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SEPARATION AND CHARACTERIZATION OF NITROGEN HETEROCYCLE AND HYDROXYL AROMATIC COMPOUNDS IN NON-DISTILLABLE COAL-DERIVED LIQUIDS

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SUMMARY

The extent of compound class overlap for a previously developed fluorocarbon/basic alumina chromatographic method was investigated. It was found that the extent of hydroxyl aromatic and nitrogen aromatic compound overlap was minimal for the chromatographic method with oils and asphaltenes isolated from a Wyodak coal-derived liquid. A high-performance liquid chromatographic method was developed which very effectively grouped nitrogen aromatic compounds and hydroxyl aromatic compounds isolated from oils and asphaltenes with the fluorocarbon/basic alumina chromatographic approach. The high-performance liquid chromatographic method consisted of silica and various dimethyl sulfoxide–carbon tetrachloride mobile phases. Accurate elemental analysis data could not be obtained from the high-performance liquid chromatography subfractions because inorganic material was removed from the silica stationary phase with the dimethyl sulfoxide–carbon tetrachloride mobile phases. The hydroxyl aromatic and nitrogen aromatic compound fractions from the high-performance liquid chromatographic steps were characterized by proton nuclear magnetic resonance, infrared, and field-ionization mass spectrometry. The combination of the fluorocarbon/basic alumina and high-performance liquid chromatography steps with the field-ionization mass spectrometry and infrared spectrometry permitted a high degree of compound-class separation and general spectral characterization of coal-liquid fractions.

INTRODUCTION

Nitrogen heterocycles and hydroxyl aromatics, which constitute a majority of the polar compounds in coal-derived liquids, are important because of their role in refining processes and in the stability of feedstocks and upgraded products. The detrimental effects of nitrogen compounds in transportation fuels and fuel oils is demonstrated by relatively high NO_x emissions and by fuel instability[1]. Nitrogen

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compounds are present in coal-liquids mainly as azaarenes, pyrrolic types, and aromatic amines, all of which are considered environmentally important[2,3]. The presence of hydroxyl aromatic compounds in coal-liquids is well established[4]. Hydroxyl aromatic compounds play an important role in coal liquefaction processes due to their ability to enhance the conversion to fuels and increase the solubility of coal products in solvent refined coal (SRC) processes[5–8].

A large amount of research has focused on the separation and characterization of components in coal liquids in the last decade. Many of these investigations concentrated on the separation of polycyclic aromatic hydrocarbons (PAHs), while relatively fewer reports have appeared involving the analysis of the more polar nitrogen heterocycle and hydroxyl-aromatic constituents in coal liquids. A number of investigations have been published on polar compounds in fuels using gas chromatography–mass spectrometry (GC–MS)[9–15]. However, GC–MS, while useful in determining individual, volatile components in fuels, is difficult to apply to non-volatile, high-boiling samples. Green *et al.*[16] commented that adding up several hundred members of a particular compound class using GC–MS was not a very accurate method for determining the abundance of a compound class as a whole.

The combined use of high-performance liquid chromatography (HPLC) and GC–MS was utilized by Schmitter *et al.*[17] to identify nitrogen heterocycles in crude oils. Schabron *et al.*[18] were able to separate alkyl phenols from distillable coal-derived liquids using open-column chromatography and HPLC. Burke *et al.*[19] separated phenols from solvent refined coal (SRC) samples and recycle distillates. Boduszynski *et al.*[20–23] and Allen *et al.*[24] have reported a low-pressure liquid chromatography method[25,26] in conjunction with HPLC–field-ionization mass spectrometry (FIMS) for the separation and characterization of SRC samples. The HPLC–FIMS method of analysis yielded detailed compositional information not available previously[20]. Ruckmick *et al.*[27] also used the low-pressure liquid chromatography/HPLC–FIMS approach to separate and characterize large-ring number PAHs in non-distillable SRC oils and asphaltenes. Cooper *et al.*[28,29] also used low-pressure liquid chromatography, HPLC, and FIMS to separate and characterize hydroxyl-aromatics in non-distillable oils and asphaltenes.

Green *et al.*[16] compared non-aqueous titrametric, infrared spectrometric, and HPLC methods of analysis for polar classes of compounds in SRC-II liquids. Wallace *et al.*[30] isolated basic nitrogen compounds from coal-derived asphaltenes and preasphaltenes using an acid-modified silica chromatographic system. Chmielowiec[31] separated a variety of functional classes from coal-related liquids using carbon tetrachloride–dimethyl sulfoxide (DMSO) mobile phases on silica. Ruckmick and Hurtubise[32] utilized a silica/carbon tetrachloride–DMSO HPLC system to separate model nitrogen heterocycles from hydroxyl aromatics and found a high degree of selectivity with the silica/DMSO–carbon tetrachloride system for the separation of nitrogen compounds from sterically hindered hydroxyl aromatics.

Due to the selectivity obtained with the silica/DMSO–carbon tetrachloride chromatographic system[31,32], it was of interest to apply the separation approach to SRC fractions obtained from a fluorocarbon/basic alumina chromatographic method developed by Boduszynski *et al.*[25,26]. The fluorocarbon/basic alumina approach separates coal-derived components into compound classes. The purpose of this work was threefold: (a) to investigate the extent of the compound class overlap in the

fluorocarbon/basic alumina chromatographic method[26,26]; (b) to evaluate the ability of the HPLC silica/DMSO–carbon tetrachloride system to separate coal-liquid fractions into functional classes after obtaining the fractions with the fluorocarbon/basic alumina separation method; (c) to characterize the isolated fractions by various spectral techniques.

