

CHROMSYMP. 2083

## **Chemical class separation of coal liquids by high-performance liquid chromatography on a semi-preparative, phosphoric acid-modified amino-bonded-phase column**

JOHN W. HAAS, III<sup>a</sup> and PETER C. UDEN\*

*Department of Chemistry, Lederle Graduate Research Tower A, University of Massachusetts, Amherst, MA 01003-0035 (USA)*

---

### **ABSTRACT**

A amino-bonded stationary phase, modified by treatment with phosphoric acid to form an amino phosphate, permits the high-performance liquid chromatographic separation of aliphatic, non-polar aromatic, neutral/acidic polar aromatic and basic polar aromatic hydrocarbon chemical classes. It was employed to fractionate coal liquid samples on a semi-preparative scale.

---

### **INTRODUCTION**

Among fuel sources being investigated as alternatives to petroleum, coal-derived liquids have generated considerable interest because of the abundance and low cost of coal feedstock. Various sources and processing methods produce coal liquids with different chemical compositions. When evaluating the overall usefulness and acceptability of these various coal liquids as fuel sources, it is important to include measurements of utile energy content and health risk assessments using biological tests. The energy content of a fuel can often be determined using easily measured properties such as C/H ratios. However, biological testing to date has shown that in many instances only a few potent chemical compounds, present at trace levels in a coal liquid, account for most of the biological activity. Consequently, samples must be characterized extensively so that these species can be identified and determined. This task is made difficult, however, by the complexity of coal liquids; they are known to contain numerous hydrocarbons including aliphatics, "simple" aromatics (including benzene and polycyclic aromatics), alkyl- and other substituted aromatics, hydroaromatics and heterocyclics. Therefore, a combination of several high-resolution analytical methods is usually required to characterize fully a particular coal liquid sample.

Prefractionation can both simplify and reduce the number of high-resolution analyses needed to characterize a coal liquid thoroughly. Prefractionation by normal-

---

<sup>a</sup> Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37832-6113, USA.

phase high-performance liquid chromatography (HPLC) using silica, amino and amino-cyano columns has been reported [1-4]. All of the reported prefractionations, however, required the use of a back-flush in order to elute the aromatic fraction. Although the use of a back-flush is acceptable, a simplified prefractionation procedure that does not require the switching of valves in the middle of the chromatographic run would be of value. Also, the prefractionation steps reported achieved class separations of the aliphatic and aromatic fractions only. The separation of the aromatic fraction into the "simple" aromatics (including benzene and polycyclic aromatics), alkyl- and other substituted aromatics, hydroaromatics and heterocyclics was not accomplished.

In response to the limitations of existing polar bonded stationary phases and liquid-solid chromatographic (LSC) adsorbents, we recently developed a phosphoric acid-modified amino-bonded phase that, in a preliminary study, separated model compounds into aliphatic, non-polar aromatic, neutral/acidic polar aromatic and basic polar aromatic hydrocarbon chemical classes [5]. In the study described here, the phosphoric acid-modified column was investigated further and used to fractionate coal liquid samples on a semi-preparative scale.

## EXPERIMENTAL

### *Reagents*

Standard compounds were obtained from Aldrich (Milwaukee, WI, USA) and were used as received. HPLC-grade hexane and dichloromethane and 85% phosphoric acid were purchased from Fisher Scientific (Fair Lawn, NJ, USA). HPLC-grade isopropanol and glacial acetic acid were obtained from J. T. Baker (Phillipsburg, NJ, USA) and MCB Manufacturing Chemists (Cincinnati, OH, USA), respectively. All solvent mixtures were prepared volumetrically. The 10- $\mu$ m Chromosorb LC-9 amino-bonded phase was from Manville Products (Denver, CO, USA).

### *Samples*

The coal liquid and Illinois No. 6 heavy fuel oil (b.p. 435-900°F) was obtained from an H-coal pilot plant at Oak Ridge National Laboratory (Oak Ridge, TN, USA). Of primary interest to us was the hexane-soluble fraction of the SRC-II sample; the work reported here was part of an effort to develop methods to remove biologically active compounds from synthetic fuels. Thus, prior to HPLC fractionation, 10 g of the coal liquid were shaken with 10 ml of hexane and the asphaltene precipitate was removed by filtration. A spiked coal liquid sample was prepared by dissolving four standard compounds in a portion of the coal liquid-hexane mixture which had been diluted further (1:75) with hexane. The final concentrations of the four components were 50-150 mg/l in the spiked sample. Samples used for column recovery studies and as model polar hydrocarbons were individual standard compounds dissolved in hexane at concentrations of 75-200 mg/l. The mixture of standard *n*-alkanes was obtained from Supelco (Bellefonte, PA, USA).

