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CLASS SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS, NITROGEN HETEROCYCLES AND HYDROXYL AROMATICS BY LIQUID CHROMATOGRAPHY

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SUMMARY

High-performance liquid chromatography has been used to separate polycyclic aromatic hydrocarbons, nitrogen heterocycles, and hydroxyl aromatics which are known or suspected to be present in solvent refined coal samples. The separation of these model compounds by compound-class was accomplished with normal-phase μPorasil and Nucleosil NO_2 columns. *n*-Heptane, *n*-heptane–chloroform, carbon tetrachloride–chloroform and carbon tetrachloride–dimethyl sulfoxide mobile phases were used to separate the model compounds. Polar standards were chromatographed with mobile phases of several solvent strengths to observe the different migration behavior of the functional classes. It was found that the μPorasil column utilizing a carbon tetrachloride–chloroform mobile phase offered the best separation of polycyclic aromatic hydrocarbons and nitrogen heterocycles. μPorasil also yielded superior separation of nitrogen heterocycles from hydroxyl aromatics when a carbon tetrachloride–dimethyl sulfoxide eluent was employed.

INTRODUCTION

Due to the eventual limits in supply of high quality crude oil, much recent research has been focused around the chemical characterization of alternative fuel feedstocks such as tar sands, shale oils and coal liquids. It is important to elucidate the chemical nature of these materials so that fossil fuel technology can be improved and the environmental impact of these fuels can be assessed. The extreme complexity and heterogeneity of these organic mixtures requires a compound-class separation prior to detailed chemical analysis. Various separation procedures have been reported for preliminary separation steps[1–8]. Much more work is needed, however, to develop additional schemes for compound-class separation.

Normal- and reversed-phase high-performance liquid chromatography (HPLC) have been used to separate components in fossil fuels because of the fast and efficient nature of these systems compared to more classical and time consuming open column procedures. Wise *et al.*[9] reported using normal-phase μBondapak NH_2 to separate polycyclic aromatic hydrocarbons (PAHs) from crude oil based on the

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number of aromatic rings. Boduszynski *et al.*[10,11] used μBondapak NH_2 combined with field-ionization mass spectrometry (FIMS) to separate and characterize PAHs isolated from a solvent refined coal (SRC) sample. Novotny *et al.*[12] reported the separation and characterization of PAHs in fossil fuels using a combination of open column chromatography, analytical HPLC and micro liquid chromatography–mass spectrometry (MS). Holstein and Severin[13] and Matsunaga[14] compared various stationary phases and were able to obtain profiles of fossil fuel liquids and predict where various functional classes would appear. Holstein and Severin[15] identified the major compound types in a recycle oil by using normal-phase HPLC–MS. Green and Grizzle[16] reported enhanced selectivity for various functional classes on unmodified silica using mobile phase additives.

Reversed-phase HPLC has been used by Schabron *et al.*[17] to characterize aromatic and hydroaromatic compounds in coal-derived recycle solvents. They were also able to separate alkylphenols from coal-derived liquids using reversed-phase HPLC[18]. Various other reports on the chromatography of alkylphenols have also appeared[19,20]. Colin *et al.*[21] and Schronk *et al.*[22] have reported the reversed-phase chromatography of various nitrogen heterocycles thought to be present in coal derived liquids. The use of reversed-phase HPLC combined with gas chromatography–MS has been reported by Schmitter *et al.*[23] who were able to identify triaromatic nitrogen heterocycles in crude oil. Although reversed-phase techniques have been applied to some coal liquids, the sample capacity of these systems is often very low due to the limited solubility of these complex organic mixtures in aqueous mobile phases. Schmitter *et al.*[23] reported that the low sample capacity of a crude oil extract in aqueous mobile phases made NMR analysis impossible while Amateis and Taylor[24] have reported similar solubility problems.

Although HPLC has been applied to the separation of various components in coal liquids there have been few reports dealing with the separation of the major compound classes using this technique. Blumer and Zander[25] compared normal-phase Nucleosil NO_2 and reversed-phase C_{18} for their ability to separate a large number of PAHs from nitrogen heterocycles. Both stationary phases investigated yielded overlap of large PAHs into the nitrogen heterocycle fraction. Ruckmick and Hurtubise[26] compared a number of normal-phase and reversed-phase columns for their ability to separate model PAHs and nitrogen heterocycles known to be in coal liquids. It was reported that reversed-phase systems separated these functional classes, but the low solubility of coal-derived liquids limited the usefulness of the technique. The model nitrogen compounds and PAHs were completely separated with a μPorasil–*n*-heptane–chloroform system, however.