EXPERIMENTAL

Material studied

A coal-derived liquid was produced from Wyodak subbituminous coal obtained from the Canyon-Anderson seams in the Powder River Basic of north-eastern Wyoming by Catalytic, Inc., in the Southern Company Services, Inc., SRC pilot plant at Wilsonville, AL, U.S.A. This liquid was distilled in the laboratory to 427°C and the non-distillable, mineral-free residue (solvent refined coal) was analyzed.

Apparatus and chemicals

The liquid chromatograph used was a Waters Model ALC/GPC 244 equipped with a Model U6K injector, a Model 6000A pump, a Model 440 UV absorbance detector, a strip chart recorder, and a Bascom-Turner Model 8120 computerized recorder.

The separation procedure was first evaluated by using a 10-μm particle size μPorasil analytical column (300 × 3.9 mm) from Waters. The experimental procedure, model compounds, and k' values have been reported[32]. The procedure was then scaled up by using a 7-μm particle size LiChrosorb silica semipreparative column (250 × 10 mm) with a carbon tetrachloride–DMSO mobile phase at 7.0 ml/min.

Sample fractionation

The nitrogen heterocycle and hydroxyl-aromatic rich low-pressure chromatographic fractions were isolated from the coal-derived sample (> 427°C) by using previously described procedures[20,25,26].

The nitrogen heterocycle and hydroxyl aromatic rich low-pressure chromatographic fractions from both oils (hexane soluble) and asphaltenes (toluene soluble, hexane insoluble) were further separated by using a semipreparative silica column with a carbon tetrachloride–DMSO mobile phase at 7.0 ml/min. The nitrogen-compound and hydroxyl-compound rich fractions were each dissolved in tetrahydrofuran and approximately 20 mg of sample were injected onto the silica column.

A carbon tetrachloride–dimethyl sulfoxide (99:1, v/v) mobile phase was used to elute the low-pressure liquid chromatographic nitrogen compound fraction of oils (fraction O2) or asphaltenes (fraction A2) from the silica semi-preparative HPLC column. The material eluting in the first 12 min corresponded to the elution range of model nitrogen heterocycles. The HPLC fractions collected in the first 12 min were obtained for fractions O2 (designated as O2N) and A2 (designated as A2N) for the oils and asphaltenes, respectively. The material eluting after 12 min corresponded to the range of model hydroxyl-aromatic compound elution, and the material was collected for fractions O2 (designated as O2OH) and A2 (designated as A2OH) for the oils and asphaltenes, respectively. The column was then physically reversed, and the strongly retained material was backflushed and collected from the HPLC column

with carbon tetrachloride–DMSO (85:15, v/v) for O2 (designated as BFO2) and A2 (designated as BFA2) for the oils and asphaltenes, respectively.

A carbon tetrachloride–DMSO (98:2, v/v) mobile phase was used to elute the low-pressure chromatographic hydroxyl aromatic fractions of oils (fraction O3) and asphaltenes (fraction A3) from the silica semi-preparative HPLC column at a flow-rate of 7.0 ml/min. The material eluting in the first 8 min from the HPLC column corresponded to the region of model nitrogen heterocycle compound elution. The HPLC fractions, which were collected in the first 8 min, were collected for low-pressure fractions of O3 (designated as O3N) and A3 (designated as A3N). The material eluting after 8 min from the HPLC column corresponded to the region of model hydroxyl aromatic compound elution. This material was collected for fractions O3 (designated as O3OH) and A3 (designated as A3OH). The strongly retained material was backflushed and collected from the column with carbon tetrachloride–DMSO (85:15, v/v) for O3 (designated as BFO3) and A3 (designated as BFA3). Several injections of the nitrogen-compound and hydroxyl-compound rich fractions of oils and asphaltenes were made, and the respective subfractions from each run were combined. The fractions were concentrated, transferred into pre-weighed 1/2 dram vials, dried with a dry stream of nitrogen gas, and weighed.

Field ionization mass spectrometry

Field ionization mass spectrometry was applied to the analysis of the HPLC subfractions separated from the nitrogen-compound and hydroxyl-compound rich oil and asphaltene fractions. Since FIMS produces unfragmented molecular ions, the molecular-weight distribution profiles of the subfractions could be obtained. The FI mass spectra were obtained at SRI International, Menlo Park, CA, U.S.A., using procedures and instrumental parameters previously described[20,23,33].

Infrared spectroscopy

A Perkin-Elmer Model 621 grating infrared spectrophotometer was used to record the spectra of HPLC subfractions in methylene chloride at a concentration between 10 and 30 mg/ml, using 0.5-mm sodium chloride cells.

^{1}H NMR spectrometry

The ^{1}H NMR measurements were made on a JEOL FX 270 MHz instrument at 269.73 MHz. A total of 8192 points were collected over a spectral width of 3000 Hz utilizing a pulse delay of 5 s and a pulse width of 45°. Samples were dissolved in deuterochloroform and tetramethylsilane (TMS) was used as an internal standard.

Elemental analyses

Determination of carbon, hydrogen, nitrogen, sulfur, chlorine, oxygen, and % ash in HPLC subfractions were conducted at Huffman Laboratories, Wheatridge, CO, U.S.A. Average results of duplicate runs were reported.