### *High-performance liquid chromatography*

HPLC was performed with an IBM Instruments (Wallingford, CT) Model 9533 ternary gradient chromatograph equipped with a fixed-wavelength (254 nm) UV ab-

sorbance detector and a 250- $\mu$ l injection loop. The semi-preparative stainless-steel column (25 cm  $\times$  1 cm I.D.) was packed with 15 g of amino-bonded phase using isopropanol as both slurry and packing solvent [5]. The amino-bonded phase was modified with phosphoric acid by pumping 75 ml of 0.5% phosphoric acid in isopropanol solution through the column. The modified bonded phase, considered to consist primarily of ammonium phosphate groups [5], was then washed with 75 ml each of isopropanol and dichloromethane prior to equilibration with hexane.

The ternary solvent gradient program developed to separate model synthetic compounds [5] was modified for fractionation of the coal liquid samples. The complete solvent program is included in Table I and was also used for the recovery studies. The initial low flow-rate allowed a fraction to be collected from the beginning of the run until the first detectable species eluted from the column (at higher flow-rates it was difficult to change collection vessels before the second fraction began to elute into the vessel for the first fraction). The switch to 100% hexane after 35 min kept acetic acid out of the isopropanol fraction, from which it cannot be extracted. After 50 min, the flow-rate was again reduced because the pressure increased when 100% isopropanol was pumped through the column. The bonded phase was regenerated to full activity by pumping 0.5% phosphoric acid in isopropanol through the column for 5 min at the end of the chromatographic run. Coal liquid fractions or recovery standards were collected manually and concentrated by blowing nitrogen over the solutions as they were warmed on a hot-plate. Fractions containing acetic acid were extracted with 3  $\times$  15 ml of distilled, dionized water and dried over sodium sulfate prior to concentration.

### Gas chromatography

The coal liquid fractions and recovery standards were analyzed by GC using a Varian (Palo Alto, CA, USA) Model 2760 chromatograph equipped with a 22 m  $\times$  0.31 mm I.D. SE-52 capillary column and both flame ionization detection (FID) and

TABLE I

TERNARY HPLC MOBILE PHASE PROGRAM FOR THE SEMI-PREPARATIVE CHEMICAL CLASS FRACTIONATION OF COAL LIQUIDS USING A PHOSPHORIC ACID-MODIFIED AMINO-BONDED-PHASE COLUMN

Time (min)	Solvent	Flow-rate (ml/min)
0	100% hexane	2.00
8	100% hexane	5.00
20	100% hexane <sup>a</sup>	5.00
30	hexane-acetic acid (96.5:3.5) <sup>b</sup>	5.00
35	Switch to 100% hexane	5.00
40	100% hexane <sup>a</sup>	5.00
50	100% isopropanol <sup>b</sup>	3.50
65	Switch to 0.5% phosphoric acid in isopropanol	3.50
70	Switch to 100% isopropanol	3.50
80	100% isopropanol <sup>a</sup>	3.50
90	100% hexane <sup>b</sup>	5.00

<sup>a</sup> Begin a linear mobile phase gradient.

<sup>b</sup> End a linear mobile phase gradient.

nitrogen-phosphorus detection (NPD) were used. The column oven was programmed from 60 to 275°C at 8°C/min. Fractions were also analyzed with a Hewlett-Packard (Palo Alto, CA, USA) Model 5985 gas chromatographic-mass spectrometric (GC-MS) system employing the same GC column and temperature program. Electron impact ionization was used to obtain individual mass spectra, which were compared the NIH-EPA-MSDC mass spectral database using the GC-MS computer system.

## RESULTS AND DISCUSSION

### Recovery studies

Ideally, an HPLC prefractionation method should provide quantitative (100%) recovery of all sample components. In practice, bonded stationary phases normally give better recoveries than LSC adsorbents such as silica gel, silicic acid or alumina, which adsorb some polar compounds irreversibly. Recoveries from the phosphoric acid-modified amino bonded phase were determined for compounds representing some of the most abundant (*e.g.*, polycyclic aromatics) or bioactive (*e.g.*, amino aromatics) chemical classes found in coal liquids. The results are compared in Table II with those reported for low-pressure alumina and silicic acid columns [6]. Recoveries of non-polar aromatic hydrocarbons, neutral nitrogen-containing aromatic hydrocarbons and acidic hydroxy aromatic hydrocarbons from all three columns were nearly quantitative. The neutral alumina column provided better recoveries of the nitrogen-containing aromatic bases than did the two acidic columns. However, the modified amino-bonded phase yielded significantly higher recovery (72%) of the amino aromatic hydrocarbon 9-aminophenanthrene than did either the alumina adsorbent (57%) or the silicic acid adsorbent (39%). Overall, recoveries from the modified amino-bonded-phase column were excellent, comparing favorably with those obtained from the solid alumina and silicic acid adsorbents.