Recently Chmielowiec[27] separated a wide variety of compounds known to be in coal related liquids by using dimethyl sulfoxide–carbon tetrachloride mobile phases on plain silica. Chmielowiec[27] obtained impressive separations of model compounds based on functional class and was able to apply his system to coal liquids. While some model compounds were observed to overlap into other class fractions, the overall procedure provided a good functional class separation.

The purpose of this work was to compare the Nucleosil NO_2 and the μPorasil stationary phases for their ability to separate model PAHs, nitrogen heterocycles, and hydroxyl aromatics which are known to be in coal liquids. Dimethyl sulfoxide–carbon tetrachloride mobile phases are particularly attractive for this ap-

plication since SRC samples appear to be highly soluble in this binary solvent mixture.

EXPERIMENTAL

High-performance liquid chromatography

The liquid chromatograph used was a Waters Model ALC/GPC 244 equipped with a Model 6000A pump, a U6K injector, a dual-channel UV detector set at 254 nm and 280 nm, and a dual-channel 10 mV strip chart recorder.

Columns

Nucleosil NO_2 and μPorasil columns were both 300 × 3.9 mm and contained 10-μm particles. The Nucleosil NO_2 column was obtained from Phenomonex/HPLC Technology (Palo Verdes Estates, CA, U.S.A.). The μPorasil column was obtained from Waters Assoc. (Milford, MA, U.S.A.).

Procedure

All separations were carried out at ambient temperature (25 ± 1°C) with a 2 ml/min flow-rate. Solutes were dissolved in HPLC grade chloroform and sample amounts between 0.01 μg and 20 μg were injected depending on the molar absorptivity and retention characteristics of the solute. The capacity factor (k') was calculated from the relationship $k' = (V_R - V_M)/V_M$ where V_R (ml) is the measured retention volume and V_M (ml) is the column void volume. V_M was measured by the small baseline peak from chloroform in which the solutes were dissolved. Following a change in mobile phase, 1–2 h of equilibration time with the new mobile phase were allowed. Equilibrium conditions were confirmed by repetitive injection of the same solute until constant k' values were obtained. The Nucleosil NO_2 column was flushed with 100% chloroform overnight at 0.2 ml/min after every 4 days of operation to maintain reproducible capacity factors.

Reagents

The PAHs, nitrogen heterocycles, 1-hydroxybenzo[*c*]phenanthrene, 3-hydroxybenzo[*c*]phenanthrene, 2-indanol and 1-naphthol were purchased from Aldrich (Milwaukee, WI, U.S.A.). The remaining hydroxyl aromatic compounds were purchased from the Alfred Bader Library of rare chemicals, Division of Aldrich (Milwaukee, WI, U.S.A.). HPLC grade *n*-heptane and chloroform were obtained from Baker (Phillipsburg, NJ, U.S.A.). HPLC grade carbon tetrachloride and dimethyl sulfoxide were obtained from Burdick and Jackson (Muskegon, MI, U.S.A.). All solvents were filtered through a Millipore type F-H 0.45-μm filter prior to use. *n*-Heptane was degassed by bubbling helium through the solvent for approximately 1 h.

RESULTS AND DISCUSSION

Polycyclic aromatic hydrocarbons and nitrogen heterocycles

Table I gives the names and structures of the model compounds investigated. Table II lists the chromatographic data from PAHs and nitrogen heterocycle standards studied with the Nucleosil NO_2 and μPorasil columns. It was found that large