RESULTS AND DISCUSSION

Application of silica/carbon tetrachloride–DMSO systems in the separation of compound classes

Previous work by Chmielowiec[31] and Ruckmick and Hurtubise[32] showed a high degree of selectivity for the separation of several nitrogen heterocycles as a group and several hydroxyl-aromatics as a group with silica/carbon tetrachloride–DMSO chromatographic systems. The silica/carbon tetrachloride–DMSO systems were applied to a Fluoropak/basic alumina chromatographic method[25,26] to determine the extent of compound overlap in the Fluoropak/basic alumina method and to evaluate the HPLC silica/carbon tetrachloride–DMSO systems in separating coal-liquid fractions into functional classes from fractions obtained by the Fluoropak/basic alumina approach. Recently, the Fluoropak was replaced by Chromosorb-T and was found equivalent to the Fluoropak[34].

Initially, a nitrogen-compound fraction from oils (fraction O2) of Wyodak SRC and a nitrogen-compound fraction from asphaltenes (fraction A2) of Wyodak SRC were isolated by the Chromosorb-T/basic alumina method[25,26,34]. Each fraction was chromatographed on a semi-preparative HPLC silica column with a carbon tetrachloride–DMSO (99:1, v/v) mobile phase. Because of the strong retention of polyfunctional compounds in fractions O2 and A2, the column was backflushed after approximately 40 min for O2 and after approximately 50 min for A2. The backflush eluent was carbon tetrachloride–DMSO (85:15, v/v), which was able to more efficiently remove the backflush material than the carbon tetrachloride–DMSO (99:1, v/v) eluent. Earlier work with several model aromatic nitrogen compounds and hydroxyl aromatics showed that nitrogen compounds eluted in the first 12 min and model hydroxyl compounds eluted from 12 min to 20 min[32]. The elution range was then defined as the first 12 min for HPLC nitrogen-compound subfractions O2N from oils and A2N from asphaltenes. HPLC nitrogen-compound subfractions O2OH from oils and A2OH from asphaltenes were then defined as the material eluting from 12 min to the point at which the column was backflushed. The backflush material from O2 and A2 was then defined as BFO2 for oils and BFA2 for asphaltenes, respectively.

Low-pressure liquid chromatographic hydroxyl aromatic fractions from oils (fractions O3) and asphaltenes (fractions A3) isolated with the Chromosorb-T/basic alumina approach were then chromatographed on the silica semi-preparative column with a carbon tetrachloride–DMSO (98:2, v/v) mobile phase. Model nitrogen heterocycles eluted within 8 min while the model hydroxyl-aromatics eluted from 8 min to 17 min[32]. HPLC subfractions O3N and A3N were then defined as the material eluting in the first 8 min, and HPLC subfractions O3OH and A3OH were defined as the material eluting from 8 min to the point at which the column was backflushed. Low-pressure liquid chromatographic fractions O3 and A3 were backflushed with carbon tetrachloride–DMSO (85:15, v/v) after approximately 40 min and 50 min, respectively, to elute polyfunctional compounds. A typical chromatogram for the silica/carbon tetrachloride–DMSO separation is offered in Fig. 1 for the HPLC separation of the low-pressure hydroxyl aromatic asphaltene fraction (A3).

Very few model polyfunctional compounds which had two hydroxyl groups or a hydroxyl and a basic nitrogen could be eluted in the forward direction from the

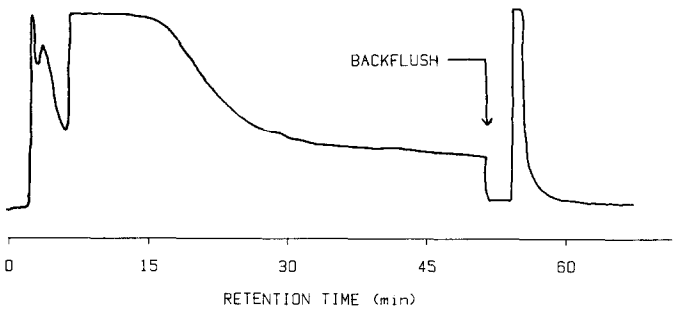

Fig. 1. Chromatogram obtained on silica semi-preparative column with carbon tetrachloride–DMSO (98:2, v/v) at 7.0 ml/min. Column backflushed with carbon tetrachloride–DMSO (85:15, v/v). UV detection at 313 nm. Sample: 14 mg of fraction A3.

TABLE I

DESCRIPTIONS OF HPLC SUBFRACTIONS ISOLATED FROM CHROMOSORB-T/BASIC ALUMINA LOW-PRESSURE LIQUID CHROMATOGRAPHIC FRACTIONS

HPLC subfraction	*Description*
O2N	Large PAH and nitrogen compounds in oils eluting in the region of model nitrogen heterocycles (in the first 12 min).
O2OH	Nitrogen compounds in oils eluting in the region of model hydroxyl aromatics (from 12 to 20 min).
BFO2	Polyfunctional compounds in the nitrogen fraction of oils. Isolated by backflushing the column.
O3N	Hydroxyl compounds in oils eluting in the region of model nitrogen heterocycles (in the first 8 min).
O3OH	Hydroxyl compounds in oils eluting in the region of model hydroxyl aromatics (from 8 to 17 min).
BFO3	Polyfunctional compounds in the hydroxyl fraction of oils. Isolated by backflushing the column.
A2N	Large PAH and nitrogen compounds in asphaltenes eluting in the region of model nitrogen heterocycles (in the first 12 min).
A2OH	Nitrogen compounds in asphaltenes eluting in the region of model hydroxyl aromatics (from 12 to 20 min).
BFA2	Polyfunctional compounds in the nitrogen fraction of asphaltenes. Isolated by backflushing the column.
A3N	Hydroxyl compounds in asphaltenes eluting in the region of model nitrogen heterocycles (in the first 8 min).
A3OH	Hydroxyl compounds in asphaltenes eluting in the region of model hydroxyl aromatics (from 8 to 17 min).
BFA3	Polyfunctional compounds in the hydroxyl fraction of asphaltenes. Isolated by backflushing the column.

silica column using either carbon tetrachloride–DMSO mobile phases (99:1, v/v or 98:2, v/v). This suggested that the backflush material in the coal-liquid fractions was polyfunctional in nature. These polyfunctional model compounds could be eluted by backflushing, however. This supports the hypothesis that the backflush material was predominantly polyfunctional in nature.