TABLE II

RECOVERIES OF MODEL COAL LIQUID COMPOUNDS FROM PHOSPHORIC ACID-MODIFIED AMINO, ALUMINA AND SILICIC ACID LC COLUMNS

Compound	Chemical class	Recovery (%)		
		Modified Amino	Alumina <sup>a</sup>	Silicic Acid <sup>a</sup>
Phenanthrene	Non-polar aromatic	99	98	—
1-Naphthol	Hydroxy aromatic	94	—	—
1-Acenaphthol	Hydroxy aromatic	—	85	—
Carbazole	Neutral nitrogen-containing aromatic	94	87	88
2-Methylindole	Neutral nitrogen-containing aromatic	82	—	—
Pyridine	Basic nitrogen-containing aromatic	84	—	—
Quinoline	Basic nitrogen-containing aromatic	—	100	81
Acridine	Basic nitrogen-containing aromatic	—	99	90
3-Aminofluoranthene	Amino aromatic	68	64	64
9-Aminophenanthrene	Amino aromatic	72	57	39

<sup>a</sup> Ref. 2.

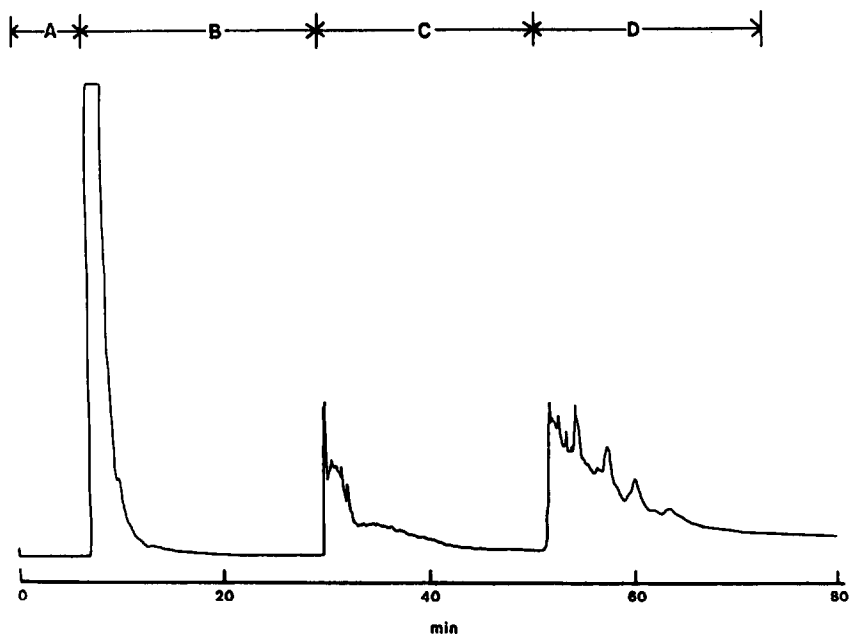


Fig. 1. Chemical class fractionation of hexane-treated Illinois No. 6 coal liquid on the semi-preparative, phosphoric acid-modified amino-bonded-phase HPLC column. Fractions: (A) non-polar aliphatics; (B) non-polar aromatics; (C) neutral/acidic polar hydrocarbons; (D) basic polar hydrocarbons.

#### *HPLC fractionation of coal liquid samples*

Three groups of peaks are observed in the chromatogram for the diluted coal liquid-hexane mixture (Fig. 1) and were collected as fractions B-D when the original hexane-soluble fraction (75 times more concentrated) was separated. A fourth fraction, A, expected to contain non-polar aliphatic hydrocarbons which are not detected at 254 nm, was collected from the beginning of the chromatographic run until the first peak was detected for fraction B.