TABLE I

MODEL COMPOUNDS INVESTIGATED WITH NUCLEOSIL NO_2 AND μPORASIL STATIONARY PHASES

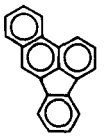
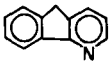
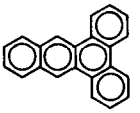
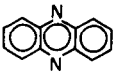
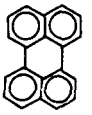
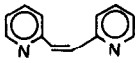
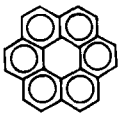
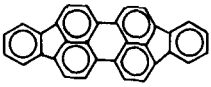
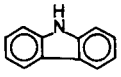
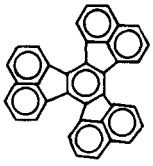
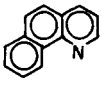
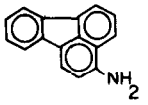
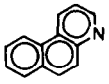
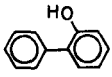
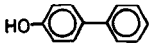
No.	*Compound*	*Structure*	*No.*	*Compound*	*Structure*
1	Acenaphthene		11	Acridine	
2	3,4-Benzofluoranthene		12	4-Azafluorene	
3	1,2,3,4-Dibenzanthracene		13	Phenazine	
4	Perylene		14	1,2-Bis[2-pyridyl]-ethylene	
5	Coronene		15	7-Methylindole	
6	Diindeno[1,2,3-*c*-*d*: 1′,2′,3′: *im*]perylene		16	Carbazole	
7	Decacyclene		17	*n*-Azaindole	
8	7,8-Benzoquinoline		18	3-Aminofluoranthene	
9	5,6-Benzoquinoline		19	2-Phenylphenol	
10	Quinoline		20	4-Phenylphenol	

TABLE I (*continued*)

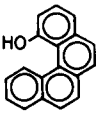
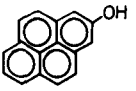
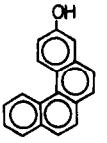
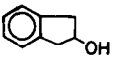
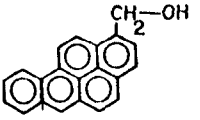
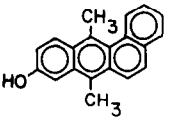
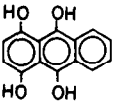
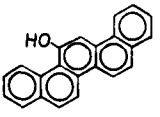
No.	*Compound*	*Structure*	*No.*	*Compound*	*Structure*
21	1-Hydroxybenzo[*c*]-phenanthrene		26	2-Hydroxypyrene	
22	3-Hydroxybenzo[*c*]-phenanthrene		27	2-Indanol	
23	1-Naphthol		28	1-(Hydroxymethyl)-benzo[*a*]pyrene	
24	7,12-Dimethyl-9-hydroxy-benz[*a*]anthracene		29	1,4,9,10-Tetrahydroxy-anthracene	
25	13-Hydroxypicene				

TABLE II

CAPACITY FACTORS FOR POLYCYCLIC AROMATIC HYDROCARBONS AND NITROGEN HETEROCYCLES ON μPORASIL AND NUCLEOSIL NO_2 STATIONARY PHASES

No.	*Compound*	*Nucleosil NO_2*		*μPorasil*	
		n-Heptane	*n-Heptane–chloroform (95:5)*	*Carbon tetrachloride–dimethyl sulfoxide (99.975:0.025)*	*Carbon tetrachloride–chloroform (95:5)*
1	Acenaphthene	0.80	0.20	0.03	0.15
2	3,4-Benzofluoranthene	7.66	2.00	0.18	0.15
3	1,2,3,4-Dibenzanthracene	13.1	3.00	0.18	0.18
4	Perylene	9.60	2.33	0.12	0.15
5	Coronene	12.3	3.66	0.23	0.20
6	Diindeno[1,2,3-*c-d*: 1′,2′,3′:*im*]perylene	*	5.01	0.76	0.23
7	Decacyclene	55.1	5.66	0.47	0.23
8	7,8-Benzoquinoline	31.0	4.33	0.47	6.64
9	5,6-Benzoquinoline	*	31.6	0.50	*
11	Acridine	*	22.1	1.20	*
12	4-Azafluorene	*	22.3	1.76	*
13	Phenazine	*	12.4	0.76	*
14	1,2-Bis(2-pyridyl)ethylene	*	*	10.2	*
15	7-Methylindole	*	16.7	5.06	*
16	Carbazole	*	19.7	5.94	*

* Very strongly retained.