The HPLC subfractions O2N, O2OH, BFO2, O3N, O3OH, BFO3, A2N, A2OH, BFA2, A3N, A3OH, and BFA3 were collected for infrared spectroscopic analysis. A description of the subfractions is presented in Table I. The descriptions of the subfractions are based on chromatographic data and other information provided later in this paper. The large-ring PAH material found in subfractions O2N and A2N were discussed in an earlier reference[27]. The approximate percentage of each subfraction with respect to the corresponding whole low-pressure liquid chromatographic fraction from which it was derived is given in Table II.

Characterization of HPLC subfractions isolated from Chromosorb-T/basic alumina nitrogen compound and hydroxyl-aromatic low-pressure liquid chromatographic fractions

Infrared spectroscopy. The HPLC subfractions isolated from nitrogen-compound low-pressure liquid chromatographic fractions (O2N, O2OH, BFO2, A2N, A2OH, and BFA2) were characterized by infrared spectroscopy and all showed absorption bands at 3460 cm^{-1} which was indicative of the N–H functionality. An example of the strong N–H infrared band observed for these HPLC subfractions is given in Fig. 2 for fraction O2OH which shows the IR spectrum over the 2500–4000 cm^{-1} range. None of these fractions showed any absorption between 3585 and 3602 cm^{-1} which is characteristic of the OH functionality. This indicated that there were

TABLE II

APPROXIMATE PERCENTAGE OF EACH HPLC SUBFRACTION WITH RESPECT TO THE LOW-PRESSURE LIQUID CHROMATOGRAPHIC FRACTION FROM WHICH IT WAS DERIVED

O2 = Low-pressure nitrogen compound fraction of oils; O3 = Low-pressure hydroxyl aromatic fraction of oils; A2 = Low-pressure nitrogen compound fraction of asphaltenes; A3 = Low-pressure hydroxyl aromatic fraction of asphaltenes.

HPLC subfraction	*Approximate percentage of low-pressure liquid chromatographic fraction*
O2N	80% of O2
O2OH	5% of O2
BFO2	15% of O2
O3N	50% of O3
O3OH	25% of O3
BFO3	25% of O3
A2N	90% of A2
A2OH	7% of A2
BFA2	3% of A2
A3N	25% of A3
A3OH	35% of A3
BFA3	40% of A3

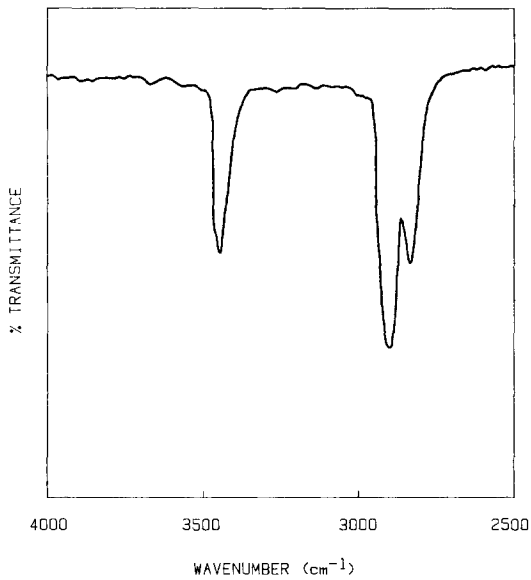

Fig. 2. Infrared spectrum of HPLC subfraction O2OH. Spectrum obtained in methylene chloride at approximately 30 mg/ml.

relatively few hydroxyl aromatic compounds in the Chromosorb-T/basic alumina nitrogen fractions. Since the detection limit of conventional infrared spectroscopy is approximately 1%, it is reasonable to assume that the HPLC subfractions isolated from the low-pressure liquid chromatographic nitrogen fractions contained $< 1.0\%$ hydroxyl aromatic compounds. This supports earlier work which concluded that the Chromosorb-T/basic alumina procedure is efficient in separating nitrogen heterocycles from hydroxyl-aromatics[24,25]. However, recently it was shown that the Chromosorb-T/basic alumina procedure allows overlap of large-ring PAHs into the nitrogen-compound fractions of O2 and A2[27]. Because of the overlap of the large-ring polycyclic aromatic hydrocarbons, HPLC subfractions A2N and O2N contained sizable amounts of large PAH compounds since they would elute very quickly with the carbon tetrachloride–DMSO (99:1, v/v) mobile phase used to collect fractions O2N, O2OH, A2N, and A2OH[27].

