. This difference was due primarily to the fact that, during the bottoms recycle operation, the distillation range of the PS was increased to include higher boiling material.

In the microbial mutagenicity assays the N-PAC fractions showed greater activity than did the aliphatic hydrocarbon, hydroxy-PAH, or PAH fractions, although mutagenicity was detected in certain PAH fractions by a modified version of the standard microbial mutagenicity assay. Mutagenic activities for the EDS materials were lower, overall, than those for the corresponding materials from the SRC II process. For the crude distillate cut materials, mutagenic activity increased monotonically with increasing distillation temperature. A similar trend was observed for the N-PAC chemical class fractions of the distillate cuts. However, for the PAH isolates, the 650-700°F cut showed more activity than either the 700-750°F or the 750-800°F distillate cuts. The PAH fractions from the four highest boiling distillate cut materials were further separated by high performance liquid chromatography (HPLC). The HPLC subfractions were subjected to microbial mutagenicity assays, as well as further chemical analysis. Results from the microbial mutagenicity testing of HPLC subfractions revealed that substantial masking of mutagenic activity was occurring as a result of matrix effects in the neutral PAH fractions from some of the higher boiling distillate cut materials.

The EDS materials produced under different operational modes had distinguishable differences in both their chemical constituency and biological activity. The primary differences between the EDS materials studied here and their SRC II counterparts used for comparison are most likely attributable to the incorporation of catalytic hydrogenation in the EDS process.

INTRODUCTION

The EDS program objective of developing a direct coal liquefaction process to a state of commercial readiness for commercial application when warranted by economics has been achieved for a broad range of coals. The EDS development program was funded by the U.S. Department of Energy (DOE) and private industry sponsors and employed an integrated approach to the development and scale-up of the technology. This included not only the design, construction and operation of a 250-ton-per-day pilot plant, but also a continuing program of laboratory and bench-scale research, engineering design and economic studies, product quality studies, and environmental studies. The environmental studies focused on control of plant emissions, waste treatment, occupational health, and toxicity of coal liquefaction products.

In general, coal-derived products have been associated with adverse health effects to a greater degree than have analogous petroleum-based materials (1-10). As a component of the overall coal liquefaction program, DOE and process developers have cooperated in efforts to define potential health effects and industrial hygiene concerns as coal utilization technologies develop. Samples of EDS process-derived materials have been supplied by Exxon for evaluation in extramural programs sponsored by the Office of Health and Environmental Research and the Office of Fossil Energy, DOE. The investigations described in this report were performed as part of that effort.

The EDS process is distinguished from other modern, direct coal liquefaction processes by the use of a distilled, catalytically hydrogenated recycle solvent. The EDS design allows a high degree of flexibility in feed coal, process configuration and product slate selection. Since market trend projections in 1981 showed a decreasing demand for heavy-end products and in-

creasing demand for middle distillates, process development has recently focused on production of the latter materials.

The EDS process has been successfully operated in two basic modes. The first distillate recycle mode was the "once-through" or "coal only" mode. In this mode, the process solvent (PS) is distilled, hydrogenated light vacuum gas oil (VGO), which is recycled to the front end of the process for coal slurry. In the second, or bottoms recycle mode, vacuum bottoms are mixed with the hydrogenated PS and feed coal in the slurry drier prior to entering the liquefaction reactor. Furthermore, in this mode, heavy VGO is added to the light VGO prior to hydrogenation and distillation for production of the recycle PS. This document reports the results of the initial biological and chemical screening work performed on the EDS PS materials from both operational modes as well as a raw naphtha, a vacuum bottoms solid material from the bottoms recycle mode, and a heavy VGO (from the once-through mode).

Along with this set of representative process materials, a set of 50°F distillate cuts from a blend of materials produced in the bottoms recycle mode were also analyzed. A full-boiling-range material was simulated by blending, in appropriate proportions, the raw naphtha and process recycle solvent sampled during the processing of Illinois No. 6 coal. This reblended material was distilled and 50°F samples were collected. Solvent refined coal (SRC) 700-850°+F distillate cuts are known to be responsible for most of the observable biological activity of the SRC materials in terms of both carcinogenicity and mutagenicity. Therefore, particular attention was given to the complete chemical and biological analyses of the >700°F EDS distillates.

The microbial mutagenicity assay with Salmonella typhimurium, TA98 is relatively inexpensive and has become a standard assay for screening complex fossil fuel mixtures for genetic activity. Mutagenicity results observed for

other coal liquefaction materials have shown the test to be differentially sensitive toward the nitrogen-containing polycyclic aromatic compounds (N-PAC) in the materials, particularly toward the amino-polycyclic aromatic hydrocarbons (amino-PAH; 1-10). In the work reported here, a modification of the standard plate incorporation assay has been specifically used to assess genetic activity of the neutral PAH fractions from the EDS materials. This modified test, the "microtiter" fluctuation assay, is more sensitive to mutations induced by neutral PAH than the standard plate incorporation test (7). Carcinogenicity assessments for the recycle solvent (produced during the bottoms recycle mode) and the two higher boiling distillate cuts (750-800°F and 800°+F), as tested in the mouse skin initiation/promotion (I/P) tumorigenicity assay, are also presented in this report. The I/P mouse skin assay results have, to date, shown good correlation with results obtained for coal-derived matrials using the longer term and more expensive chronic skin painting studies on mice (7).

In conjunction with these bioassays, chemical analyses of EDS process materials were conducted in an effort to understand the chemical basis for the observed biological activity. Preparation of the samples for mutagenicity testing and instrumental chemical analysis was achieved by chromatographic separation procedures that yielded class-specific chemical fractions. Identification of those chemical constituents that are most probably responsible for the observed biological activity of the EDS process materials was made based on correlations with chemical composition and biological activity of comparative coal liquefaction materials from other processes.

Studies to date have focused on a limited number of chemical parameters related to the mutagenicity, carcinogenicity and teratogenicity of coal liquefaction materials. These include molecular weight, aromaticity, PAH content,

N-PAC content, amino-PAH content and/or hydroaromatic content. These parameters are again used in this document to correlate the biological activity and the chemical composition of EDS materials. (Because the nature and concentration of hydroaromatic species in the EDS materials are considered proprietary information, neither their identification nor their concentration levels will be reported or discussed in detail.) In addition, detailed comparisons are made between the results of this investigation and earlier studies of SRC materials performed in this laboratory. These comparisons will add perspective to the EDS results and emphasize the major differences in chemical composition and biological activity of these materials as compared with two other direct coal liquefaction processes. In general, the EDS materials had higher upper-limit boiling point (bp) ranges than coal liquefaction process materials previously studied.

ENGINEERING

The EDS Coal Liquefaction pilot plant (ECLP) was designed to process 200 tons/day of dry coal. The plant has been 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.

Raw coal was either crushed and dried in a gas swept rotary mill or crushed in an impact mill and subsequently dried in a slurry drier. When operated on prepared, dried, and crushed coal, the slurry drier mixed the recycled, hydrogen-rich donor solvent and the coal. When operating on crushed "as-received" coal, it served as a drier and as a mixer. The mixture of coal and solvent was pumped to pressures over 2,000 psig; gaseous hydrogen was added; and the three phases were heated to about 840°F in either of the two slurry preheat furnaces. The heated mixture flowed through the liquefaction reactor system, which consisted of four reactors. Two serially coupled reactors provided the desired residence time of 40 to 60 minutes. Effluent from the reactors passed through a series of separator drums into an atmospheric fractionator, where the naphtha was taken as an overhead, and gas/oil side streams were withdrawn. Sour water, H_2S, and acidic gas streams were processed at a nearby Exxon petroleum refinery. The atmospheric bottoms were then pumped through a preheat furnace to a vacuum stripper. Light VGO and heavy VGO were withdrawn from the vaccuum stripper; and the bottoms from the tower were solidified on a cooling belt. During bottoms recycle operation, liquid vacuum bottoms were recycled to the slurry drier and mixed with the recycle solvent and feed coal. Vacuum and atmospheric gas oils were sent to a solvent hydrogenation unit for catalytic hydrotreatment. The mixture was preheated and sent through a series of four fixed-bed, catalytic reactors to in-

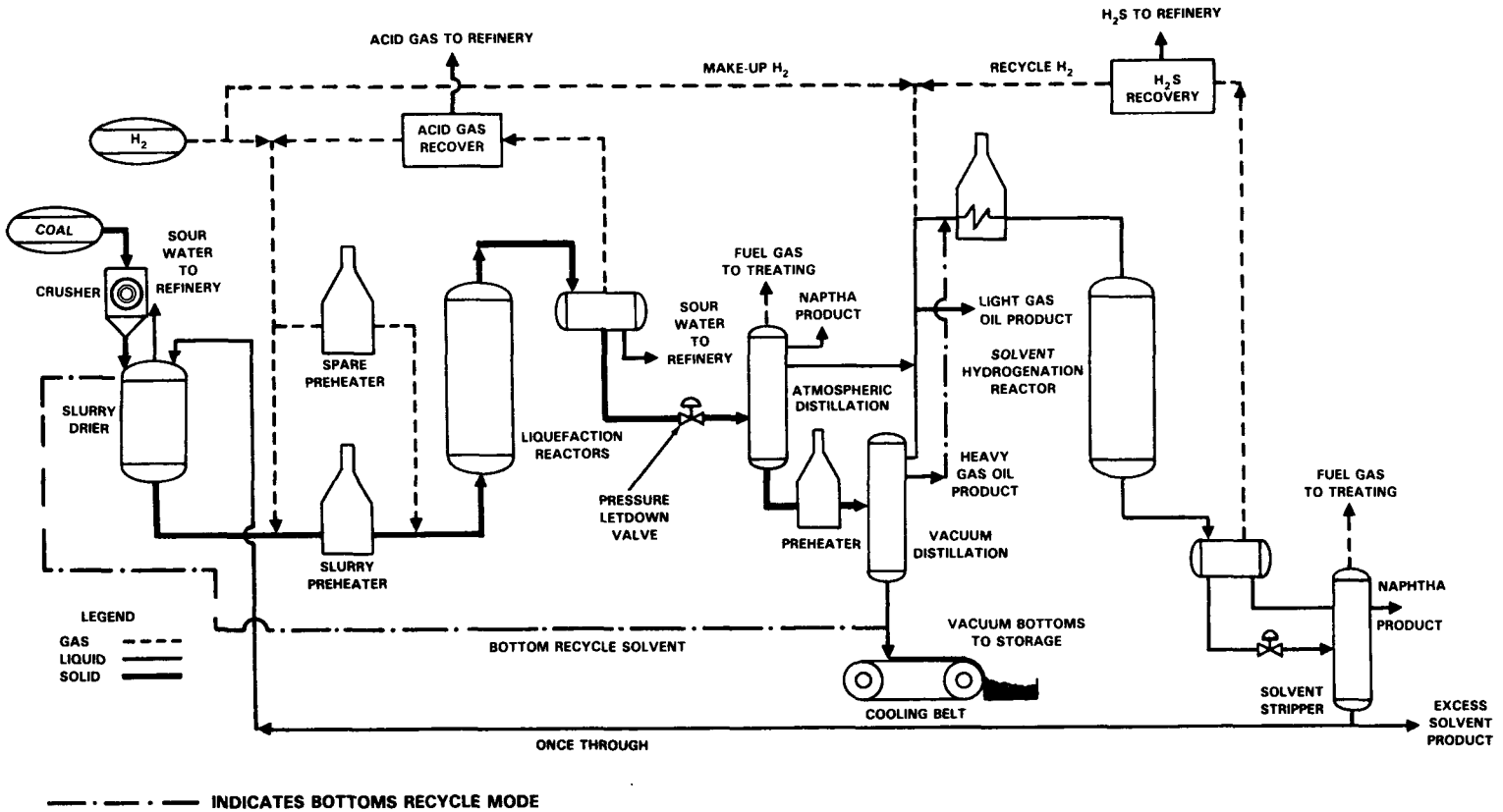


FIGURE 1. Simplified Flow Schematic for the EDS Coal Liquefaction Pilot Plant (ECLP)

crease the hydrogen donor capability of the solvent. The hydrogenated product was fractionated by distillation to provide the recycle solvent for return to the slurry drier. Naphtha and excess gas oils were sent to tankage. The types of materials that have been collected for chemical and toxicological characterization are summarized in Table 1.

TABLE 1. Summary of Materials for Chemical/Toxicological Characterization from the EDS Coal Liquefaction Pilot Plant (ECLP)

Nominal Reactant Feedrates		Nominal Reaction Conditions[a]	
Coal:	200 tons/day, MF[b]	Liquefaction Temperature:	800-850°F
Solvent/Coal:	1-2 lb/lb MF coal	Liquefaction Pressure:	1500-2500 psig
H_2/Coal:	4-8 wt. % MF coal	Slurry Residence Time:	40-100 minutes
Bottoms/Coal:	0-0.7 lb/lb MF coal		
VGO/Coal:	0-0.3 lb/lb MF coal		

Material Description	Material Characteristics
Raw naphtha	Volatile hydrocarbons from atmospheric fractionation that boil below 400°F
Spent solvent	Mixture of atmospheric gas oil (boiling point [bp] range 350-650°F, VGO (bp range 650-900°F) and vacuum distillate (bp range 400-650°F)
Recycle solvent	Hydrocarbons boiling nominally in the range of 400-1000°F
VGO	Heavy VGO boiling in the range of 700-1000°F
Fuel oil	Blend of recycle solvent/VGO at a 70/30 volume ratio, boiling in the range of 400-1000°F
Vacuum bottoms	Ash-bearing residuum containing hydrocarbons boiling above 1000°F
Liquefaction sour water	Sour water from recycle gas cold separator water drum, containing dissolved organics, inorganics and trace metals
Atmospheric fractionator sour water	Sour water containing dissolved organics, inorganics and trace metals
Cold atmospheric fractionator sour water	Cold sour water containing dissolved organics, inorganics and trace metals

[a]Solvent hydrotreating conditions not specified
[b]Moisture-free basis

MATERIALS

Two sets of EDS samples were used in this study. The first set consisted of materials that were generally representative of the EDS process. This sample set was specifically selected for a combined chemistry/toxicology study. The materials included in this sample set are listed in Table 2. Samples were collected on-site, blanketed under nitrogen and stored at 4°C. Aliquots were shipped (blanketed under nitrogen) in individually wrapped containers packed in a 55-gallon drum filled with zeolite absorbant. The PS from both bottoms recycle and "once-through" or "coal-only" runs were included in this set.

The second sample set consisted of materials that had been fractionally distilled into 50°F cuts from a 60/40 volume percent blend of the raw naphtha and recycle solvent collected during processing of Illinois No. 6 coal in the bottoms recycle mode (samples described in Table 2). This blended material was considered to be representative of a full-boiling-range product for the EDS process. Sample information and distillation data are given in Tables 3A and B and Figure 2. In general, correlated chemical and biological studies were conducted only on those distillates with bp ranges greater than 650°F.

TABLE 2. EDS Sample Set 1 Used for the Combined Chemistry/Toxicology Study

EDS Identity Number	Exxon Tag Number	Quantity (Gallons)	Description	PNL Sample Number
ETP-11	105179	2	ECLP raw naphtha from Illinois coal, bottoms recycle operations (Source: ERE Bbl. No. 104269)	5226-002
ETP-13	105180	2	ECLP recycle solvent from Illinois coal, bottoms recycle operations (Source: ERE Bbl. No. 104270)	5226-003
ETP-14	105181	5	ECLP vacuum bottoms from Illinois coal, bottoms recycle operations (Source: ERE Bbl. No. 104275)	5226-004
ETP-3	105182	1	ECLP recycle solvent from Illinois coal, once-through operations (Source: ERE Bbl. No. 102232)	5226-005
ETP-4	105183	5	ECLP heavy vacuum gas oil from Illinois coal, once-through operations (Source: ERE Bbl. No. 102235)	5226-006

TABLE 3A. Distillation of ECLP Product Blend from Bottoms Recycle Operations with Illinois #6 Coal

Charge: 60 LV% Naphtha ETP-11, Bbl. No. 104273 } Bottoms recycle mode
40 LV% Recycle Solvent ETP-13, Bbl. No. 104270

Coal: Illinois No. 6; Monterey Mine

Still: Exxon Crude Assay Laboratories - Still No. 2
20 L, 15/5 distillation

Boiling Range, °F	PNL Sample Numbers (5226-xxx)	Distillation Data				
		LV%	Cum. LV%	Wt. %	Cum. Wt. %	°API
IBP/150	---	1.81	1.81	1.40	1.40	76.3
150/200	027	6.70	8.51	5.67	7.07	58.0
200/250	028	9.86	18.37	8.63	15.70	51.4
250/300	029	12.14	30.51	11.00	26.70	45.3
300/350	030	14.81	45.32	14.15	40.85	36.4
350/400	031	17.25	62.57	17.39	58.24	27.5
400/450	032	9.73	72.30	10.15	68.39	22.1
450/500	033	5.28	77.58	5.59	73.98	20.0
500/550	034	5.30	82.88	5.77	79.75	15.7
550/600	035	4.02	86.90	4.54	84.29	10.5
600/650	036	3.40	90.30	3.93	88.22	7.0
650/700[a]	037	2.68	92.98	3.16	91.38	4.6
700/750[a]	038	2.35	95.33	2.83	94.21	1.4
750/800[a]	039	1.78	97.11	2.15	96.36	0.6
800+[a]	040	2.89	100.00	3.64	100.00	-4.1
		100.00		100.00		28.7

[a]Bioassayed for mutagenesis and/or tumorigenesis

TABLE 3B. Gas Chromatographic Distillation of EDS Process Solvents

Percent Off	Bottoms Recycle PS (ETP-13) Temperature (°F)	Once-Through PS (ETP-3) Temperature (°F)
0.1	278.9	287.3
0.3	331.2	330.8
0.5	350.2	342.6
1.0	369.5	355.2
2.5	389.5	368.7
5.0	395.3	381.0
10.0	408.9	395.4
15.0	423.8	404.2
20.0	438.0	414.1
25.0	451.6	428.1
30.0	470.2	441.9
35.0	488.0	455.0
40.0	509.7	471.0
45.0	529.9	485.9
50.0	546.4	501.5
55.0	569.8	519.2
60.0	592.2	535.0
65.0	617.9	548.9
70.0	646.1	567.2
75.0	676.2	586.8
80.0	707.7	611.3
85.0	744.4	638.6
90.0	791.9	672.0
95.0	866.4	724.2
97.5	927.7	772.6
99.0	988.5	832.6
99.5	1018.6	868.7
99.7	1036.6	891.5
100.0	1112.4	944.4

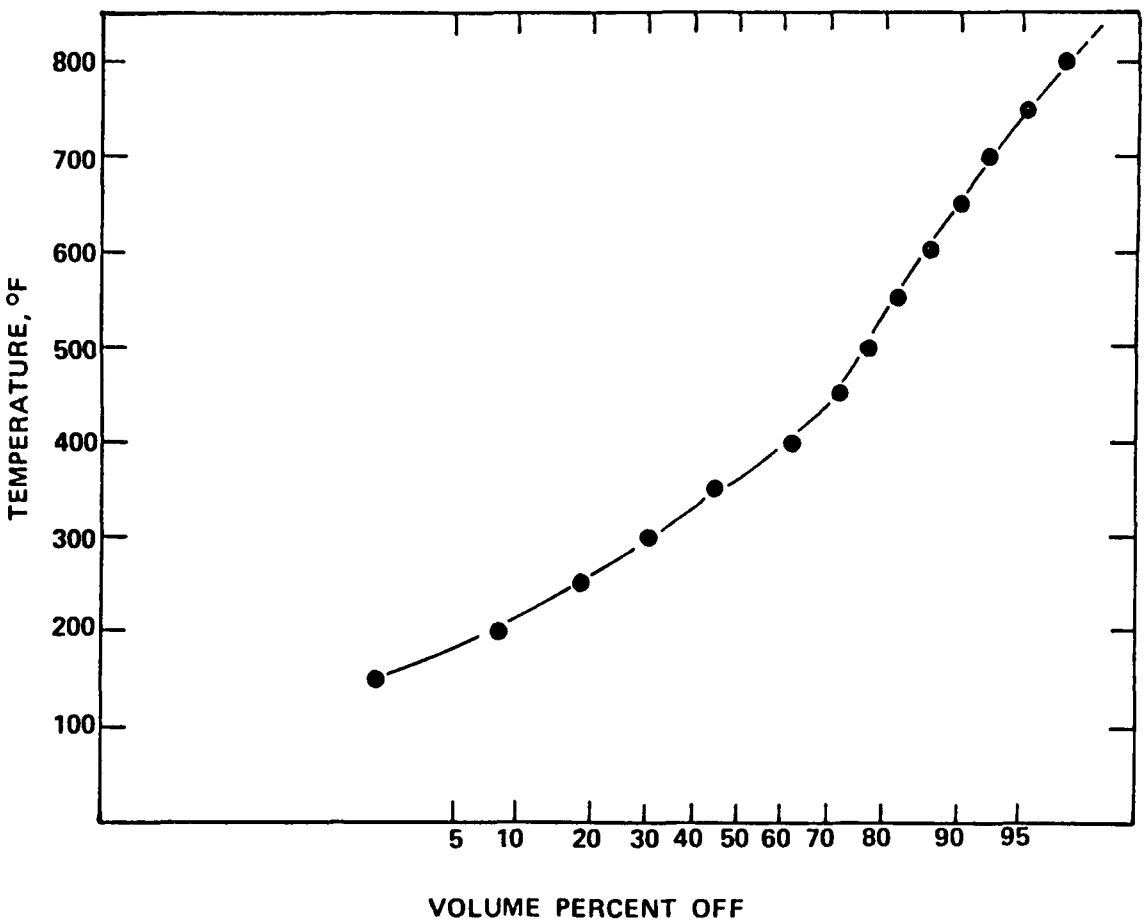


FIGURE 2. Distillation Curve for the Naphtha/PS Blended EDS Material

METHODS AND BACKGROUND

BIOLOGICAL ASSAYS

The mutagenic potencies for the crude materials, and their chemical class fractions, were estimated using the standard plate incorporation assay method of Ames and coworkers (11). In addition, a fluctuation version of this assay was performed on selected class fractions of the EDS materials.

Selected crude materials from both sample sets were assayed for skin tumor initiating activity in the I/P mouse skin assay. Promotion of initiated mouse skin was achieved using a phorbol ester. The specific details of the assays used to study the genotoxicity of the EDS process materials are outlined below.

Standard Mutagenicity Test

Standard agar plate mutagenicity assays were performed as described by Ames et al. (11) using a *S. typhimurium*, TA98 microbial tester strain. Dimethylsulfoxide was used as a solvent. In addition to the mutagens used to check the phenotypes of *Salmonella* strains, fixed concentrations of 2-aminoanthracene, benzo[a]pyrene and a complex basic fraction from SRC II heavy distillate (HD) were tested with Aroclor induced rat liver (S9) homogenates used for metabolic activation. Optimum levels for S9 were established and monitored daily during the course of the experiments. Negative controls included the *Salmonella* test strains with and without microsomal enzymes (S9), and appropriate solvent controls. Revertant colonies per petri plate were counted electronically using a Biotran II automated colony counter.

The specific mutagenic activity of crude products and chemical fractions were expressed as revertant colonies of S. typhimurium, TA98/μg of test material, estimated by linear regression analysis of dose response data. A positive test was one that had a maximum mutagenic response in revertant colonies twofold (or greater) above background. Mutagenic potency was estimated by linear regression analysis of dose response data. The complete set of raw data are presented in Appendix A for all EDS materials tested with TA98 and TA100, along with data on positive and negative controls.

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 doubling of dose concentration; a correlation coefficient of 0.8 or greater; an intercept on the response (ordinate) axis within 20% of the negative control for the day. To estimate recovery of genetic activity, mutagenicity experiments were replicated several times to obtain an average value for the slope of the regression line, or mutagenic potency in revertants/μg. To normalize the response of the chemical class fractions for comparison with the crude and other fractions, the average slope value was multiplied by the weight percent of a given fraction to yield a weighted mutagenic activity.

Fluctuation Mutagenicity Test

The fluctuation bioassay with S. typhimurium, TA98, used the microtiter technique of Gatehouse and Delow (12). Briefly, all exposure ingredients, including the S9 enzyme used in the standard microbial mutagenicity test, and the chemical (or chemical mixture) were placed in sterile 5-ml test tubes. The reaction mixtures were maintained at 37°C, with shaking at 200 rpm (revolutions per minute), for 2 hours. At the end of the 4-hour exposure period,

the contents of each exposure tube were dispersed in 10-μl aliquots into a 96-well microtiter plate along with 20 μl of bromthymol blue indicator medium. Viable cell counts were also made to determine survival of TA98 in the exposure step. Microtiter plates were incubated for 48 hours and then scored for turbid yellow microtiter wells, indicating growth of induced mutants. The number of turbid wells from exposed cells was compared with the number of turbid wells from unexposed cells, and the level of significance of the response was determined from chi-square statistics (12).

Initiation/Promotion (I/P) Mouse Skin Carcinogenicity Assay

The I/P skin tumor assay is based on the concept initially proposed by Barenblum (13) that skin tumorigenesis consists of at least two separate events: initiation and promotion. Initiation occurs rapidly, is essentially nonreversible, and probably involves interaction of the initiator with DNA. Promotion is reversible and requires repeated application of the promoting agent. The concept of I/P may be readily demonstrated experimentally by applying a single small dose of an agent such as 7,12-dimethylbenz[a]anthracene or benzo[a]pyrene to mouse skin. If the initial application is followed by repeated application of phorbol myristate acetate (PMA), tumors develop. If no promoter is used, or if an initiator does not precede application of the promoter, no tumors develop. Complete carcinogens, such as benzo[a]pyrene and 7,12-dimethylbenz[a]anthracene, can be used in high doses for both initiation and promotion. However, initiation occurs at doses much smaller than those required for promotion. PMA is a more effective promoter than equivalent amounts of benzo[a]pyrene or 7,12-dimethylbenz[a]anthracene.

Work by Calkins et al. (14) suggested that the I/P system may be useful for screening synthetic fuel mixtures for skin carcinogenic activity. Numer-

ous coal-derived materials have been screened at Pacific Northwest Laboratory (PNL) for their ability to initiate skin tumors. Some of these have also been assayed in chronic skin painting studies (15) as well as in *in vitro* mutagenicity tests (16).

The I/P assay for mouse skin carcinogenicity was described by Calkins et al. (14). Female CD-1 mice (Charles River, Portage, ME) at 6 weeks of age were housed, five/cage, on standard bedding material (Sani-Cel, Paxton Processing Co., Paxton, IL) with food (Wayne Lab-Blox, Allied Mills, Libertyville, IL) and tap water available *ad libitum*. Prior to administration of the test materials, the animals were ear-tagged for identification, weighed, shaved, and assigned to a test group (28 to 30 mice/group). Each test material was diluted 1:1 with acetone, and 50 µl of the diluted material was applied to the shaved backs of the mice. Two groups of animals were initiated with 50 µg of 7,12-dimethylbenz[a]anthracene (Eastman Chemical Company) or benzo[a]pyrene (Sigma Chemical Company) to serve as positive controls. In addition, 50 µg of several amino-PAH (9-aminophenanthrene, 3-aminopyrene, 6-aminochrysene and 2-aminoanthracene) were applied separately as initiators for reference purposes. Two weeks after initiation, 50 µl of PMA (Sigma Chemical Company, 0.1 mg/ml of acetone) were applied to the initiated area twice weekly for a period of 6 months. The mice were shaved as necessary throughout the study, usually once/week. Animals were observed regularly for tumor growth. Sketches of approximate tumor location and size were recorded each week to record progression of papilloma development.

CHEMICAL ANALYSES

The EDS samples were chemically analyzed and prepared for biological testing using an integrated analytical approach based on separation according to chemical class. This method was developed at PNL for the qualitative and quantitative measurement of components in complex coal liquefaction process materials. The development of these analytical methods has been principally directed by the requirements of identifying the biologically active agents in coal conversion materials.

A general overview of the current separation methodology is shown in Figure 3. This methodology employs an initial adsorption column chromatographic separation (16) of the major chemical classes that generally occur in coal conversion materials: aliphatic hydrocarbons, neutral PAH, N-PAC, and polar or hydroxy-PAC. The neutral alumina used for the separation of EDS materials was standardized with respect to adsorbent activity (17) to insure reproducible class separations. A secondary chromatographic separation of the neutral PAH into less-complex subfractions is achieved by high performance liquid chromatography (HPLC; 18). A combination of adsorption and gel permeation chromatography are used for the secondary separation of N-PAC species: carbazoles, azaarenes and amino-PAH (19,20). The various classes of polycyclic aromatic compounds (PAC) determined in this study are listed in Table 4, along with typical structures and the acronyms used in this report. High resolution capillary column gas chromatography (GC) and both low- and high-resolution mass spectrometry (MS) were used for the detailed identification and quantitative determination of specific compounds in each class-specific isolate obtained from the initial and secondary chromatographic separations. This integrated analytical approach has been applied to the chemical characterization

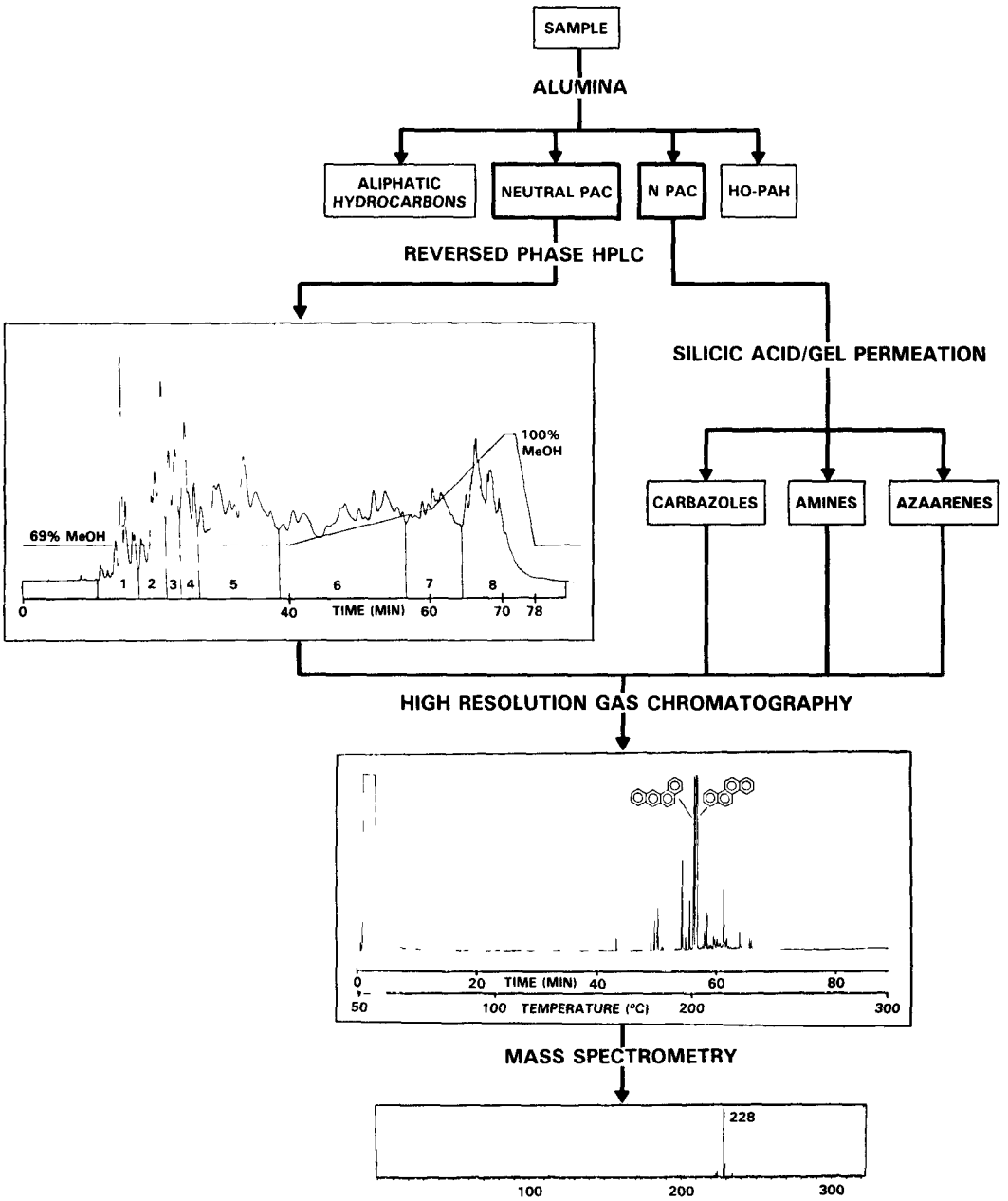
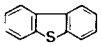
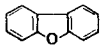
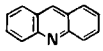
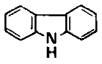
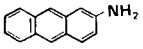
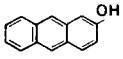


FIGURE 3. A Schematic Overview of PNL's Separation Methodology

TABLE 4. Polycyclic Aromatic Compound (PAC) Classes in Coal-Derived Materials

STRUCTURE	CLASS	ACRONYM
	NEUTRAL PAH	
	POLYCYCLIC AROMATIC HYDROCARBONS	PAH
	POLYCYCLIC AROMATIC SULFUR HETEROCYCLES	PASH
	POLYCYCLIC AROMATIC OXYGEN HETEROCYCLES	PAOH
	N-PAC	
	3°-POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES	3°-PANH
	2°-POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES	2°-PANH
	AMINO POLYCYCLIC AROMATIC HYDROCARBONS	AMINO-PAH[a]
	HYDROXY-PAH	
	HYDROXY POLYCYCLIC AROMATIC HYDROCARBONS	HYDROXY-PAH

[a]ALSO COMMONLY REFERRED TO AS PRIMARY AROMATIC AMINES (PAA)

of coal liquefaction materials from the SRC, Integrated Two-Stage Liquefaction (ITSL), and EDS processes.

HPLC Separation of the Neutral PAH

The neutral PAH, as a chemical class, appear to be the most potent dermal carcinogenic components in coal liquefaction materials (7,10,21). This observation applies particularly to the higher molecular weight species having from four to six aromatic rings. Distillation of blended process materials, followed by chemical class separation of the distillate fractions on alumina, has been used to study the composition of these high-boiling neutral PAH. However, even in a 50°F distillate cut, the neutral PAH fraction is highly com-

plex. Direct probe (70 eV) mass spectral analysis of such materials generally suggested the presence of compounds that were not fully separated even by high resolution capillary column gas chromatography. Therefore, prior to gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) analyses, the neutral PAH isolates of the EDS bp cuts from the alumina step (Figure 3) were subjected to a lower resolution separation by HPLC (18) according to schemes similar to that shown in Figure 4.

A Spectra Physics 8100 HPLC was operated in the reverse phase mode using a Supelcosil LC-8DB column (5 μm particle size; 250 x 10 mm). The mobile phase composition and solvent gradient were optimized to provide the best possible separation for each individual 50°F distillate fraction. Typically, the eluent was a mixture of methanol in water, with the methanol concentration gradient linearly programmed from approximately 70% up to 100%. An Ultraviolet (UV) monitor at 254 nm was used for detection. Subfractions of the neutral PAH fraction were collected for biological and chemical analysis. This HPLC method has been used primarily to isolate and quantitatively determine the mutagenic and carcinogenic neutral PAH components from the SRC II and EDS process distillates.

Gas Chromatography (GC)

High resolution GC was performed using a Hewlett Packard (HP) 5880 GC equipped with a 25 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 to a film thickness of 0.25 μm (J & W Scientific Inc.). The capillary vaporization injection system was operated in the splitless mode at 260°C as samples were introduced. In general, the oven temperature was held for 2 minutes at 50°C, then temperature-programmed at a rate of either 3 or 4°C/minute to 280°C. Other temperature programs employed for specific GC analyses are

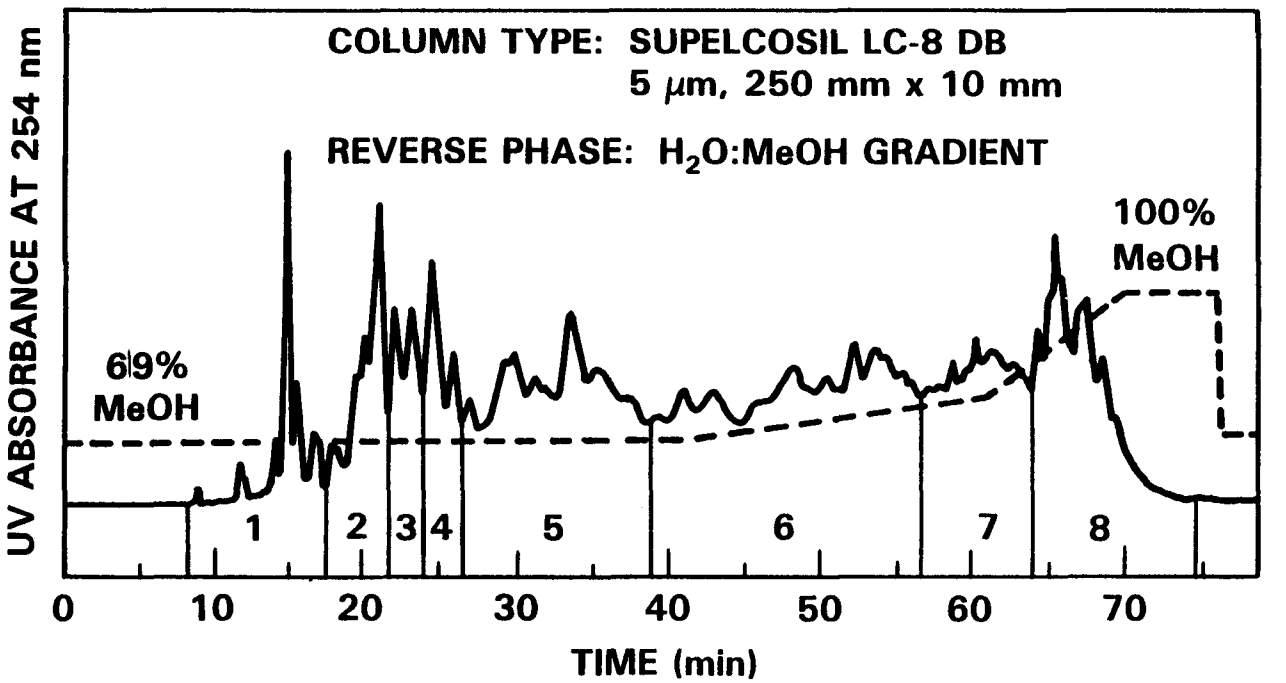


FIGURE 4. HPLC Separation of the Neutral PAH Isolate of an SRC II 800-850°F Distillate Fraction

defined in the appropriate figure legends. A flame ionization detector (FID) was used to analyze for neutral PAC and N-PAC fractions. A ^{63}Ni electron capture detector (ECD) was used for the selective detection of amino-PAH components that had been derivatized with pentafluoropropionic anhydride (22). The detectors were operated at 285 and 300°C, respectively.