Fig. 1 shows that fraction B, assigned to the non-polar aromatic hydrocarbon class, was eluted as a relatively narrow band with hexane. The compact elution profile was produced when a short equilibration with hexane was used prior to sample separation. Longer equilibrations (up to 1 h or more) removed residual isopropanol, water and phosphoric acid from the column and resulted in stronger adsorption and better resolution of components within the fraction. Thus, longer equilibrations can be used when "subfractionation" of the non-polar aromatic class is needed to facilitate the determination of single compounds. It has been demonstrated that polycyclic aromatics are separated by the modified amino-bonded phase according to the number of condensed rings in the range 2-5 [5]. This ring number-based separation is characteristic of polar stationary phases, including bonded phases and traditional LSC adsorbents, when non-polar solvents are used to separate parent and alkylated aromatic hydrocarbons [7-10]. Although these aromatics have been labelled "non-polar", they are in fact weakly polar and interacted enough with the polar stationary phase to elute after the aliphatic hydrocarbons, which were not retained at all on the

column. However, hydrocarbons substituted with polar functional groups, especially those capable of interacting with the polar stationary phase through strong hydrogen bonds, were retained on the column longer than the "non-polar" aromatics.

Fraction C was eluted from the HPLC column when acetic acid was added to the hexane mobile phase. Early in the gradient, increasing solvent strength caused polar species forming weak hydrogen bonds with the phosphate bonded phase groups (*e.g.*, neutral aromatics) to elute rapidly from the column after the non-polar aromatics. At higher concentrations of acetic acid, polar hydroxy aromatics and other acids capable of forming stronger hydrogen bonds with the stationary phase were displaced, leaving bases on the column. Because of their abundance in fossil fuels, only phenolic-type hydroxy aromatics were tested in our previous study [5]. In this study, however, it was confirmed with standard compounds that stronger acids such as aliphatic (*e.g.*, stearic) and aromatic (*e.g.*, benzoic) carboxylic acids were eluted in this fraction. Thus, the fraction can be classified more broadly as containing neutral aromatics and acidic hydrocarbons (both aliphatic and aromatic). It is also notable that the use of acetic acid in the mobile phase was critical for the selective elution of acids in fraction C. For example, when isopropanol (another strong hydrogenbonding solvent, but weaker than acetic acid) was added to the hexane mobile phase instead of acetic acid, the acids and bases eluted together [5]. Acetic acid's levelling effect on acids, strengthening of bases and strong competition for sites active for adsorbing acids could all have contributed to the preferential elution of the acids. The unique selectivity of acid-containing mobile phases employed with the modified amino-bonded-phase column is currently under further investigation.

The final acetic acid concentration, 3.5% in hexane, was not high enough to remove strongly adsorbed nitrogen-containing bases from the column. They were eluted in fraction D with a gradient to 100% isopropanol. The especially strong retention of the bases was presumably due to hydrogen bonds formed between the nitrogens of the bases and acidic hydroxyl protons of the phosphate stationary phase groups. It is well known that the strongest hydrogen bonds are formed between the most acidic proton donors and the most basic proton acceptors [11]. Further, it was confirmed with standard compounds such as 2-amino-octane that aliphatic bases eluted in this fraction along with the aromatic bases. Hence, fraction D can be assigned more generally to hydrocarbon bases.

The HPLC results provide some useful initial characterization of the hexane-soluble coal liquid sample. It is clear from Fig. 1 that the hexane-treated sample used in our study, similarly to a related whole oil which contained about 20% polar compounds [12], contained more non-polar aromatics than the more biologically active and less energetically useful polar aromatics. However, when a sample of whole oil was separated with the modified amino-bonded-phase column, the UV absorbances of fractions C and D increased relative to fraction B, indicating that the hexane dilution/precipitation procedure had enriched the non-polar hydrocarbon content of the fuel. More detailed HPLC characterization could be achieved if a variable-wavelength absorbance detector set near 200 nm or a refractive index detector was employed. Then the non-polar aliphatics would have been detected along with the aromatics, providing a non-polar aliphatic/aromatic hydrocarbon ratio which is one useful measure of energy content.