The HPLC subfractions obtained from hydroxyl low-pressure liquid chromatographic fractions (O3N, O3OH, BFO3, A3N, A3OH, and BFA3) all showed absorption in the 3585–3602 cm^{-1} region while none of these HPLC subfractions showed absorption at 3460 cm^{-1}. An example of the strong OH absorption band observed for these fractions is given in Fig. 3 for fraction A3N which shows the infrared spectrum over the 2500–4000 cm^{-1} range. The spectra indicated that the HPLC subfractions from the Chromosorb-T/basic alumina separation were predominantly hydroxyl aromatics with $< 1.0\%$ nitrogen compounds present as N–H. The presence of basic nitrogen compounds (*e.g.*, pyridine, quinoline, etc.) could not be detected because of the overlap of spectral bands in the aromatic C–C region at 1600 cm^{-1}.

In general, the infrared analyses of the HPLC subfractions indicated that the

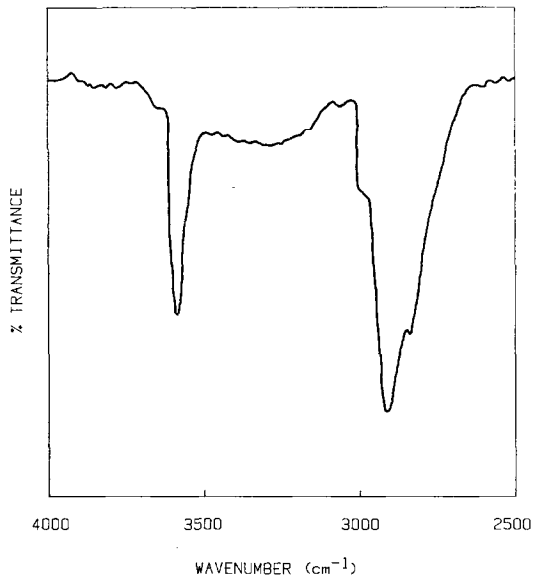

Fig. 3. Infrared spectrum of HPLC subfraction A3N. Spectrum obtained in methylene chloride at approximately 30 mg/ml.

Chromosorb-T/basic alumina procedure produced fractions which were rich in nitrogen heterocycles and hydroxyl aromatics with relatively little overlap of these two functional classes. The infrared results for the HPLC subfractions readily support the conclusions reached by Boduszynski *et al.*[25] about compound-class separation of hydroxyl aromatics and aromatic nitrogen compounds in coal-derived samples. Overlap of large PAH compounds into nitrogen compound low-pressure chromatographic fractions O2 and A2 was observed in earlier work[26]. Percent recovery was 90–95% when the respective nitrogen compound or hydroxyl-aromatic HPLC subfractions (O2N, O2OH, BFO2, O3N, O3OH, BFO3, A2N, A2OH, BFA2, A3N, A3OH, and BFA3) were combined for the various low-pressuire chromatographic fractions. For example, when fractions O2N, O2OH and BFO2 were combined, between 90 and 95% of the 20 mg of the O2 fraction which was injected was recovered.

Elemental analysis. Elemental analysis of the HPLC subfractions O2N, O2OH, A2N, A2OH, A3N, and A3OH were obtained for carbon, hydrogen, oxygen and nitrogen. The mass balance for the subfractions was $< 100\%$ and in some subfractions was considerably less than 100% which indicated that compounds containing elements other than carbon, hydrogen, oxygen, and nitrogen were present. The silica semi-preparative column was suspected of contaminating the samples with trace amounts of metals which are known to be in commercial silica stationary phases[35]. In general, many workers who use silica gel are probably unaware of the metal content in this adsorbent[36,37]. Verzele *et al.*[35] found approximately 42 ppm iron in silica produced by Merck. Various metals could be leached out of the silica column because DMSO can form stable complexes with many metal salts[38]. Considering that large volumes of DMSO–carbon tetrachloride mobile phases were used to collect the fractions for elemental analysis, there was a strong possibility that sizable amounts of

sulfur, chlorine, aluminum, calcium, iron, and sodium (and probably other elements) were extracted from the silica gel by the mobile phase. DMSO may also have dissolved trace amounts of metals from the liquid chromatograph. Evidence for this was the observation of various colored liquids leaking from the liquid chromatograph and corrosion of some of the metal parts of the liquid chromatograph.

Due to the presence of various elements in the silica semi-preparative column, and the corrosion of metallic parts of the chromatograph, it was decided to flush the chromatographic system with pure carbon tetrachloride at the end of each working day. This would minimize the amount of inorganic material extracted by the DMSO. A new silica semi-preparative column was used and fractions A3N, A3OH and BFA3 were collected for elemental analysis using the precaution of flushing the chromatographic system which carbon tetrachloride at the end of each working day. The elemental analysis results for these HPLC subfractions are given in Table III. The % total data in the last column of Table III indicate that, in general, most of the mass can be accounted for by obtaining elemental analysis data for chlorine, sulfur and ash in addition to carbon, hydrogen, oxygen, and nitrogen. However, the elemental analysis data does not accurately represent the actual elemental composition of carbon, hydrogen, oxygen, and nitrogen of the coal-liquid fractions because of the high present ash, percent sulfur, and percent chlorine values. Thus, the silica/DMSO–carbon tetrachloride chromatographic system could not be used to obtain reliable elemental analysis data for the fractions. However, additional precautions such as extensive cleaning of the HPLC silica prior to use could improve the elemental analysis data. Also, more extensive drying of the fractions could improve the data. These aspects were not pursued.

Elemental analysis of Wyodak coal showed sulfur to be at 0.3% and the ash content at 0.5%[26]. The compound-class fractions from oils and asphaltenes isolated by the Fluoropak/basic alumina method gave a sulfur content of 0.0% or 0.1% depending on the compound-class fraction[22]. Although chlorine was not determined in previous work, it is presumed to be very low in the fractions from the Fluoropak/basic alumina step because of the excellent mass balances obtained for the elements C, H, N, O, S[22].