A retention index system specially designed for the determination of PAC using temperature-programmed capillary GC (23,24) was one of two means used to identify the compounds in EDS samples. This retention system uses the intervals between naphthalene, phenanthrene, chrysene, and picene PAH standards to calculate indices of retention for other PAC. Using standard compounds, a retention index library of approximately 500 PAC compounds has been established (23,24). Identification of PAC in the sample fractions involved comparing retention indices of actual sample components with library values.

A second GC method, based on absolute retention and calibrated internal standard data (assisted by the HP-5880 computerized integrator), was used for both the quantitative and qualitative analyses of the majority of fractionated EDS samples. An internal standard, 2-chloroanthracene, was added to all fractions at a final concentration of 50 ng/μl and used in conjunction with calibrated response factors, as measured with standard compounds, for the quantitative analysis of sample components. The absolute retention times of all available PAC standard compounds were measured, and detector response factors were calculated at eight concentration levels ranging two orders of magnitude for each standard. These values were then used to identify and quantify sample constituents with respect to the 2-chloroanthracene internal standard. A related or average response factor of a closely eluting or similar compound was used to quantify components for which standard compounds were not available. For example, a response factor was calculated for benzo[b]fluorene from

the available standard, however, a benzo[a]fluorene standard was not available, so the same response factor was used for both quantitative calculations. All samples were analyzed at two or more dilutions to ensure analyses were within the range of the calculated response factors: 1.0, 2.5, 5.0 or 10.0 mg/ml. Results are reported in parts per million (ppm), μg/g, or parts per thousand (ppt), mg/g, as noted for a given fraction or crude, with a minimum detectable limit of approximately 20 ppm. The mean and standard deviations for at least three determinations are given as the amount for each component quantified in the fractions.

This method was also used for the quantitative/qualitative GC analysis of the amino-PAH isolates of the EDS materials in conjunction with the selective ECD (22). Response factors for a total of 19 amino-PAH, ranging from aminonaphthalenes to aminobenzopyrenes, were calculated and used for quantitation. Comparisons of absolute retention times of the standard compounds and sample components were used for identification purposes. GC/MS was used to confirm the qualitative assignments. As with the other PAC fractions, 2-chloroanthracene was used as an internal calibration standard. The 2-chloroanthracene gives a selective, reproducible, and sensitive ECD response due to the halogen functionality. The minimum detectable limits with this ECD method were below the ppm level for the amino-PAH.

Gas Chromatography/Mass Spectrometry (GC/MS)

Most GC identifications were supplemented with MS identification using coupled GC/MS. The GC/MS analyses were performed on a HP5982A quadrupole MS interfaced to a HP5710 GC equipped with a 15 m x 0.30 mm i.d., SE-52 or DB-5 fused-silica capillary column. The GC transfer line was modified so that the fused silica could be inserted to within 5 to 10 mm of the ionizing electron

beam within the ion source. This modification enhanced the resolution and interpretability of the GC/MS chromatograms. Gas chromatographic conditions were similar to those previously described. The quadrupole was operated in the electron impact mode at 70 eV, and scan rates were, typically, 100 atomic mass units per second (amu/sec). Spectra of the capillary GC peaks were acquired and processed on a HP 5934A data system.

Probe Inlet MS

To determine compounds present in higher molecular weight materials which may not be amenable to GC owing to their low volatilities, and to compare the relative average molecular weights of the samples, the crude materials, alumina fractions and selected HPLC fractions were analyzed by probe inlet MS on a VG ZAB 1F double-focusing MS. The ZAB system was typically operated in the electron impact mode with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 seconds/mass decade, a source temperature of 250°C, and at a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000.

Each sample (10 to 20 μg) was loaded into a glass capillary tube, which was 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°C, slowly desorbing the sample from the capillary tube in what amounted to fractional distillation. The MS was scanned repetitively throughout this desorption period, and data were collected across the entire desorption profile. By using the data system to sum the intensities of each mass across the entire profile, an average spectrum representing the entire sample was generated. These averaged spectra were then used to estimate the mean molecular weight of each sam-

ple and were compared to GC data to confirm the rank order of average molecular weights assigned to the various samples.

Averaged spectra were acquired for most samples using ionizing electron energies of both 70 and 10-12 eV. The 70 eV spectra display the molecular ions, the major fragments, and doubly charged ions for each species, thus providing structural information. However, 70 eV spectra do not accurately depict either the average molecular weight profiles of the samples or the relative concentration of alkylated components, as represented by the intensities of their molecular ions. The 10-12 eV spectra are composed primarily of signals representing molecular ions only, resulting in a profile that more accurately represents the average molecular weight distribution of the sample. Relative cross-sections for ionization are, of course, widely different for dissimilar classes of compounds, and can lead to discrimination and inaccurate results when assessing relative abundances of different types of compounds measured simultaneously. For example, aliphatic hydrocarbons do not give spectra composed only of molecular ions at low voltage conditions as do PAH, and are, in fact, badly discriminated against at low voltage. Thus a mixture composed of alipatic hydrocarbons and PAH could not be accurately examined quantatively at low voltage. Within a given chemical class of PAC, however, the ionization cross sections were found to be roughly equivalent for all the components. Qualitatively accurate profiles that were roughly quantitative were acquired at a low ionization voltage. More quantitatively accurate data would require the measurement and use (or calculation) of a response factor for each individual component of the mixture and this process was not deemed necessary for the level of accuracy required in these experiments.

RESULTS AND DISCUSSION

BIOLOGICAL ASSAYS

EDS Distillate Cuts

A full boiling range EDS liquid, representative of the bottoms recycle mode of liquefaction (Materials Section), was simulated by blending raw naphtha and PS (Table 3), then separating the blend into 50°F fractions by distillation. Crude distillate cuts and their chemical class fractions were tested for mutagenicity in the standard plate incorporation and fluctuation mutagenesis assay systems. Mutagenicity assays were carried out on only the 650-700°, 700-750°, 750-800° and 800°+F EDS distillate cuts, based on the results from previous work on SRC I, II, and ITSL coal liquids, which showed little or no genetic activity in the <700°F distillate cuts.

Plate Incorporation Mutagenicity Assay. The mutagenicity data presented in Tables 5-8 were obtained with *S. typhimurium*, TA98 as the microbial test organism. This strain is more sensitive than other microbial tester strains to mutagens present in coal liquids (25,26). Mutagenicity data for *S. typhimurium*, TA100, which also responds to mutagens in coal liquids, are presented in Appendix A.

The data in Tables 5-8 illustrate that the mutagenic activity of the EDS crude distillates and most of their chemical fractions tended to increase with increasing distillation temperatures, as has been shown previously for SRC and ITSL liquids (4,6,8). However, for a given temperature range, the EDS distillate was usually of much lower activity than its SRC II counterpart. For example, for the crude (unfractionated) EDS distillates, mutagenic response in-

TABLE 5. Comparison of the EDS and SRC II Crude Distillates for Mutagenicity against *S. typhimurium*, TA98

Bp Cut (°F)	EDS Crude: Dose Response in rev/μg	EDS Crude: Maximum Response in rev/Plate	SRC II Crude:	SRC II Crude: Dose Response in rev/μg	SRC II Crude:	SRC II Crude: Maximum Response in rev/Plate
800+	34.4 (1)[a]	189 ± 1 (2)[b]	850°+F:	258 ± 31 (2)[a]	850°+F:	1820 ± 56 (2)[b]
			800-850°F:	61 ± 8 (2)	800-850°F:	943 ± 15 (2)
750-800	0	103 ± 4 (2)		67 ± 0 (2)		524 ± 211 (2)
700-750	0	60 ± 2		37 ± 14 (2)		220 ± 0 (2)
650-700	0	47 ± 3 (2)		NA[c]		NA
639-689	NA	NA		0 (1)		59 ± 10 (2)
600-650	0	79 ± 2 (2)		NA		NA
300-700	NA	NA		0 (1)		79 ± 2 (2)

[a]Number of dose-response experiments used to estimate mutagenicity; results of two or more experiments were averaged. Potency in rev/μg was derived from the slope of a dose-response curve estimated by linear regression (Methods).

[b]Total number of sample points (petri plates) counted to obtain the average maximum response. Each exposure consisted of two points (plates) for each concentration assayed. A full dose range consisted of six concentrations (Methods).

[c]NA = not applicable

TABLE 6. Comparison of the Mutagenicity of EDS and SRC II N-PAC Chemical Class Fractions for *S. typhimurium*, TA-98. Mutagenicity expressed as rev/μg or average rev/μg from linear regression of dose-response data, using criteria discussed in Methods, and as maximum response in rev/plate (Methods and Appendix A).

Bp Cut (°F)	EDS N-PAC		SRC II N-PAC	
	Dose Response in rev/μg	Maximum Response in rev/Plate	Dose Response in rev/μg	Maximum Response in rev/Plate
800+	60.6 (1)[a]	362 ± 11 (2)[b]	230 ± 20 (2)[a]	1908 ± 750 (4)[b]
750-800	34.4 (1)	251 ± 5 (2)	275 ± 46 (2)	1455 ± 170 (4)
700-750	13.1 (1)	118 ± 6 (2)	407 ± 271 (2)	1713 ± 406 (4)
650-700	0	64 ± 3 (2)	NA[c]	NA
639-689	NA	NA	30 (1)	200 ± 0 (2)
600-650	0	49 ± 1 (2)	NA	NA
300-700	NA	NA	114 ± 5 (2)	265 ± 96 (4)

[a]Number of dose-response experiments used to estimate mutagenicity; results of two or more experiments were averaged. Potency in rev/μg was derived from the slope of a dose-response curve estimated by linear regression (Methods).
[b]Total number of sample points (petri plates) counted to obtain the average maximum response. Each exposure consisted of two points (plates) for each concentration assayed. A full dose range consisted of six concentrations (Methods).
[c]NA = not applicable

TABLE 7. Comparison of the Mutagenicity of EDS and SRC II Hydroxy-PAH Fractions with *S. typhimurium*, TA-98

Bp Cut (°F)	EDS Hydroxy-PAH		SRC II Hydroxy-PAH	
	Dose Response in rev/μg	Maximum Response in rev/Plate	Dose Response in rev/μg	Maximum Response in rev/Plate
800+	0 (3)[a]	72.5 ± 9.2 (3)[b]	850°+F: 5.13 ± 2.23 (3)[a] 800-850°F: 0.95 ± 0.49 (3)	850°+F: 529 ± 180 (3)[b] 800-850°F: 272 ± 113 (3)
750-800	0 (3)	52.5 ± 0.7 (3)	0 (3)	74 ± 24 (3)
700-750	0 (3)	44.5 ± 2.1 (2)	0 (3)	60 ± 31 (3)
650-700	0 (3)	45.0 ± 1.4 (3)	NA[c]	NA
639-687	NA	NA	0 (3)	42.7 ± 5.5 (3)
600-650	0 (3)	31 ± 1 (2)	NA	NA
300-700	NA	NA	0 (1)	73 ± 7 (2)

[a]Number of dose-response experiments used to estimate mutagenicity; results of two or more experiments were averaged. Potency in rev/μg was derived from the slope of a dose-response curve estimated by linear regression (Methods).

[b]Total number of sample points (petri plates) counted to obtain the average maximum response. Each exposure consisted of two points (plates) for each concentration assayed. A full dose range consisted of six concentrations (Methods).

[c]NA = not applicable

TABLE 8. Comparison of the Mutagenicity of the EDS and SRC II PAH Fractions with *S. typhimurium*, TA-98

Bp Cut (°F)	EDS PAH Dose Response in rev/μg	EDS PAH Maximum Response in rev/Plate	SRC II PAH Dose Response in rev/μg	SRC II PAH Maximum Response in rev/Plate
800+	0.17 ± 0.10 (3)[a]	106 ± 55 (3)[b]	850°+F: 0.79 ± 0.15 (4)[a]	850°+F: 245 ± 41 (4)[b]
			800-850°F: 0.44 ± 0.07 (4)	800-850°F: 152 ± 43 (4)
750-800	0 (3)	98 ± 6 (3)	0.23 ± 0.05 (3)	111 ± 16 (3)
700-750	0 (3)	68 ± 4 (3)	0 (3)	92 ± 5 (3)
650-700	0.11 ± 0.05	139 ± 9 (3)	NA[c]	NA
639-687	NA	NA	0 (3)	58.7 ± 19.1 (3)
600-650	0	38 ± 0 (2)	NA	NA
300-700	NA	NA	0 (3)	50 ± 13 (3)

[a]Number of dose-response experiments used to estimate mutagenicity; results of two or more experiments were averaged. Potency in rev/μg was derived from the slope of a dose-response curve estimated by linear regression (Methods).

[b]Total number of sample points (petri plates) counted to obtain the average maximum response. Each exposure consisted of two points (plates) for each concentration assayed. A full dose range consisted of six concentrations (Methods).

[c]NA = not applicable

creased monotonically, with temperature reaching maximum levels in the 800°+F material (Table 5). The EDS crude 800°+F distillate (34 rev/μg) exhibited much less mutagenic potency in S. typhimurium, TA98, as compared to the SRC II 800°+F distillates (800-850°F = 61 rev/μg; 850°+F = 258 rev/μg). The potency in maximum revertants/plate of the crude 750-800°F EDS distillate (103 rev/plate) was less than one-fifth that of the SRC II 750-800°F distillate (524 rev/plate). Furthermore, a detectable dose response for this EDS distillate was not observed, while the equivalent SRC II distillate yielded 67 rev/μg. No genetic activity was detected in the EDS crude distillates with upper distillation temperature cut points at 750°F or below, although the comparable SRC II distillates were all mutagenically active (see Table 5).

The low activity observed for the EDS distillates boiling below 800°F was due, at least in part, to compositional masking effects, as shown by the data for the chemical fractions of these materials (Tables 6 to 8). For example, the N-PAC constituents from both the EDS 700-750° and 750-800°F distillate cuts were mutagenic (Table 6), although the crudes showed little or no activity (Table 5). The comparable SRC II N-PAC fractions were, again, considerably more active in the standard Ames bioassay with S. typhimurium, TA98. Little or no mutagenic activity was observed for the hydroxy-PAH chemical fractions from the EDS distillate cuts (Table 7). The hydroxy-PAH fractions from the less than 800°F SRC II distillates were also not mutagenically active. However, the hydroxy-PAH from the greater than 800°F SRC II distillates were significantly active mutagens against S. typhimurium, TA98 (Table 7).

Distribution of the genetic activity of the EDS PAH fractions (Table 8) was bimodal, with one activity peak associated with the 800°+F distillates and a second peak associated with the EDS 650-700°F distillate. The PAH isolate from the 700-750°F EDS distillate was not measurably active against S. typhi-

murium, TA98. The distribution of activity in the PAH fractions from the SRC II distillates was not bimodal but increased monotonically with increasing distillation temperature, attaining maximum specific mutagenic activities in the 800°+F SRC II distillate cuts. The PAH fractions from the SRC II 800°+F distillate cuts were again more active than comparable fractions from the EDS distillate cuts.

Fluctuation Mutagenicity Assay. A series of bacterial mutagenicity assays, using the fluctuation test system with TA98, was performed to supplement the data set obtained with the standard plate incorporation assay. These tests were prompted by the greater sensitivity of the fluctuation assay as compared to the standard plate incorporation assay reported for certain pure compounds (12). Results of the fluctuation mutagenesis bioassays on EDS fractions with S. typhimurium, TA98 are shown by the data in Table 9.

The aliphatic hydrocarbons, PAH, and hydroxy-PAH fractions (but not the N-PAC fraction) were tested for mutagenicity by the fluctuation method. All of the aliphatic hydrocarbon fractions were inactive in the fluctuation bioassay system, as were those hydroxy-PAH fractions from cuts distilled below 800°F. This confirms the results of the standard plate incorporation test. The >650°F PAH fractions all showed significant genetic activity in this bioassay system, but the 600-650°F PAH isolate was inactive; this was in agreement with the results of the standard plate incorporation bioassay. The neutral PAH fractions of the greater than 650°F distillate cuts that were not mutagenically active in the standard plate incorporation assay with S. typhimurium, TA98 showed low but significant levels of activity in the fluctuation assay with the same organism. The aliphatic hydrocarbon fractions and hydroxy-PAH fractions up to 800°F were still inactive in the fluctuation as-

TABLE 9. Mutagenicity of EDS Distillate Cuts in the Fluctuation Mutagenicity Bioassay with *S. typhimurium*, TA-98

Bp Cut (°F)	Fraction[a]	Dose (µg/ml)	S9	µl/ml	Viability Count (S/S_0)	No. Positive Wells From Exposed (Nonexposed) Cells	X^2[b]	P[c] Value
650-700 (037)	A_1	100	+	100	1.8	8 (12)		NS[d]
		100	-	0	1.5	35 (29)	0.84	NS
	A_2	100	+	100	1.6	36 (12)	16	<0.005
		100	-	0	1.5	22 (22)	0	NS
	A_4	100	+	100	1.7	7 (7)	0	NS
		100	-	0				
700-750 (038)	A_1	100	+	100	3.1	12 (11)	0.05	NS
		100	-	0	1.8	36 (79)	1.14	NS
	A_2	100	+	100	1.9	37 (19)	8.17	<0.01
		100	+	100	2.5	63 (44)	7.62	<0.01
		100	+	100	1.5	47 (20)	16.71	<0.005
		100	-	0		31 (22)	2.12	NS
	A_4	100	+	100	1.9	6 (7)		NS
		100	+	100	1.4	16 (27)	(4.43)	NS
		100	-	0				
750-800 (039)	A_1	100	+	100	1.8	15 (12)	0.39	NS
		100	+	100	3.3	5 (11)	(2.45)	NS
		100	-	0	2.0	27 (29)	0.1	NS
	A_2	5	+	100	1.6	15 (12)	0.39	NS
		10	+	100	1.8	10 (12)	0.21	NS
		25	+	100	1.4	13 (12)	0.05	NS
		100	+	100	1.5	96 (44)	71.31	<0.005
		100	+	100	1.8	36 (20)	6.45	<0.02
		100	-	0	1.6	24 (22)	0.11	NS
	A_4	100	+	100	1.9	17 (27)	(3.57)	NS
800+ (040)	A_1	100	+	100	1.4	15 (12)	0.39	NS
		100	+	100	1.8	16 (11)	1.08	NS
		100	-	0		23 (29)	0.95	NS

TABLE 9. (continued)

Bp Cut (°F)	Fraction[a]	Dose (μg/ml)	S9	μl/ml	Viability Count (S/S_0)	No. Positive Wells From Exposed (Nonexposed) Cells	X^2[b]	P[c] Value
800+	A_2	5	+	100	ND	24 (12)	4.92	<0.05
		10	+	100	ND	26 (12)	6.43	<0.05
		25	+	100	ND	24 (12)	4.92	<0.05
		100	+	100	ND	73 (44)	18.4	<0.005
		100	+	100	ND	37 (20)	7.21	<0.005
		5	-	0	ND	36 (11)	17.61	<0.001
		10	-	0	ND	37 (11)	18.7	<0.001
		25	-	0	ND	25 (11)	6.7	<0.01
	A_4	100	+	100	ND	7 (3)	1.69	NS[d]
		100	-	0	ND	42 (27)	10.79	<0.01

[a]A_1 = aliphatic hydrocarbon alumina column fraction
A_2 = neutral PAH alumina column fraction
A_4 = hydroxy-PAH alumina column fraction
[b]Chi-squared values are an estimate of significance; values ≥ 3.0 are positive correlates of activity, with increasing numerical value corresponding to increasing significance.
[c]<Probability; $P \leq 0.05$ is a positive response
[d]NS = not significant

say. Results of the standard plate incorporation and fluctuation microbial mutagenicity assays were in agreement and set the temperature boundary between activity and inactivity of the crude distillates and alumina chemical fractions at 700°F.

In all cases the genetic activity of the 700-750°F and 750-800°F neutral PAH fractions was S9 dependent, suggesting that only promutagens were contained in these fractions. However, the PAH fraction from the 800°+F distillate cut showed mutagenic activity in the absence of a metabolic activation

system, indicating that direct-acting mutagens were present in this chemical fraction.

Plate Incorporation Mutagenicity Assay of the Neutral PAH HPLC Subfractions. The PAH fractions from the EDS 650-700°F, 700-750°F, 750-800°F, and 800°+F distillate cuts were further separated by the HPLC method discussed earlier, and the resulting fractions were analyzed for chemical composition (see Chemical Analysis section of Results and Discussion) and assayed for mutagenic activity with S. typhimurium, TA98. The bioassay results are shown in Figures 5 to 8. Figure 5 shows the mutagenic activity associated with the PAH fraction from the 800°+F distillate cut (Table 9) was concentrated in HPLC Subfraction #2, which was enriched in parent five-ring PAH. The specific mutagenic activity of this 800°+F HPLC subfraction was more than 25-fold greater than that associated with the unfractionated 800°+F PAH starting material (Figure 5 versus Table 8). It is therefore apparent that mutagenic activity was purified by HPLC fractionation of the initial PAH isolate. The chemical composition of these HPLC subfractions is presented in the next section and will be discussed in detail there in relation to the biological activity. It is interesting to note that little or no mutagenic activity was associated with any other HPLC subfractions from the 800°+F PAH isolate. The recovery of weight normalized mutagenic potency of the HPLC subfractions (i.e., HPLC cut #2 in Figure 5) was approximately as expected for the unfractionated EDS 800°+F PAH isolate.

The HPLC subfractions from the EDS 750-800°F PAH were essentially devoid of mutagenic activity with S. typhimurium, TA98 (Figure 6). However, a low but significant response was obtained for the fourth subfraction from the 700-750°F cut (Figure 7). Subfraction #5 from the 650-700°F PAH isolate (Fig-

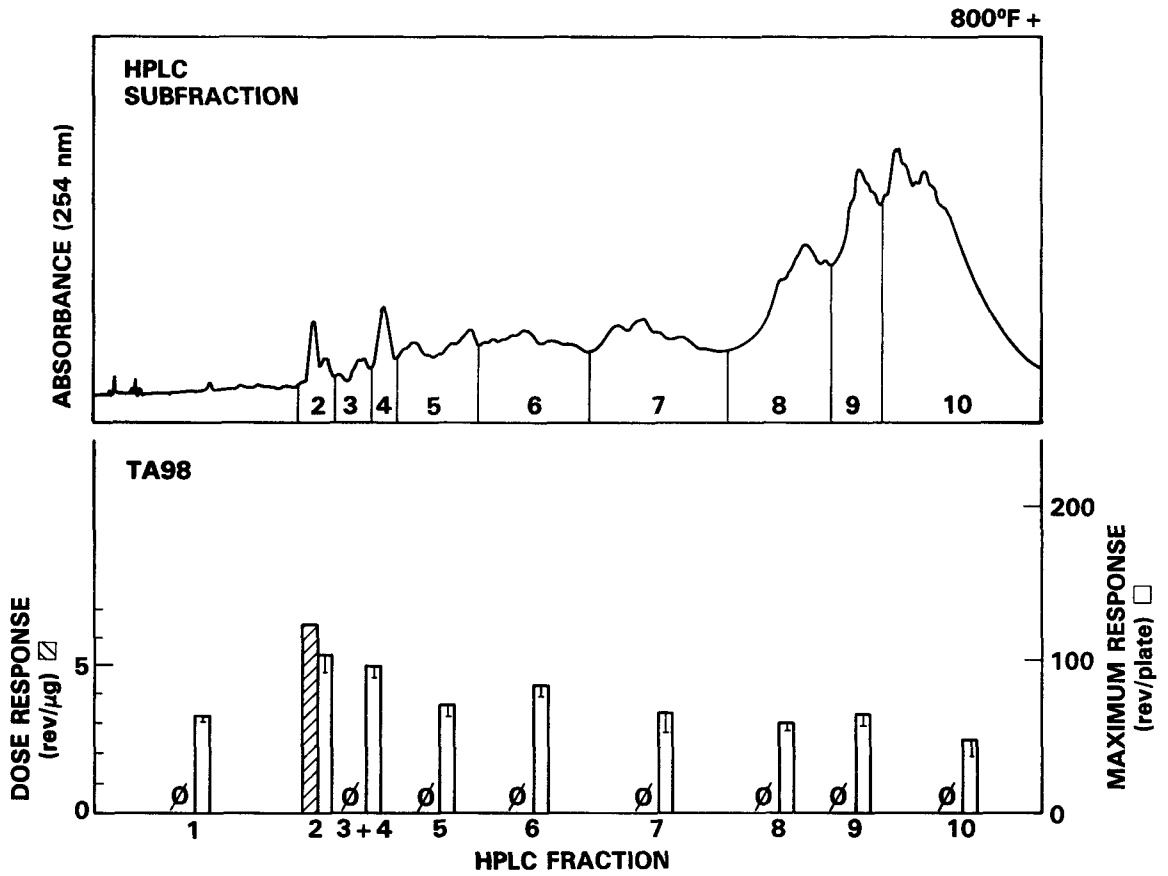


FIGURE 5. Mutagenic Response with S. typhimurium, TA98 by HPLC Subfractions from the Neutral PAH Fractions of the EDS 800°+F Distillate Cut

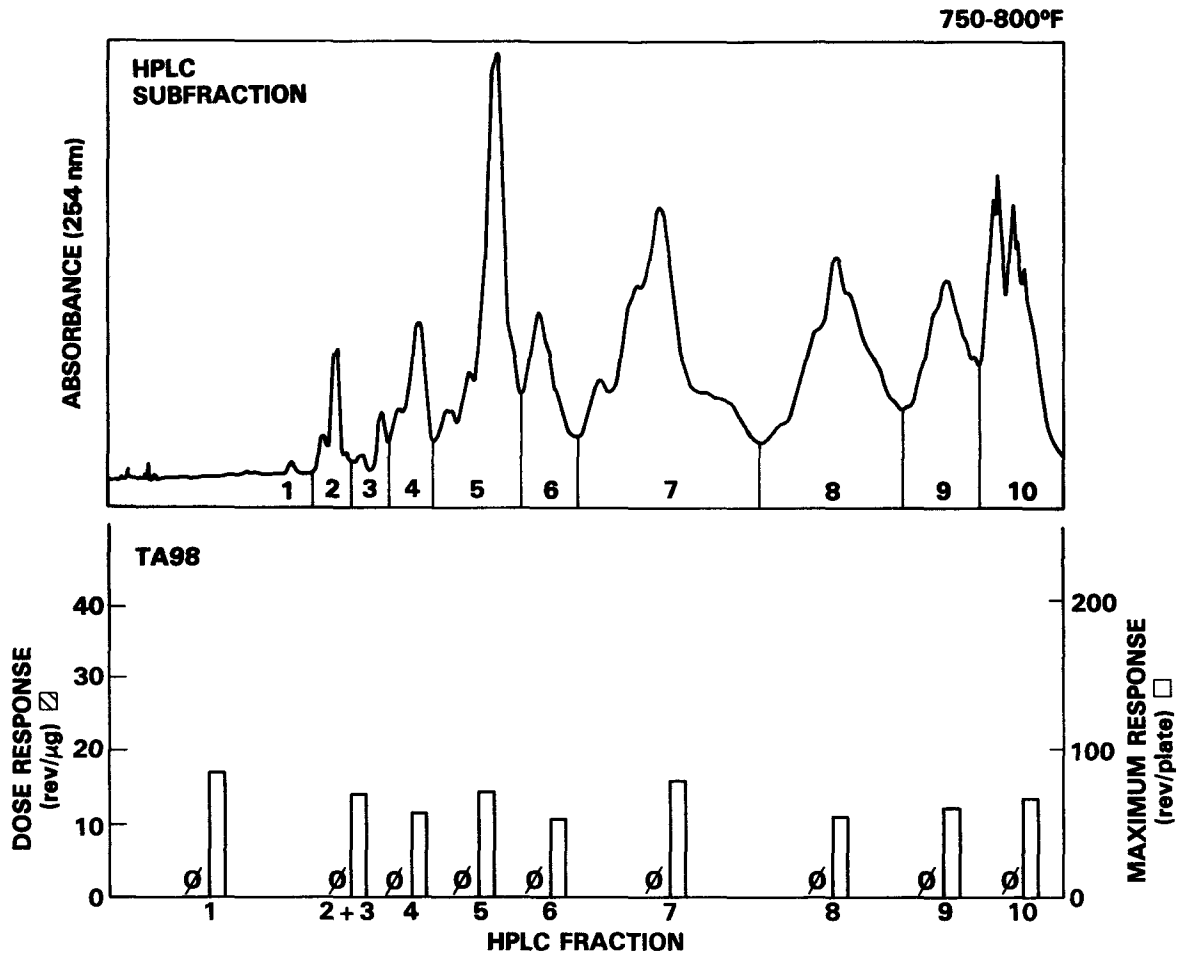


FIGURE 6. Induced Mutagenic Response in S. typhimurium, TA98 by HPLC Subfractions from the Neutral PAH Fractions of the EDS 750-800°F Distillate Cut

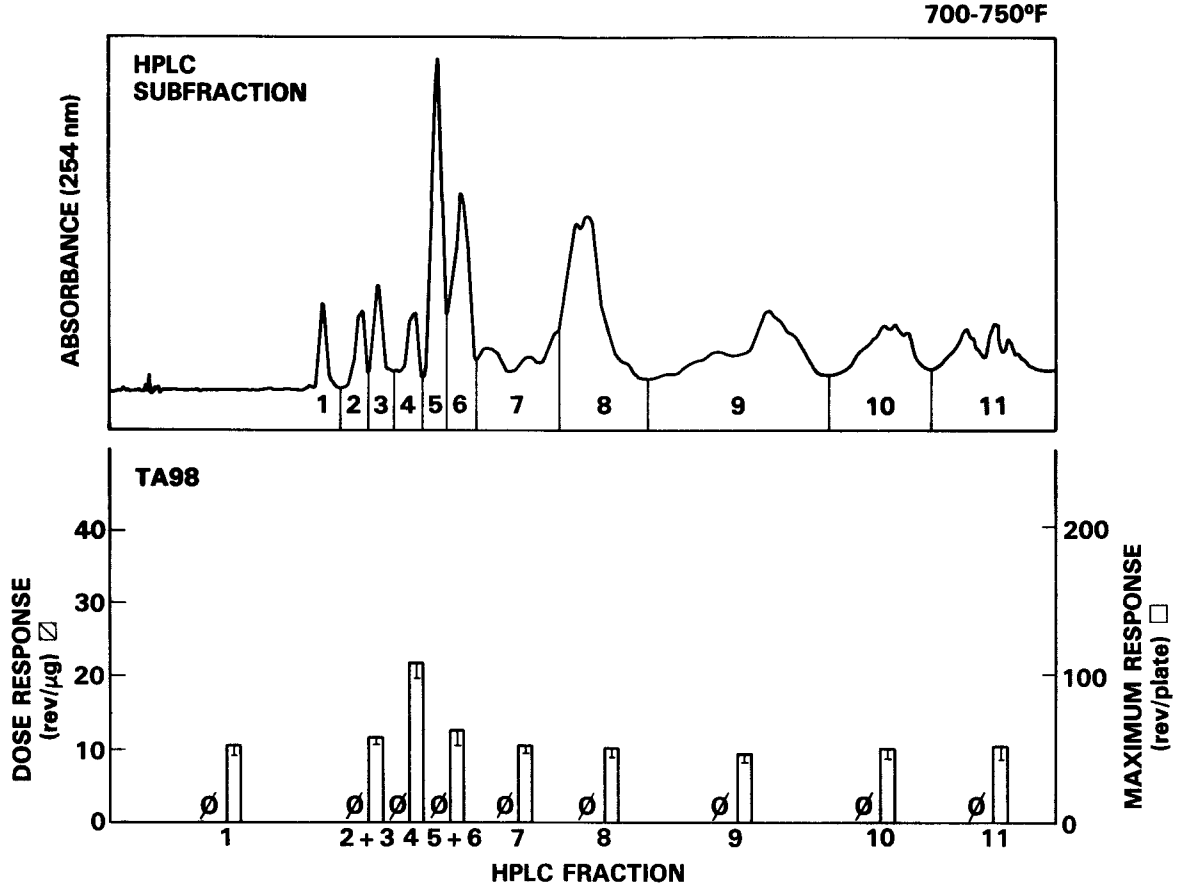


FIGURE 7. Induced Mutagenic Response in S. typhimurium, TA98 by HPLC Subfractions from the Neutral PAH Fractions of the EDS 700-750°F Distillate Cut

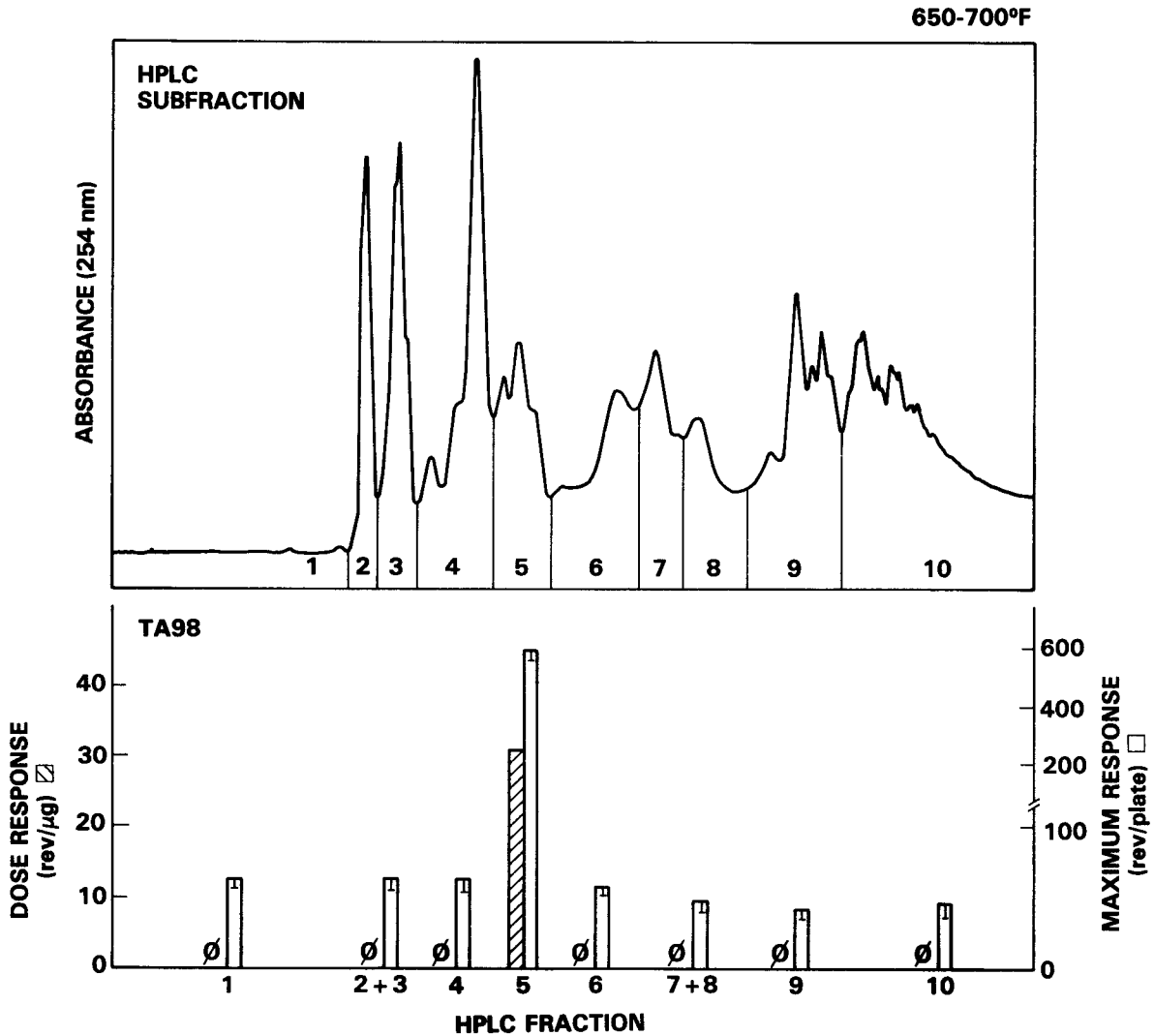


FIGURE 8. Induced Mutagenic Response in S. typhimurium, TA98 by HPLC Subfractions from the Neutral PAH Fractions of the EDS 650-700°F Distillate Cut

ure 8) was also mutagenically active with S. typhimurium, TA98. Its weight normalized specific mutagenic activity (based on linear regression) and its weight normalized maximum response were both many times greater than those observed for either the EDS 800°+F PAH fraction (Figure 5) or the SRC II 850°+F PAH fraction (Figure 9). Essentially all of the genetic activity of the EDS PAH 650-700°F isolate was localized in an HPLC subfraction that constituted only 1% of the total mass (see Table 22). Evidently, the genetic activity of the 650-700°F PAH fraction was heavily masked, as evidenced by the increased recovery of activity in the fifth HPLC subfraction (Figure 8). The detailed chemical analysis of these HPLC fractions will be discussed with respect to specific chemical composition in a subsequent section.

EDS Process Materials: Plate Incorporation Mutagenicity Assay

Several representative EDS process streams were tested for mutagenic activity in the histidine reversion microbial mutagenicity assay. The results from these bioassays are shown in Figure 10. As expected, the raw naphtha (002, bp <400°F) was without significant genetic activity with S. typhimurium, TA98. The vacuum bottoms from bottoms recycle mode (004, bp >1000°F), and the heavy VGO (006, bp 700-1000°F) were mutagenically active with S. typhimurium, TA98; activity was concentrated in the N-PAC and hydroxy-PAH fractions. The PAH fractions from these two high boiling materials showed no dose-dependent activity in the standard microbial mutagenicity assay with S. typhimurium, TA98. Considerable masking of genetic activity was observed as shown by the increased recovery of activity in the chemical fractions of the vacuum bottoms over that predicted from the activity demonstrated by the crude. Conversely, the recovery of genetic activity in the chemical fractions of the heavy VGO was less than expected, based on the mutagenicity of the crude.