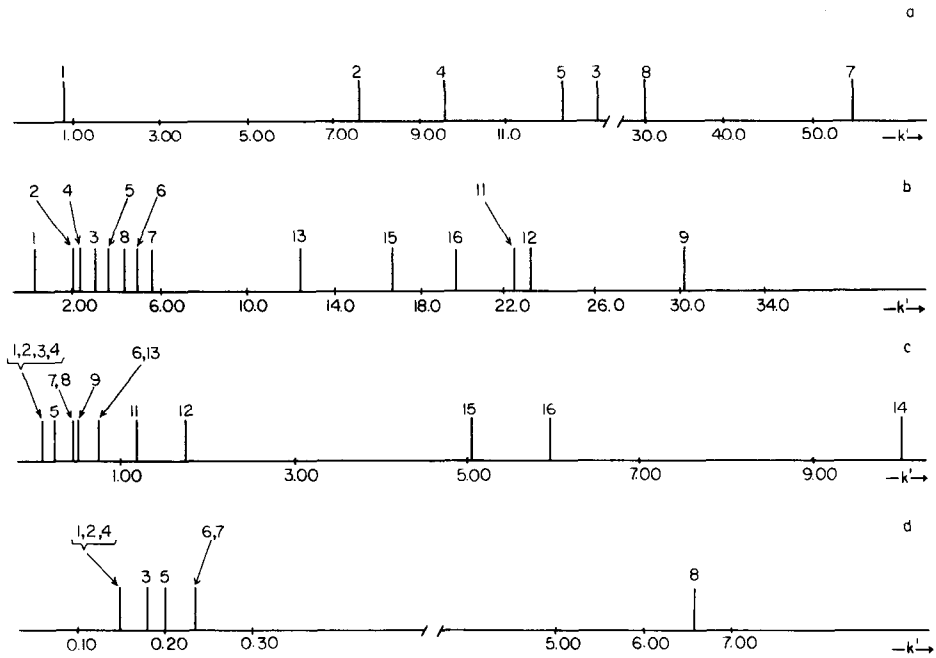


Fig. 1. Migration behavior of model compounds in Table II on μPorasil and Nucleosil NO_2. (a) Nucleosil NO_2–*n*-heptane, (b) Nucleosil NO_2–*n*-heptane–chloroform (95:5), (c) μPorasil–carbon tetrachloride–dimethyl sulfoxide (99.975:0.025), (d) μPorasil–carbon tetrachloride–chloroform (95:5).

PAHs were retained longer on Nucleosil NO_2 than on μPorasil with *n*-heptane as the mobile phase. This indicated that as the number of π-electrons increased in the PAH the interaction between the PAH and the nitrophenyl electron acceptor group of the Nucleosil NO_2 also increased. The long retention of PAHs resulted in overlap of PAHs and sterically hindered nitrogen heterocycles when using the Nucleosil NO_2 column and *n*-heptane mobile phases (Table II). Fig. 1 diagramatically illustrates the retention behavior of the model compounds in Table II. It can be seen that sterically hindered nitrogen heterocycles such as 7,8-benzoquinoline would overlap into the PAH fraction for the Nucleosil NO_2–*n*-heptane, Nucleosil NO_2–*n*-heptane–chloroform (95:5) and μPorasil–carbon tetrachloride–dimethyl sulfoxide (99.975:0.025) chromatographic systems.

Employing an *n*-heptane mobile phase with the μPorasil column, it was found that large PAHs were eluted with relatively smaller k' values of approximately 16.0. Nitrogen heterocycles were retained more strongly on μPorasil with this eluent due to strong acid–base interactions of the basic nitrogen atom with the acidic silanol groups in the silica gel. Due to this interaction, even the sterically hindered 7,8-benzoquinoline was not observed to elute after 200 ml of *n*-heptane passed through the μPorasil column (k' of *ca.* 58). Although the Nucleosil NO_2 column also retained nitrogen heterocycles strongly, 7,8-benzoquinoline eluted with a k' value of approximately 28 with *n*-heptane as the mobile phase. While acid–base interactions have been used to explain the nitrogen heterocycle mechanism of retention on silica[14,21,26,28], electron donor–acceptor complexes have been reported as the mech-

anism of retention on nitrophenyl stationary phases[25,29]. Since the μPorasil-*n*-heptane system preferentially eluted PAHs, but strongly retained hindered nitrogen heterocycles, this stationary phase was able to separate these two compound classes more effectively than the Nucleosil NO_2 column. The major drawback to using the μPorasil-*n*-heptane system was the long analyses times required to elute the large PAHs. However, a carbon tetrachloride mobile phase on μPorasil offered unique selectivity toward PAHs compared to *n*-heptane. A 100% carbon tetrachloride mobile phase eluted all the PAHs in Table II from the μPorasil column within a k' value of about 1.64 while no nitrogen heterocycles were observed to elute after a calculated k' value of 35.0 had been reached. Thus, the selectivity for non-polar compounds in the μPorasil–carbon tetrachloride system appeared to be due to the high solubility of these compounds in the carbon tetrachloride mobile phase.