^1H nuclear magnetic resonance (NMR) analysis. Results from ^1H NMR analysis of the HPLC subfractions provided only limited information on the composition of the fractions. The proton signals were divided into six regions corresponding to six proton types: 4.5–9.5 ppm, aromatic and phenolic; 3.3–4.5 ppm, ring joining methylene; 2.0–3.3 ppm, hydrogen α to an aromatic ring; 1.5–2.0 ppm, CH_2 and CH β to an aromatic ring in hydroaromatic and alkyl groups; 1.0–1.5 ppm, CH_2 and CH

TABLE III

ELEMENTAL ANALYSIS RESULTS (%) FOR FRACTIONS ISOLATED WITH A SILICA GEL/DIMETHYL SULFOXIDE–CARBON TETRACHLORIDE CHROMATOGRAPHIC SYSTEM

Sample	*C*	*H*	*O*	*N*	*Cl*	*S*	*Ash*	*Total*
A3N	75.2	5.9	6.3	1.2	4.3	2.7	0.9	96.5
A3OH	71.8	6.1	8.2	1.1	6.0	3.0	2.2	98.4
BFA3	64.7	6.4	10.7	1.0	2.8	6.9	3.9	96.4

further than β from an aromatic ring; and 0.5–1.0 ppm, CH_3 γ or further from an aromatic ring[20,22].

In general, the proton absorption peaks were all broad, except for the α to an aromatic ring proton signal at 2.6 ppm, which was quite sharp in all the HPLC subfractions. The proton signal at 2.6 ppm was very strong in all the fractions except fraction A3N which showed a weak proton signal at 2.6 ppm indicating less alkyl substitution for this fraction.

All the spectra showed aromatic hydrogen response and peaks at 2.5 ppm and 1.2 ppm indicating that, in addition to these fractions being aromatic in character, the fractions all contained sizable amounts of alkyl substitution (with the exception of A3N which showed a weak α proton signal). Interestingly, A3N showed a strong proton signal at 1.2 ppm indicating a sizable amount of CH_2 and CH further than β from the aromatic ring system. A strong proton signal was also observed at 3.7 ppm for fraction A3N. None of the other fractions showed proton signals between 3 and 4 ppm.

Field-ionization mass spectrometry (FIMS) analysis. FIMS is ideally suited to the analysis of complex mixtures due to its ability to produce virtually only molecular ions and essentially no fragmentation ions[39]. Therefore, FIMS yields spectra are much simpler compared to conventional mass spectrometry.

FIMS separates according to molar mass and Z number, where Z corresponds to the general formula $C_nH_{2n+Z}O$ for hydroxyl aromatics and $C_nH_{2n+Z}N$ for nitrogen heterocycles. The Z number can be affected by the number of double bonds in a ring system or by the number of saturated rings[23]. The total FIMS spectra for fractions O2N, O2OH, O3N, O3OH, A2N, A2OH, A3N, and A3OH were obtained from SRI International. However, these spectra exhibited low percent volatility. The low percent volatility was probably caused by inorganic contaminants such as sulfur, chlorine, aluminum, calcium, iron, sodium, and possibly other elements which were extracted from the HPLC column with the DMSO–carbon tetrachloride mobile phases as considered earlier. Because the percent volatility of these fractions was low, other samples of fractions A2N, A2OH, A3N, and A3OH were submitted for analysis, which were collected from a new semi-preparative column and the chromatographic system was flushed with carbon tetrachloride at the end of each working day. Also included in the second set of samples sent to SRI International for FIMS analysis

TABLE IV

PERCENT VOLATILITY BY FIMS FOR NITROGEN COMPOUND AND HYDROXYL AROMATIC FRACTIONS ISOLATED USING THE SILICA SEMI-PREPARATIVE COLUMN

See Table I for a description of the HPLC subfractions.

Fraction	*Volatility (%)*
A2N	91
A2OH	65
A3N	79
A3OH	81
BFA2	60
BFA3	77

were fractions BFA2 and BFA3. Table IV gives the percent volatility for the second set of samples sent to SRI International.

The ^{13}C corrected FIMS spectra of the HPLC subfractions A2N, A2OH, A3N, A3OH, BFA2, and BFA3 showed the extreme complexity of the fractions. Fig. 4 shows a typical FIMS spectrum for the fraction A3N. Table V lists the number average molecular weight values for the fractions which were determined by the FIMS analysis. From Table V it can be seen that the molecular weight of the fraction has little influence on the retention or polarity of the fraction. For example, Table V shows that the least polar fraction, A2N, has a number average molecular weight of 496 while the most polar fraction, BFA3, has a number average molecular weight of 491. However, it should be recalled that none of the fractions were completely volatile (Table IV).

Table VI lists the odd/even mass ratios for the HPLC subfractions obtained by FIMS analyses. The highest odd/even mass ratios corresponded to the HPLC subfractions which were derived from nitrogen-compound fractions from the Chromosorb-T/basic alumina method (A2N, A2OH, and BFA2). The highest odd/even mass ratio was found for HPLC subfractions A2OH, (odd/even ratio of 1.32), indicating that this fraction contained predominately nitrogen compounds. Fraction A2N had a relatively low odd/even mass ratio of 0.79, but this fraction also contained a substantial amount of PAH material (see ref. 27). Fraction BFA2 gave an odd/even mass ratio of 0.83 which was substantially less than the ratio obtained for fraction A2OH. This may be due to more hydroxyl aromatic material in this very polar backflush fraction. Also, recall that fraction BFA2 comprises only about 3% of fraction A2 (see Table II).