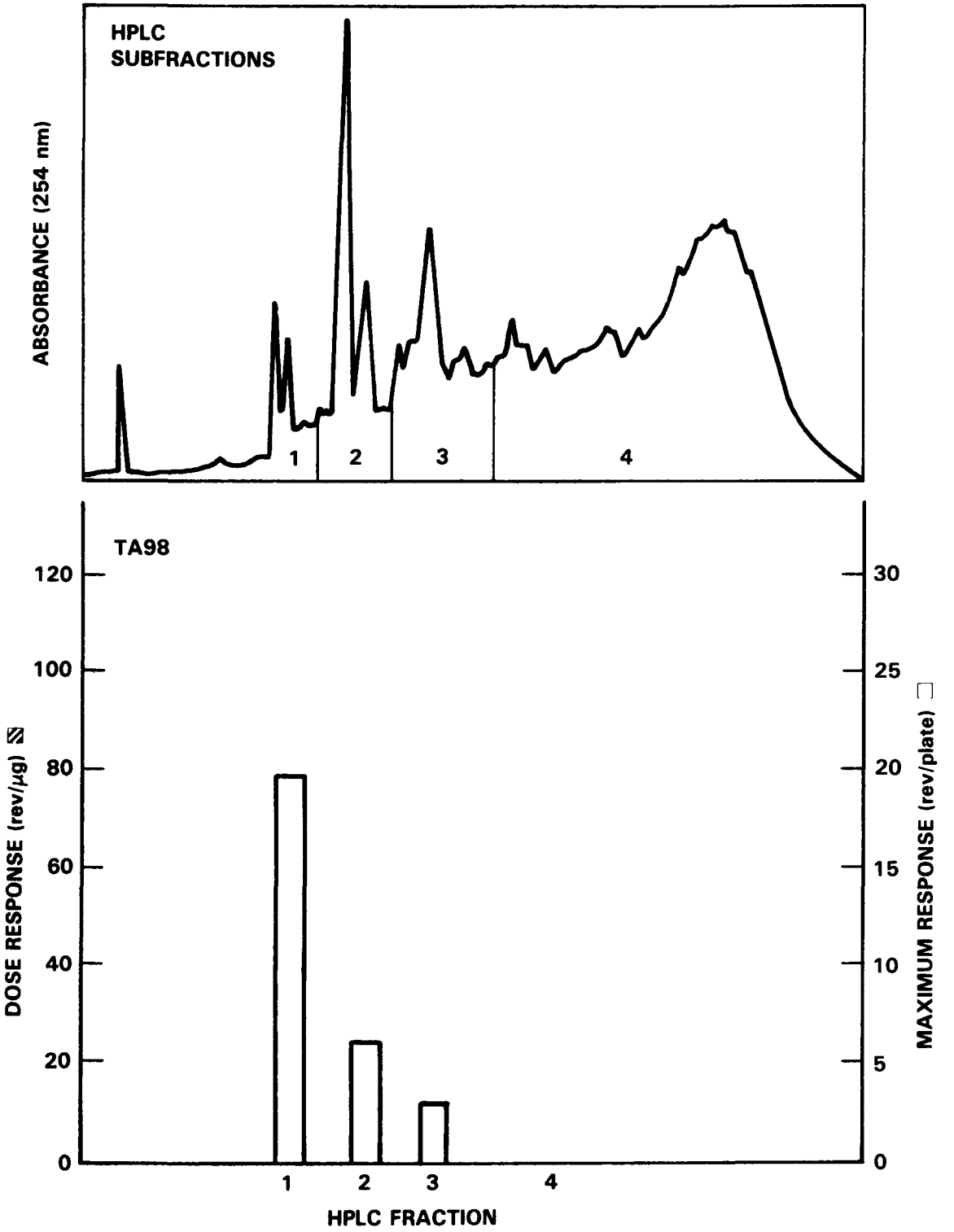


FIGURE 9. Induced Mutagenic Response in S. typhimurium, TA98 by HPLC Subfractions from the Neutral PAH Fractions of the SRC II 850°+F Distillate Cut

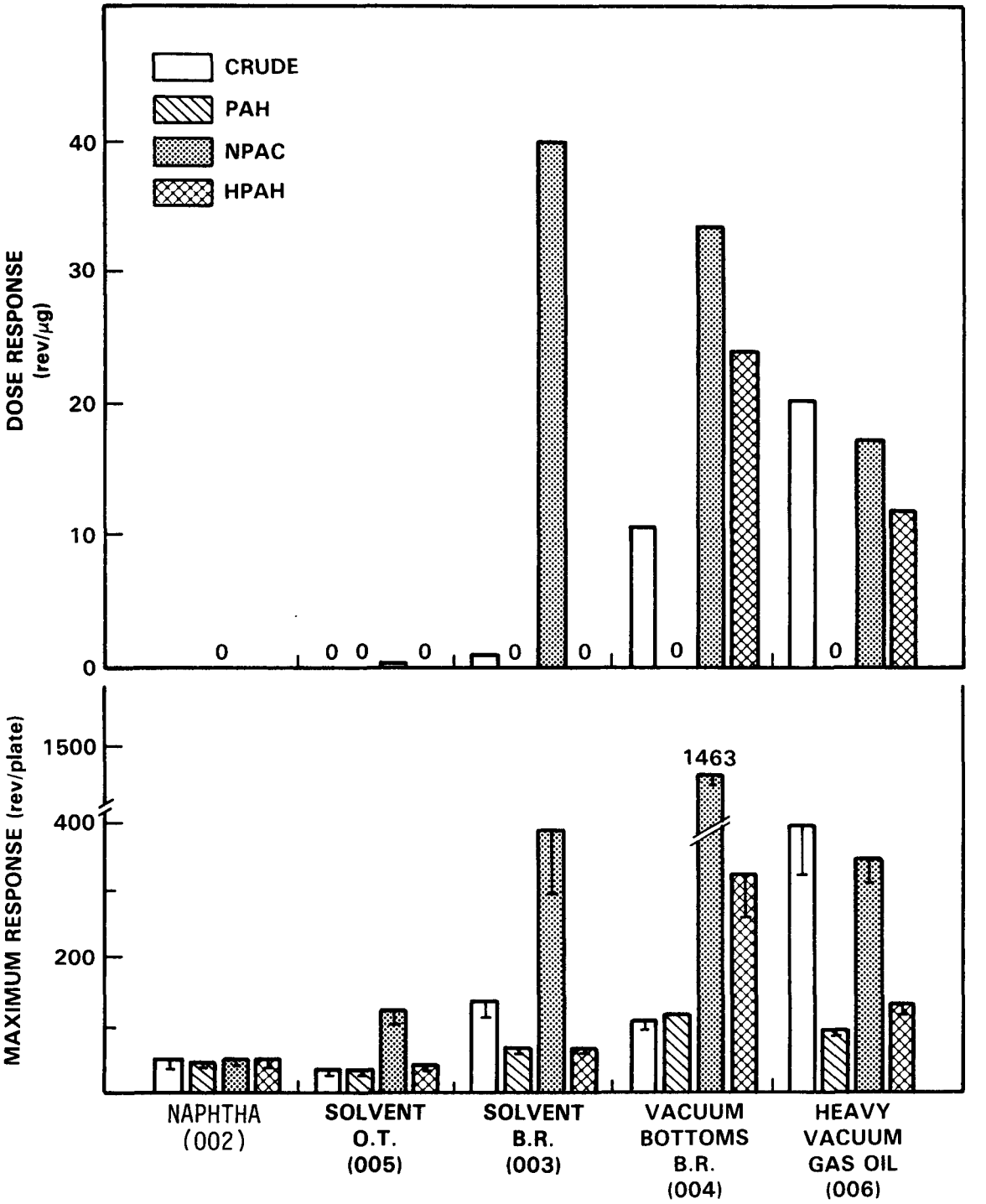


FIGURE 10. Mutagenicity of EDS Process Streams with S. typhimurium, TA98 in the Standard Ames Assay System

The once-through mode PS (005, bp 400-800°F) showed only slight dose-dependent activity in the N-PAC fraction and none in the hydroxy-PAH isolate and crude solvent. The bottoms recycle PS (003, bp 400 to 800°F) showed comparatively high activity in the N-PAC fraction and crude but no activity in the PAH or hydroxy-PAH fractions.

EDS Process Materials and Distillate Cuts: I/P Assay

The crude 750-800°F and 800+°F EDS distillate cuts were assayed for tumorigenicity in the I/P mouse skin painting system. As shown in Figures 11 and 12, the distillate cuts as well as the recycle solvent (bottoms recycle mode) were tumorigenic. The 800°+F distillate cut was more active than either the 750-800°F distillate cut or the recycle solvent, confirming similar results for SRC I and II distillates (21).

Figure 13 compares the mutagenic responses of the PAH fractions (A_2) with *S. typhimurium*, TA98 for the EDS 750-800 and 800°+F distillate cuts with tumorigenic responses induced by the unfractionated materials (Figure 13). The same data for three comparable SRC II distillate cuts are also presented in Figure 14. Mutagenic response induced in *S. typhimurium*, TA98 by the neutral PAH (A_2 fractions) for both the EDS and SRC materials appeared to be a good predictor for tumorigenic response based on either the rate of tumor initiation or the maximum number of tumors formed. Furthermore, for distillates spanning a comparable temperature range, the SRC II PAH isolates were considerably more tumorigenic than the EDS crude distillate cuts.

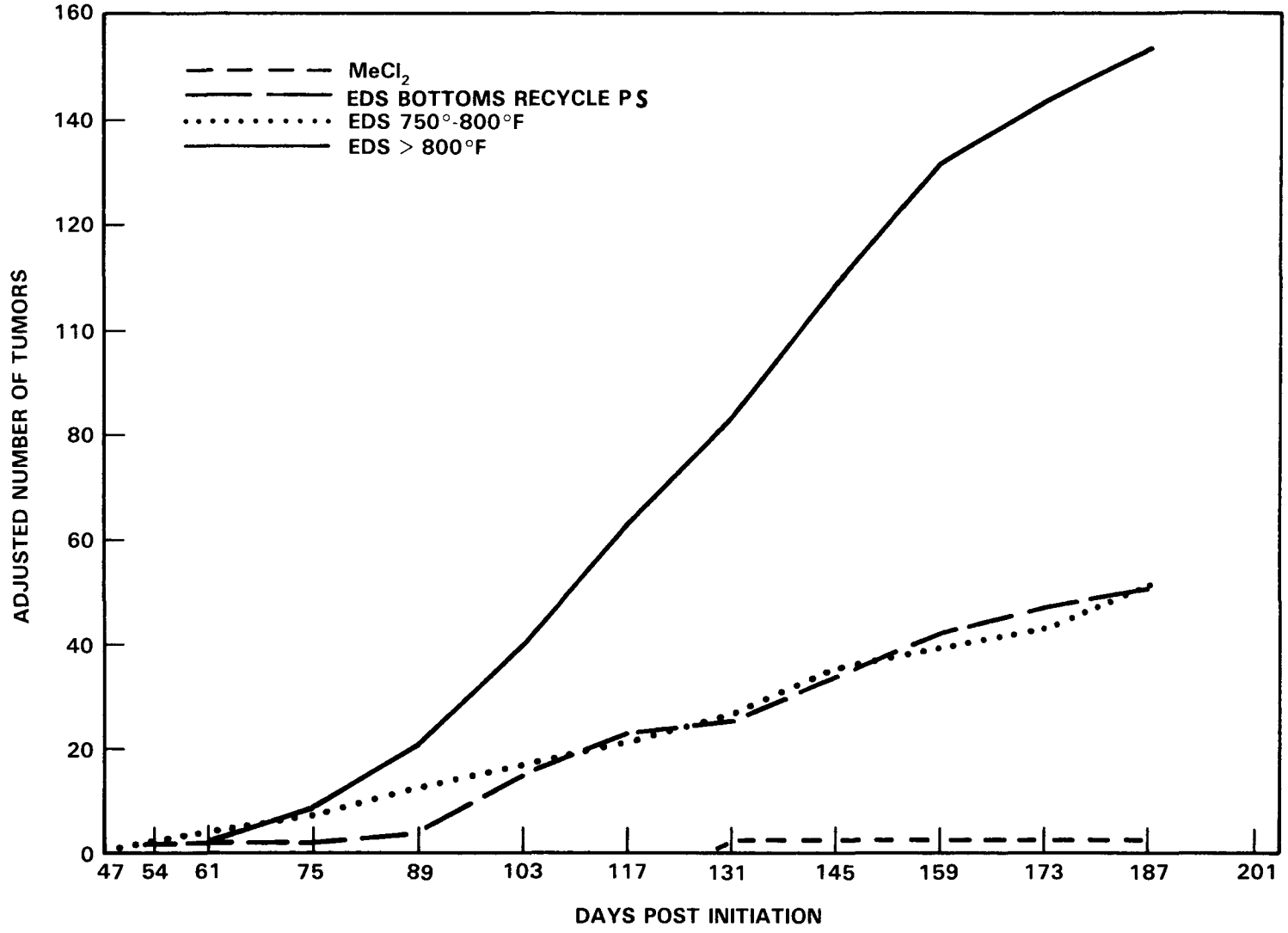


FIGURE 11. Adjusted Number of Tumors (versus Days after Initiation) Induced by EDS 800°+F and 750-800°F Distillate Cuts and EDS Bottoms Recycle PS

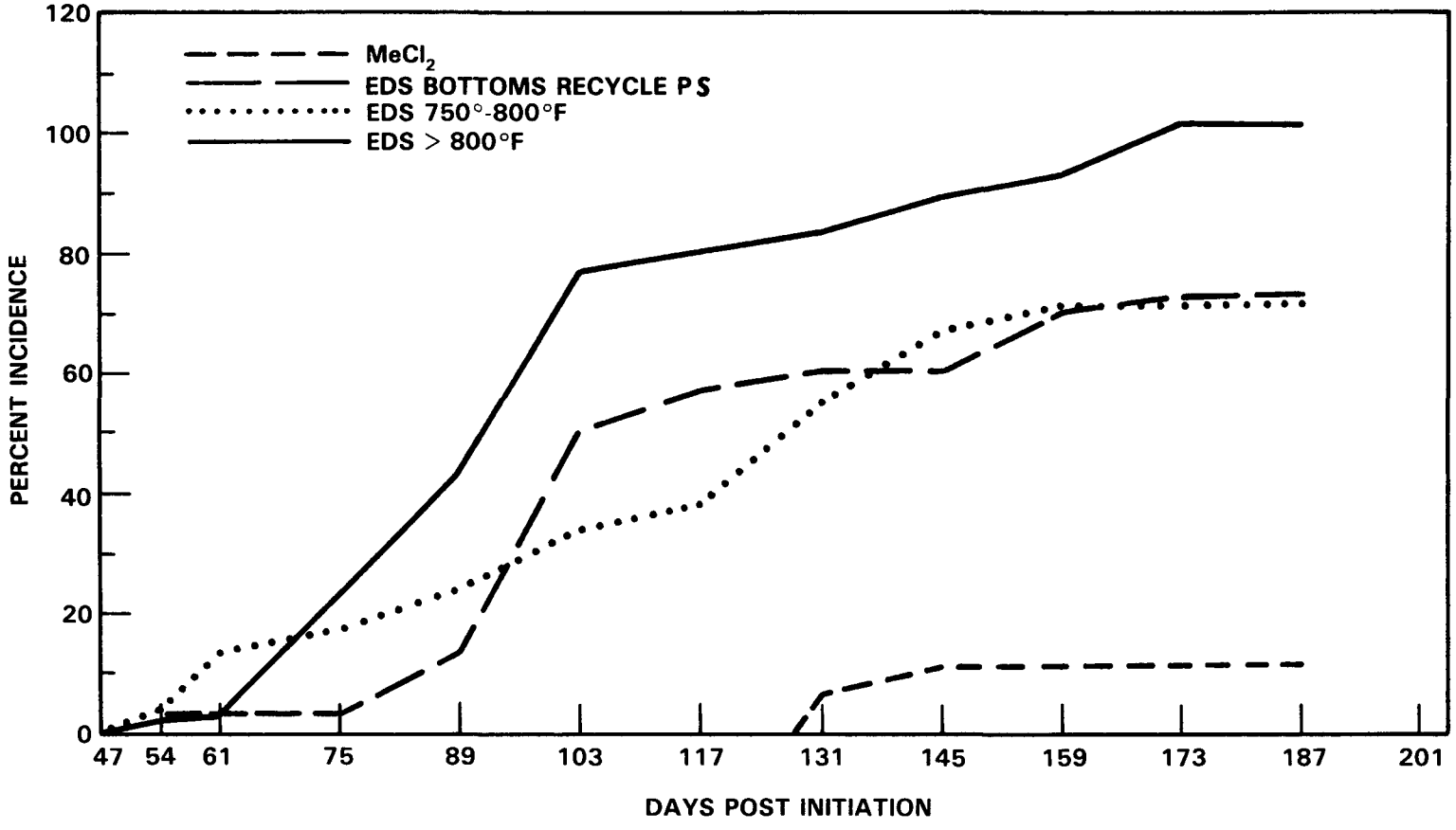


FIGURE 12. Percent of Tumor Incidence (versus Days after Initiation) for EDS 800°+F and 750-800°F Distillate Cuts and Bottoms Recycle PS

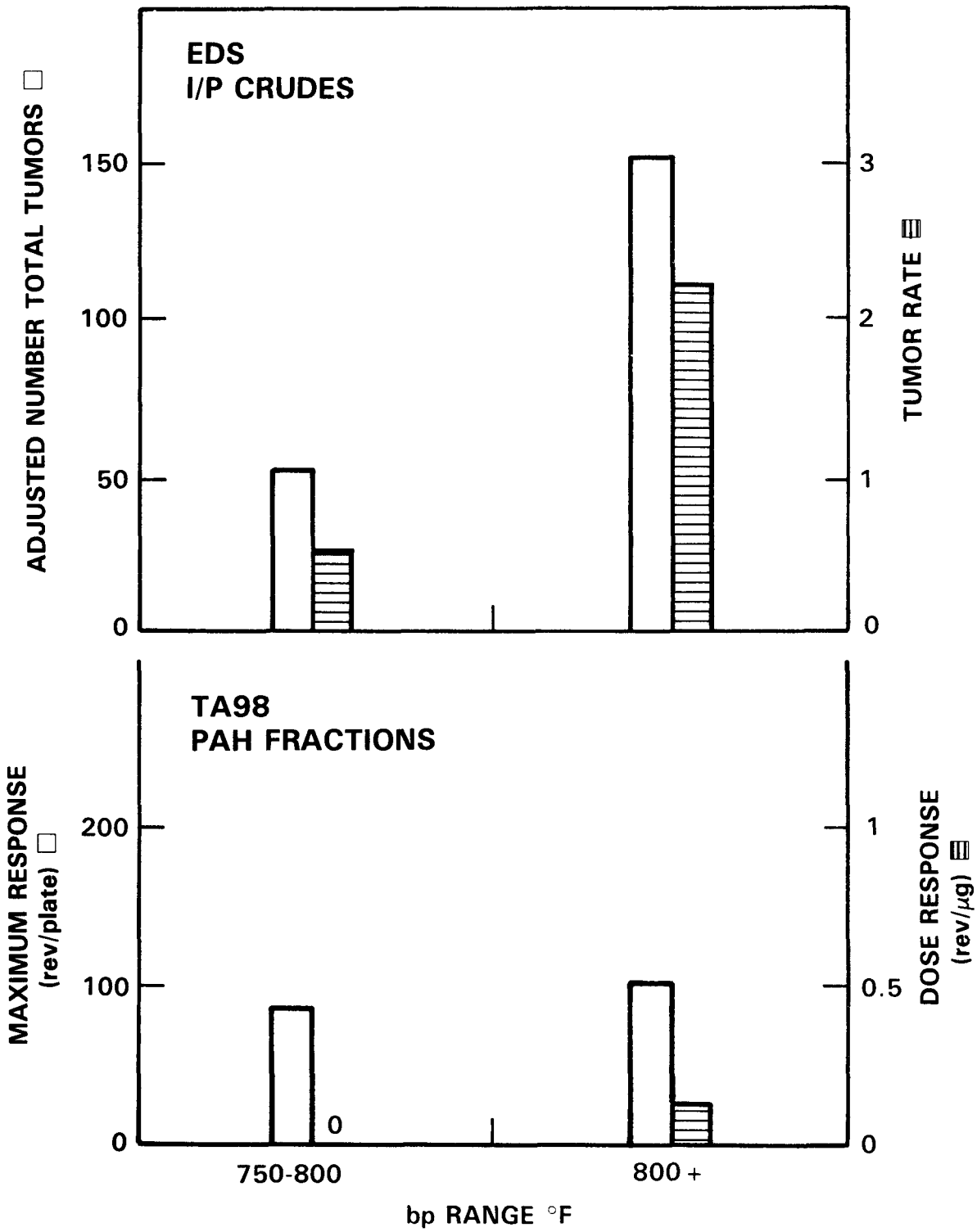


FIGURE 13. Dose and Maximum Mutagenic Response Induced by the PAH Fraction in *S. typhimurium*, TA98 Compared with Initiation Rate and Maximum Initiation Response of Dermal Tumors in Mice by the Crudes of the EDS 750-800°F and 800°+F Distillate Cuts

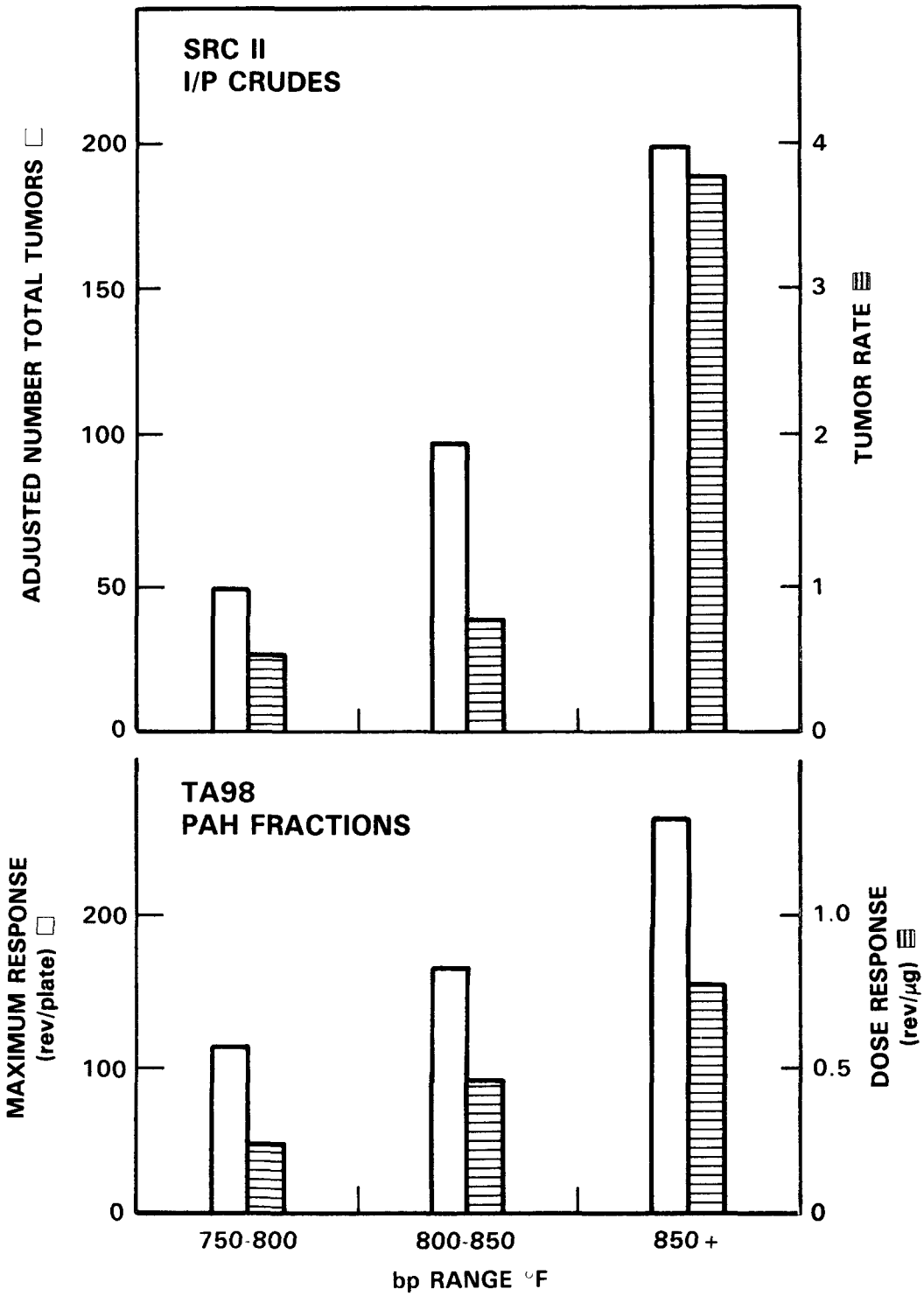


FIGURE 14. Dose and Maximum Mutagenic Response Induced by the PAH Fraction in *S. typhimurium*, TA98 Compared with Initiation Rate and Maximum Initiation Response of Dermal Tumors in Mice by the Crudes of the SRC II 750-800°F, 800-850°F, and 850°+F Distillate Cuts

CHEMICAL ANALYSES

Chemical characterization of EDS process materials and distillate fractions was carried out for two major reasons. The first, for the purpose of this report, was the correlation of chemical information and observed biological response. Secondly, detailed information on the chemical composition of these process materials and distillation cuts has also been generated. Similar data sets for several operational modes of SRC and TSL coal liquefaction processes have also been accumulated. Although these data sets have been generated as a component of toxicological studies on the various process materials, they also offer insights into the different chemical properties of materials from different coal liquefaction processes and the effects that different process technologies such as hydrotreatment, heavy-end recycling, and reduced liquefaction severity might have on the chemical composition of product materials. In this section, the results of the chemical analyses for both the representative process materials (Sample Set 1, Table 2) and distillate fractions of the reblended naphtha/recycle solvent (Sample Set 2, Table 3) will be presented.

EDS Process Materials

The relative chemical compositions of the five EDS process materials, as determined by the alumina column chemical class fractionations, are shown in Table 10. The low overall recovery from the alumina separation observed for the raw naphtha was probably due to sample component loss while evaporating the solvents used to elute the class fractions. The sample constituents in the raw naphtha were relatively volatile; they boiled at less than 400°F. The naphtha also appeared to be mainly aliphatic in nature, with greater than 65%

TABLE 10. Chemical Composition of Selected EDS Process Materials

Compound Class	Fraction	Weight Distribution (%)[a] Raw Naphtha 002	Bottoms Recycle PS 003	Vacuum Bottoms 004	Once-Through PS 005	Heavy VGO 006
Alumina Separations						
Aliphatic hydrocarbons	A_1	28	46*	2	69*	5
Neutral PAH	A_2	4	37	7	21	31
N-PAC	A_3	<1	7	24	2	22
Hydroxy-PAH	A_4	11	13	27	8	41
Total Recovery (%)		43	103	60	100	99
Picric Acid/Alumina Separation[b]						
Aliphatic hydrocarbons	PA_1		26		40	
Hydroaromatic PAH	PA_2		37		36	
Dihydro-PAH + PAH	PA_4		15		8	
>4-ring-PAH	PA_5		9		2	
Total Recovery (%)			87		86	

[a]Values are the average of two individual determinations except for the two values marked with asterisks, which are single values.
[b]Fractions obtained by the method of Wozniak and Hites (26)

of the recoverable material being eluted in the aliphatic hydrocarbon fraction. Additionally, only a low concentration of neutral PAH was observed in the raw naphtha, with almost no N-PAC components. The most concentrated chemical class, next to the aliphatic hydrocarbons, was the hydroxy-PAH fraction, presumably phenol, alkyl phenols, and related low molecular weight hydroxy-PAH found in the crude raw naphtha.

Several general observations can be made by comparing the weight distribution of the chemical classes for the PS from the bottoms recycle (003) and once-through (005) operational modes (Table 10). First, the once-through PS had a higher level of aliphatic hydrocarbons than the bottoms recycle PS. Compounds with a high degree of hydroaromaticity can also elute in the A_1 fraction of the alumina separation. A picric acid-doped alumina separation method recently developed by Wozniak and Hites (26) for class distinction of the hydroaromatic-type compounds was employed to gain further insight into the hydroaromatic PAH versus aliphatic hydrocarbon composition. Except for general chemical composition studies for mass balance purposes, detailed investigations of the hydroaromatic PAH composition in the picric acid/alumina fractions were not undertaken due to the proprietary nature of these types of compounds in the EDS process materials. The observation from the alumina separation that the aliphatic hydrocarbons were more concentrated in the once-through PS compared with the bottoms recycle PS, is supported by the chemical class distribution results from the picric acid/alumina separation. Fraction PA_1 was 40% for the once-through PS and can be directly compared to 26% for the bottoms recycle PS. The hydroaromatic PAH portion of each PS was a constant 36% of the crude. Both PS were highly aliphatic, with 76% of the once-through PS and 63% of the bottoms recycle PS being accounted for in the ali-

phatic hydrocarbon and hydroaromatic PAH fractions. The high aliphatic/hydroaromatic content of these materials was a result of hydrogenating the PS.

The fact that the once-through PS has a higher aliphatic content than the bottoms recycle PS is related to two factors. First, both liquefaction and solvent hydrogenation conditions were changed to decrease aliphatic content and increase hydroaromatic content in the bottoms recycle PS. These changes were made to improve process operability and yield and were made possible by information acquired after the once-through operation had been completed. Second, the boiling range of the process solvent was purposely changed to increase the upper boiling point limit and, consequently, increase the concentration of high boiling materials in the bottoms recycle PS relative to the once-through PS. Comparison of the GC distillation data previously shown in Table 3B substantiates the overall presence of higher boiling materials in the bottoms recycle PS as compared to the once-through PS. Again, the driving force was process operability and yield considerations. The higher boiling fractions contained more aromatics and less aliphatics, and higher levels of N-PAC and hydroxy-PAH. The change in boiling range as well as changes in hydrogenation and liquefaction conditions probably accounted for the higher levels of PAH, N-PAC, and hydroxy-PAH observed in the bottoms recycle PS versus the once-through PS.

Further investigation of the PS alumina fractions by probe MS and capillary GC revealed, as expected, that the bottoms recycle PS contained higher molecular weight material than the once-through PS. Figure 15 shows capillary column gas chromatograms detailing the neutral PAH components of these two PS; the concentrations of PAH identified are given in Table 11.

A noticeable inclusion of PAH with molecular weights greater than pyrene (202 m/z) was observed for the bottoms recycle PS. Inspection of the data in

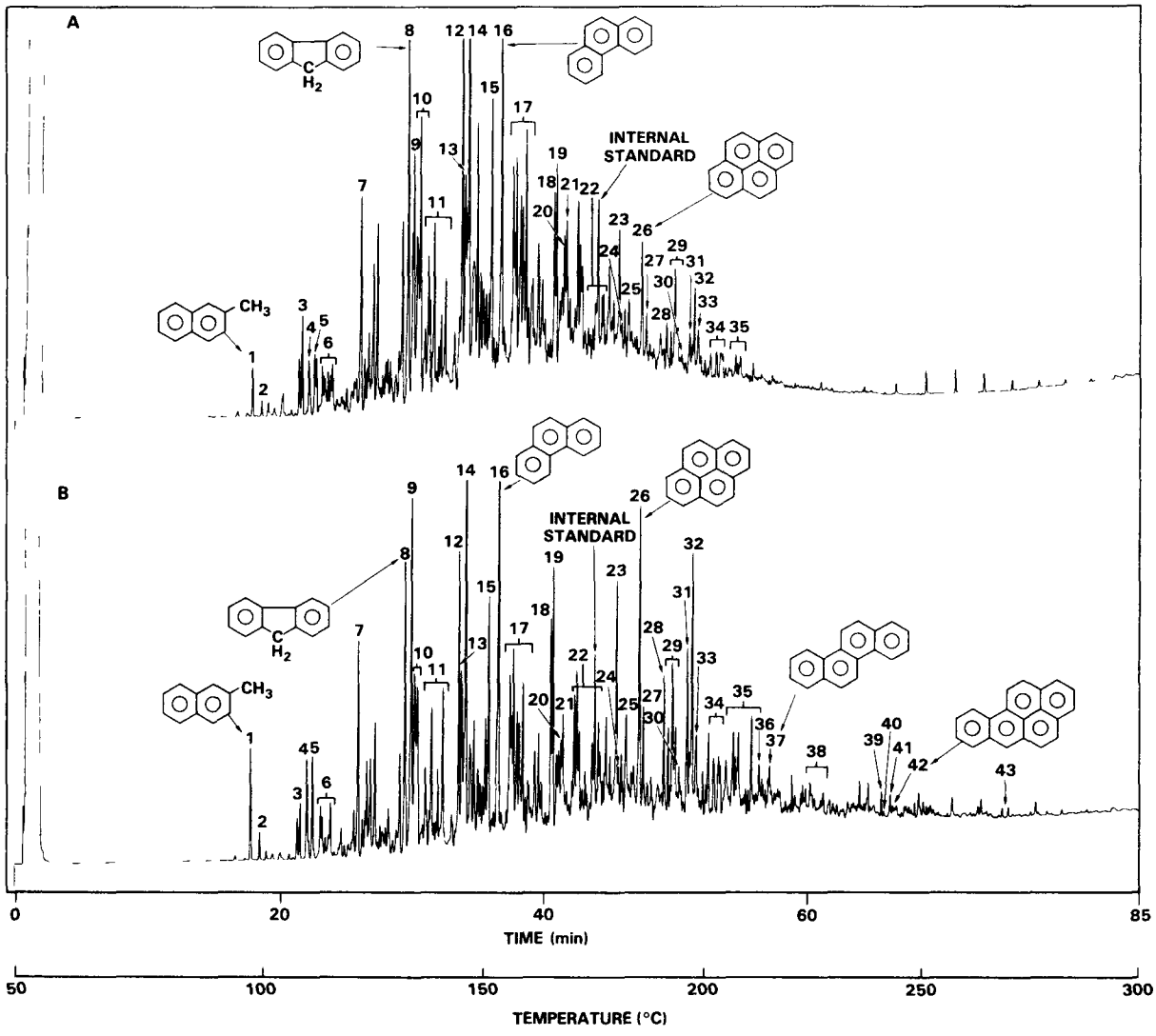


FIGURE 15. Capillary Column Gas Chromatogram of the PAH Fractions from the (A) Once-Through PS and (B) Bottoms Recycle PS. See Table 11 for qualitative and quantitative peak identifications.

TABLE 11. Peak Identifications and Concentrations of PAH from Fraction A_2 of the Bottoms Recycle and Once-Through Recycle Solvents

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g PAH Fraction) Bottoms Recycle	Once-Through
1	142	2-Methylnaphthalene	5400 ± 200	2000 ± 100
2	142	1-Methylnaphthalene	1300 ± 50	600 ± 50
3	154	Biphenyl	5100 ± 1800	2700 ± 100
4	156	2-Ethylnaphthalene	ND[c]	ND
5	156	2,3- or 2,6-Dimethylnaphthalene	6100 ± 200	3200 ± 200
6	156	C_2-Naphthalenes	ND	ND
7	170	C_3-Naphthalene	5000 ± 1300	6300 ± 400
8	166	Fluorene	12600 ± 1500	17000 ± 900
9	168	Dihydrofluorene	16800 ± 3100	6500 ± 500
10	168	C_1-Biphenyls	ND	ND
11	182	C_2-Biphenyls	ND	ND
12	180	2-Methylfluorene	11200 ± 1400	13200 ± 1700
13	180	1-Methylfluorene	6300 ± 1600	14800 ± 2800
14	180	Methylfluorene	15400 ± 1000	17100 ± 2300
15	196	C_3-Biphenyls	ND	ND
16	178	Phenanthrene	21700 ± 100	13600 ± 2200
17	194	C_2-Fluorenes	22900 ± 2550[d]	26200 ± 1680[d]
18	192	3-Methylphenanthrene	8400 ± 100	6400 ± 1100
19	192	2-Methylphenanthrene	7500 ± 700	5700 ± 600
20	192	9- or 4-Methylphenanthrene	3800 ± 200	4500 ± 100
21	192	1-Methylphenanthrene	5000 ± 300	5400 ± 500
22	206	C_2-Phenanthrenes	ND	ND
23	204	Dihydrofluoranthene	7000 ± 300	4600 ± 200

[a]Refers to peaks in Figure 15
[b]Tentative identification by GC/MS and retention times
[c]No quantitative data
[d]A composite of more than one peak

TABLE 11. (continued)

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g PAH Fraction) Bottoms Recycle	Once-Through
24	202	Fluoranthene	1400 ± 200	1200 ± 200
25	220	C_3-Phenanthrene	ND	ND
26	202	Pyrene	9500 ± 800	3300 ± 1000
27	204	Dihydropyrene	3100 ± 300	1500 ± 100
28	218	C_1-Dihydrofluoranthene/pyrenes	ND	ND
29	234	C_4-Phenanthrene	ND	ND
30	216	Benzo[a]fluorene	1000 ± 800	250 ± 50
31	216	Benzo[b]fluorene, 2- or 4-methylpyrene	5800 ± 800	1300 ± 150
32	218	Methylphenylnaphthalene	ND	ND
33	216	1-Methylpyrene	1200 ± 200	1700 ± 400
34	234	Benzonaphthothiophenes	ND	ND
35	232	C_2-Dihydrofluoranthene/pyrenes	ND	ND
36	228	Benz[a]anthracene	900 ± 200	100[e]
37	228	Chrysene	1700 ± 100	380[e]
38	242	C_1-Chrysenes	4300 ± 250	657[d,e]
39	252	Benzo[j or b]fluoranthene	300 ± 100	58[e]
40	252	Benzo[k]fluoranthene	ND	110[e]
41	252	Benzo[e]pyrene	570 ± 120	ND
42	252	Benzo[a]pyrene	170 ± 60	ND
43	276	Benzo[ghi]perylene	320 ± 30	ND

[a]Refers to peaks in Figure 15
[b]Tentative identification by GC/MS and retention times
[c]No quantitative data
[d]A composite of more than one peak
[e]Value derived from one determination only

Table 11 emphasizes this difference: compounds above the pyrene "cut-point" were much less concentrated (or undetectable) in the once-through as opposed to the bottoms recycle materials. In most cases, the concentration of PAH was greater for components of the bottoms recycle PS as compared to the once-through PS. For example, increased concentrations of PAH, such as phenanthrene, pyrene, chrysene, and the benzopyrenes/fluoranthenes, were observed in the bottoms recycle PS. Those species in Table 11 which were more concentrated in the once-through PS either had a lower molecular weight (e.g., fluorene) or were alkylated PAH species (e.g., methylfluorene).

Generally, the EDS process materials contained higher levels of alkylated PAH than previously observed in SRC-type materials. Alkylation as high as C_{10} was typically observed by GC, HPLC, GC/MS and probe inlet MS for parent PAH such as biphenyl, fluorene, phenanthrene, pyrenes, chrysene and the benzopyrenes/fluoranthenes. A more detailed discussion emphasizing this observation as it relates to the distillate cuts will be presented later.