Support for the chemical assignments and retention mechanisms proposed

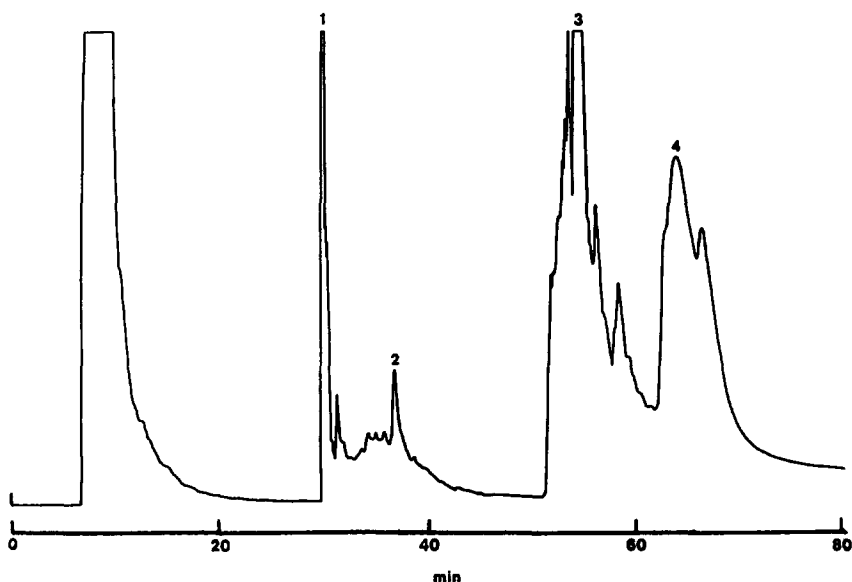


Fig. 2. Chemical class fractionation of hexane-treated Illinois No. 6 coal liquid hexane extract spiked with four model synthetic fuel compounds. Peak identities: (1) carbazole; (2) 1-naphthol; (3) phenanthridine; (4) 4-picoline.

above was obtained for the two polar fractions by spiking the hexane-soluble coal liquid fraction with four model compounds. The results (Fig. 2) indicate that the assignments were correct. Carbazole, a neutral nitrogen-containing compound, eluted early in the neutral/acidic polar hydrocarbon fraction C. Capable of forming a stronger hydrogen bond through its acidic hydroxyl group, 1-naphthol eluted later in the same fraction. Phenanthridine and 4-picoline are bases and eluted as expected in the basic polar hydrocarbon fraction D. Although both compounds were able to interact with the acidic phosphate groups of the stationary phase through a heterocyclic nitrogen, the hydrogen bond formed was stronger for 4-picoline, the stronger base ( $pK_a = 6.02$ ). Hence, it eluted after phenanthridine ( $pK_a = 5.58$ ). The nitrogen in phenanthridine is also sterically hindered by its ring system, a factor which probably contributes to its weaker retention.

#### GC analysis of coal liquid fractions

GC and GC-MS analyses were used to confirm the chemical class assignments for the coal liquid fractions and demonstrate the usefulness of prefractionation when there is a need for individual compound identification. It may be noted that no evidence was seen of any GC column degradation and performance loss resulting from the presence in samples of phosphoric acid removed from the column.

Chromatograms for HPLC fractions A-C obtained with FID and NPD are presented in Fig. 3-5. The FID trace in Fig. 3 shows that fraction A contained an abundance of non-polar aliphatic hydrocarbons even though the fraction was not visible in the HPLC trace (Fig. 1). Appreciable amounts of  $n$ -C<sub>15</sub>-C<sub>27</sub> alkanes are

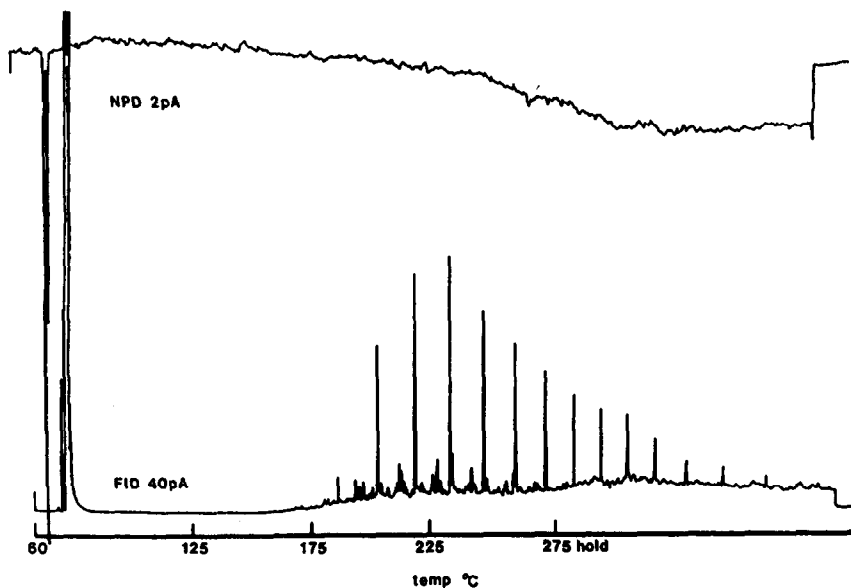


Fig. 3. Dual FID-NPD capillary gas chromatogram of the non-polar aliphatic hydrocarbon fraction A recovered from the HPLC separation of hexane-treated Illinois No. 6 coal liquid.