Contrastingly, the HPLC subfractions isolated from hydroxyl compound fractions from the Chromosorb-T/basic alumina approach showed relatively lower odd/even mass ratios corresponding to higher concentrations of hydroxyl aromatic

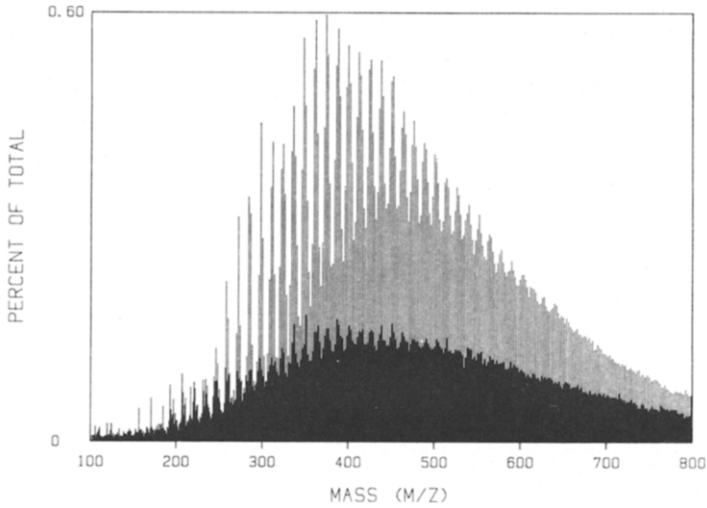

Fig. 4. Total FI ^{13}C corrected mass spectrum of HPLC subfraction A3N from the Wyodak coal-liquid sample.

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHT VALUES FOR FI MASS SPECTRA OF HPLC SUBFRACTIONS

Fraction		*Number average molecular weight*
Least Polar	A2N	496
	A2OH	463
	A3N	477
	A3OH	468
	BFA2	447
Most Polar	BFA3	491

compounds in these fractions. All three fractions isolated from fraction A3 (A3N, A3OH, and BFA3) yielded odd/even mass ratios which were roughly similar (see Table VI). The somewhat higher odd/even mass ratio for fraction BFA3 was probably due to the increased number of compounds containing both a nitrogen and hydroxyl functionality. These polyfunctional compounds would retain very strongly and would be expected to be present in the backflush fraction.

Selected homologous Z series

Boduszynski *et al.*[22] showed that the main difference between the oils and asphaltenes fractions from the fluorocarbon/alumina separation method was the concentration of hydrocarbons, nitrogen compounds, and hydroxyl aromatics in the fractions. Field-ionization mass spectrometry was also used in their work. In this work, FIMS was used to characterize HPLC fractions obtained from the fluorocarbon/alumina approach. As was previously discussed, FIMS separated according to molar mass and Z number, where Z corresponds to the general formula $C_nH_{2n+Z}N$ for nitrogen heterocycles. The parent ion peaks in the FIMS spectra were separated into seven odd mass series and seven even mass series (14 series total). The general approach was described earlier[20–24]. A visual, qualitative determination of the relative amount of even mass (hydroxyl compound) *versus* odd mass (nitrogen compound) material in an HPLC fraction is accomplished by plotting the even homologous series and odd homologous series. Fig. 5 shows the even homologous series $C_nH_{2n-26}O$

TABLE VI

ODD/EVEN MASS RATIOS FOR THE HPLC SUBFRACTIONS DETERMINED BY FIMS ANALYSIS

Fraction	*Odd/even mass ratio*
A2N	0.79
A2OH	1.32
A3N	0.45
A3OH	0.47
BFA2	0.83
BFA3	0.57

(-26 Z series) and C_nH_{2n-40} (-40 Z series) for the sample A3OH. Fig. 6 shows the odd homologous series $C_nH_{2n-39}N$ (-39 Z series) and C_nH_{2n-53} (-53 Z series) for sample A3OH. By comparing the two spectra, it appears the even mass (hydroxyl compound) material predominates in the A3OH fraction.

The interpretation of the FI mass spectra is based on the assignment of a parent-structure to the lowest molecular weight homologue in the spectrum. The peaks following the parent structure, occurring every 14 mass units, are assumed to be alkyl substituted parent structures[21–24]. Combining this method of FIMS interpretation with the chromatographic retention behavior of model compounds allows a possible structure assignment to be made for mass peaks believed to be parent structures. However, it should be emphasized that many possible structures can be drawn for any given mass. Because of this, the structures given in Figs. 5 and 6 are only representative of the general type of compounds believed to be in the fraction. Because A3OH is predominantly hydroxyl aromatic material eluting in the region of model hydroxyl aromatics, structures given in Fig. 5 are similar to the structures of model hydroxyl compounds. For odd mass compounds such as those in Fig. 6, a nitrogen atom most likely is present in the molecule in addition to the hydroxyl group. Because very few of these types of model compounds could be eluted, the nitrogen or hydroxyl group must be sterically hindered in order for it to be more weakly retained than model compounds which had neither group sterically hindered. Based upon work done with standards, when the nitrogen or hydroxyl group is not sterically hindered, the compound will not elute from the column and will appear in the backflush fraction. This is why the structure in Fig. 6 has the nitrogen atom sterically hindered. An alternative structure could have the hydroxyl group sterically hindered instead. For backflush fractions BFA3 and BFA2, structures would be drawn with neither group sterically hindered.