The trends observed by capillary column GC for the neutral PAH alumina fractions of the PS were supported and confirmed by low voltage, low resolution probe inlet MS. The probe mass spectra for the PAH isolates from the two recycle solvents are shown in Figure 16. Additional spectra for all of the chemical classes for the four EDS process materials (003-006) are presented in Appendix B. The spectra of Figure 16 emphasize the high degree of alkylation present in the EDS process materials. For example, the homologous series of peaks at m/z 166, 180, 194, 208, 222, 236, 250, etc. represent the molecular ions of alkylated fluorene, starting with the parent ion structure at m/z 166. The dominant presence of peaks at m/z 165, 179, 193, etc. in the 70 eV spectra for the PS provides additional confirmation for the assignment of fluorene as the parent structure for this alkylated series. Probe MS data confirm that

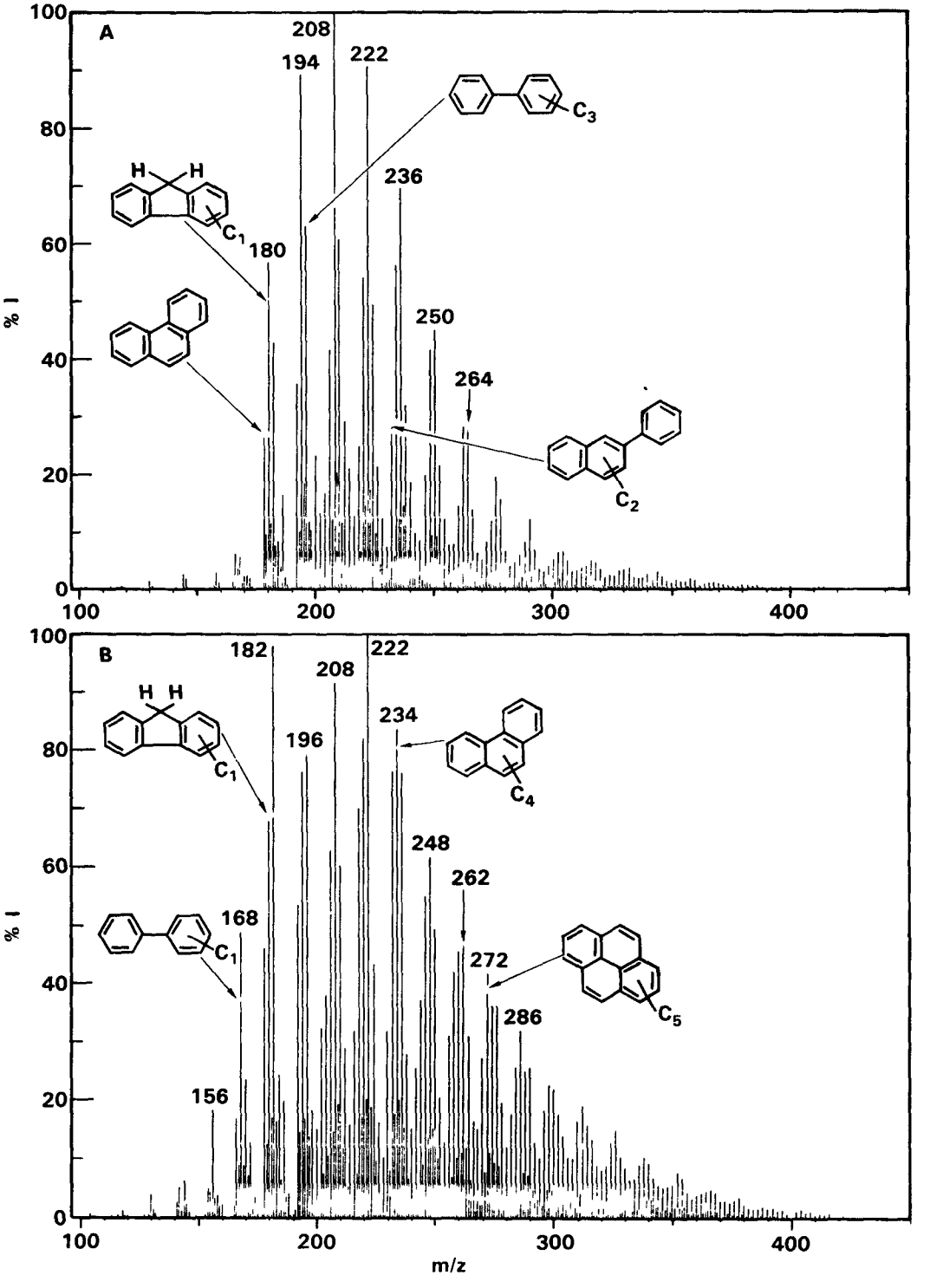


FIGURE 16. Low Voltage, Low Resolution Probe Inlet Mass Spectra of the PAH Fractions from the (A) Once-Through PS and (B) Bottoms Recycle PS

the PS in the once-through mode was lower in molecular weight than the bottoms recycle PS.

The heteroatomic content of the two PS follows the same trends as those discussed for the neutral PAH. The N-PAC (bottoms recycle: 7%, once-through: 2%) and hydroxy-PAH (bottoms recycle: 13%, once-through: 8%) concentrations were lower in the once-through PS than in the bottoms recycle PS (Table 10). As discussed, this trend is probably due to changes in the PS boiling range and processing conditions.

Figure 17 shows capillary column gas chromatograms of the N-PAC isolates of the recycle solvents; Table 12 quantitatively lists those compounds identified in these two PS. The major N-PAC species observed in these PS materials were the indole/carbazole-type compounds, with only slight concentrations of the quinoline/benzoquinoline azaarene species present. As with the neutral PAH, the concentrations of those compounds identified were generally higher in the bottoms recycle PS than in the once-through PS. Again, a high degree of alkylation was observed; the alkylated species were present in generally higher concentration than the nonalkylated parent structures. These observations have also been confirmed by probe inlet MS, with alkylation detected in these isolates up to C_8 for the carbazole series (Appendix B).

A chromatogram of the hydroxy-PAH fraction (A_4) is shown in Figure 18, with corresponding qualitative information in Table 13. The major species present in the recycle solvents were the alkylated phenols and hydroxybiphenyls. Infrared (IR) spectrophotometric analyses of the once-through PS and bottoms recycle PS supported the presence of hydroxy-PAH in these materials, with a strong adsorption band in the 3600 cm^{-1} region (hydroxy stretch). Detail on the differences in hydroxy-PAH concentration of these two PS have been outlined by Dauble and coworkers in a previous PNL Status Report (27).

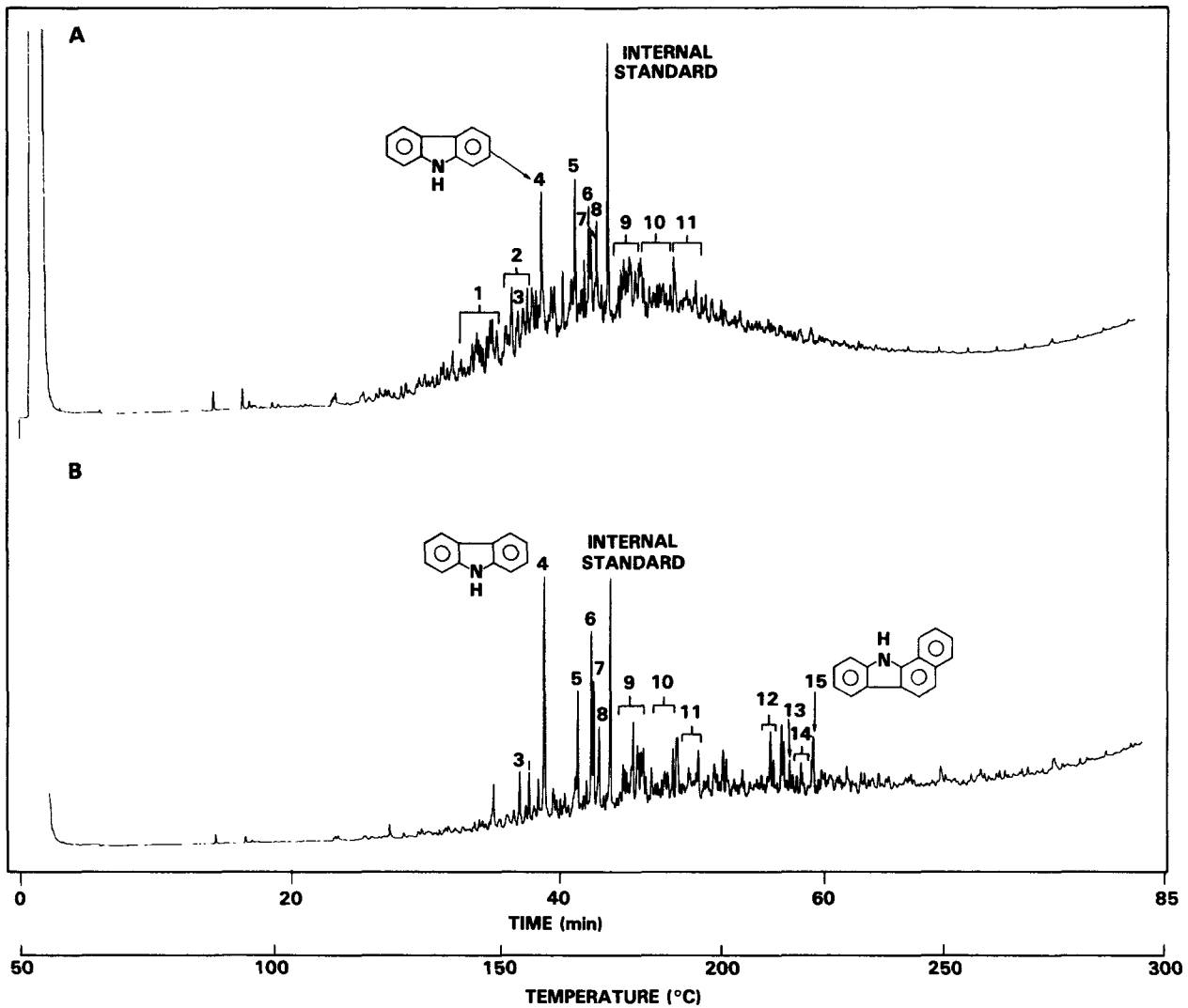


FIGURE 17. Capillary Column Gas Chromatogram of the (A) Once-Through and (B) Bottoms Recycle PS, N-PAC Fraction A_3. See Table 12 for qualitative and quantitative peak identifications.

TABLE 12. Peak Identifications and Concentrations of N-PAC from Fraction A_3 of the Bottoms Recycle and Once-Through PS

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g N-PAC Fraction) Bottoms Recycle	Once-Through
1	187,197	C_5-Indole, C_3-azabiphenyl	ND[c]	ND
2	201,211	C_6-Indole, C_4-azabiphenyl	ND	ND
3	201	C_6-Indole	1270 ± 240	1000 ± 300
4	167	Carbazole	5940 ± 940	3140 ± 640
5	181	1-Methylcarbazole	2270 ± 380	2530 ± 190
6	181	3-Methylcarbazole	3800 ± 250	2200 ± 630
7	181	2-Methylcarbazole	2740 ± 210	1940 ± 500
8	181	4-Methylcarbazole	2920 ± 370	1780 ± 1050
9	195	C_2-Carbazoles	ND	ND
10	209	C_3-Carbazoles	ND	ND
11	223	C_4-Carbazoles	ND	ND
12	221	C_3-Azaphenanthrenes	ND	ND
13	217	Benzo[a]carbazole	900 ± 190	280[d]
14	235	C_4-Azaphenanthrenes	ND	ND
15	217	Benzo[c]carbazole	2460 ± 510	250[d]

[a]Refers to peaks in Figure 17
[b]Tentative identification from GC/MS and retention time
[c]No quantitative data
[d]Value derived from one determination

Briefly, phenol and alkylated phenols constituted a higher percentage of the total hydroxy-PAH fraction from the PS produced in the once-through compared with the bottoms recycle mode of operation. This correlates well with observations made in this report for the other chemical classes: the once-through PS was composed of lower molecular weight compounds and the bottoms recycle PS contained a wider range of higher molecular weight PAC.

The other two process materials investigated were the heavy VGO and vacuum bottoms. The vacuum bottoms sample was a high molecular weight material with a high heterocyclic PAC content. The total weight recovered from the

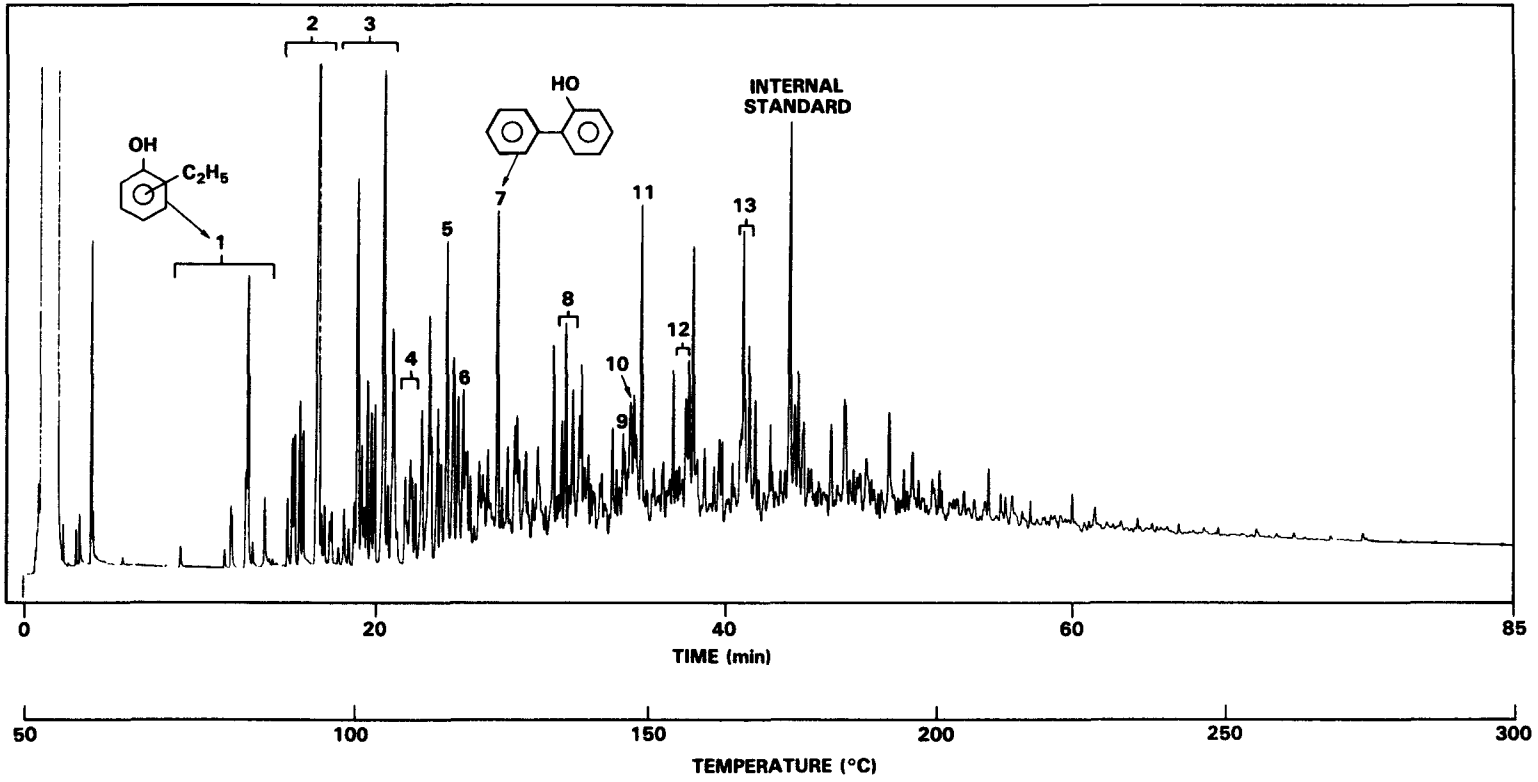


FIGURE 18. Capillary Column Gas Chromatogram of the Hydroxy-PAH Fraction A_4 of the Bottoms Recycle PS. See Table 13 for peak identification.

TABLE 13. Peak Identifications of Hydroxy-PAH from Fraction A_4 of the Bottoms Recycle Solvent

Peak Number[a]	Molecular Weight	Compound[b]
1	122	C_2-Phenols
2	136	C_3-Phenols
3	150	C_4-Phenols
4	164	C_5-Phenols
5	164	C_5-Phenol
6	162	C_2-Indanol
7	170	2-Hydroxybiphenyl
8	184	C_1-Hydroxybiphenyls
9	198	C_2-Hydroxybiphenyl
10	170	Hydroxybiphenyl
11	190	C_4-Indanol
12	184	C_1-Hydroxybiphenyls
13	198	C_2-Hydroxybiphenyls

[a]Refers to peaks in Figure 18
[b]Tentatively identified by GC/MS

alumina adsorption column was only 60% of the initial starting material (Table 10). Component loss during the solvent reduction step of sample preparation, as seen for the raw naphtha, was not likely, due to the high molecular weight of this material. There are two possible explanations for the observed low recovery of this process material. First, the vacuum bottoms material typically contained 22-24% ash. In addition, they contained a considerable amount of carbonaceous material that was insoluble in most organic solvents. These two factors probably accounted for roughly 40% by weight of the vacuum bottoms material.

The observation that the vacuum bottoms were highly polar and were composed of high molecular weight PAC that were not eluted from alumina even with polar solvents such as tetrahydrofuran or methanol is also supported by mass

spectral data. The average molecular weights for the neutral PAH and N-PAC fractions were ∿350 amu and ∿380 amu, respectively. (See the low voltage probe mass spectra of the class fraction of the vacuum bottoms in Appendix B.) The low voltage mass spectra for fraction A_4 (Figure 19) indicated that the major constituents were the highly alkylated four-, five-, and six-ring hyroxy-PAH; compounds with more than six aromatic rings were also present. Hence, the soluble portion of the vacuum bottoms material is also composed of high molecular weight, polar PAC.

The heavy VGO was also mostly polar and aromatic, with greater than 60% of the gross chemical composition attributable to the N-PAC and hydroxy-PAH classes (Table 10, Sample 006). The neutral PAH isolates from the vacuum bottoms and heavy VGO are compared in the capillary column gas chromatograms of Figure 20; quantitative differences are tabulated in Table 14. These data, along with the low voltage mass spectra (Appendix B), indicate that although the heavy VGO has a relatively high molecular weight range (from approximately that of fluorene to that of benzo(ghi)perylene), the vacuum bottoms are still higher in molecular weight, with the distribution starting only around the chrysene (m/z 228) region. Again, high levels of alkylation are present in both materials. The main N-PAC constituents in the heavy VGO were again the carbazoles, alkylated carbazoles, benzocarbazoles, and alkylated benzocarbazoles as shown in Table 15. Fraction A_4 contained highly alkylated three- to six-ring hydroxy-PAH (see Appendix B).

Since the amino-PAH have been demonstrated to be the determinant mutagens in coal liquefaction materials, quantitative and qualitative analyses of this chemical class were also conducted on four of the five process materials (003-006). Secondary separation of the N-PAC on silicic acid prior to pentafluoropropionic anhydride derivatization and selective ECD-GC detection of the

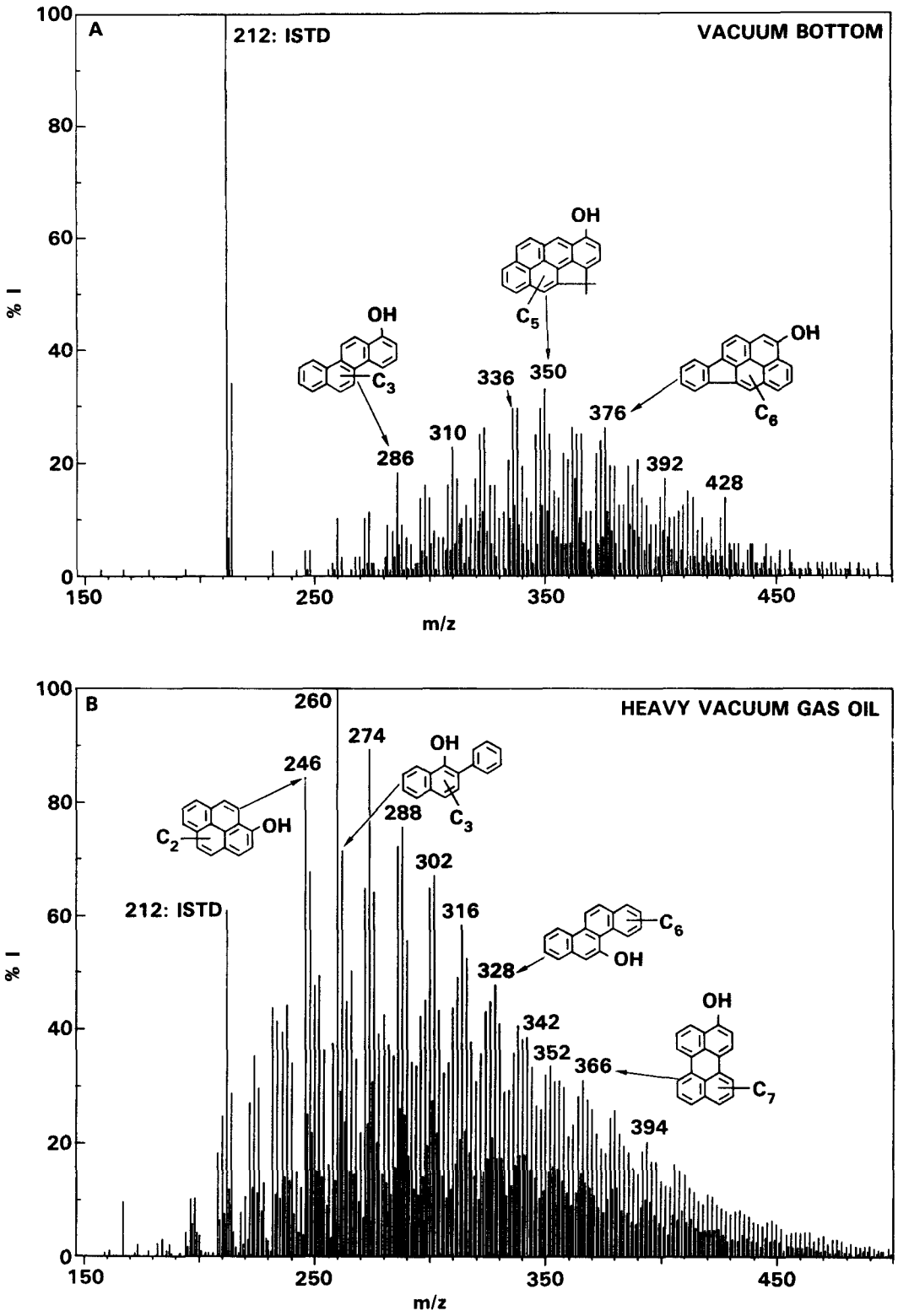


FIGURE 19. Low Voltage, Low Resolution Probe Inlet Mass Spectra of the Hydroxy-PAH Fraction from the Vacuum Bottoms and Heavy VGO

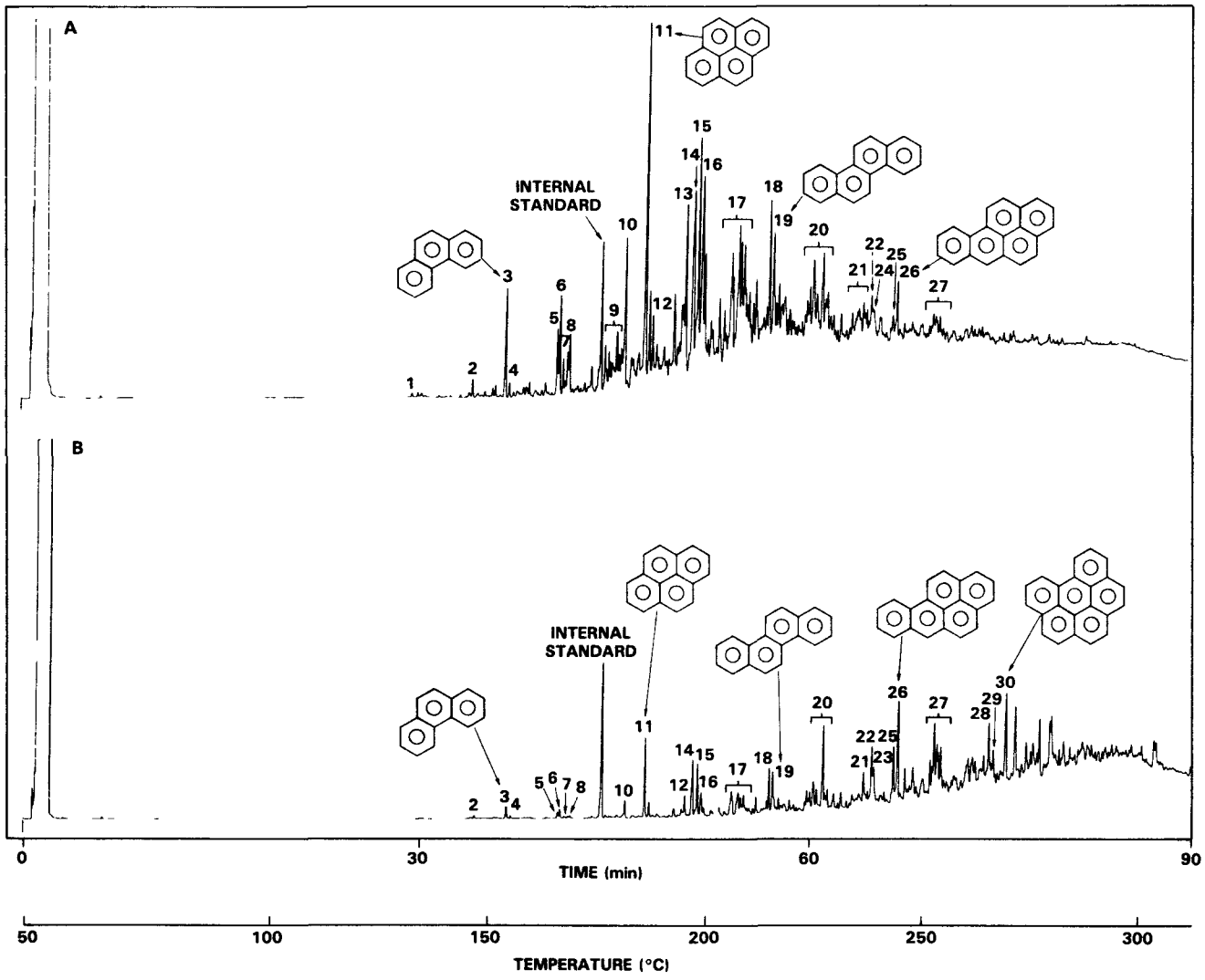


FIGURE 20. Capillary Column Gas Chromatogram of the PAH Fraction A_2 of the EDS (A) Heavy VGO and (B) Vacuum Bottoms. See Table 14 for peak identification.

TABLE 14. Peak Identifications and Concentrations for the Neutral PAH Fraction A_2 of the Vacuum Bottoms and Heavy VGO

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g PAH Fraction) Heavy VGO (006)	Vacuum Bottoms (004)
1	166	Fluorene	150[d]	
2	180	Methylfluorene	750 ± 50	
3	178	Phenanthrene	4200 ± 300	400 ± 100
4	178	Anthracene	600 ± 50	
5	192	3-Methylphenanthrene	2700 ± 400	
6	192	2-Methylphenanthrene	3300 ± 300	220 ± 45
7	192	9- or 4-Methylphenanthrene	1800 ± 400	
8	192	1-Methylphenanthrene	2100 ± 300	
9	206	C_2-Phenanthrenes	ND[e]	
10	202	Fluoranthene	5200 ± 1300	350 ± 100
11	202	Pyrene	13000 ± 3000	2200 ± 64
12	218	C_1-Phenylnaphthalene	ND	ND
13	216	Benzo[a]fluorene	5700 ± 700	500 ± 100
14	216	Benzo[b]fluorene, 2- or 4-methylpyrene	8100 ± 1500	2100 ± 50
15	218	C_1-Phenylnaphthalene	ND	ND
16	216	1-Methylpyrene	9800 ± 2300	1000 ± 100
17	230	C_1-Benzofluorenes, C_2-pyrenes	ND	ND
18	228	Benz[a]anthracene	4400 ± 600	1200 ± 50
19	228	Chrysene	4500 ± 600	1200 ± 400
20	242	C_1-Chrysenes[c]	12000 ± 1600	5600 ± 290
21	256	C_2-Chrysenes	ND	ND
22	252	Benzo[j or b]fluoranthene	1000 ± 100	1900 ± 100
23	252	Benzo[k]fluoranthene	400 ± 100	1600 ± 50
24	256	7,12-Dimethylbenzanthracene	92	ND
25	252	Benzo[e]pyrene	1000 ± 600	1800 ± 300
26	252	Benzo[a]pyrene	1900 ± 350	3300 ± 100
27	266	C_1-Benzopyrenes, C_1-benzofluoranthenes	ND	
28	276	Indeno[1,2,3-cd]pyrene	ND	2400 ± 280
29	278	Dibenz[a,c or a,h]anthracene	490 ± 140	1600 ± 500
30	276	Benzo[ghi]perylene	180 ± 66	4000 ± 490

[a]Refers to peaks in Figure 20
[b]Tentatively identified by GC/MS and retention times
[c]Composite of four peaks
[d]Value derived from one determination
[e]No quantitative data

TABLE 15. Quantitative Data for N-PAC Detected in Fraction A_3 of the Heavy VGO

Molecular Weight	Compound	Concentration (μg/g N-PAC Fraction) Heavy VGO (006)
167	Carbazole	141[a]
181	1-Methylcarbazole	127[a]
181	3-Methylcarbazole	280 ± 83
181	2-Methylcarbazole	205 ± ND
181	4-Methylcarbazole	ND[b]
195	Dimethylcarbazole	159[a]
209	Trimethylcarbazole	297 ± 0
209	Trimethylcarbazole	302 ± 26
223	Tetramethylcarbazole	257[a]
223	Tetramethylcarbazole	413 ± 137
217	Benzo[a]carbazole	446 ± 55
217	Benzo[b]carbazole	729 ± 50
217	Benzo[c]carbazole	939 ± 41
251	Methylbenzocarbazole	1387 ± 91
245	Dimethylbenzocarbazole	383 ± 79

[a]Based on a single determination
[b]No quantitative data

amino-PAH isolates enabled the semi-quantitation of several known mutagenic compounds. Table 16 lists the concentrations of 19 amino-PAH as determined by comparative retention and response factor data (see Methods Section for details). The 19 components for which analyses were conducted represented only a small portion of the amino-PAH detected by this method. A complex mixture of many amino-PAH was observed in each of the EDS process materials.

In general, the amino-PAH are in much lower relative concentrations in the EDS materials than in analogous SRC I or II materials. (This will be demonstrated in the next section by comparing equivalent distillation cuts of materials from the two processes.) Comparison of the PS from both operational

TABLE 16. Concentration Levels of Selected Amino-PAH in EDS Process Materials

Compound[b]	Concentration (μg/g Crude)[a]			
	Bottoms Recycle PS (003)	Vacuum Bottoms (004)	Once-Through PS (005)	Heavy VGO (006)
1-Aminonaphthalene	1.6	---[c]	---	---
2-Aminobiphenyl	1.1	---	---	0.6
2-Aminonaphthalene	1.7	---	0.2	1.1
3-Methyl-2-aminonaphthalene	0.8	---	0.1	1.1
4-Aminobiphenyl	2.6	---	0.4	1.1
4-Aminofluorene	2.0	---	0.4	0.8
2-Aminofluorene	3.7	---	1.4	---
9-Aminophenanthrene, and/or 1-aminophenanthrene, and/or 1-aminoanthracene	9.6	3.3	1.3	2.9
2-Aminophenanthrene, and/or 3-aminophenanthrene	3.1	1.5	1.0	5.4
2-Aminoanthracene	2.7	0.6	2.1	3.1
3-Aminofluoranthrene	4.5	---	1.2	3.8
1-Aminopyrene	2.9	---	2.5	48.8
2-Aminopyrene	2.5	4.4	0.3	2.8
8-Aminofluoranthene	3.9	9.4	2.1	9.0
3-Aminochrysene	3.8	13.0	0.5	29.8
6-Aminochrysene	1.9	13.0	0.7	5.1

[a]Values are the average of three independent measurements at three concentration levels.
[b]Tentatively identified by GC/MS and GC retention times
[c]Not detected

modes shows that the bottoms recycle PS had higher levels of a wider range of amino-PAH than the once-through PS. Inspection of the ECD-GC chromatograms in Figure 21, where only the derivatized amino-PAH were detected, reveals a noticeable difference in the composition of these two materials. The once-through PS (bottom chromatogram) was not nearly as complex and had a more restricted distribution of amino-PAH than the bottoms recycle PS. The latter contained a greater number of compounds at higher concentrations (Table 16).

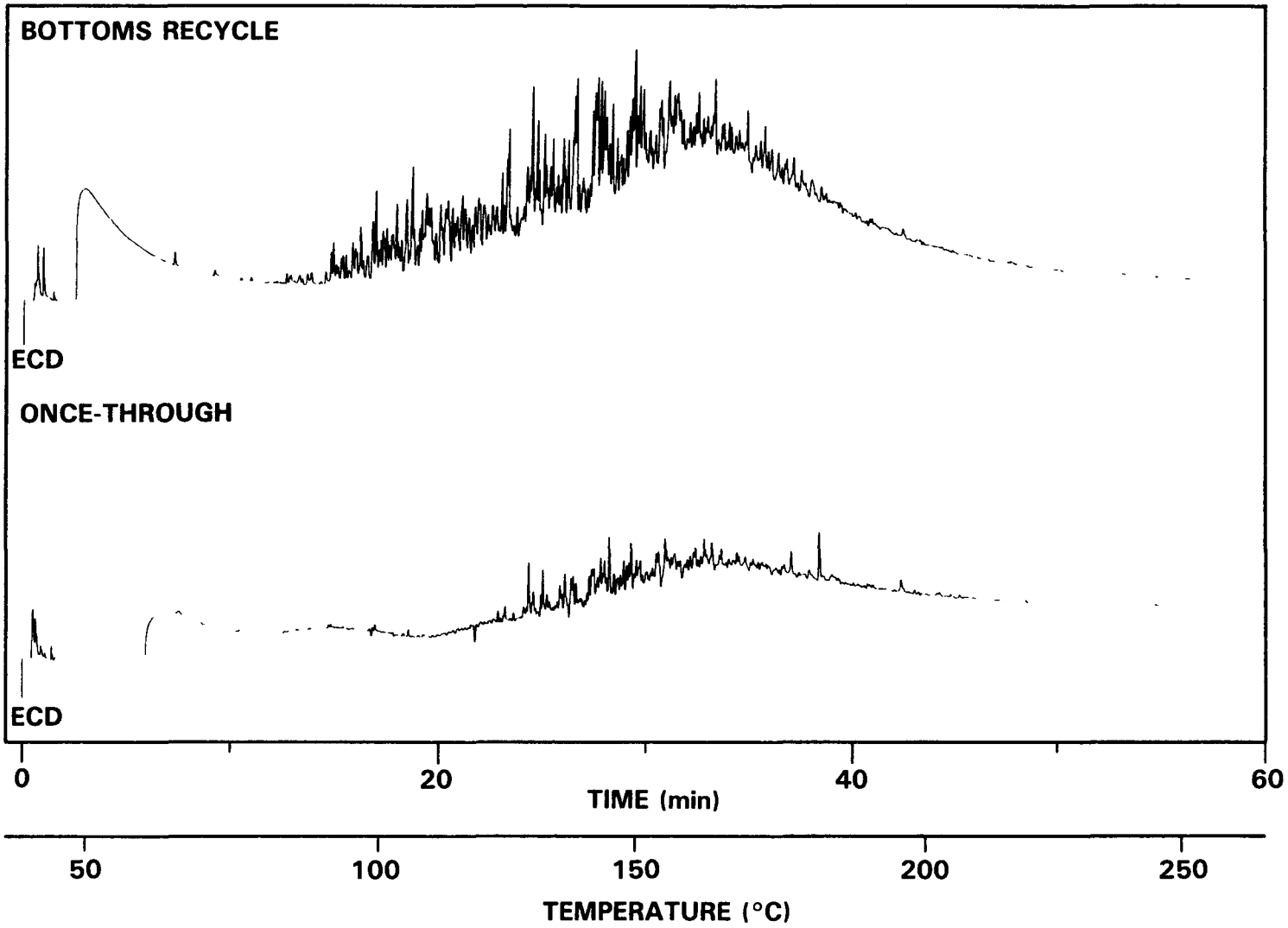


FIGURE 21. Selected ECD Capillary Column Gas Chromatograms of the Derivatized Amino-PAH Isolates of (A) Bottoms Recycle and (B) Once-Through PS

Again, these differences are probably related to differences in the boiling range of the two solvents, as well as differences in liquefaction hydrogenation conditions. As predicted from these data, the bottoms recycle PS A_3 fraction was more mutagenic as determined by both dose response and maximum response (see Figure 10, Biology section of Results). A dose response mutagenicity was not observed for the N-PAC fraction A_3 of the once-through PS, as would be anticipated from the concentrations of amino-PAH shown in Table 16. Amino-PAH data for the vacuum bottoms and heavy VGO also support the biological activity observations. The vacuum bottoms contained mostly high molecular weight amines, while the VGO was composed of a wider range of amino-PAH with high levels of the higher molecular weight amino compounds. Both materials showed strong dose response and maximum mutagenic response in S. typhimurim, TA98 (see Figure 10).

EDS Distillate Cuts

Distillation has been used in the petroleum industry for the gross separation of full-boiling-range products according to their relative volatility. A full-boiling-range process-derived EDS liquid was simulated by blending the raw naphtha and recycle solvent (Table 3). This material, which contained compounds in the 150-800°+F boiling range, was then fractionally distilled into 50°F cuts (Table 3). The weight distributions for the four major chemical classes are shown in Table 17 for the four highest boiling cuts. Approximately 88% of the reblended material was distilled below 700°F (see Figure 2 and Table 3 for distillation data). Although the four distillate materials listed in Table 17 represent only approximately 12% of the total distillation mass, the bulk of the biological activity for the full-boiling-range material was observed in these higher boiling materials (see Biological Assays: Re-

TABLE 17. Chemical Class Composition of Selected EDS Distillates

Compound Class	Weight Percent Distribution			
	650-700°F	700-750°F	750-800°F	800°+F
Aliphatic Hydrocarbons	23	19	16	4
Neutral PAH	52	60	58	58
N-PAC	10	9	13	23
Hydroxy-PAH	8	9	12	17
Total Recovery	93	97	99	102

sults and Discussion). With regard to specific chemical composition, aliphatic hydrocarbon content decreased with a concomitant increase in the levels of N-PAC and polar hydroxy-PAH with increasing distillation temperature (see Table 17). The neutral PAH portion of each distillate cut generally remained constant, 52-60%, with increasing temperature.

The effect of distillation temperature on molecular weight was clearly manifested in the results of the GC, GC/MS, and probe inlet MS studies. As a general rule, compounds of increasing molecular weight correlated with increasing distillation temperature. The gas chromatograms of the PAH fraction shown in Figure 22 illustrate this point for the four highest boiling distillates; corresponding peak identifications and quantitative data are given in Table 18. Compounds of increasing molecular weight are distilled in higher temperature distillate cuts. For example, pyrene is at approximately the same maximum concentration in the 650-700°F and 700-750°F, but levels decrease in the next two higher distillates. However, carcinogenic compounds of higher molecular weight, such as benzo[a]pyrene, are distilled entirely in the 800°+F cut (see Table 18).