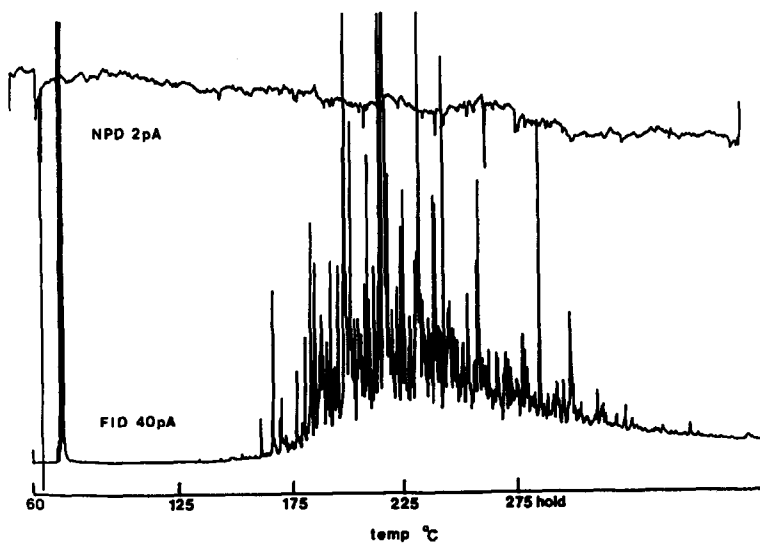


Fig. 4. Dual FID-NPD capillary gas chromatogram of the non-polar aromatic hydrocarbon fraction B recovered from the HPLC separation of hexane-treated Illinois No. 6 coal liquid.



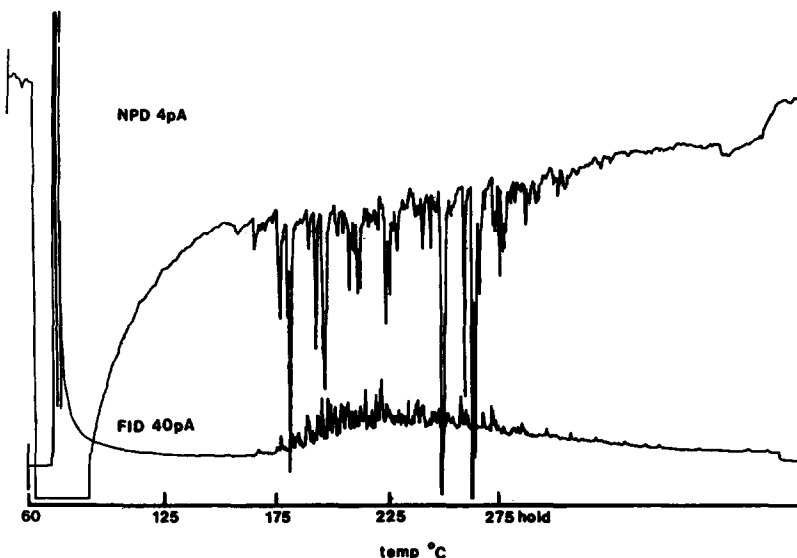


Fig. 5. Dual FID-NPD capillary gas chromatogram of the neutral/acidic polar hydrocarbon fraction C recovered from the HPLC separation of hexane-treated Illinois No. 6 coal liquid.

observed with the largest peak being at  $n$ -C<sub>17</sub> (heptadecane). Peak identities were confirmed by comparing retention times and mass spectra with those for a standard mixture of normal aliphatic hydrocarbons. Lower molecular weight hydrocarbons, up to *ca.* C<sub>10</sub>-C<sub>11</sub>, were certainly lost during the concentration step. This was relatively unimportant, however, for this study, as they would elute prior to the alkanes which were observed. Only very small amounts of other compounds are evident in the FID trace. Mass spectra indicated that these species were primarily branched aliphatics, although most of the small peaks in the FID trace were below the MS detection limits. No aromatics were detected by MS. Further, using NPD no nitrogen-containing species were detected in this fraction. This is not surprising as any nitrogen-containing compound would probably have been polar enough to be retained more than the non-polar aliphatic or aromatic hydrocarbons.