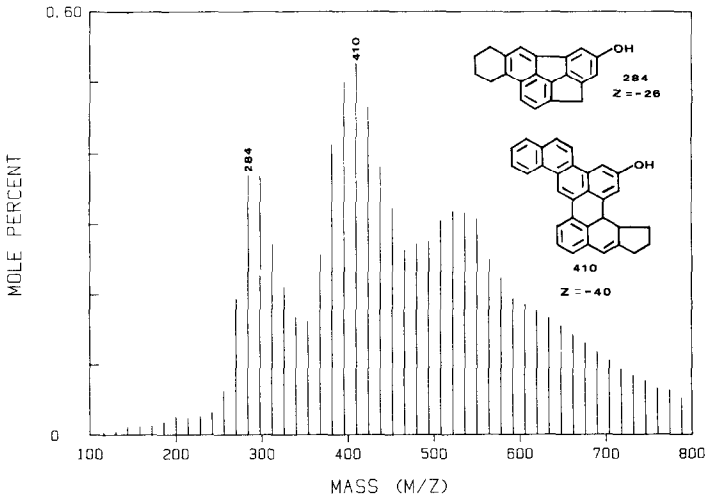

Fig. 5. Even mass Z series $C_nH_{2n-26}O$ and $C_nH_{2n-40}O$ in the FI mass spectrum of HPLC subfraction A3OH. Structures are only representative because other structures could be drawn for masses 284 and 410.

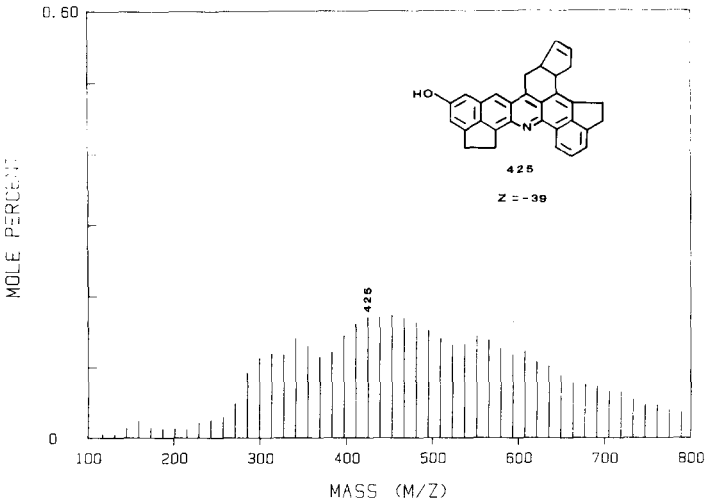

Fig. 6. Odd mass Z series $C_nH_{2n-39}N$ and $C_nH_{2n-53}N$ in FI mass spectrum of HPLC subfractions A3OH. Structures are only representative because other structures could be drawn for mass 425.

Fraction A3N contains mostly hydroxyl compounds (see section *Infrared spectrometry*) which elute in the region of model nitrogen heterocycles. This type of weak retention for this hydroxyl fraction suggests that the hydroxyl compounds in the fraction are either sterically hindered or aliphatically substituted. Table VI shows that this fraction has the lowest odd/even mass ratio, indicating that this fraction has relatively few nitrogen compounds.

HPLC subfraction A2OH contained predominantly nitrogen compounds eluting in the region of model hydroxyl aromatic elution. From Table VI it can be seen that fraction A2OH contained the most nitrogen material of all the HPLC subfractions. These nitrogen compounds are probably similar to the model nitrogen heterocycles, but are retained more strongly because of their higher average molecular weight. In addition, a small amount of the compounds in this fraction may contain a basic nitrogen atom and an aliphatically substituted hydroxyl group. The hydroxyl group may also be very sterically hindered or in a position to intramolecularly hydrogen bond. These types of hydroxyl substitutions would make the nitrogen-hydroxyl compound retain more strongly than the basic nitrogen heterocycles but not strong enough to be present in the backflush fraction. However, since infrared analyses showed no hydroxyl band, the number of these polyfunctional types would be expected to be small. In addition, the stronger retention of the material in fraction A2OH could be explained by compounds containing three nitrogen atoms. Such compounds would probably have one of the nitrogen atoms sterically hindered because model nitrogen heterocycles with three unsterically hindered nitrogen atoms would not be eluted.

CONCLUSION

The chromatographic and spectral results showed that the extent of hydroxyl-aromatic and nitrogen-aromatic compound overlap in the Chromosorb-T/basic

alumina procedure was minimal. However, as reported earlier, large-ring PAHs could appear in some of the fractions[27]. The HPLC silica/DMSO–carbon tetrachloride chromatographic system can be used to group specifically the nitrogen aromatic compounds and hydroxyl aromatic compounds isolated by the Chromosorb-T/basic alumina procedure mainly by the polarity of a given compound class.

Elemental analyses results may be used to obtain a very rough estimate of the amount of C, H, O, and N in the fractions; however, the results are not very accurate. This is due to the relatively large amounts of inorganic material which can be removed from the silica stationary phase with the DMSO–carbon tetrachloride mobile phases.

Overall, it was shown that the Chromosorb-T/basic alumina–silica/DMSO–carbon tetrachloride approach permitted a rather high degree of compound-class separation. When the HPLC approach was combined with FIMS and infrared spectrometry a method for the general characterization and the estimation of the compound-classes was developed for the coal-liquid fractions isolated by the Chromosorb-T/basic alumina approach[25,26].

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