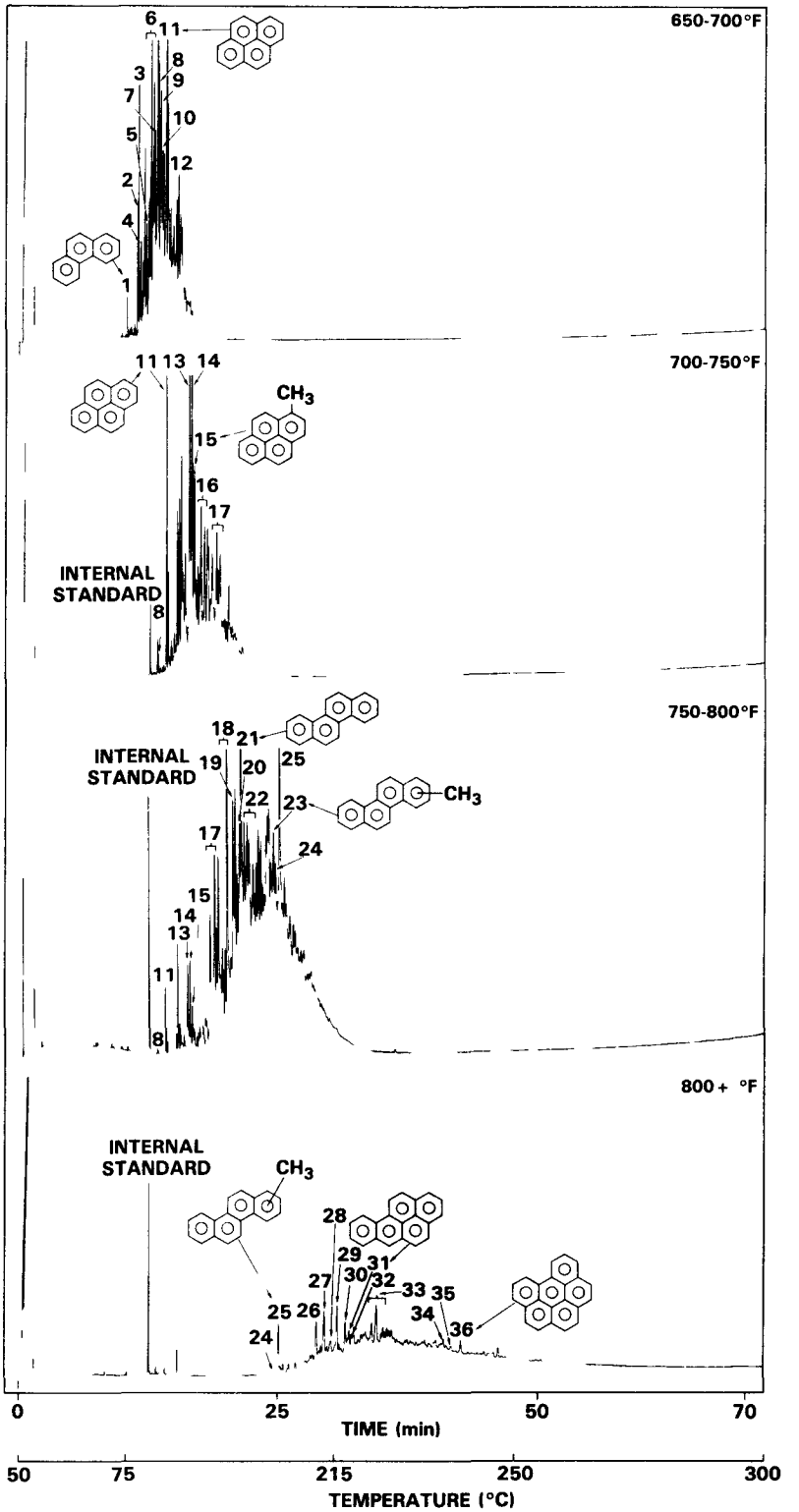


FIGURE 22. Capillary Column Gas Chromatograms of the Neutral PAH Fractions of the Four Highest Boiling EDS Distillates. See Table 18 for peak identification and concentrations.

TABLE 18. Peak Assignments and Concentrations of PAH in Fraction A_2 for the Four Highest-Boiling EDS Distillates

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g PAH Fraction) 650-700°F (037)	700-750°F (038)	750-800°F (039)	800°+F (040)
1	178	Phenanthrene	800 ± 86			
2	192	3-Methylphenanthrene	3900 ± 480			
3	192	2-Methylphenanthrene	6600 ± 700			
4	192	1-Methylphenanthrene	2830 ± 250			
5	204	2-Phenylnaphthalene	6000 ± 620			
6	206	C_2-Phenanthrenes[c]	24000 ± 1000			
7	208	C_3-Fluorene	6300 ± 2600			
8	202	Fluoranthene	9800 ± 900	1100 ± 16	41[e]	
9	220	C_3-Phenanthrene	22000 ± 1800	ND[d]	ND	
10	218	C_1-Phenylnaphthalene	8900 ± 1000	500 ± 67	ND	
11	202	Pyrene	30000 ± 2200	30000 ± 1000	1200 ± 21	170 ± 6
12	234	C_4-Phenanthrene	5700 ± 580	ND	ND	
13	216	Benzo[b]fluorene, 2- or 4-Methylpyrene		47000 ± 12000	2600 ± 230	
14	218	C_1-Phenylnaphthalene		55000 ± 11000	2200 ± 310	
15	216	1-Methylpyrene		27000 ± 6400	1400 ± 100	
16	232	C_2-Phenylnaphthalene		ND	ND	
17	230	C_1-Benzofluorenes, C_2-Pyrenes[c]		38000 ± 1000	16000 ± 610	
18	232	C_2-Phenylnaphthalene		ND	ND	
19	244	C_2-Benzofluorene, C_3-Pyrene		ND	8600 ± 440	

[a]Refers to peaks in Figure 22
[b]Tentatively identified by GC/MS and retention times.
[c]Composite of two peaks
[d]No quantitative data
[e]Value derived from one determination only

TABLE 18. (continued)

Peak Number[a]	Molecular Weight	Compound[b]	Concentration (μg/g PAH Fraction) 650-700°F (037)	700-750°F (038)	750-800°F (039)	800°+F (040)
20	228	Benz[a]anthracene		300 ± 23	5500 ± 2000	
21	228	Chrysene		1600 ± 340	22000 ± 13000	
22	258	C_3-Benzofluorenes, C_4-Pyrenes[c]			21000 ± 6600	
23	242	3-Methylchrysene			9500 ± 4300	
24	242	2-Methylchrysene			5700 ± 5000	290
25	242	6- or 4-Methylchrysene			21000 ± 13000	4200 ± 290
26	256	C_2-Chrysene				4600 ± 470
27	252	Benzo[j or b]fluoranthene				6400 ± 1100
28	252	Benzo[k]fluoranthene				920 ± 340
29	256	C_2-Chrysene				4500 ± 410
30	252	Benzo[e]pyrene				3600 ± 920
31	252	Benzo[a]pyrene				2200 ± 1200
32	252	Perylene				160 ± 70
33	262	C_6-Phenanthrene				ND
34	276	Indeno[1,2,3-cd]pyrene				680 ± 160
35	278	Dibenz[a,h, or a,c]anthracene				37
36	276	Benzo[g,h,i]perylene				1800 ± 400

[a]Refers to peaks in Figure 22
[b]Tentatively identified by GC/MS and retention times.
[c]Composite of two peaks
[d]No quantitative data
[e]Value derived from one determination only

This trend was also observed for the N-PAC, mutagenic amino-PAH, and hydroxy-PAH. Table 19 lists the concentrations of major N-PAC species detected in the A_3 fractions of the four highest boiling distillates. These were the pyrrolic-PAH such as indoles, carbazoles, benzocarbazoles, dibenzocarbazoles, and their alkyated homologues. Tertiary amines or azaarenes, such as the quinolines, acridines, phenanthridines, benzoquinolines, etc., were detected in much lower concentrations, relatively, than the pyrrolic-PAH components. The effect of distillation observed for the PAH was also noted for the N-PAC, with higher molecular weight N-PAC distilled in the higher boiling cuts (see Table 19).

Probe inlet MS data supported the above observations and confirmed the highly alkylated character of the PAC found in the distillate fractions. Table 20 provides the low voltage MS compositional data for the major components in the PAH and N-PAC fractions of the 600-650°F distillate. The base peak for each fraction is denoted as 100%, with the other peaks given as percentage intensity of the base peaks. The numbers in parentheses represent the intensity of each nominal mass ion peak as compared to the total sum of intensities for all peaks present in the spectrum. Similar data are compiled in Tables C1 to C5 of Appendix C for the 650-700°F, 700-750°F, 750-800°F, and 800°F EDS distillates. These low voltage mass spectra were acquired only at low resolution, and structural differences among isobars cannot be readily distinguished from these data. For example, C_6-indane and pyrene both have a nominal mass of 202 amu and require high resolution MS for their differentiation. In general, however, it is clear from the tables in Appendix C that the EDS distillate materials are composed mostly of alkylated species, with alkylation starting at methyl (or C_1) and ranging as high as C_{10}-C_{12} in the 800°+F distillate cut for PAH, N-PAC and hydroxy-PAH chemical components.

TABLE 19. Concentrations of N-PAC in Fraction A_3 for the Four Highest-Boiling EDS Distillates

Molecular Weight	Compound[a]	Boiling Point Range, °F 650-700 (037)	700-750 (038)	750-800 (039)	800+ (040)
129	Quinoline	15[b]			
179	Benzo[h]quinoline	280 ± 43	140		
179	Acridine	170 ± 15			
179	Phenanthridine, and or Benzo[f]quinoline	850 ± 170			
167	Carbazole	4100 ± 340	270 ± 19		
181	1-Methylcarbazole	510 ± 120	---		
181	3-Methylcarbazole	18000 ± 2300	670 ± 10		
181	2-Methylcarbazole	14000 ± 580	650 ± 27		
181	4-Methylcarbazole	9700 ± 690	320 ± 33		
195	C_2-Carbazoles[c]	28000 ± 3200	2700 ± 96		
209	C_3-Carbazoles[c]	17000 ± 1200	34000 ± 5900	1200 ± 68	
223	C_4-Carbazoles[c]		46000 ± 9800	2000 ± 450	
237	C_5-Carbazole		4100 ± 490	1700 ± 68	
221	C_3-Benzoquinolines[c]		4900 ± 1200	46000 ± 1900	
235	C_4-Benzoquinolines[d]			18000 ± 1000	
217	Benzo[c]carbazole			31000 ± 8000	400 ± 66
249	C_5-Benzoquinolines[d]			11000 ± 1700	
231	C_1-Benzocarbazoles[c]			2300 ± 320	2400 ± 350
245	C_2-Benzocarbazoles[d]				1300 ± 320
253	Azabenzopyrene				720 ± 460
259	C_3-Benzocarbazoles				440 ± 310
273	C_4-Benzocarbazoles[c]				2000 ± 310
287	C_5-Benzocarbazoles				400 ± 510
267	Dibenz[c,g or a,g]carbazole				180

[a]Tentatively identified by GC/MS and retention times
[b]Value derived from one determination only
[c]Composite of three peaks
[d]Composite of two peaks

TABLE 20. Low Voltage, Probe Inlet MS Compositional Data for the PAH and N-PAC Fractions of the 600-650°F EDS Distillate[a]

Compound	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
PAH												
Phenanthrene	42 (5.9)	82 (11.4)	39 (4.1)	7 (0.9)								
Fluorene		11 (1.5)	78 (10.8)	100 (13.8)	47 (6.5)	11 (1.4)						
Biphenyl			10 (1.3)	46 (6.3)	49 (6.7)	29 (4.1)	9 (1.2)					
N-PAC												
Carbazole	100 (14.5)	80 (11.6)	6 (0.9)									
Quinoline			18 (2.5)	41 (6.0)	25 (3.6)	60 (0.9)						
Indole					12 (1.7)	26 (3.8)	22 (3.1)	9 (1.3)				

[a]Masses with peak intensities lower than 5% of base peak not included

Extensive GC and GC/MS analysis of the hydroxy-PAH fraction, A_4, was not conducted. However, each of these isolates was analyzed by low voltage, probe inlet MS. Figure 23 is a composite of three selected low voltage mass spectra that emphasize the general trends observed for this chemical class as a function of distillation temperature. These analyses revealed sharply defined divisions among the components with respect to the number of aromatic rings in their molecular structure. Distillate fractions boiling below 500°F were composed primarily of phenol and alkylated phenols (Figure 23A). Those components in the distillate cuts boiling between 500-650°F were identified as alkylated indanols, indenols, acenaphthols, and hydroxybiphenyls (Figure 23B). Distillates boiling above 650°F contained highly alkylated hydroxy-PAH with three or more condensed rings (Figure 23C). Although GC retention data were not acquired on these isolates, almost all masses present in the probe spectra could be accounted for by mono-hydroxy, fully aromatic PAH constituents. Furthermore, from IR analyses of selected distillate cuts (800°+F, 550-600°F, and 400-450°F) a strong hydroxy group stretch in the ~3600 cm^{-1} region was observed. A complete compositional summary of the major hydroxy-PAH present in each of the 50°F distillates boiling above 250°F is provided in Table C5 of Appendix C.

Table 21 and Figure 24 summarize the results of the amino-PAH analysis for the distillate cuts. Components of highest concentration in the amino-PAH isolates of the EDS distillates were identified by GC/MS as alkylated homologues of parent compounds such as aminobiphenyl, aminofluorene, aminoanthracene, and aminophenanthrene. The parent amino-PAH were generally present at lower concentration levels. As with the other chemical classes, higher molecular weight components were distilled in increasingly higher boiling distillate cuts. The mutagenicity of the A_3 isolates for the higher boiling distil-

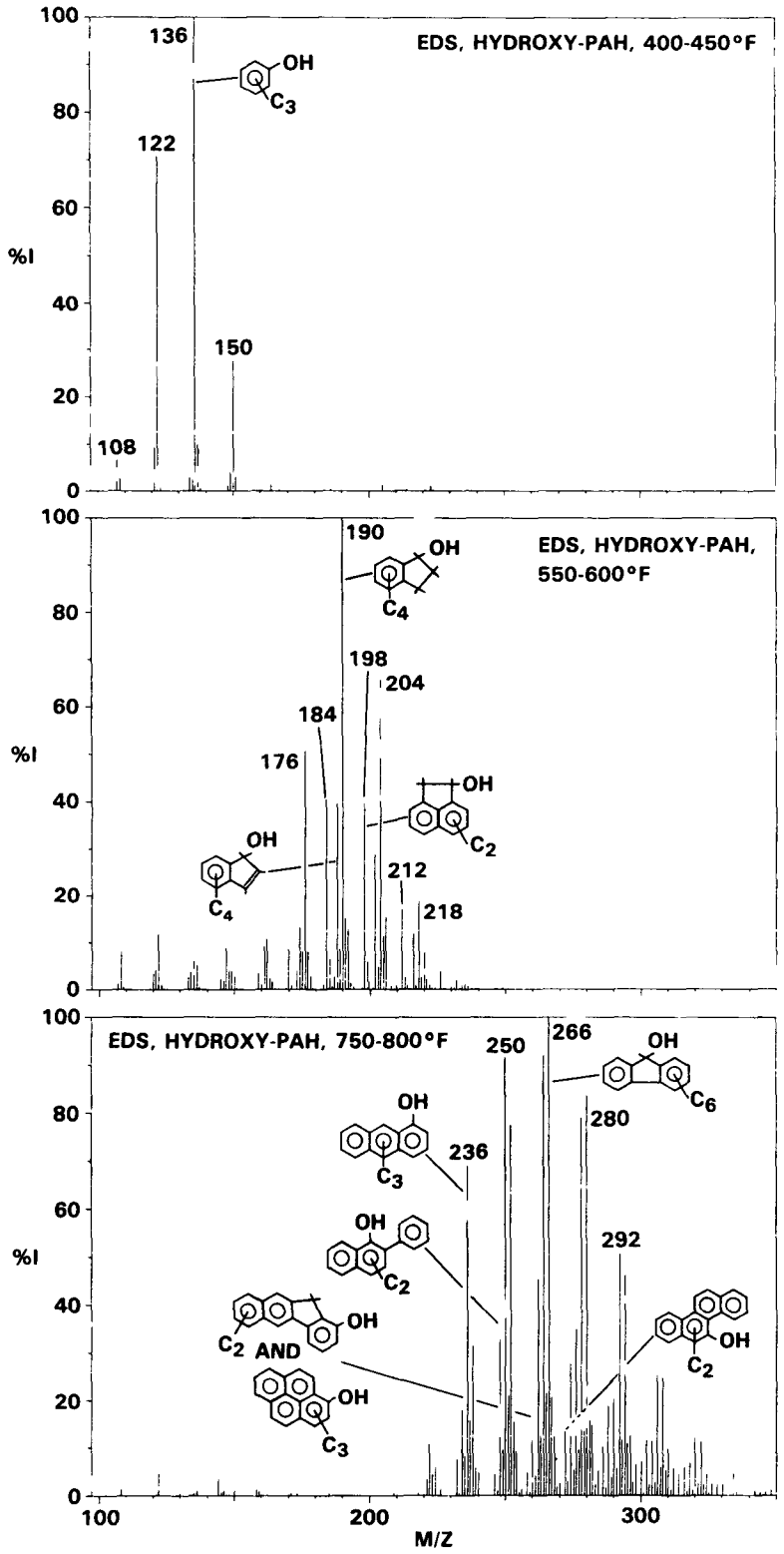


FIGURE 23. 12-eV Mass Spectra of Selected Hydroxy-PAH Fractions A_4 from the EDS Distillate Cuts; Boiling Ranges: (A) 400-450°F, (B) 550-600°F, and (C) 750-800°F

TABLE 21. Concentrations of Selected Amino-PAH in EDS Process Distillates

Compound[a]	Molecular Weight[b]	Concentration (μg/g N-PAC Fraction), °F[c] 700-600 (037)	700-750 (038)	750-800 (039)	800+ (040)
1-Aminonaphthalene	289	---	2.1	2.8	---
2-Aminobiphenyl	315	0.3	3.1	3.3	---
2-Aminonaphthalene	289	0.3	2.5	2.9	0.7
3-Methyl-2-aminonaphthalene	293	2.2	1.5	1.8	---
4-Aminobiphenyl	315	10.3	4.2	3.3	---
4-Aminofluorene	327	25.0	15.5	5.0	---
2-Aminoflurene	327	---	80.7	7.2	1.1
C_2-Aminofluorene	355	---	902	---	---
9-Aminophenanthrene and/or 1-aminophenanthrene and/or 1-aminoanthracene	339	22.9	194	16.2	13.8
C_3-Aminofluorene	369	---	1680	---	---
3-Aminophanthrene and/or 2-aminophenanthrene	339	10.6	130	73.2	1.8
C_3-Aminobiphenyl	357	---	757	---	---
2-Aminoanthracene	339	17.2	305	73.1	---
C_2-Aminophenanthrene	367	---	648	1170	---
C_3-Aminophenanthrene	381	---	---	601	---
C_3-Aminophenanthrene	381	---	---	895	---
3-Aminofluoranthene	363	8.4	41.2	389	3.0
1-Aminopyrene	363	6.9	14.8	173	5.1
2-Aminopyrene	363	---	44.6	193	5.1
8-Aminofluoranthene	363	---	28.0	157	12.6
6-Aminochrysene	389	---	---	33.1	46.9
3-Aminochrysene	389	---	---	12.8	20.3
7-Aminobenzo[a]pyrene	413	---	---	---	8.2

[a]Tentatively identified by GC/MS and GC retention times
[b]Pentafluoropropylamide-derived mass as determined by GC/MS
[c]Values reported are the average of three separate determinations

lates has already been presented and discussed in the Biological Assay section of Results and Discussion (Table 6).

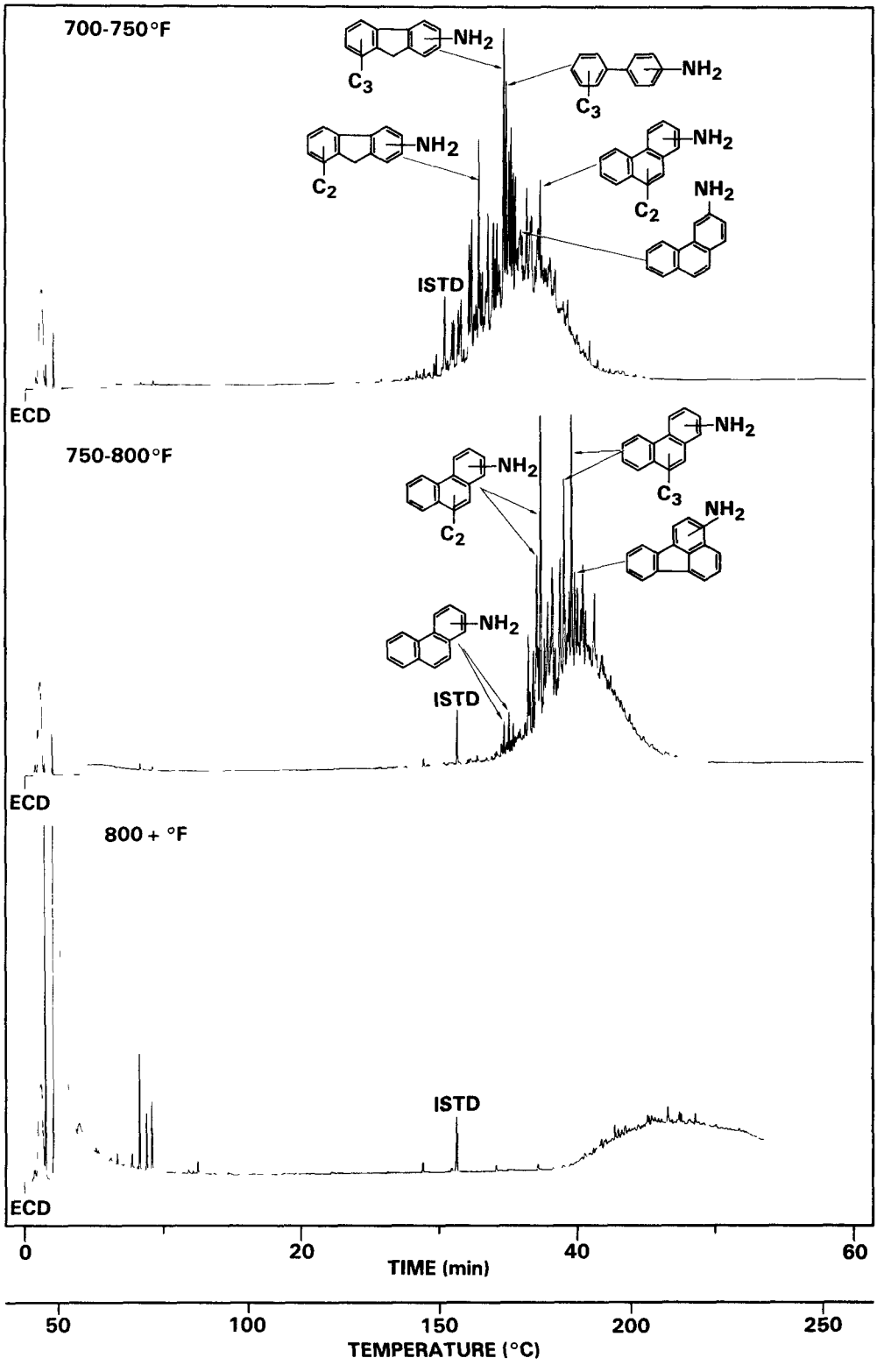


FIGURE 24. Selected Capillary Column Gas Chromatograms of the Amino-PAH (Pentafluoropropyl Amide Derivatized) Isolates of the 700-750°F, 750-800°F, and 800°+F EDS Distillate Cuts

HPLC Subfractionation of Neutral PAH Isolates

Detailed chemical and biological studies were conducted on the neutral PAH isolates of the four highest boiling distillates to determine the chemical components that might give rise to the carcinogenic and mutagenic activity observed for the >700°F EDS process materials (see Figures 11 and 12). In general, mouse skin tumorigenicity of coal liquefaction materials has been associated with their neutral PAH components (21). Therefore, the neutral PAH isolates were subfractionated by HPLC with mutagenicity and further chemical analyses conducted on the subfractions. The HPLC chromatograms for the 650-700°F, 700-750°F, 750-800°F, and 800°+F distillates were already shown in conjuction with the microbial mutagenicity data in Figures 5 through 8. The mass contribution of each HPLC subfraction is summarized in Table 22. As a general trend, the higher numbered cuts (8-11) are responsible for more than 50% of the mass of the initial PAH fraction.

Detailed GC, GC/MS and low voltage probe inlet MS analyses were performed in an effort to identify the specific components in these HPLC subfractions. A summary of the results are provided in Tables 23 through 25 for the 700-750°F, 750-800°F, and 800°+F distillates, respectively. The highly alkylated nature of these EDS process distillates is quite apparent from these data. It must be noted that several mass assignments made to alkylated species may in fact arise partially or completely from hydroaromatic PAH. For example, mass 206 could be either tetrahydropyrene or C_2-phenanthrene. However, mass spectral fragmentation patterns tended to support alkylated PAH assignments. Due to the proprietary nature of the EDS hydroaromaticity, differentiation of these two species was not pursued. It is likely that a complex combination of hydroaromaticity and alkylation exist in these samples. In any case, the net

TABLE 22. Weight Distribution of HPLC Subfraction of the Neutral PAH Isolates for the Four Highest Boiling EDS Distillates

HPLC Fraction	Weight Percent Distribution of EDS A_2 (°F)			
	800+ (040)	750-800 (039)	700-750 (038)	650-700 (037)
1	2.6	1.7	0.5	5.8
2	1.8	1.4	0.3	1.7
3	3.1	0.5	2.5	1.4
4	2.4	2.1	5.0	2.2
5	4.7	9.2	5.6	1.0
6	6.9	4.5	3.0	10.2
7	8.8	18.3	3.0	5.0
8	12.4	16.2	12.5	0.6
9	14.6	15.3	14.2	13.8
10	42.6	30.7	22.4	58.2
11	---	---	33.4	---
Recovery (%)	99.9	99.9	102.4	99.9

effect is an increased hydrogen/carbon ratio and enhanced overall quality of these process materials relative to analogous SRC II materials.

A combined capillary chromatogram and mass spectrum of the three mutagenically active HPLC fractions for the 800°+F and 700-750°F are shown in Figures 25 through 27. Note the degree of separation achieved by this HPLC method as well as the high level of mass focusing achieved. For example, several PAH isomers are usually detected by capillary GC in each HPLC subfraction, however, the masses for the components in each subfraction is either the same or within a very small mass window (±10 amu). The most mutagenically active HPLC subfraction from the PAH isolate for the 800°+F distillate was the second subfraction and was composed almost exclusively of benzo[a]pyrene, benzo[e]pyrene and the benzofluoranthenes (Figure 25 and Table 25). Less activity was detected in the third HPLC subfraction (Figure 26 and Table 25) of the

TABLE 23. Quantitative Results for HPLC Fractions for the PAH Fraction Isolates from EDS 700-750°F Distillate Cuts

Compound	Molecular Weight	Concentration (ppt) mg/g in HPLC Fractions 1	2	3	4	5	6	7	8	9	10	11
GC												
Pyrene	202	32.6 ± 4.7										
C_1-Fluoranthenes[a]	216			187	14.5 ± 1.0							
Benzo[a]fluorene	216			123	2.54 ± 1.1							
Benzo[b]fluorene, and/or 2- or 4-Methylpyrene	216			113	308 ± 1.4							
1-Methylpyrene	216			28.2	33.8 ± 2.2							
C_1-Phenylnaphthalenes, and/or C_2-Cyclopentaphenanthrenes[b]	218		4.04 ± 1.70	27.3	21.7 ± 7.6	881 ± 2.2	517 ± 60.6					
C_3-Phenanthrenes[c]	220							31.1 ± 1.6	192 ± 2.0			
C_4-Fluorenes[d]	222										14.5 ± 2.9	
C_2-Pyrenes, and/or C_1-Benzofluorenes[e]	230				7.7 ± 0.3	68.3 ± 2.6	89.2 ± 2.3	148 ± 10.6				
C_2-Phenylnaphthalenes, and/or C_3-Cyclopentaphenanthrenes[f]	232							76.7 ± 9.5	522 ± 8.6			
C_4-Phenanthrenes[g]	234									464 ± 40.3	62.7 ± 9.7[j]	
C_5-Fluorenes[h]	236										53.4 ± 2.6	
C_3-Pyrene, and/or C_2-Benzofluorene	244								19.1 ± 0.6			
C_3-Phenylnaphthalenes, and/or C_4-Cyclopentaphenanthrenes[c]	246									77.0 ± 8.5	27.1 ± 0.9	
C_5-Phenanthrenes[e]	248										118 ± 7.3	
C_6-Fluorene	250										39.0 ± 7.3	
C_4-Phenylnaphthalenes, and/or C_5-Cyclopentaphenanthrenes[h]	260										25.3 ± 0.5	
C_6-Phenanthrene	262											2.8 ± 0.04
C_7-Fluorenes[h]	264											15.7 ± 3.1
C_8-Fluorenes[a]	278											23.3 ± 2.0[k]
MS												
Mass[l] (Relative Intensity)		202(100)	218(100)	216(100)	216(100)	218(100)	218(100)	230(100)	232(100)	234(100)	248(100)	250(100)
		244(91)	248(79)	204(2)	218(16)	230(10)	230(24)	220(47)	220(31)	246(37)	236(53)	262(79)
		242(44)	212(73)	212(<1)	230(4)	216(2)	232(9)	218(27)	244(11)	222(16)	234(43)	264(79)
		256(37)	234(29)		212(1)	212(<1)	212(<1)	232(17)	230(5)	236(11)	250(25)	276(40)
		258(36)	260(27)					212(<1)	212(<1)	248(9)	260(18)	278(39)
		226(31)								258(6)	246(17)	266(23)
		278(30)								212(<1)	262(9)	252(18)
		212(17)									212(1)	212(3)

(a) Combination of four isomers
(b) Combination of eight isomers
(c) Combination of five isomers
(d) Combination of two isomers
(e) Combination of six isomers
(f) Combination of ten isomers
(g) Combination of thirteen isomers
(h) Combination of three isomers
(i) One chromatographic run
(j) Also m/e 248, C_5-phenanthrene which co-elutes
(k) Also m/e 276, C_7-phenanthrene which co-elutes
(l) Mass 212 is 2-Chloroanthracene internal standard.

TABLE 24. Quantitative Results for HPLC Fractions for the PAH Fraction Isolates from EDS 750-800°F Distillate Cuts

Compound	Molecular Weight	Concentration (parts per thousand) mg/g in HPLC Fractions 1	2	3	4	5	6	7	8	9	10
GC											
Pyrene	202										
C_1-Fluoranthene	216	0.58 ± 0.03									
Benzo[a]fluorene	216			0.96 ± 0.07							
Benzo[b]fluorene, and/or 2- or 4-Methylpyrene	216	0.11 1.71 ± 0.9	16.2 ± 2.2 19.7 ± 3.5	0.07 ± 0.01 6.3 ± 0.4							
1-Methylpyrene	216										
C_1-Phenylnaphthalenes and/or C_2-Cyclopentaphenanthrenes[a]	218			1.9 ± 0.2 3.4 ± 0.2	17.2 ± 0.5						
Benz[a]anthracene	228										
Chrysene	228		57.6 ± 24.4	12.6 ± 0.8						See MS Data	See MS Data
Naphthacene	228	0.14	475 ± 80.9	9.9 ± 2.4							
C_2-Pyrenes, and/or C_1-Benzofluorenes[b]	230			22.7 ± 1.3							
C_2-Phenylnaphthalenes and/or C_3-Cyclopentaphenanthrenes[c]	232			13.2 ± 1.0	236 ± 18.8	167 ± 5.6 248 ± 19.1					
Cyclopentachrysene	240										
C_1-Benzanthracenes[d]	242			14.7 ± 1.1							
3-Methylchrysene	242				144 ± 6.8	35.6 ± 1.3					
2-Methylchrysene	242				13.8 ± 0.1	22.4 ± 2.3					
5-Methylchrysene	242				94.0 ± 1.5	7.86					
6- and/or 4-Methylchrysene	242				43.8 ± 0.8	2.8 ± 0.4					
1-Methylchrysene	242				6.4 ± 0.4	122 ± 8.5	19.4 ± 0.6				
C_3-Pyrenes, and/or C_2-Benzofluorenes[e]	244				19.6 ± 0.5	11.7 ± 0.9 41.5 ± 10.5	456 ± 18.9	88.2 ± 10.9			
C_3-Phenylnaphthalenes C_4-Cyclopentaphenanthrenes[b]	246			7.2 ± 1.1				212 ± 26.7			
C_5-Phenanthrenes[f]	248										
C_2-Chrysenes and/or C_2-Benzanthracenes[d]	256						53.1 ± 1.1		51.5 ± 11.4		
C_4-Pyrenes and/or C_3-Benzofluorenes[g]	258						38.0 ± 0.6	114 ± 20.0	73.6 ± 7.9		
C_4-Phenylnaphthalenes, and/or C_5-Cyclopentaphenanthrenes[a]	260		6.3 ± 2.0						130 ± 16.1		
C_3-Chrysene, and/or C_3-Benzanthracene	270							18.4 ± 8.0			
MS											
Mass[h] (Relative Intensity)			228(100) 260(9) 216(6) 212(<1)	228(100) 274(59) 262(48) 246(42) 230(37) 240(28) 216(27) 212(7)	230(100) 242(76) 228(24) 244(12) 218(5) 212(<1)	232(100) 242(49) 230(42) 244(30) 256(7) 254(4) 212(<1)	244(100) 256(20) 232(15) 258(10) 246(9) 242(7) 212(1)	246(100) 258(63) 244(25) 260(10) 270(9) 256(8) 212(<1)	260(100) 272(42) 248(31) 258(21) 262(12) 274(11) 284(8) 212(1)	274(100) 262(85) 286(33) 276(33) 288(17) 272(15) 212(<1)	276(100) 290(74) 288(46) 278(38) 304(37) 292(33) 264(26) 302(25) 306(20) 212(5)

(a) Combination of five isomers
(b) Combination of eight isomers
(c) Combination of two isomers
(d) Combination of three isomers
(e) Combination of nine isomers
(f) Combination of seven isomers
(g) Combination of four isomers
(h) Mass 212 is 2-chloroanthracene internal standard

TABLE 25. Quantitative Results for HPLC Fractions for the PAH Fraction Isolates from EDS 800°+F Distillate Cuts

Compound	Molecular Weight	Concentration (parts per thousand) in HPLC Fractions 1	2	3	4	5	6	7	8	9	10
GC											
Benzo[a]fluorene	216			0.04							
Benzo[b]fluorene, and/or 2- or 4-Methylpyrene	216			0.54 ± 0.30							
1-Methylpyrene	216			0.16 ± 0.01							
Cyclopentachrysenes[a]	240		64.7 ± 7.6						See MS Data		
C_1-Benzanthracene	242		29.5 ± 3.8								
3-Methylchrysene	242		27.6 ± 3.1	71.2 ± 2.8						See MS Data	
2-Methylchrysene	242			0.02	6.3 ± 3.9						
5-Methylchrysene	242			0.21 ± 0.05							
6- and/or 4-Methylchrysene	242		15.8 ± 2.6	57.5 ± 4.5	11.6 ± 3.4						See MS Data
1-Methylchrysene	242			1.3 ± 0.20	24.6 ± 5.6						
Benzo[j or b]fluoranthene	252		295 ± 66.0								
Benzo[k]fluoranthene	252		34.3 ± 8.2								
Benzo[e]pyrene	252		304 ± 67.5								
Benzo[a]pyrene	252		132 ± 30.7								
Perylene	252		9.3 ± 1.7								
C_1-Cyclopentachrysenes, and/or Binaphthyls[b]	254		19.9 ± 3.1	36.6 ± 1.7							
C_2-Chrysenes, and/or C_2-Benzanthracenes[b]	256				78.4 ± 6.4						
7, 12-Dimethylbenzanthracene	256					390 ± 50.6					
C_4-Pyrenes, and/or C_3-Benzofluorenes[c]	258						90.9 ± 4.2				
C_1-Benzofluoranthenes, and/or C_1-Benzopyrenes,[d]	266			27.5 ± 4.4	190.0 ± 18.1						
C_2-Cyclopentachrysenes, and/or C_1-Binaphthyls[e]	268					95.2 ± 9.9					
C_3-Chrysenes, and/or C_3-Benzanthracenes[c]	270						74.7 ± 13.3	69.5 ± 4.7			
C_5-Pyrenes, and/or C_4-Benzofluorenes[e]	272							80.7 ± 10.6			
Indeno[1,2,3-cd]pyrene	276				43.3 ± 5.1	6.7 ± 0.7					
Benzo[ghi]perylene	276				69.6 ± 7.7	5.3 ± 0.1					
Bibenz[a,h or a,c]anthracene	278				6.6 ± 0.8	2.7 ± 0.1					
C_2Benzofluoranthenes, and/or C_2-Benzopyrenes[e]	280					65.6 ± 5.6					
C_3-Cyclopentachrysenes, and/or C_2-Binaphthyls[b]	282						97.9 ± 11.6	32.8 ± 5.3			
C_3-Benzofluorantabenes, and/or C_3-Benzopyrenes[a]	294							9.55 ± 0.6			
Coronene	300					2.9 ± 0.4					
MS											
Mass[f] (Relative Intensity)			252(100)	242(100)	266(100)	256(100)	270(100)	272(100)	286(100)	300(100)	326(100)
			254(7)	266(54)	256(51)	268(34)	282(68)	284(58)	296(65)	312(87)	314(97)
			242(7)	254(54)	276(40)	280(30)	258(43)	270(47)	298(57)	310(75)	328(82)
			240(2)	268(14)	268(29)	258(12)	292(35)	282(43)	284(55)	324(58)	352(78)
			212(<1)	212(3)	242(24)	278(10)	280(27)	306(40)	308(46)	298(57)	340(78)
					278(16)	270(9)	294(25)	296(30)	310(36)	288(51)	316(75)
					212(2)	282(9)	290(19)	294(28)	320(33)	322(50)	338(74)
						212(1)	284(17)	308(20)	274(29)	334(39)	354(59)
							256(16)	304(13)	322(16)	336(38)	324(58)
							212(2)	212(2)	312(16)	302(16)	350(57)
									212(2)	212(4)	212(<1)

(a) Combination of two isomers
(b) Combination of seven isomers
(c) Combination of five isomers
(d) Combination of four isomers
(e) Combination of three isomers
(f) Mass 212 is 2-chloroanthracene internal standard