In an attempt to decrease the retention of the nitrogen heterocycles and maintain the desired selectivity, carbon tetrachloride–dimethyl sulfoxide (99.975:0.025), and carbon tetrachloride–chloroform (95:5) mobile phases were investigated with the μPorasil column. In Table II and Fig. 1 it is evident that the carbon tetrachloride–dimethyl sulfoxide (99.975:0.025) mobile phase dramatically alters the retention characteristics of nitrogen heterocycles on μPorasil compared to the carbon tetrachloride–chloroform (95:5) mobile phase. As shown in Table II, with carbon tetrachloride–chloroform (95:5), 7,8-benzoquinoline was the only nitrogen heterocycle observed to elute from the μPorasil column while all the nitrogen compounds in Table II were readily eluted with the carbon tetrachloride–dimethyl sulfoxide (99.975:0.025) mobile phase. Chmielowiec[27] has reported that concentrations as low as 0.03% dimethyl sulfoxide in the carbon tetrachloride mobile phase can moderate the silica surface and increase the selectivity for various functional classes. Recent work in our laboratory has indicated that concentrations as low as 0.01% dimethyl sulfoxide in the carbon tetrachloride mobile phase can cause significant changes in the chromatographic behavior of the model compounds studied. These effects may be explained by the fact that dimethyl sulfoxide is a well known hydrogen bond acceptor[30–32] which can form stable association complexes with compounds containing proton donating functional groups such as –COOH, –NH and –OH[30]. Looking at Table II and noting the strong hydrogen bonding properties of dimethyl sulfoxide, it is evident that even very low concentrations of dimethyl sulfoxide in carbon tetrachloride can coat the surface of the μPorasil stationary phase, altering the chromatographic characteristics of the column significantly.

Due to the strongly modifying characteristics of the dimethyl sulfoxide, the PAHs and nitrogen heterocycles were not adequately resolved on μPorasil and thus chloroform was chosen to modify the carbon tetrachloride mobile phase in an attempt to increase the separation between these compound classes. It can be seen in Table II and Fig. 1 that with the carbon tetrachloride–chloroform (95:5) mobile phase that the largest PAH is eluted with a k' value of only 0.23 while the weakest retained nitrogen heterocycle, 7,8-benzoquinoline, elutes with a k' value of 6.64. This is a significant improvement in selectivity over the *n*-heptane–chloroform mobile phase which we reported previously for the separation of PAHs and nitrogen heterocycles on μPorasil[26]. Due to the large difference in retention obtained for these compound classes, the μPorasil stationary phase utilizing a carbon tetrachloride–chloroform (95:5) mobile phase is superior to Nucleosil NO_2–*n*-heptane and *n*-

heptane–chloroform (95:5) systems for separating PAHs from nitrogen heterocycles. In addition, the μPorasil–carbon tetrachloride–chloroform system is more useful in separating PAHs from nitrogen heterocycles than the μPorasil–carbon tetrachloride–dimethyl sulfoxide system in Table II.

Nitrogen heterocycles and hydroxyl aromatics

Generally the Nucleosil NO_2 column utilizing chloroform–*n*-heptane mobile phases retained unhindered hydroxyl aromatic compounds rather strongly (Table III and Fig. 2). The Nucleosil NO_2–chloroform–*n*-heptane (40:60) system yielded k' values of approximately 50 for the most strongly retained hydroxyl compound while the μPorasil–carbon tetrachloride–dimethyl sulfoxide (99.75:0.25) system yielded k' values near 13.0 (Table IV). Although the Nucleosil NO_2 column retained most of the hydroxyl aromatic compounds substantially longer with chloroform–*n*-heptane mobile phases compared to the μPorasil column with dimethyl sulfoxide–carbon tetrachloride mobile phases, Nucleosil NO_2 did not give a superior separation of these compounds from the nitrogen heterocycles. The μPorasil system is better for separating model nitrogen heterocycles from hydroxyl aromatics for two reasons: (1) nitrogen heterocycles eluted very rapidly with dimethyl sulfoxide–carbon tetrachloride mobile phases on μPorasil and (2) μPorasil retains sterically hindered hydroxyl aromatic compounds longer than Nucleosil NO_2–chloroform–*n*-heptane systems, yielding a better functional group separation. In Table IV and Fig. 3 it can be seen