Overall, the GC results for fraction A indicate that the HPLC separation of non-polar aliphatics from other hydrocarbons, most notably the non-polar aromatics, was efficient, allowing individual aliphatics to be easily determined without interference. This is not the case when whole coal liquids are analyzed by GC; the aliphatics are difficult to detect and determine in FID traces dominated by aromatic hydrocarbon peaks (see the discussion of fraction B below). Based on the strong FID responses for fraction A, it can be concluded that most of the valuable aliphatic hydrocarbon content of the SRC-II sample was maintained through the hexane dilution/precipitation procedure. This conclusion seems reasonable considering that non-polar aliphatic compounds such as octadecane are not retained on the HPLC column [5] (resulting in quantitative recovery) and are highly soluble in hexane. As discussed earlier, the use of a non-selective detector with the HPLC method would help to

confirm this conclusion by quantifying the non-polar aliphatic contents of dilute and whole oil comparison samples.

The second HPLC fraction, B, contained more gas chromatographable material (see Fig. 4) than did the other fractions. GC-MS analysis confirmed the predominance of unsubstituted and alkylated polycyclic aromatics in the fraction. These were the only species detected; the primary compounds identified are included in Table III. The abundance of aromatics in the sample was consistent with previous analyses which indicated that non-polar aromatic compounds comprised about 47% of a similar whole oil sample [12]. The GC results were also consistent with the HPLC data which indicated that the non-polar aromatics were enriched relative to the polar compounds during hexane pretreatment of the whole oil. It is clear that hexane pretreatment did not reduce significantly the non-polar aromatic content relative to the whole coal liquid. The excellent recoveries of polycyclic aromatics such as phenanthrene (99%) from the HPLC columns and their generally favorable solubility in hexane support this conclusion.

TABLE III

SOME OF THE COMPOUNDS IDENTIFIED IN HPLC FRACTIONS B AND C OF HEXANE-TREATED ILLINOIS NO. 6 COAL LIQUID

HPLC fraction	Compound
(B) Non-polar aromatic hydrocarbons	C <sub>1</sub> -naphthalenes C <sub>4</sub> -naphthalenes Anthracene/phenanthrene Fluoranthene/pyrene
(C) Neutral/acidic polar hydrocarbons	Phenol Cresols C <sub>2</sub> -phenols Carbazole

Fig. 4 also shows that the composition of fraction B was complicated and it would be difficult to determine many of the individual aromatic hydrocarbons. In this instance, the capability of the amino-bonded phase to provide ring number-based subfractions could be used to simplify subsequent GC analysis, including the identification and determination of biologically active compounds. A few nitrogen-containing species can be observed at trace levels in the NPD trace in Fig. 4. These species were probably neutral nitrogen-containing compounds in which the nitrogens were sterically hindered by alkyl groups or aromatic rings so that they were restricted from interacting with the stationary phase. However, the concentrations of these compounds were far below those of polycyclic aromatic hydrocarbons, and they could not be detected by MS.

The FID trace in Fig. 5 shows that HPLC fraction C contained many species at low concentrations. The low polar hydrocarbon levels were consistent with the HPLC results for hexane-treated and whole oil samples; this indicated that non-polar compounds were enriched relative to the polars compounds during hexane dilution/precipitation. This enrichment reflects the low solubility of polar compounds in hexane

and demonstrates that a simple precipitation scheme can be used to reduce the levels of undesirable polar compounds in synthetic fuels. GC-MS analysis confirmed the presence of neutral/acidic polar compounds in fraction C through identification of carbazole and various alkylated phenols (Table III). Non-polar aromatics were not detected, however, demonstrating that the separation of polar species from non-polar aromatics was efficient using the modified amino-bonded-phase column. These results illustrate again the merits of HPLC prefractionation, *i.e.*, GC analysis of the whole liquid would not have identified any of the polar compounds listed in Table III.

The NPD trace in Fig. 5 shows that many of the compounds in HPLC fraction C contained nitrogen, suggesting that all the neutral nitrogen-containing species, except the few observed in fraction B, were efficiently recovered and eluted in this fraction. The excellent recovery of carbazole (94%) from the modified amino-bonded phase supports this conclusion. Although the concentrations of the nitrogen-containing species were low and the hydroxy aromatics interfered with their analyses by GC-MS, there was no evidence that basic nitrogen compounds were present in the fraction. Specifically, selected ion monitoring was used to screen for amino compounds and heterocyclic nitrogen bases such as acridine but they were not detected. In a similar way to fraction B, subfractionation could be used to help identify and determine biologically active compounds in fraction C.