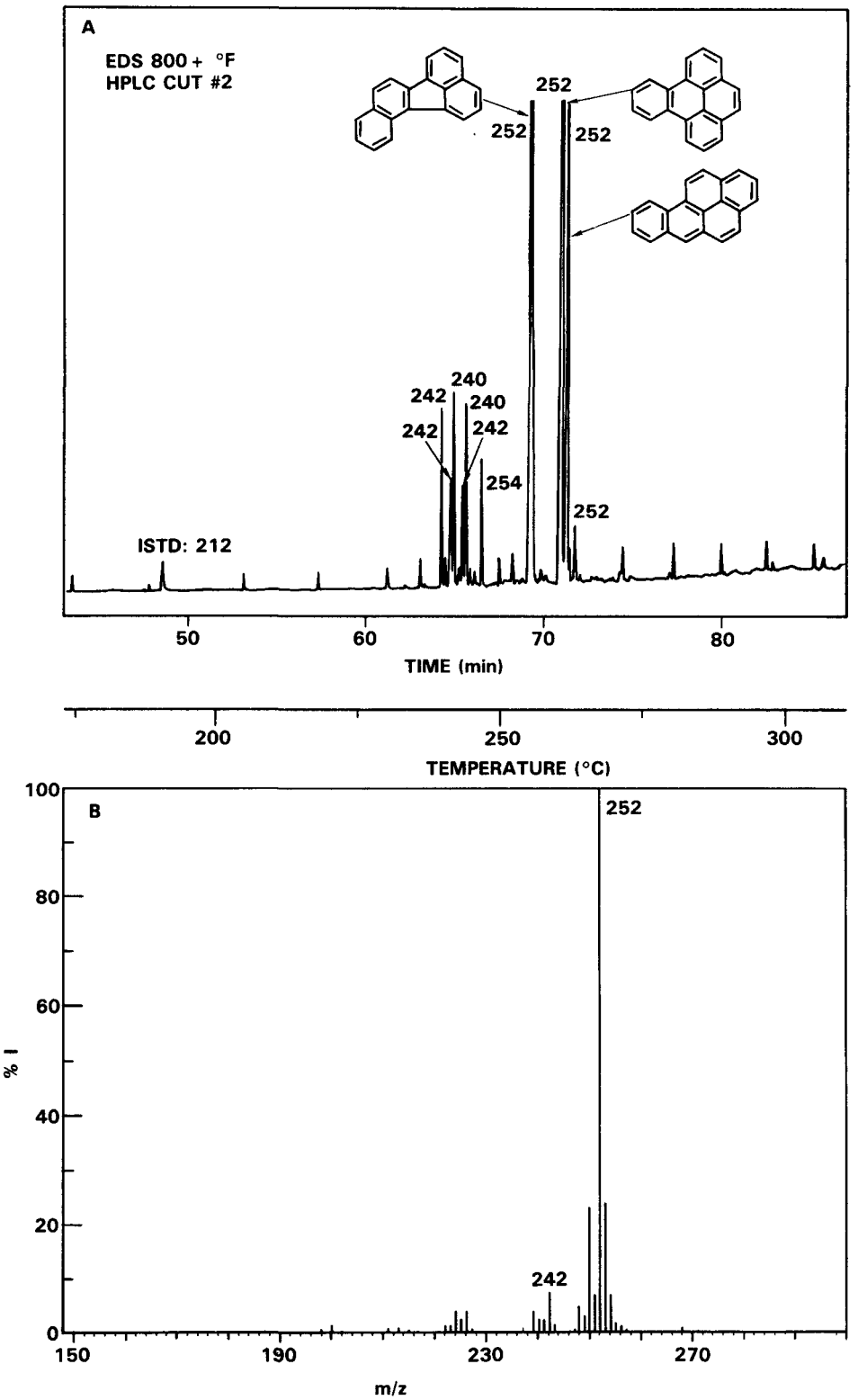


FIGURE 25. Capillary Column Gas Chromatogram and Mass Spectrum (12 eV) of HPLC Cut #2 of the Neutral PAH Isolate of the 800°+F EDS Distillate Cut

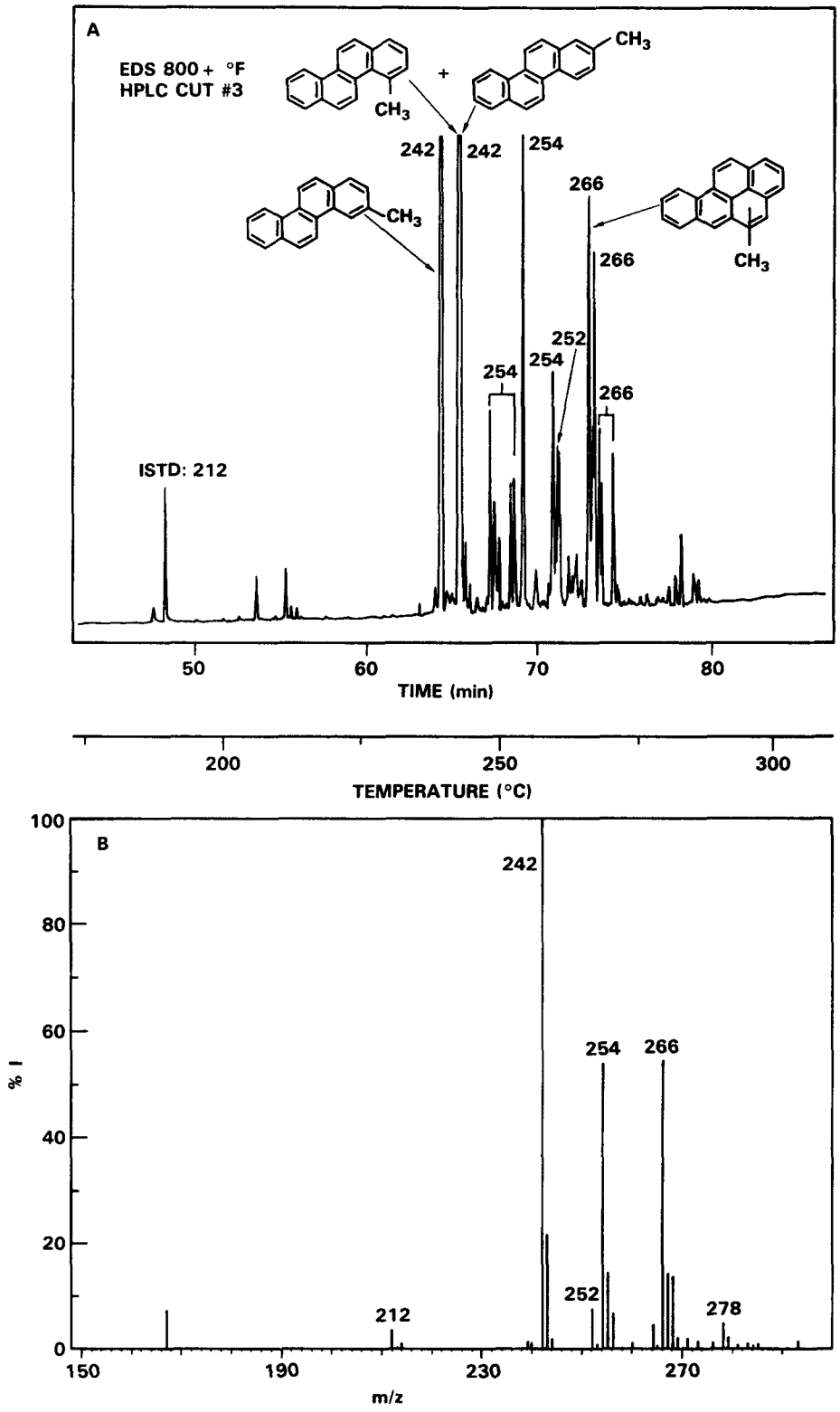


FIGURE 26. Capillary Column Gas Chromatogram and Mass Spectrum (12 eV) of HPLC Cut #3 of the Neutral PAH Isolate of the 800°+F EDS Distillate Cut

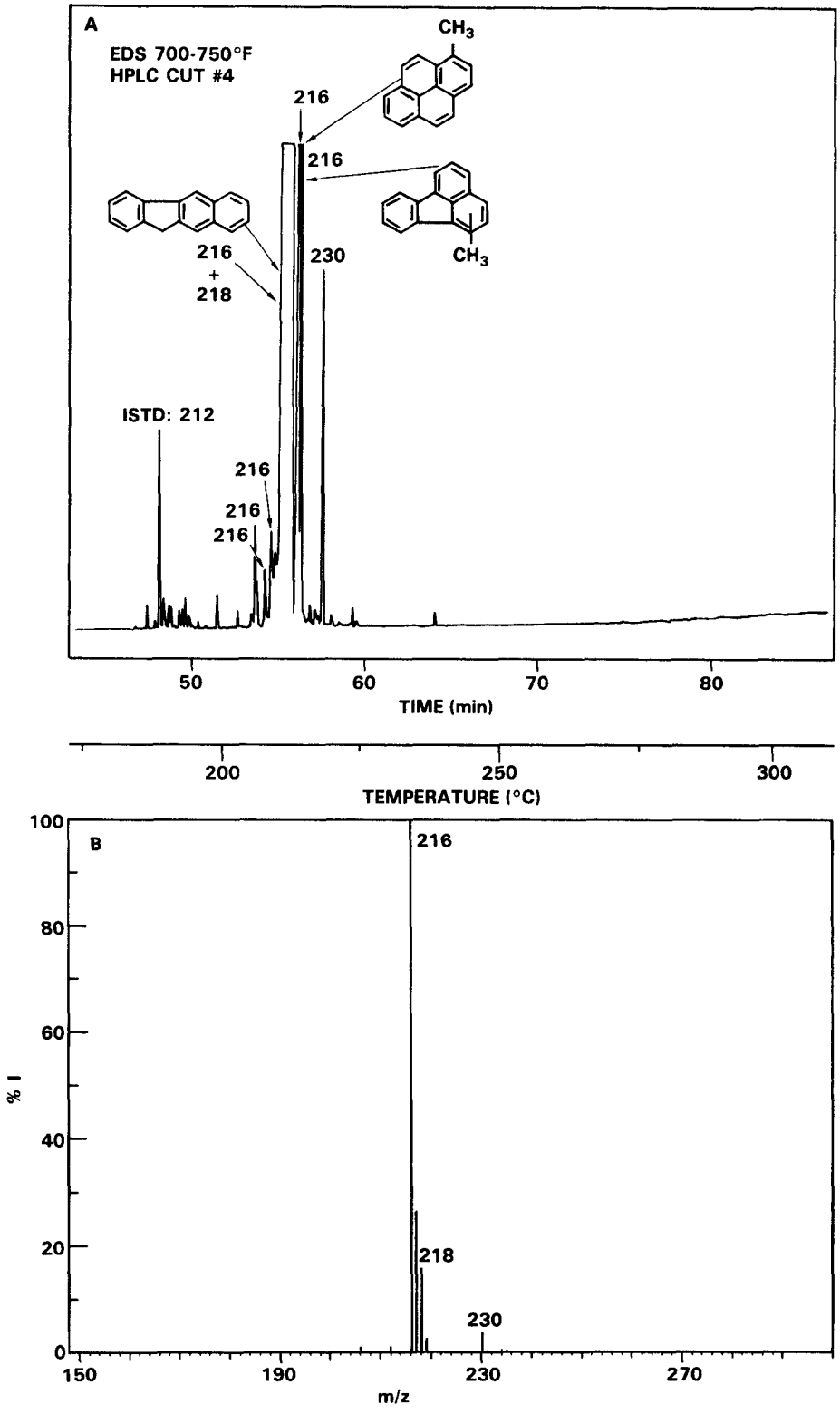


FIGURE 27. Capillary Column Gas Chromatogram and Mass Spectrum (12 eV) of HPLC Cut #4 of the Neutral PAH Isolate of the 700-750°F EDS Distillate Cut

800°+F PAH isolate; 3- and 4- and/or 6-methylchrysenes as well as methyl-substituted benzopyrene/benzofluoranthenes were identified in this subfraction (254 m/z could be cyclopentachrysenes, binaphthyls, and/or dihydro-252s). These data are consistent with the observed concentration of mutagenic activity in the second HPLC subfraction.

For the 700-750°F distillate, the fourth HPLC subfraction was mutagenically active. Figure 27 shows that this is due to isomers of mass 216. From GC retention data (see Table 23), the major component was benzo[b]fluorene and/or 2- or 4-methylpyrene with less concentrations of 1-methylpyrene and other methylpyrenes/methylfluoranthenes. Detailed chemical analyses of the HPLC subfractions for the 650-700°F distillate have not, to date, provided data conclusive enough to determine the source of elevated activity of this distillate cut; work is currently on-going.

In summary, these multiple-step, advanced chromatographic techniques permit a high chromatographic resolution, high mass discrimination separation to be achieved, which enables the precise determination of isomeric PAH that are adverse biological agents. The component/activity correlations and observations made for the >800°+F EDS distillation materials agree very well with similarly fractionated >800°+F SRC II distillate cuts. However, unlike the SRC II 700-750 distillate, an HPLC subfraction from the analogous EDS 700-750°F distillate was active. The source(s) of this mutagenic activity in this EDS distillate as related to the chemical composition (Figure 26 and Table 23) is somewhat unique to the EDS distillate materials.

COMPARATIVE SUMMARY

The mutagenic activities of the EDS distillate cuts and process streams for S. typhimurium, TA98 in the histidine reversion, mutagenicity bioassay were lower than those observed for comparable SRC II process materials. This is largely due to lower concentrations of premutagens in the EDS materials than in the SRC II materials. For example, if the levels of mutagenic amino-PAH are compared, the concentrations of these compounds in the EDS distillates were roughly two orders of magnitude less than those of comparable SRC II distillates. This point is illustrated in Table 26 for the EDS and SRC II distillate cuts boiling above 800°F. The amino-PAH are the primary determinants of mutagenic response in the N-PAC isolates; therefore, the lower concentration levels of these compounds in the EDS distillates resulted in a marked reduction in mutagenicity, whereas the higher levels in the SRC materials resulted in elevated mutagenic responses. The TA98 mutagenicity of the 800°+F PAH fractions is mainly associated with the HPLC subfraction containing benzo[a]pyrene. The concentration of benzo[a]pyrene in the EDS 800°+F PAH fraction was roughly 10% of that in corresponding SRC II distillate PAH fractions. Furthermore, the EDS distillates generally had higher neutral PAH content and lower levels of N-PAC than comparable SRC II distillates (Figure 28), presumably due to denitrogenation via hydrogenation in the EDS process.

Another chemical difference between the EDS and SRC coal liquefaction materials is the absence of the sulfur-containing PAH (PASH) in the EDS process materials and distillate cuts. The PASH are usually isolated in the neutral PAH fraction A_2; however, for the EDS materials, PASH-type compounds were not detected in these isolates. In contrast, PASH were readily detected in the neutral PAH fractions of the SRC materials, particularly in the HPLC sub-

TABLE 26. Concentrations of Selected Amino-PAH in the NPAC Fractions of the EDS and SRC II Distillate Cuts

Compound[a]	Concentration (μg/g N-PAC)		
	EDS 800°+F	SRC II 800-850°F	SRC II 850°+F
2-Aminonaphthalene	0.7	18.7	3.0
2-Aminofluorene	1.1	67.9	8.7
3-Aminophenanthrene	1.8	121	11.6
8-Aminofluoranthene	12.6	2130	53.6
2-Aminopyrene	5.1	771	15.7
3-Aminochrysene	20.3	1030	119
7-Aminobenzo[a]pyrene	8.2	73.4	412

[a]Isomeric assignment determined by GC retention measurements

fractions of the 800-850°F PAH isolate. PASH have also been identified as chemical components of TSL process materials. An explanation for this observation is that a desulfurization/denitrogenation catalyst, rather than a hydro-cracking catalyst, was used in the hydrogenation step of the EDS process. This catalyst apparently releases the heteroatomic-bound sulfur from the PAH structure; therefore, the PASH were absent or were not at dectable levels in the EDS process materials and distillate cuts. Biologically related effects of the PASH are not yet understood well enough to establish concrete correlations with the reduced mutagenicity or carcinogenicity of the neutral PAH isolates of EDS materials compared with SRC process materials.

Factors other than specific chemical concentrations may play a role in modulating the genetic activity of the chemical fractions from the EDS distillate cuts. For example, reduced amino-PAH concentrations did not appear to account for the drastically reduced mutagenicity of the N-PAC isolate from the once-through relative to the bottoms recycle PS, or even relative to SRC II

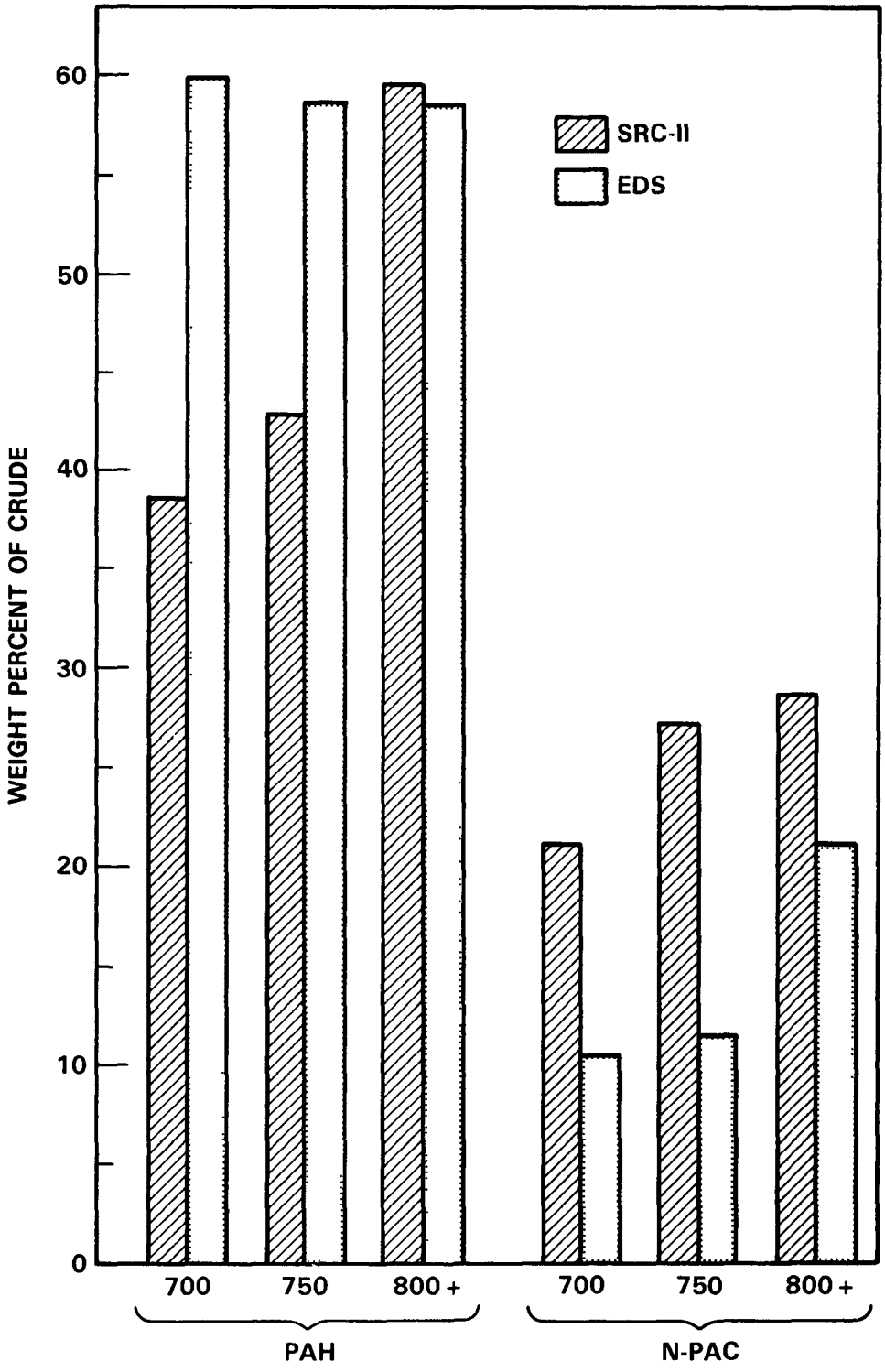


FIGURE 28. Comparative Composition of EDS and SRC Distillate Cuts

heavy distillate (4). The comparatively low activity of the N-PAC fractions from the EDS distillate cuts relative to SRC II N-PAC isolates was less than expected based solely on the levels of amino-PAH components. Considerable masking of genetic activity was also observed in the bottoms recycle PS and heavy VGO, where the mutagenicity of their N-PAC fractions was much higher than expected based on the genetic activity of the crudes.

A factor that may have contributed to the comparatively low genetic activity of the EDS distillates may be the high concentrations of alkylated PAC observed in these materials. For example, although the basic chemical composition of the individual components of 700-750°F PAH fractions are similar, the concentration of the alkylated species is higher in the EDS than in the SRC II distillate. The data in Table 27 support this observation: the pyrene/1-methylpyrene ratio is eightfold greater for the EDS than for the SRC II material. Furthermore, the HPLC subfractionation of the neutral PAH fraction of the EDS 800°+F crude distillate separated the mutagenic activity into a subfraction highly enriched in nonalkylated five-ring compounds, such as benzo[a]pyrene. The fractions containing alkylated PAH homologues, which constituted more than 50% of the PAH fraction mass, were of low activity in the microbial mutagenicity assay with S. typhimurium, TA98.

The tumorigenicity of the EDS 800°+F distillates was lower than that of comparable SRC II distillates. However, the observed tumorigenic response was still greater than expected based on the reduced mutagenicity of the same materials in the Salmonella/microsome bioassay. The reasons for this are not yet clear. Although the initiation of tumorigenesis in mouse skin may involve biochemical steps similar to those involved in mutation, the overall process is probably more complex than the induced mutation in the S. typhimurium bioassay system. Moreover, the endpoints of mutation frequency and tumor forma-

TABLE 27. Concentrations of the Major Components in the 700-750°F Distillate Fractions of the SRC II and EDS Materials

Compound	PAH Fractions (ppm)	
	EDS	SRC II
Dihydrofluoranthene	2,100 ± 36	21,800 ± 6,340
Fluoranthene	1,090 ± 16	30,200 ± 1,820
Pyrene	29,800 ± 976	276,000 ± 32,400
Dihydropyrene	6,390 ± 156	27,700 ± 8,419
2- or 4-methylpyrene	47,000 ± 11,600	258,000 ± 70,400
1-Methylpyrene	26,600 ± 6,370	343,000 ± 4,410
Benz[a]anthracene	308 ± 23	4,100 ± 942
Chrysene	1,550 ± 335	2,090 ± 561
Pyrene:1-Methylpyrene[a]	1.1[a]	8.0[a]

[a]Ratio of pyrene concentration to 1-methylpyrene concentration

tion are achieved by different types of experiments. Mutagenicity was based on dose-response data; tumorigenicity was determined by response to a single concentration of the EDS distillate. Obtaining dose response data for the I/P assay would most likely allow the data to be more easily compared. However, when I/P dose response experiments have been carried out with SRC II heavy distillate, the results suggested that tumor response for the levels of coal liquids used in the I/P experiments increased almost linearly with concentration of coal liquid. In any case, the microbial mutagenicity assay data and the I/P skin painting data were in agreement in rank-ordering the SRC II and EDS distillate cuts for biological activity. Both endpoints may, therefore, be useful in assessing the genotoxicity and carcinogenicity of the EDS materials relative to other coal liquids.

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TABLE A1. Averaged Positive and Negative Control Data for *S. typhimurium* TA98 and TA100 for the Dose-Response Data of Tables A2 and A3

Compound	µg/Plate	S9 (µl)	Number of Average Revertant Colonies/Plate	Strain
2-AA	2	10	4258 ± 385 (LL)	TA98
BII	5.7	20	1993 ± 866 (LL)	TA98
BaP	10	100	326 ± 118	TA98
9-AA	100	100	58 ± 7	TA98
MNNG	1	0	77 ± 18	TA98
None	0	20	52 ± 2	TA98
None	0	20	168 ± 4 (LL)	TA98
None	0	100	64 ± 18	TA98
None	0	100	145 ± 17 (LL)	TA98
2-AA	1	10	3900 ± 1273 (LL)	TA100
BII	5.7	20	459 ± 86 (LL)	TA100
BaP	10	100	869 ± 180	TA100
9-AA	100	100	190 ± 23	TA100
MNNG	1	0	2690 ± 70 (LL)	TA100
None	0	20	139 ± 10	TA100
None	0	20	--- (LL)	TA100
None	0	100	151 ± 11	TA100
None	0	100	--- (LL)	TA100

2-AA = 2-aminoanthracene
BII = SRC II basic tar
BaP = benzo[a]pyrene
MNNG = n-methyl-N'-nitro-N-nitrosoguanidine

TABLE A2. Reverse Mutation Dose-Response Data for *S. typhimurium* TA98 and TA100 in Standard Ames Plate Incorporation Bioassay

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 650-700°F (5226-037)	A1 (23)	20	0	51 ± 11	
			2	50 ± 5	
			4	34 ± 3	
			8	41 ± 3	
			10	42 ± 7	
			20	40 ± 1	
			50	37 ± 1	
		100	0	67 ± 5	159 ± 6
			100	50 ± 8	168 ± 19
			250	47 ± 2	191 ± 10
			500	36 ± 2	143 ± 6
	A2 (52)	100	0	45 ± 4	
			2		51 ± 3
			4		42 ± 1
			8		48 ± 7
			10		41 ± 1
			20		56 ± 10
			50		52 ± 1
		100	0	67 ± 5	159 ± 6
			100	62 ± 10	199 ± 6
			250	77 ± 9[a]	211 ± 24
			500	89 ± 5	238 ± 5

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 650-700°F (5226-037)	A3 (10)	20	0	51 ± 11	139 ± 10
			2	52 ± 4	130 ± 5
			4	64 ± 4	116 ± 2
			8	61 ± 2	132 ± 2
			1	59 ± 2	146 ± 5
			2	72 ± 8[a]	148 ± 6
			5	60 ± 7	147 ± 8
		10	0	51 ± 11	139 ± 10
			2	50 ± 5	147 ± 3
			4	34 ± 3	142 ± 7
			8	41 ± 3	122 ± 1
			10	42 ± 7	144 ± 12
			20	40 ± 1	144 ± 10
			50	37 ± 1	143 ± 10
	A4 (8)	20	0	51 ± 11	
			2	38 ± 1	
			4	43 ± 2	
			8	34 ± 2	
			10	43 ± 8	
			20	37 ± 7	
			50	44 ± 12	
		100	0	67 ± 5	159 ± 6
			100	64 ± 2	160 ± 17
			250	31 ± 7	109 ± 2
			500	15 ± 4	ND

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 650-700°F (5226-036)	Crude (100)	20	0	51 ± 11	139 ± 10
			0.2	41 ± 2	131 ± 8
			0.4	43 ± 2	114 ± 0
			0.8	39 ± 3	150 ± 15
			1	32 ± 3	144 ± 10
			2	41 ± 3	137 ± 2
			5	47 ± 3	155 ± 4
			0	51 ± 11	139 ± 10
			2	47 ± 1	151 ± 12
			4	47 ± 1	148 ± 3
			8	47 ± 1	139 ± 5
			10	35 ± 4	143 ± 1
			20	46 ± 1	150 ± 2
			50	47 ± 1	144 ± 7
EDS 700-750°F (5226-038)	A1 (19)	20	0	51 ± 11	
			2	50 ± 5	
			4	34 ± 3	
			8	41 ± 3	
			10	42 ± 7	
			20	40 ± 1	
			50	37 ± 1	
		100	0	67 ± 5	159 ± 6
			100	64 ± 5	180 ± 9
			250	53 ± 2	179 ± 11
			500	67 ± 4	181 ± 2
	A2 (60)	100	0	51 ± 11	
			2	58 ± 8	
			4	55 ± 4	
			8	63 ± 9	
			10	53 ± 11	
			20	53 ± 3	
			50	78 ± 6	
		100	0	67 ± 5	159 ± 6
			100	64 ± 5	248 ± 8
			250	68 ± 7	254 ± 4
			500	63 ± 13	189 ± 5

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 700-750°F (5226-038)	A3 (9)	20	0	51 ± 11	139 ± 10
			2	55 ± 7	165 ± 12
			4	54 ± 0	174 ± 11
			8	88 ± 4	145 ± 2
			1	68 ± 6	143 ± 7
			2	91 ± 4	149 ± 12
			5	118 ± 6[a]	148 ± 12
		20	0	51 ± 11	139 ± 10
			2	119 ± 5	169 ± 15
			4	130 ± 6	187 ± 12
			8	85 ± 16	170 ± 9
			10	90 ± 28	109 ± 3
			20	121 ± 8	157 ± 2
			50	70 ± 1	146 ± 12
	A4 (9)	20	0	51 ± 11	
			2	41 ± 4	
			4	37 ± 2	
			8	29 ± 2	
			10	24 ± 5	
			20	38 ± 1	
			50	29 ± 4	
		100	0	67 ± 5	159 ± 6
			100	44 ± 1	171 ± 3
			250	36 ± 2	137 ± 4
			500	28 ± 5	ND
	Crude (100)	20	0	51 ± 11	139 ± 10
			2	41 ± 2	130 ± 1
			4	43 ± 2	149 ± 6
			8	39 ± 3	131 ± 5
			1	32 ± 3	130 ± 6
			2	41 ± 3	148 ± 3
			5	47 ± 3	176 ± 0
		20	0	51 ± 11	139 ± 10
			2	47 ± 1	159 ± 5
			4	40 ± 1	145 ± 5
			8	45 ± 15	146 ± 7
			10	35 ± 4	157 ± 7
			20	46 ± 1	149 ± 22
			50	47 ± 10	162 ± 3

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 750-800°F (5226-039)	A1 (16)	20	0	50 ± 0	
			2	50 ± 0	
			4	51 ± 6	
			8	48 ± 9	
			10	47 ± 5	
			20	54 ± 5	
			50	58 ± 8	
		100	0	67 ± 5	159 ± 6
			100	50 ± 0	211 ± 5
			250	43 ± 7	195 ± 5
			500	49 ± 5	186 ± 1
	A2 (58)	100	0	81 ± 0	
			2	48 ± 3	
			4	54 ± 3	
			8	54 ± 1	
			10	42 ± 1	
			20	65 ± 4	
			50	64 ± 2	
		100	0	67 ± 5	159 ± 6
			100	54 ± 3	203 ± 6
			250	70 ± 13[a]	227 ± 1
			500	60 ± 9	219 ± 19

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 750-800°F (5226-039)	A3 (13)	20	0	50 ± 0	139 ± 10
			2	57 ± 3	132 ± 6
			4	72 ± 8	139 ± 4
			8	53 ± 0	151 ± 10
			1	83 ± 3	150 ± 4
			2	177 ± 6[a]	143 ± 8
			5	210 ± 47	158 ± 6
		20	0	50 ± 0	139 ± 10
			2	115 ± 38	172 ± 11
			4	164 ± 1	184 ± 6
			8	203 ± 28	140 ± 1
			10	138 ± 7	165 ± 11
			20	243 ± 8	161 ± 4
			50	251 ± 5	185 ± 7
	A4 (12)	20	0	50 ± 0	
			2	32 ± 3	
			4	46 ± 5	
			8	32 ± 5	
			10	43 ± 8	
			20	52 ± 5	
			50	43 ± 3	
		100	0	67 ± 5	159 ± 6
			100	44 ± 1	187 ± 22
			250	36 ± 2	157 ± 2
			500	28 ± 5	123 ± 14

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 750-800°F (5226-039)	Crude (100)	20	0	50 ± 0	139 ± 10
			2	66 ± 2	143 ± 2
			4	82 ± 14	164 ± 4
			8	45 ± 5	153 ± 13
			1	54 ± 3	144 ± 3
			2	81 ± 6	157 ± 8
			5	76 ± 1	155 ± 0
		20	0	50 ± 0	139 ± 10
			2	66 ± 2	160 ± 5
			4	82 ± 14	159 ± 2
			8	60 ± 5	145 ± 10
			10	65 ± 2	155 ± 7
			20	93 ± 4[a]	173 ± 12
			50	103 ± 4	159 ± 8
EDS 800°+F (5226-040)	A1 (4)	20	0	50 ± 0	
			2	57 ± 10	
			4	54 ± 5	
			8	52 ± 10	
			10	47 ± 9	
			20	58 ± 2	
			50	53 ± 7	
		100	0	67 ± 5	159 ± 6
			100	59 ± 0	181 ± 23
			250	65 ± 8	176 ± 2
			500	55 ± 6	177 ± 0

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 800°+F (5226-040)	A2 (58)	100	0	81 ± 0	
			2	75 ± 9	
			4	77 ± 6	
			8	59 ± 12	
			10	64 ± 5	
			20	91 ± 4	
			50	92 ± 7	
		100	0	67 ± 5	159 ± 6
			100	89 ± 8[a]	246 ± 1
			250	101 ± 5	266 ± 1
			500	72 ± 4	219 ± 8
	A3 (23)	20	0	50 ± 0	139 ± 10
			2	73 ± 4	140 ± 5
			4	68 ± 4	150 ± 17
			8	83 ± 10	135 ± 6
			1	125 ± 10	145 ± 0
			2	230 ± 2	150 ± 6
			5	296 ± 8	157 ± 4
		20	0	50 ± 0	139 ± 10
			2	188 ± 8	187 ± 22
			4	224 ± 18	171 ± 10
			8	164 ± 15	172 ± 10
			10	253 ± 15	161 ± 10
			20	362 ± 11	143 ± 5
			50	343 ± 7	166 ± 20

[a]Underscore denotes activity greater than two times background

TABLE A2. (continued)

BP Cut	Fraction (wt %)	S9 (µl)	µg/Plate	Revertant Colonies TA98	Revertant Colonies TA100
EDS 800°+F (5226-040)	A4 (17)	20	0	50 ± 0	
			2	57 ± 3	
			4	47 ± 5	
			8	31 ± 4	
			10	49 ± 3	
			20	66 ± 6	
			50	64 ± 6	
		100	0	67 ± 5	159 ± 6
			100	81 ± 7[a]	194 ± 8
			250	91 ± 11	201 ± 4
			500	101 ± 3	166 ± 6
	Crude (100)	20	0	50 ± 0	139 ± 10
			2	51 ± 5	138 ± 18
			4	68 ± 2	111 ± 2
			8	67 ± 7	133 ± 4
			10	61 ± 3	130 ± 3
			20	123 ± 8	137 ± 6
			50	150 ± 20	168 ± 3
		20	0	50 ± 0	139 ± 10
			2	92 ± 1	158 ± 2
			4	90 ± 3	141 ± 5
			8	90 ± 26	176 ± 20
			10	92 ± 10	153 ± 8
			20	189 ± 1	179 ± 23
			50	172 ± 11	174 ± 1

[a]Underscore denotes activity greater than two times background

TABLE A3. *S. typhimurium*, TA98 Dose-Response Data for Representative EDS Process Materials (Sample Set #1)

Process Streams	Fraction (wt %)	µl S9	µg/Plate	Number of Revertant Colonies/Plate
EDS Raw Naphtha (5226-002)	A_1 (28)	100	0	47 ± 9
			2	47 ± 6
			4	56 ± 1
			8	43 ± 2
			10	32 ± 4
			20	55 ± 7
			50	53 ± 0
	A_2 (4)	100	0	47 ± 9
			2	38 ± 6
			4	44 ± 0
			8	40 ± 6
			10	35 ± 7
			20	45 ± 5
			50	40 ± 1
	A_3 (<1)	15	0	47 ± 9
			2	36 ± 1
			4	40 ± 1
			8	36 ± 3
			10	34 ± 6
			20	31 ± 3
			50	45 ± 2
	A_4 (11)	100	0	47 ± 9
			2	44 ± 6
			4	51 ± 1
			8	36 ± 0
			10	51 ± 5
			20	52 ± 1
			50	52 ± 4
	Crude (100)	100	0	24 ± 1
			2	25 ± 0
			4	16 ± 2
			8	22 ± 1
			10	24 ± 1
			20	21 ± 6
			50	20 ± 4

TABLE A3. (continued)

Process Streams	Fraction (wt %)	µl S9	µg/Plate	Number of Revertant Colonies/Plate
EDS Recycle Solvent (Bottoms Recycle mode) (5226-003)	A_1 (46)	100	0	47 ± 9
			2	47 ± 12
			4	54 ± 6
			8	38 ± 2
			10	32 ± 2
			20	36 ± 5
			50	26 ± 2
	A_2 (37)	100	0	47 ± 9
			2	38 ± 3
			4	39 ± 4
			8	38 ± 2
			10	45 ± 8
			20	50 ± 6
			50	53 ± 8
	A_3 (7)		0	47 ± 9
			2	35 ± 5
			4	52 ± 3
			8	37 ± 1
			10	70 ± 1[a]
			20	149 ± 2
			50	165 ± 2
	A_4 (13)	100	0	47 ± 9
			2	42 ± 1
			4	42 ± 4
			8	51 ± 4
			10	38 ± 4
			20	46 ± 4
			50	45 ± 3
	Crude (100)	100	0	24 ± 1
			2	37 ± 2
			4	39 ± 4
			8	61 ± 1
			10	55 ± 6
			20	70 ± 8
			50	111 ± 12

[a]Underscore denotes activity greater than two times background

TABLE A3. (continued)

Process Streams	Fraction (wt %)	µl S9	µg/Plate	Number of Revertant Colonies/Plate
EDS Vacuum Bottoms (5226-004)	A_1 (2)	100	0	47 ± 9
			2	41 ± 4
			4	29 ± 6
			8	32 ± 2
			10	38 ± 4
			20	34 ± 2
			50	52 ± 14
	A_2 (7)	100	0	47 ± 9
			2	43 ± 13
			4	37 ± 7
			8	41 ± 11
			10	52 ± 9
			20	70 ± 10
			50	87 ± 21
	A_3 (24)		0	47 ± 9
			0.2	59 ± 3
			0.4	56 ± 2
			0.8	68 ± 13
			1	44 ± 7
			2	107 ± 1[a]
			5	229 ± 16
	A_4 (27)	100	0	47 ± 9
			2	51 ± 2
			4	72 ± 12
			8	76 ± 9
			10	102 ± 2
			20	242 ± 39
			50	639 ± 75
	Crude (100)	15	0	506 ± 15(LL)
			2	507 ± 20
			4	511 ± 4
			8	760 ± 39
			10	845 ± 9
			20	1131 ± 92
			50	1440 ± 56

[a]Underscore denotes activity greater than two times background

TABLE A3. (continued)

Process Streams	Fraction (wt %)	µl S9	µg/Plate	Number of Revertant Colonies/Plate
EDS Recycle Solvent (once-through mode) (5226-005)	A_1 (69)	0		47 ± 9
		2		47 ± 3
		4		49 ± 1
		8		43 ± 8
		10		40 ± 3
		20		40 ± 3
		50		36 ± 8
	A_2 (21)	0		47 ± 9
		2		57 ± 1
		4		43 ± 6
		8		37 ± 4
		10		33 ± 1
		20		42 ± 7
		50		55 ± 8
	A_3 (2)	0		
		2		
		4		
		8		
		10		
		20		
		50		
	A_4 (8)	100	0	47 ± 9
			2	36 ± 10
			4	44 ± 8
			8	33 ± 2
			10	29 ± 7
			20	37 ± 5
			50	35 ± 4
	Crude (100)	20	0	24 ± 1
			2	18 ± 2
			4	19 ± 7
			8	17 ± 1
			10	23 ± 2
			20	28 ± 3
			50	35 ± 1

APPENDIX A

RAW DATA FOR MUTAGENIC RESPONSE OF *S. typhimurium* WITH EDS PROCESS MATERIALS AND DISTILLATE FRACTIONS

TABLE A3. (continued)

Process Streams	Fraction (wt %)	µl S9	µg/Plate	Number of Revertant Colonies/Plate
EDS Heavy vacuum gas oil (5226-006)	A_1 (5)	100	0	47 ± 9
			2	
			4	
			8	
			10	
			20	
			50	
	A_2 (31)	100	0	47 ± 9
			2	53 ± 13
			4	53 ± 13
			8	37 ± 4
			10	32 ± 1
			20	69 ± 12
			50	59 ± 7
	A_3 (22)		0	47 ± 9
			0.02	41 ± 2
			0.04	41 ± 2
			0.08	45 ± 8
			1	52 ± 3
			2	103 ± 14[a]
			5	125 ± 5
	A_4 (41)	100	0	47 ± 9
			2	54 ± 4
			4	67 ± 19
			8	134 ± 11
			10	149 ± 35
			20	154 ± 6
			50	158 ± 24
	Crude (100)		0	24 ± 1
			2	92 ± 9
			4	139 ± 3
			8	195 ± 19
			10	233 ± 13
			20	282 ± 5
			50	257 ± 7

[a]Underscore denotes activity greater than two times background

TABLE B1. Key to 10-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative Neutral PAH

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	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/Fluor-anthene	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]fluor-anthene	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
Cyclopentachry-senes/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	378	392	406
Binaphthyls	254	268	282	296	310	324	338	352	366	380	394	408
Cyclopentabenzo-pyrenes	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/ Cyclopenta-chrysenes	276	290	304	318	332	346	360	374	388	402	416	430
Dibenzanthra-cenes/Phenan-threnes	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; however, because of the proprietary nature of these compounds in the EDS materials, detailed studies to differentiate these species were not undertaken.