TABLE III

CAPACITY FACTORS FOR NITROGEN HETEROCYCLES AND HYDROXYL AROMATICS ON NUCLEOSIL NO_2 USING CHLOROFORM–*n*-HEPTANE MOBILE PHASES

No.	*Compound*	*Chloroform–n-heptane*			
		40:60	*50:50*	*60:40*	*70:30*
29	1,4,9,10-Tetrahydroxyanthracene	0.47	0.26	0.21	0.18
8	7,8-Benzoquinoline	0.55	0.35	0.33	0.28
13	Phenazine	0.64	0.45	0.36	0.30
15	7-Methylindole	0.87	0.58	0.40	0.32
16	Carbazole	1.64	1.01	0.76	0.61
19	2-Phenylphenol	1.83	1.66	1.23	0.90
10	Quinoline	2.35	1.71	1.36	0.93
12	4-Azafluorene	2.37	1.84	1.43	1.06
21	1-Hydroxybenzo[*c*]phenanthrene	2.54	2.47	1.56	1.18
9	5,6-Benzoquinoline	3.06	2.51	2.16	1.66
18	3-Aminofluoranthene	4.01	2.71	2.16	1.40
14	1,2-Bis[2-pyridyl]ethylene	7.64	5.61	4.53	3.49
23	1-Naphthol	15.2	9.84	7.83	6.30
28	1-(Hydroxymethyl)benzo[*a*]pyrene	16.0	8.80	6.16	4.13
20	4-Phenylphenol	18.3	12.0	9.34	6.91
17	7-Azaindole	19.1	13.0	9.20	7.53
24	7,12-Dimethyl-9-hydroxybenz[*a*]anthracene	28.7	23.9	16.7	11.5
26	2-Hydroxypyrene	40.7	36.4	23.2	18.9
25	13-Hydroxypicene	48.3	28.7	22.9	17.0
22	3-Hydroxybenzo[*c*]phenanthrene	51.5	31.5	22.5	16.0