Finally, HPLC fraction D contained no material detectable by FID or NPD. From the GC results alone, one might conclude that there was little or no material in this fraction. However, this further demonstrates the usefulness of preliminary HPLC characterization, which clearly showed (Fig. 1) that a significant amount of material eluted in this fraction. Evidently, the simple addition of hexane did not precipitate all of the asphaltenes from the whole oil. Multiple polar functional groups and the high molecular weight of the species eluted in this fraction probably precluded analysis by GC. We are currently analyzing the fraction further using other high-resolution methods including HPLC and supercritical fluid chromatography, which are better suited for these types of compounds. Nevertheless, the absence of nitrogen-containing bases such as amino aromatics in the NPD trace indicates that these compounds, some of which are potent carcinogens that are normally present at low levels in coal liquids, were precipitated from the sample (to below the detection limits) during hexane pretreatment. Neutral nitrogen-containing compounds and various acids were also absent from this fraction, supporting the conclusion that they were efficiently eluted in fraction C.

## CONCLUSIONS

An HPLC method employing a semi-preparative amino-bonded-phase column modified with phosphoric acid has been developed for the prefractionation of coal liquids. Separation of model compounds added to a coal liquid sample diluted with hexane and GC analysis of the HPLC fractions collected for a more concentrated coal liquid/hexane sample demonstrated that compounds were eluted according to chemical class with little or no overlap between classes. A mechanism based on hydrogen bonding can be used to explain the class separation. The HPLC results also supplied useful information about the effects of hexane pretreatment on the coal liquid and simplified subsequent GC analysis, allowing trace level species to be identified by MS.

The new method has several attractive features. First, the modification procedure is simple and rapid; many other potentially useful stationary phases could be produced as easily as the phosphoric acid-modified bonded phase using analogous acid-base chemistry. Second, the separation of hydrocarbon classes has been improved. The modified column uniquely separates the polar acids and bases into distinct fractions while demonstrating the same capability as other polar bonded phases for separating the non-polar hydrocarbon classes. Useful preliminary characterizations such as non-polar aliphatic/aromatic and polar/non-polar hydrocarbon ratios can be obtained for a variety of synfuel samples with the HPLC method and suitable non-selective detection. Third, the recovery of sample components is equal to or better than those reported for other stationary phases. This is an especially useful feature for preparative HPLC applications. Finally, the method could be scaled up to full preparative size and modified further (*e.g.*, by using a more gradual gradient program) to fractionate very complex samples more extensively, including synthetic and natural fuels or environmental samples requiring individual compound identification.

#### ACKNOWLEDGEMENTS

This study was supported in part by the US Department of Energy, Contract DE-AC02-077EV4320, and Manville Products. We thank Mark Italia and Charles Stewart for their assistance and S. B. Dave and Sidney Siggia for their continued interest in this work.

#### REFERENCES

- 1 F. Munari, A. Trisciani, G. Mapelli, S. Trestianu, K. Grob, Jr., and J. M. Colin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 601.
- 2 I. L. Davies, K. D. Bartle, G. E. Andrews and P. T. Williams, *J. Chromatogr. Sci.*, 26 (1988) 125.
- 3 G. Felix, E. Thoumazeau, J.-M. Colin and G. Vion, *J. Liq. Chromatogr.*, 19 (1987) 2115.
- 4 L. Szepeszy, M. Horvath and K. Lakszner, *Chromatographia*, 19 (1984) 431.
- 5 J. W. Haas, III, W. F. Joyce, Y.-J. Shyu and P. C. Uden, *J. Chromatogr.*, 457 (1988) 215.
- 6 D. W. Later and M. L. Lee, in C. W. Wright, W. C. Weimer and W. D. Felix (Editors), *Advanced Techniques in Synthetic Fuels Analysis*, NTIS, Springfield, VA, 1983, p. 44.
- 7 J. Chmielowiec and A. E. George, *Anal. Chem.*, 52 (1980) 1154.
- 8 S. A. Wise, S. N. Chesler, H. S. Hertz, L. R. Hilpert and W. E. May, *Anal. Chem.*, 49 (1977) 2306.
- 9 M. Popl, V. Dolansky and J. Mostecky, *J. Chromatogr.*, 117 (1976) 117.
- 10 M. Popl, V. Dolansky and J. Mostecky, *J. Chromatogr.*, 91 (1974) 649.
- 11 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley, New York, 1979, p. 257.
- 12 R. P. Khosah, *Ph. D. Dissertation*, University of Massachusetts, Amherst, MA, 1985.