TABLE B2. Key to 10-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative N-PAC

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 N-PAC have been considered.

TABLE B3. Key to 10-eV Mass Spectra: Nominal Masses for Alkylated Homologous Series of Representative Hydroxy-PAH

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.

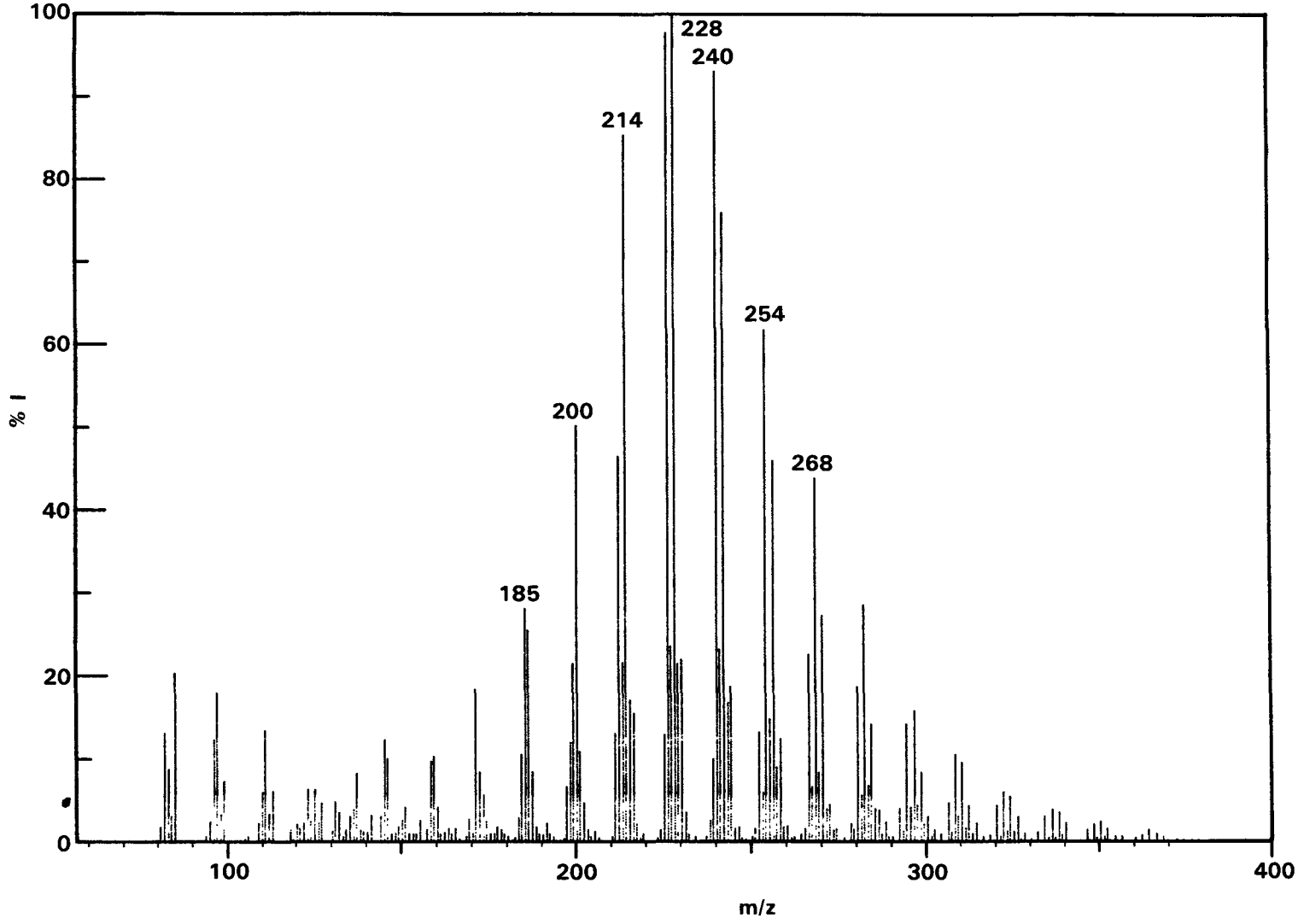

FIGURE B1. 10-eV Mass Spectrum of the A_1 Fraction from EDS Process Solvent, Bottoms Recycle Mode

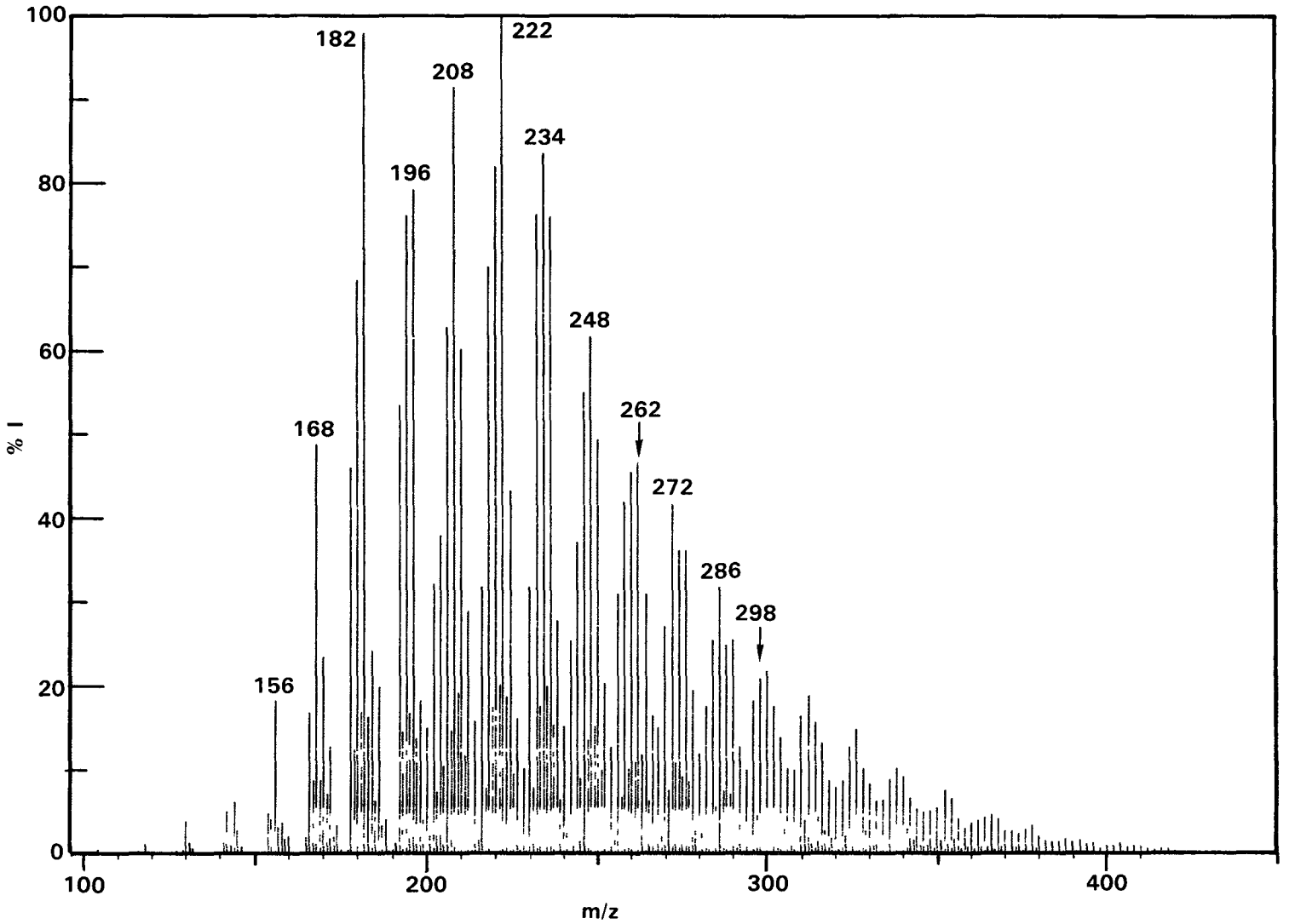

FIGURE B2. 10-eV Mass Spectrum of the A_2 Fraction from EDS Process Solvent, Bottoms Recycle Mode

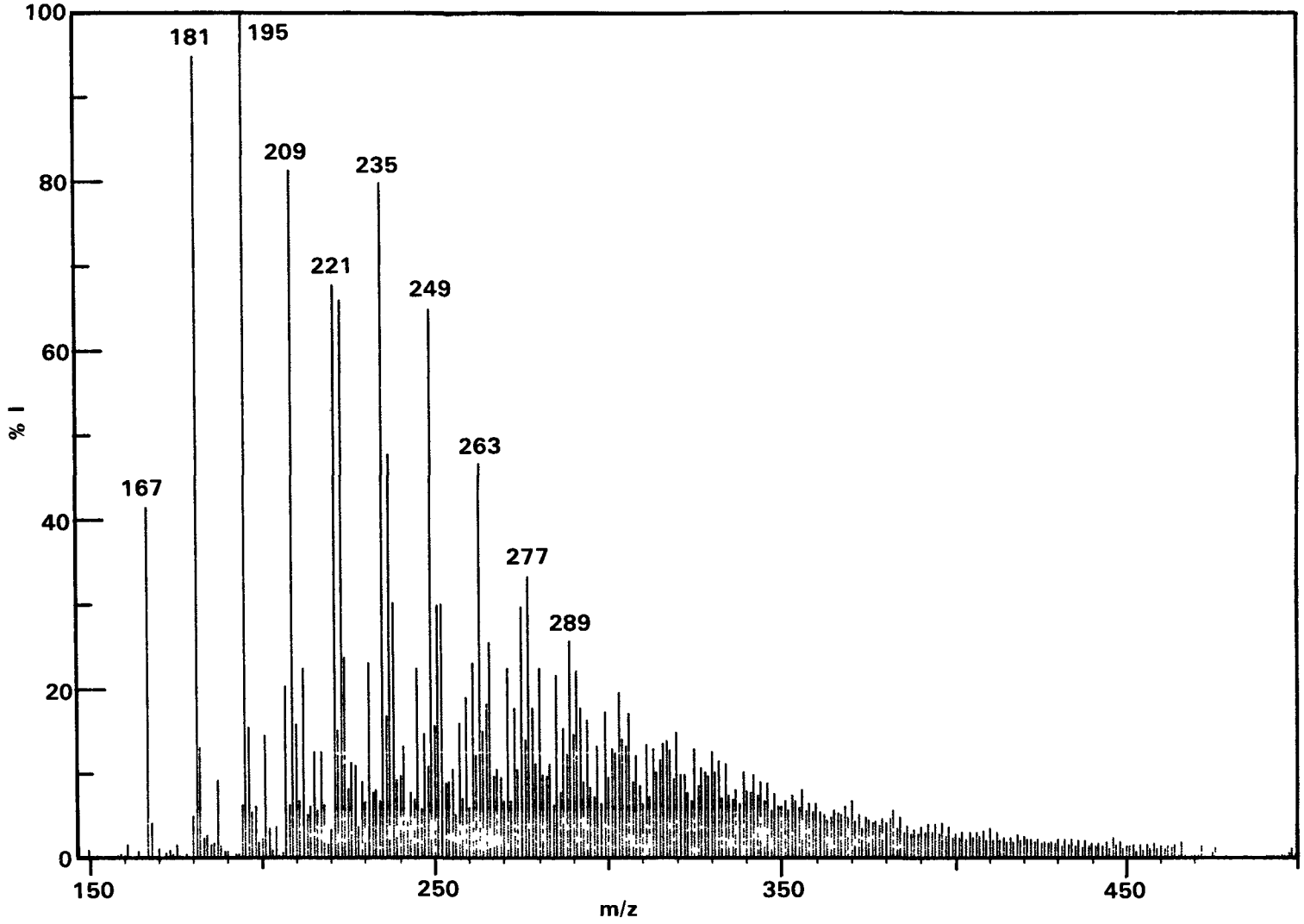

FIGURE B3. 10-eV Mass Spectrum of the A_3 Fraction from EDS Process Solvent, Bottoms Recycle Mode

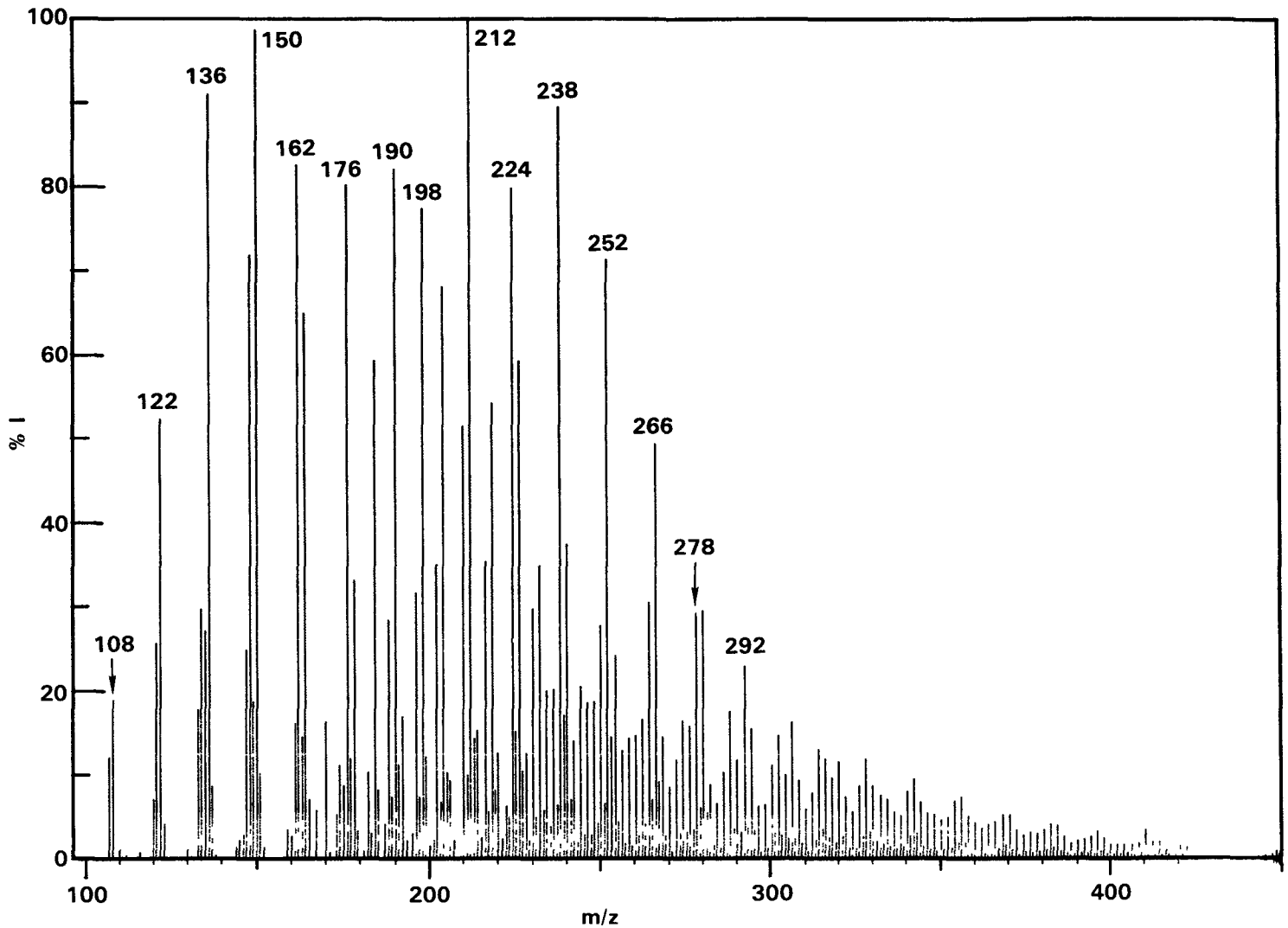

FIGURE B4. 10-eV Mass Spectrum of the A_4 Fraction from EDS Process Solvent, Bottoms Recycle Mode

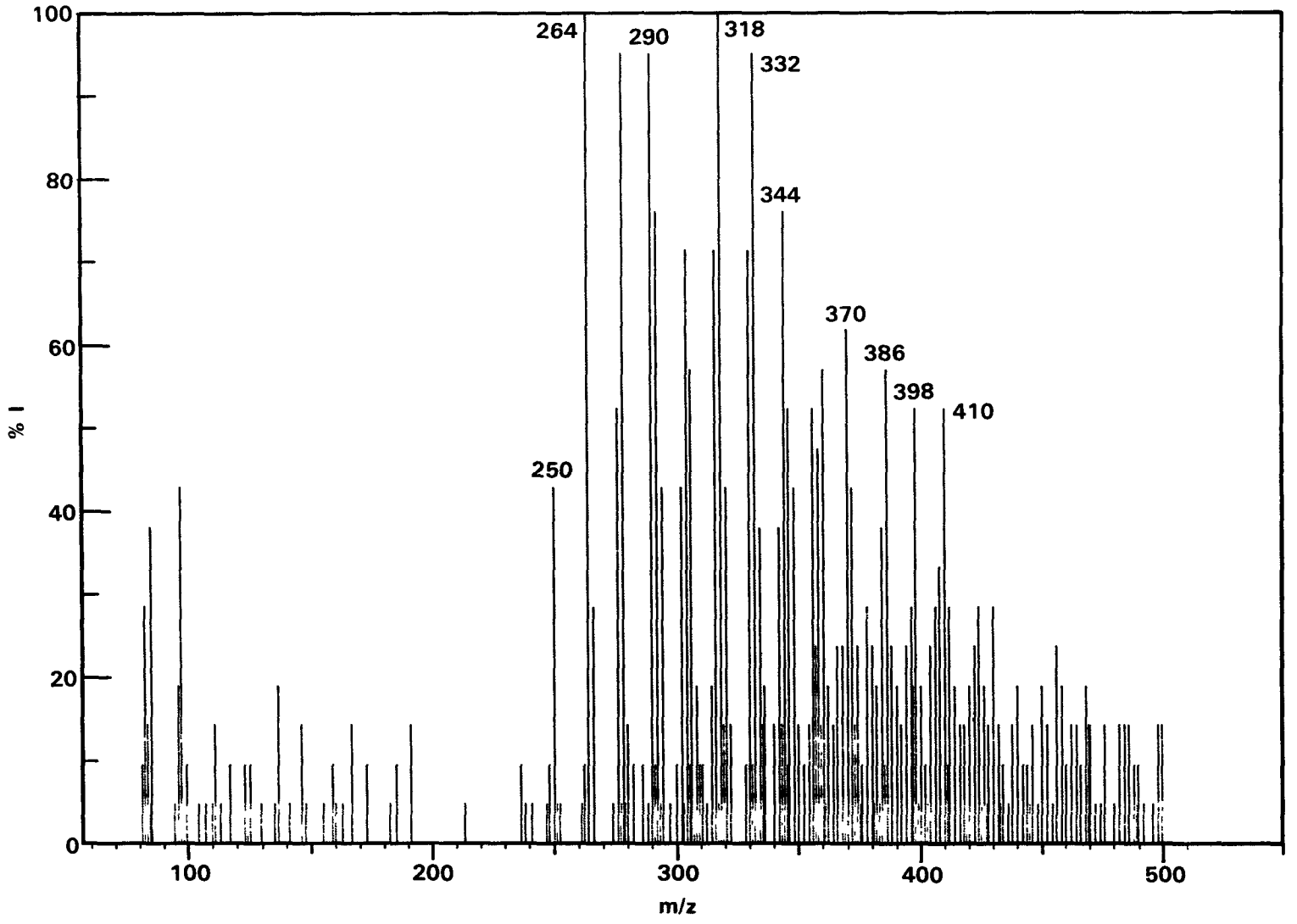

FIGURE B5. 10-eV Mass Spectrum of the A_1 Fraction from EDS Vacuum Bottoms

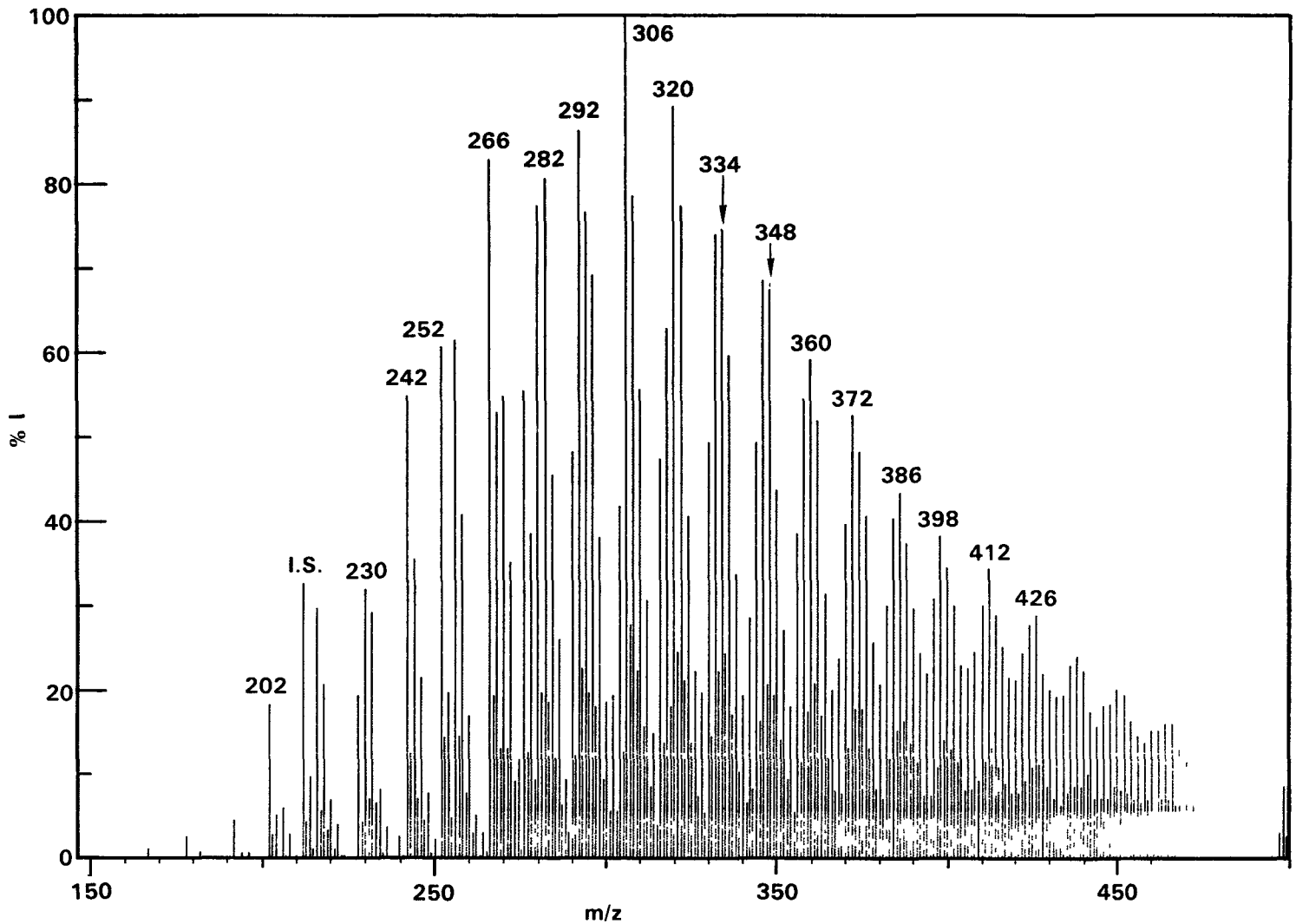

FIGURE B6. 10-eV Mass Spectrum of the A_2 Fraction from EDS Vacuum Bottoms

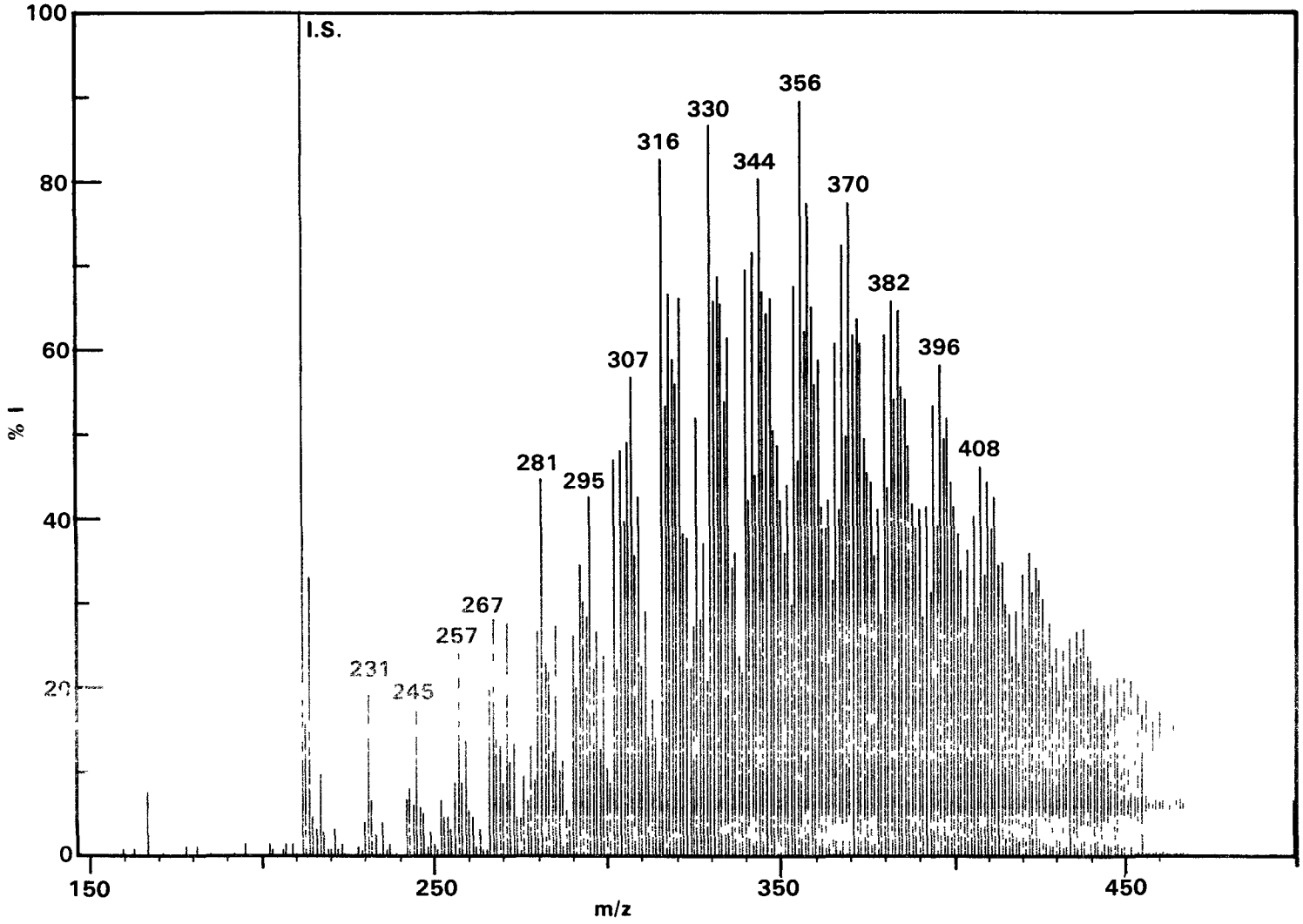

FIGURE B7. 10-eV Mass Spectrum of the A_3 Fraction from EDS Vacuum Bottoms

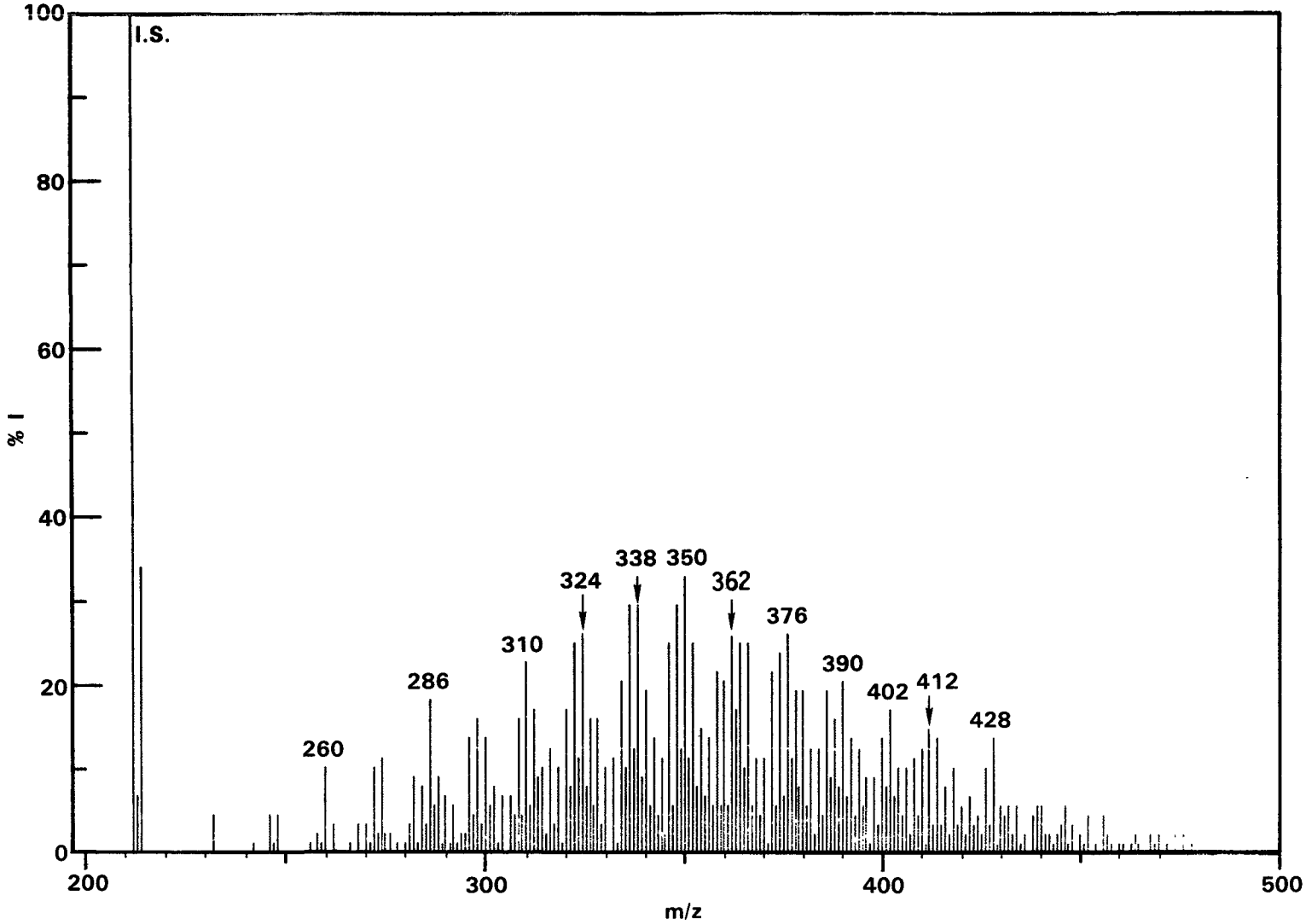

FIGURE B8. 10-eV Mass Spectrum of the A_4 Fraction from EDS Vacuum Bottoms

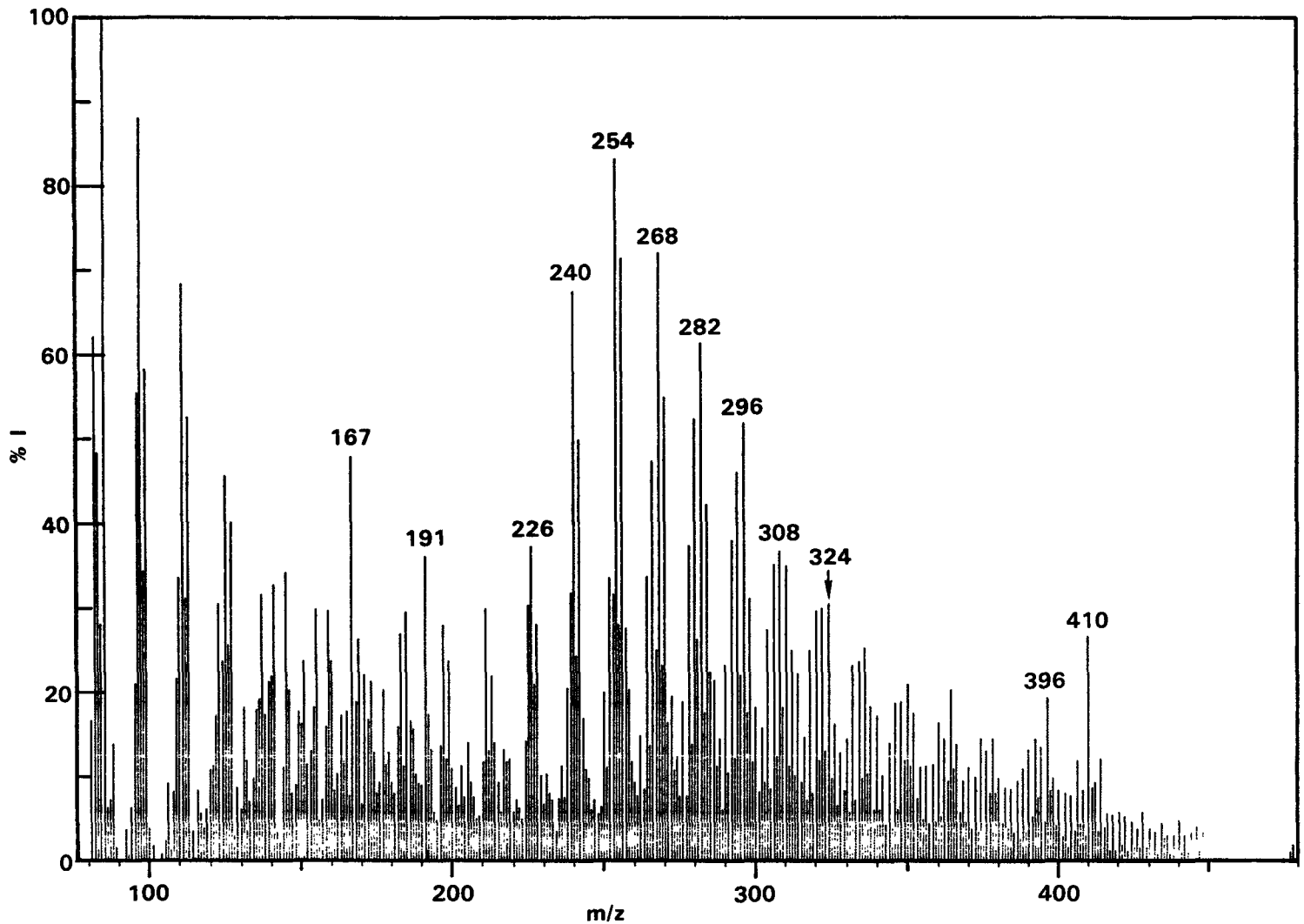

FIGURE B9. 10-eV Mass Spectrum of the A_1 Fraction from EDS Process Solvent, Once-Through Mode

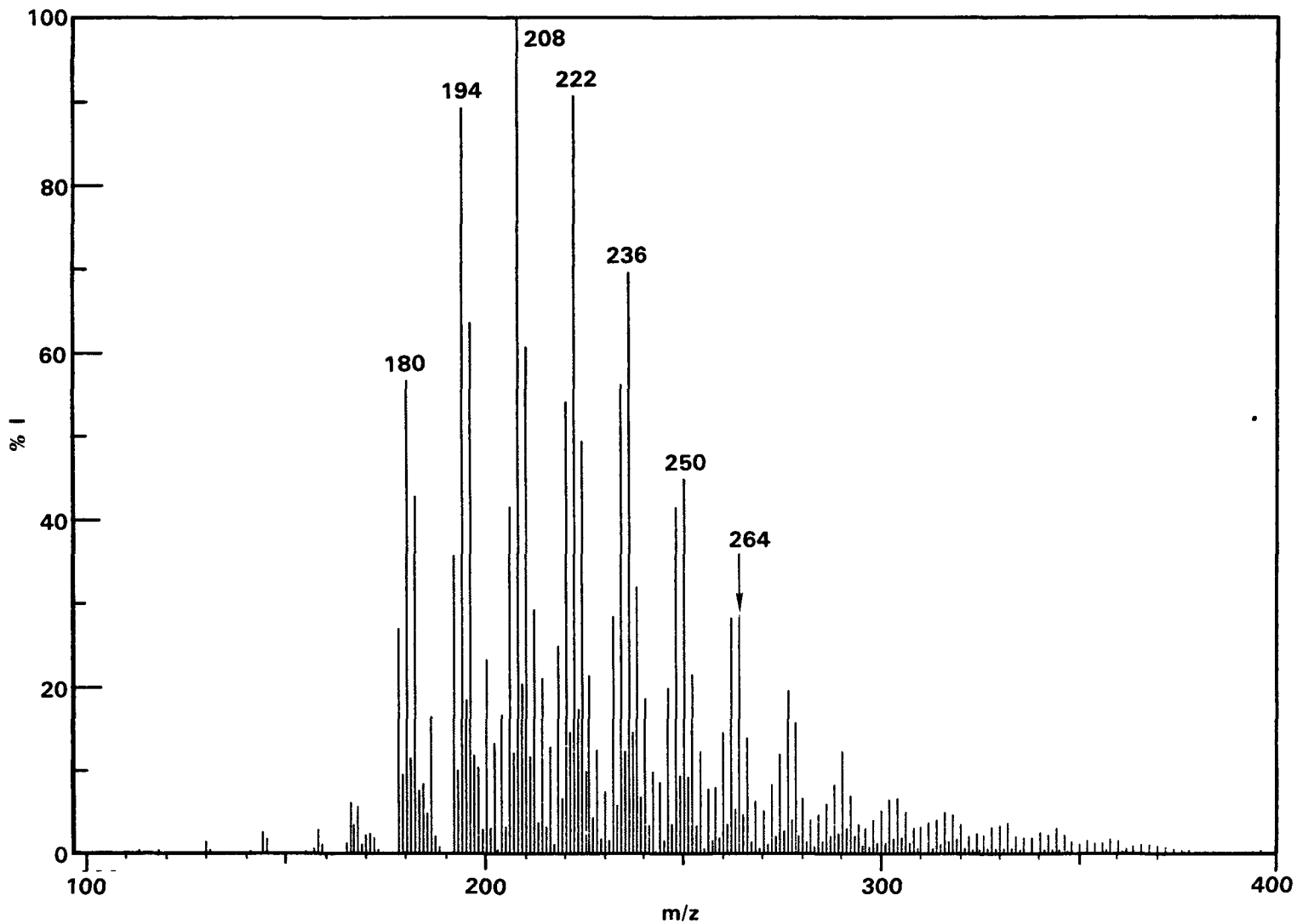

FIGURE B10. 10-eV Mass Spectrum of the A_2 Fraction from EDS Process Solvent, Once-Through Mode

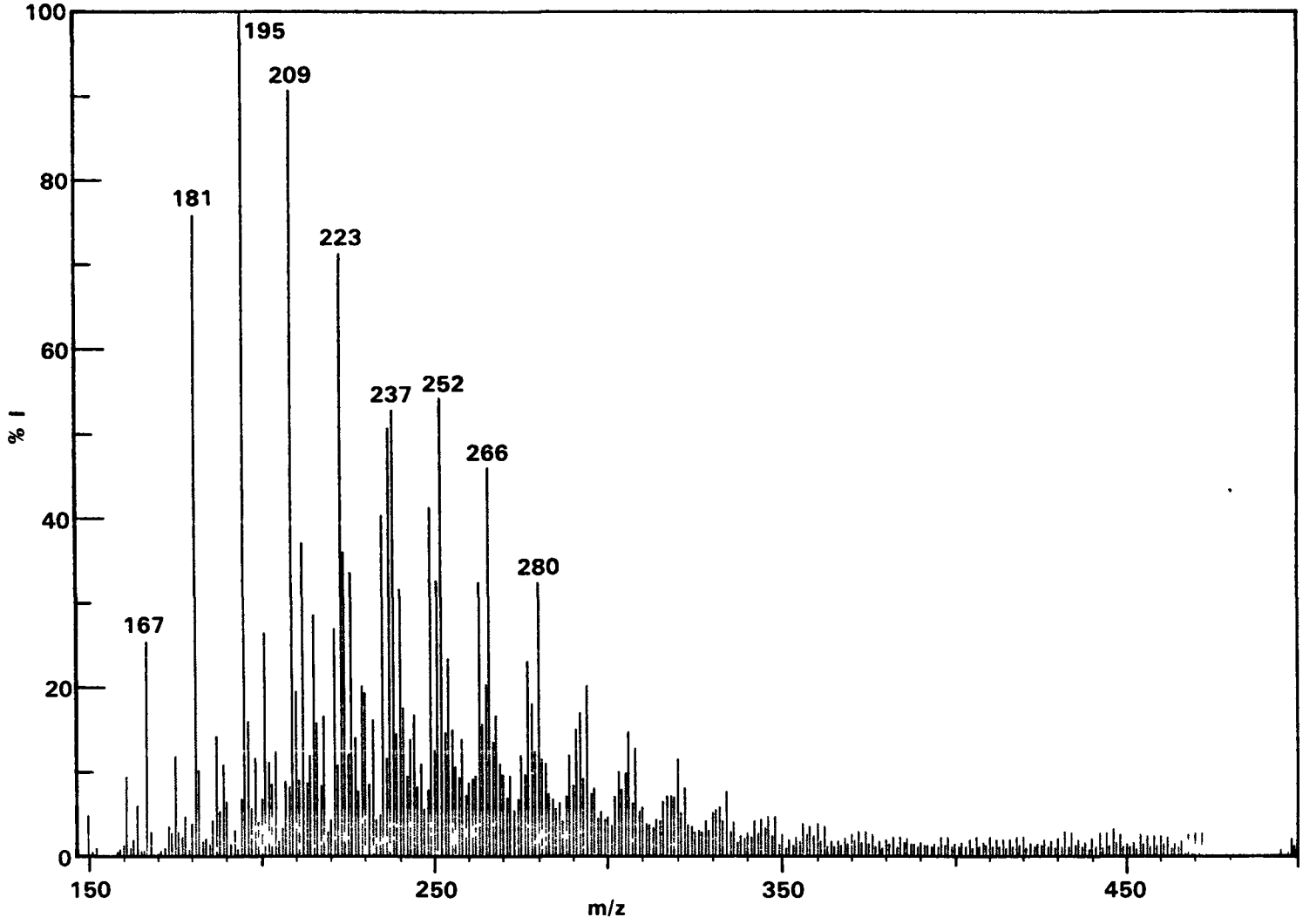

FIGURE B11. 10-eV Mass Spectrum of the A_3 Fraction from EDS Process Solvent, Once-Through Mode

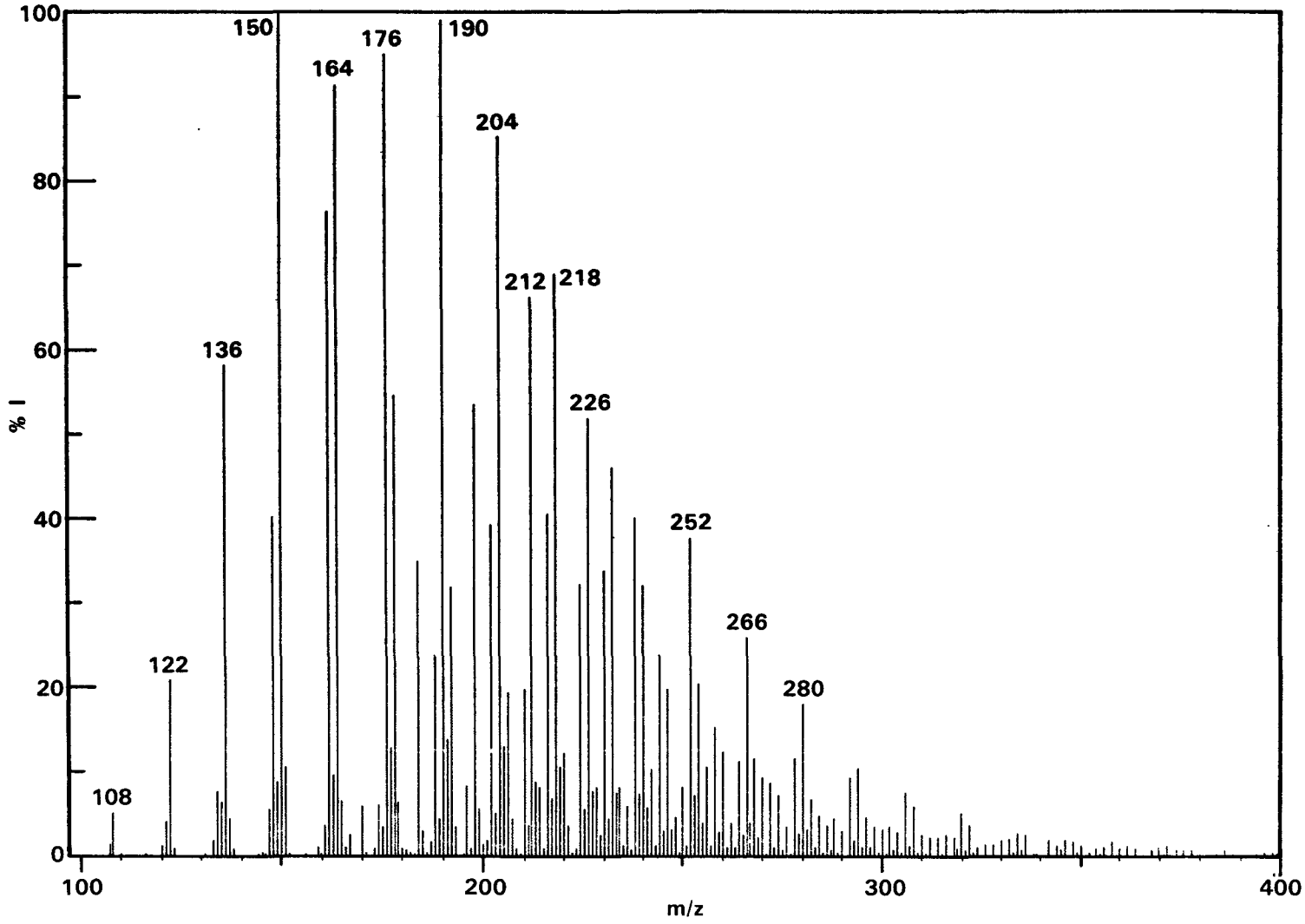

FIGURE B12. 10-eV Mass Spectrum of the A_4 Fraction from EDS Process Solvent, Once-Through Mode

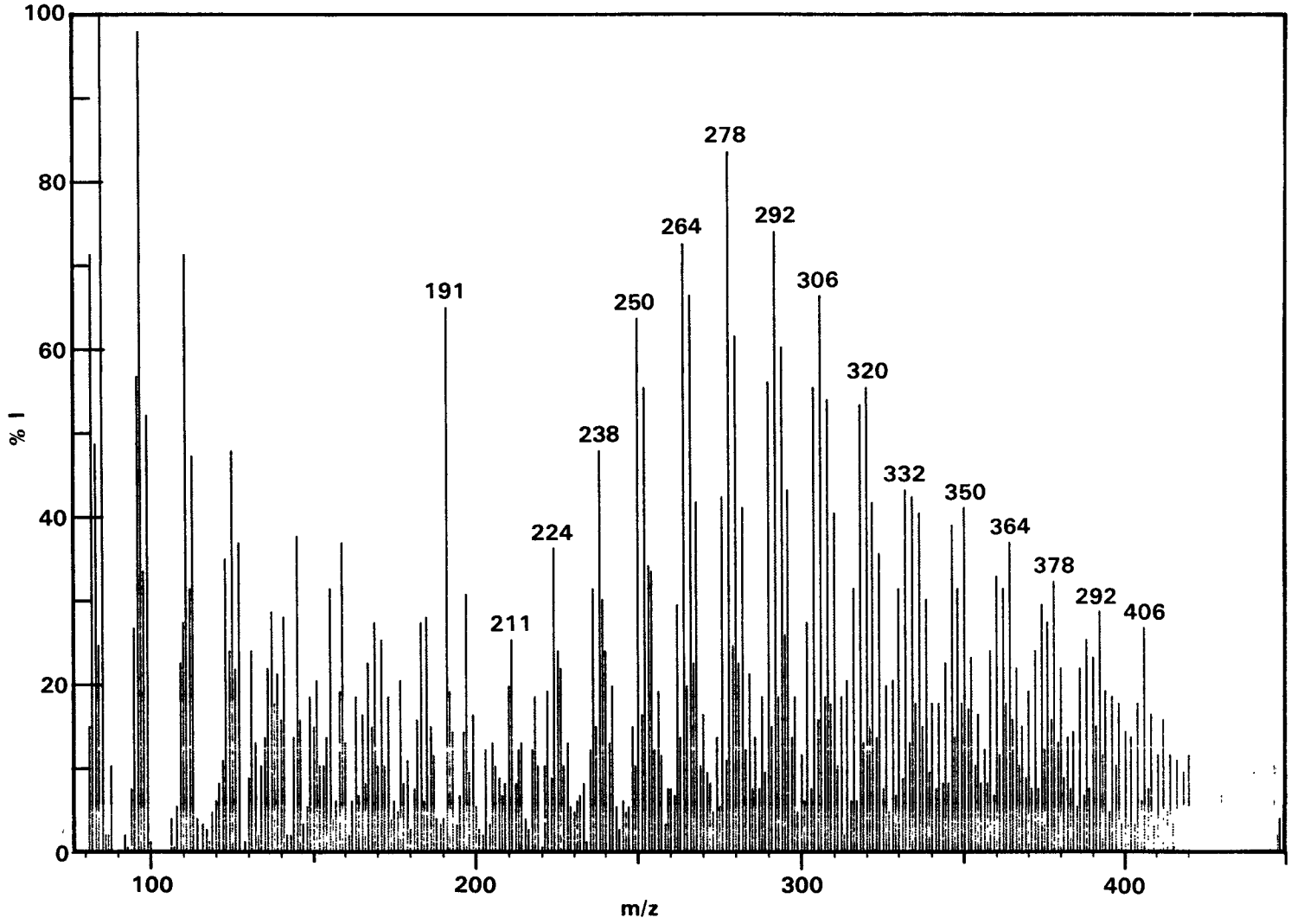

FIGURE B13. 10-eV Mass Spectrum of the A_1 Fraction from EDS Heavy Vacuum Gas Oil

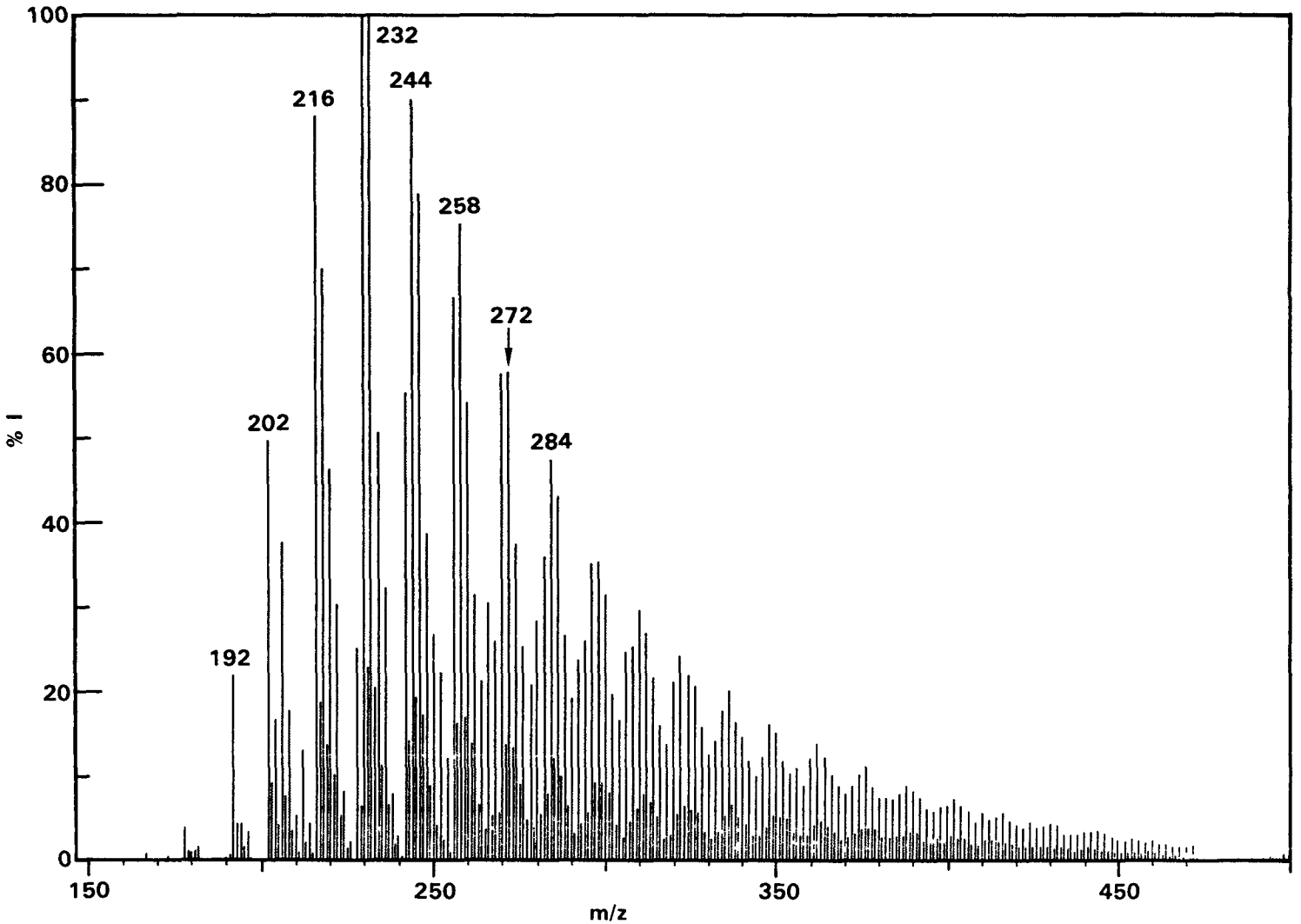

FIGURE B14. 10-eV Mass Spectrum of the A_2 Fraction from EDS Heavy Vacuum Gas Oil

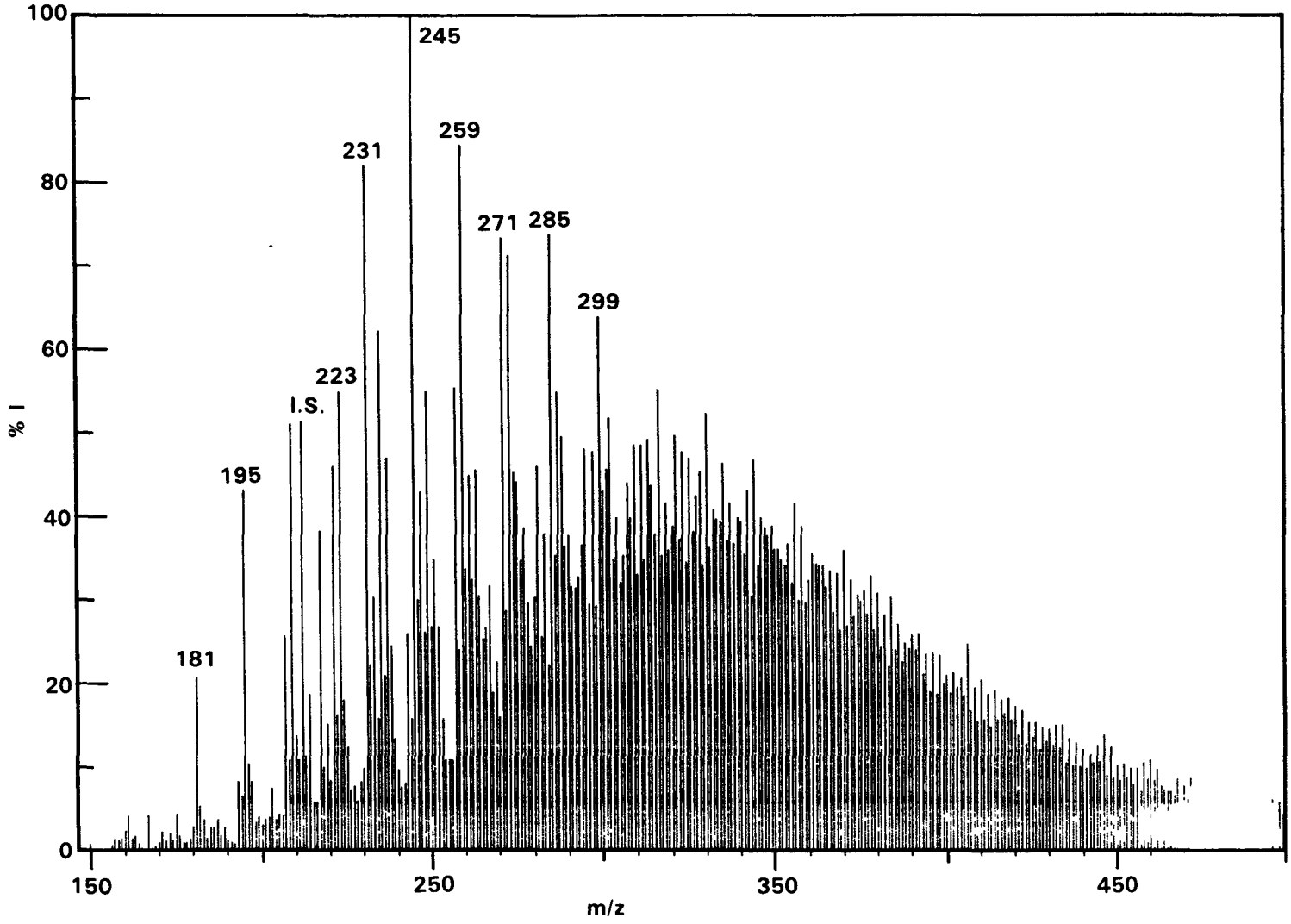

FIGURE B15. 10-eV Mass Spectrum of the A_3 Fraction from EDS Heavy Vacuum Gas Oil

APPENDIX B

LOW VOLTAGE, PROBE INLET MASS SPECTRA OF CHEMICAL CLASS FRACTIONS A_1, A_2, A_3, and A_4 OF THE FOLLOWING EDS PROCESS MATERIALS: BOTTOMS RECYCLE PS (003), VACUUM BOTTOMS (004), ONCE-THROUGH PS (005), AND HEAVY VACUUM GAS OIL (006). THREE TABLES FOR INTERPRETATION OF POSSIBLE MASS IDENTIFICATIONS FOR ALKYLATED, NEUTRAL PAH, HYDROXY-PAH, AND N-PAC HAVE ALSO BEEN INCLUDED AS KEYS TO THE DATA TABLES.

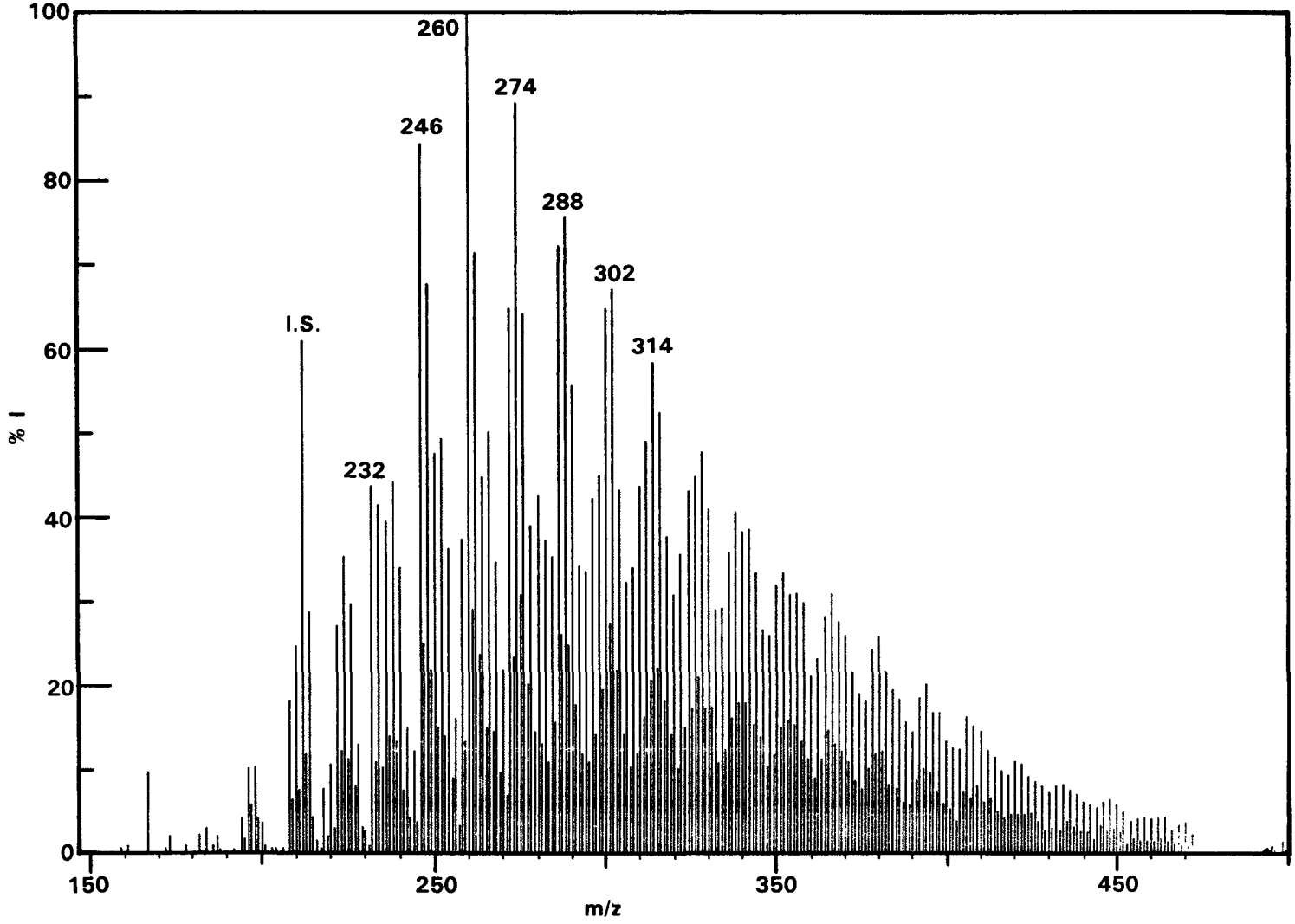

FIGURE B16. 10-eV Mass Spectrum of the A_4 Fraction from EDS Heavy Vacuum Gas Oil

TABLE C1. Low Voltage, Probe MS Compositional Data for the PAH and N-PAC Fractions of the 650-700°F EDS Distillate[a]

Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
PAH											
Biphenyl					7 (0.9)	19 (2.2)	20 (2.3)	11 (1.3)			
Fluorene			5 (0.6)	44 (5.1)	90 (10.4)	67 (7.7)	22 (2.6)	6 (0.7)			
Phenanthrene		20 (2.4)	74 (8.6)	100 (11.6)	43 (5.0)	11 (1.2)					
Phenylnaphthalene	47 (5.5)	30 (3.5)	10 (1.2)								
Pyrene and Fluoranthene	41 (4.7)										
N-PAC											
Indole								6 (1.2)	8 (1.6)	6 (1.2)	
Quinoline							5 (0.9)	8 (1.5)	6 (1.2)		
Carbazole		70 (13.7)	100 (19.7)	52 (10.2)	16 (3.1)	5 (0.9)					

[a]Masses with peak intensities lower than 5% of base peak are not included.

TABLE C2. Low Voltage, Probe MS Compositional Data for the PAH and N-PAC Fractions of the 700-750°F EDS Distillate[a]

Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
PAH											
Fluorene					21 (2.1)	39 (4.0)	31 (3.2)	19 (1.9)	7 (0.7)		
Phenanthrene			6 (0.6)	49 (5.1)	92 (9.5)	62 (6.3)	26 (2.6)	8 (0.8)			
Phenylnaphthalene	13 (1.3)	100 (10.3)	80 (8.3)	28 (2.9)	10 (1.0)						
Pyrene and Fluoranthene	47 (4.9)	70 (7.2)	29 (3.0)	10 (1.0)	5 (0.5)						
N-PAC											
Quinoline								8 (0.9)	14 (1.7)	13 (1.6)	7 (0.9)
Carbazole			16 (2.0)	66 (8.0)	100 (12.3)	70 (8.6)	34 (4.2)	9 (1.1)			
Benzoquinoline			23 (2.8)	43 (5.3)	21 (2.6)	7 (0.8)					

[a]Masses with peak intensities lower than 5% of base peak are not included.

TABLE C3. Low Voltage, Probe MS Compositional Data for the PAH and N-PAC Fractions of the 750-800°F EDS Distillate[a]

Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
PAH											
Fluorene							8 (0.7)	11 (1.0)	11 (1.0)	8 (0.7)	
Phenanthrene					13 (1.1)	36 (3.1)	53 (4.6)	42 (3.6)	20 (1.8)	8 (0.7)	
Phenylnaphthalene		11 (1.0)	79 (6.8)	100 (8.7)	81 (7.0)	48 (4.1)	19 (1.7)	7 (0.6)			
Pyrene and Fluoranthene		11 (0.9)	54 (4.6)	82 (7.1)	60 (5.2)	30 (2.6)	13 (1.1)	6 (0.5)			
Chrysene	14 (1.2)	31 (2.7)	14 (1.2)	8 (0.7)	5 (0.5)						
N-PAC											
Carbazole					6 (0.9)	14 (2.1)	20 (3.0)	17 (2.5)	11 (1.6)	6 (0.9)	
Benzoquinoline				71 (10.7)	100 (15.0)	65 (9.7)	31 (4.6)	15 (2.2)	7 (1.0)		
Benzo[def]carbazole				7 (1.1)	11 (1.6)	8 (1.3)	5 (0.7)				
Benzocarbazole	13 (1.9)	11 (1.6)									

[a]Masses with peak intensities lower than 5% of base peak are not included.

TABLE C4. Low Voltage, Probe MS Compositional Data for the PAH and N-PAC Fractions of the 800°+F EDS Dis-Distillate[a]

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
PAH													
Phenylnaphthalene						28 (1.0)	39 (1.4)	36 (1.2)	32 (1.1)	24 (0.8)	16 (0.5)	12 (0.4)	10 (0.3)
Pyrene and Fluoranthene					44 (1.5)	89 (3.1)	84 (2.9)	61 (2.1)	44 (1.5)	29 (1.0)	19 (0.7)	12 (0.4)	
Chrysene		35 (1.2)	100 (3.5)	94 (3.3)	79 (2.8)	66 (2.3)	57 (2.0)	43 (1.5)	28 (1.0)	18 (0.6)	12 (0.4)		
Benzopyrene and Benzofluoranthrene	26 (0.9)	31 (1.1)	28 (1.0)	29 (1.0)	33 (1.2)	33 (1.2)	27 (0.9)	23 (0.8)	16 (0.6)	11 (0.4)			
Binaphthyl	14 (0.5)	36 (1.2)	61 (2.1)	61 (2.1)	53 (1.8)	42 (1.4)	31 (1.1)	23 (0.8)	10 (0.1)				
Anthanthrene	16 (0.6)	21 (0.7)	19 (0.7)	19 (0.7)	19 (0.7)	17 (0.6)	15 (0.5)	11 (0.4)					
Dibenzochrysene		19 (0.7)	27 (0.9)	24 (0.8)	22 (0.8)	19 (0.7)	16 (0.6)	12 (0.4)					
N-PAC[b]													
Benzoquinoline						28 (0.5)	58 (1.1)	66 (1.2)	57 (1.0)	49 (0.9)	41 (0.8)	34 (0.6)	
Benzo[def]carbazole					21 (0.4)	63 (1.1)	100 (1.8)	92 (1.7)	65 (1.2)	52 (0.9)	41 (0.8)		
Benzocarbazole		53 (1.0)	76 (1.4)	69 (1.3)	67 (1.2)	57 (1.0)	52 (0.9)	44 (0.8)	37 (0.7)				
Benzacridine		21 (0.4)	59 (1.1)	94 (1.7)	86 (1.6)	69 (1.3)	55 (1.0)	42 (0.8)					
Dibenzo[b,def]-carbazole			25 (0.5)	38 (0.7)	51 (0.9)	57 (1.0)	51 (0.9)						

[a]Masses with peak intensities lower than 10% of base peak are not included.
[b]Masses above 330 amu not included because of hydroxy-PAH breakthrough.

TABLE C5. Low Voltage, Probe MS Compositional Data for the Hydroxy-PAH Fractions (A_4) of the 5°F Distillate Fractions Boiling from 250-800°+F

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
EDS, 250-300°F													
m/z 70 (unknown structure)	100 (28.6)												
Phenol	90 (25.8)	8 (2.3)	2 (0.7)	3 (0.9)									
EDS, 300-350°F													
Phenol	13 (7.9)	100 (62.2)											
m/z 71 (unknown)	20 (12.4)												
EDS, 350-400°F													
m/z 71 (unknown)	25 (9.6)												
Phenol		67 (25.6)	100 (38.1)	4 (1.6)									
EDS, 400-450°F													
Phenol			71 (26.2)	100 (37.2)	28 (10.2)	1 (0.4)							
Indanol	5 (0.9)												

TABLE C5. (continued)

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
EDS, 450-500°F													
Phenol			6 (1.4)	19 (3.9)	100 (20.9)	79 (16.6)	16 (3.3)						
Indanol	22 (4.7)	76 (16.0)	34 (7.0)	3 (0.7)									
EDS, 500-550°F													
m/z 71 (unknown)	100 (15.1)												
Phenol						21 (3.2)	32 (4.9)	13 (1.9)					
Indanol		36 (5.4)	95 (14.4)	73 (11.0)	18 (2.7)								
Hydroxybiphenyl	12 (1.8)	21 (3.2)											
EDS, 550-600°F													
Phenol								13 (1.8)	15 (2.2)	8 (1.1)			
Indanol			11 (1.5)	51 (7.2)	100 (14.1)	66 (9.3)	19 (2.7)						
Indenol				13 (1.9)	40 (5.6)	29 (4.1)	12 (2.4)						
Hydroxybiphenyl	9 (1.2)	40 (5.7)	40 (5.6)	17 (2.4)									

TABLE C5. (continued)

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
EDS, 600-650°F													
Phenol											8 (0.8)		
Indanol					16 (1.5)	58 (5.5)	86 (8.1)	74 (7.0)	18 (1.7)				
Indenol					14 (1.3)	49 (4.6)	69 (6.5)	16 (1.5)	10 (0.9)				
Hydroxybiphenyl		19 (1.8)	100 (9.4)	64 (6.0)	48 (4.6)	7 (0.7)							
Hydroxyfluorene	19 (1.8)	16 (1.5)	19 (1.8)	18 (1.7)									
EDS, 650-700°F													
Indanol								14 (1.2)	22 (1.8)	18 (1.5)	5 (0.4)		
Indenol							13 (1.1)	35 (2.9)	37 (3.1)	23 (1.9)	7 (0.6)		
Hydroxybiphenyl			18 (1.5)	69 (5.7)	97 (8.0)	57 (4.7)	25 (2.1)	8 (0.6)					
Hydroxyfluorene	8 (0.7)	70 (5.8)	93 (7.7)	100 (8.3)	71 (5.8)	31 (2.6)	13 (1.0)						
Naphthol						5 (0.4)	20 (1.6)	25 (2.0)	16 (1.3)	5 (0.4)			
Hydroxyphenyl-naphthalene	11 (0.9)	11 (0.9)											

TABLE C5. (continued)

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
EDS, 700-750°F													
Indenol										8 (1.0)	8 (1.0)	5 (0.6)	
Naphthol								5 (0.6)	10 (1.2)	10 (1.2)	5 (0.6)		
Hydroxybiphenyl					7 (0.9)	15 (1.9)	21 (2.7)	15 (1.9)	8 (1.0)				
Hydroxyfluorene				27 (3.4)	68 (8.5)	100 (12.6)	78 (9.8)	44 (5.6)	18 (2.3)	6 (0.7)			
Hydroxyphenanthrene			9 (1.1)	12 (1.5)	13 (1.7)	10 (1.3)	7 (0.9)						
Hydroxyphenyl-naphthalene		17 (2.2)	18 (2.2)	6 (0.8)									
EDS, 750-800°F													
Indenol										5 (0.3)	13 (0.9)	10 (0.7)	7 (0.5)
Indanol								7 (0.5)	5 (0.3)	18 (1.2)	28 (1.8)	19 (1.3)	12 (0.8)
Hydroxybiphenyl						5 (0.3)	9 (0.6)	12 (0.8)	15 (1.0)	12 (0.8)	10 (0.6)		
Hydroxyfluorene				6 (0.4)	31 (2.1)	78 (5.1)	100 (6.6)	84 (5.5)	46 (3.0)	25 (1.6)	11 (0.7)		
Hydroxyphenanthrene			11 (0.7)	70 (4.5)	92 (6.0)	92 (6.0)	79 (5.2)	51 (3.3)	26 (1.7)	12 (0.8)	5 (0.3)		
Hydroxyphenyl-naphthalene		18 (1.2)	37 (2.5)	45 (3.0)	35 (2.3)	20 (1.3)	11 (0.7)	7 (0.4)					

APPENDIX C

LOW VOLTAGE, PROBE INLET MASS SPECTRAL DATA FOR THE EDS DISTILLATE CUTS. FOR MASS ASSIGNMENTS, SEE KEY, TABLES B1-B3 OF APPENDIX B. SUMMARIES OF PROBE MS DATA FOR PAH, N-PAC, AND HYDROXY-PAH FRACTIONS ARE INCLUDED IN THIS APPENDIX.

TABLE C5. (continued)

Representative Compound Type	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
EDS, 800°+F													
Hydroxyfluorene								8 (0.2)	20 (0.4)	34 (0.7)	41 (0.8)	45 (0.9)	44 (0.9)
Hydroxyphenanthrene					18 (0.4)	35 (0.7)	58 (1.2)	66 (1.4)	66 (1.4)	64 (1.3)	50 (1.0)	46 (0.9)	36 (0.7)
Hydroxyphenyl-naphthalene				17 (0.4)	44 (0.9)	58 (1.2)	60 (1.2)	61 (1.3)	54 (1.1)	44 (0.9)	36 (0.7)	26 (0.5)	19 (0.4)
Hydroxypyrene			23 (0.5)	42 (0.9)	78 (1.6)	88 (1.8)	91 (1.9)	88 (1.8)	71 (1.5)	54 (1.1)	42 (0.9)	32 (0.7)	24 (0.5)
Hydroxychrysene		8 (0.2)	34 (0.7)	59 (1.2)	83 (1.7)	99 (2.0)	100 (2.1)	81 (1.7)	66 (1.4)	46 (1.0)	32 (0.7)	22 (0.4)	15 (0.3)
Hydroxybenzocyclo-penta[b,def]phen-anthrene		15 (0.3)	35 (0.7)	49 (1.0)	67 (1.4)	76 (1.6)	71 (1.5)	64 (1.3)	52 (1.1)	38 (0.8)	28 (0.6)	18 (0.4)	13 (0.3)
Hydroxybenzopyrene	7 (0.1)	16 (0.3)	33 (0.7)	50 (1.0)	53 (1.1)	51 (1.1)	42 (0.9)	35 (0.7)	26 (0.5)	20 (0.4)	13 (0.3)	10 (0.2)	6 (0.1)

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