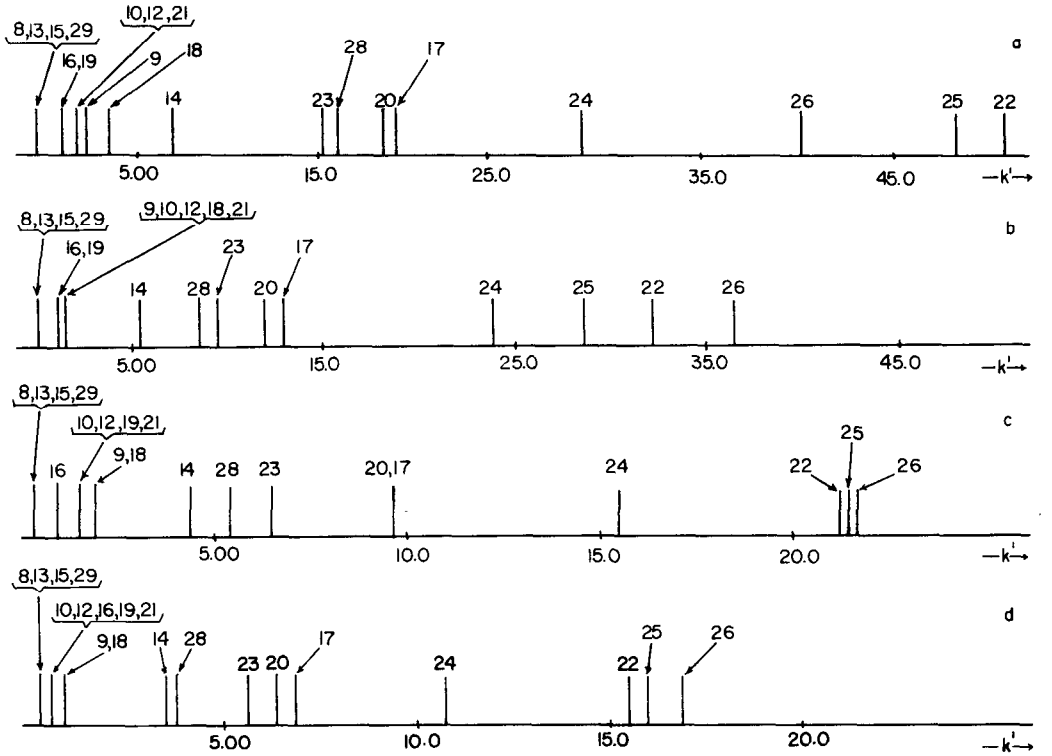


Fig. 2. Migration behavior of model compounds in Table III on Nucleosil NO_2 with chloroform–*n*-heptane mobile phases. (a) 40:60, (b) 50:50, (c) 60:40, (d) 70:30.

that generally these two functional classes are well separated on the μPorasil column utilizing a carbon tetrachloride–dimethyl sulfoxide (99:1) mobile phase. 2-Phenylphenol and 1-hydroxybenzo[*c*]phenanthrene, which are sterically hindered hydroxyl aromatic compounds (see Table I), are retained long enough on the μPorasil column to be grouped with the other hydroxyl aromatics. With the Nucleosil NO_2 column, however, these hindered hydroxyl compounds are eluted very quickly along with the nitrogen heterocycles yielding an inferior separation.

Overlap of compound classes

Although the μPorasil column separates nitrogen heterocycles from hydroxyl aromatics relatively well, there are two types of hydroxyl aromatic compounds which would be expected to appear in the nitrogen heterocycle fraction. The first hydroxyl compound has the hydroxyl functionality substituted on an aliphatic ring or alkyl group which is bonded to the aromatic system. This type of substitution decreases the acidity of the hydroxyl group[33], which in turn decreases the hydrogen bonding with the silica surface and thus reduces retention. An example of this compound type is 2-indanol which was observed to elute from the μPorasil column with a k' value of 0.64 with the carbon tetrachloride–dimethyl sulfoxide (99:1) mobile phase and with a k' value of 2.90 from the Nucleosil NO_2 column with the chloroform–*n*-hep-

TABLE IV

CAPACITY FACTORS FOR NITROGEN HETEROCYCLES AND HYDROXYL AROMATICS ON μPORASIL USING CARBON TETRACHLORIDE–DIMETHYL SULFOXIDE MOBILE PHASES

No.	*Compound*	*Carbon tetrachloride–dimethyl sulfoxide*			
		99.75:0.25	*99.50:0.50*	*99.00:1.00*	*98.75:1.25*
13	Phenazine	0.08	0.03	0.01	0.01
8	7,8-Benzoquinoline	0.13	0.11	0.10	0.08
10	Quinoline	0.32	0.18	0.12	0.06
12	4-Azafluorene	0.33	0.19	0.14	0.08
9	5,6-Benzoquinoline	0.41	0.32	0.17	0.12
14	1,2-Bis[2-pyridyl]ethylene	0.71	0.44	0.21	0.18
29	1,4,9,10-Tetrahydroxyanthracene	1.47	1.11	0.91	0.76
15	7-Methylindole	3.94	3.06	2.00	1.68
16	Carbazole	4.70	3.41	2.12	1.73
19	2-Phenylphenol	4.73	3.76	2.97	2.23
21	1-Hydroxybenzo[*c*]phenanthrene	4.88	4.21	3.00	2.57
23	1-Naphthol	8.35	5.47	3.35	2.59
17	7-Azaindole	8.82	4.59	1.65	1.01
20	4-Phenylphenol	9.41	5.94	3.62	2.82
28	1-(Hydroxymethyl)benzo[*a*]pyrene	9.47	6.23	3.65	2.85
24	7,12-Dimethyl-9-hydroxybenz[*a*]anthracene	9.66	6.42	3.49	2.82
18	3-Aminofluoranthene	10.7	9.29	6.53	5.76
25	13-Hydroxypicene	11.0	6.71	3.73	3.12
22	3-Hydroxybenzo[*c*]phenanthrene	12.4	7.56	4.29	3.44
26	2-Hydroxypyrene	13.1	8.12	4.50	3.65

tane (40:60) eluent. Similar compounds, but of higher molecular weight, may be separated by the μPorasil system, however. An example is 1-(hydroxymethyl)benzo[*a*]pyrene which is separated from the nitrogen heterocycles and would appear in the hydroxyl fraction with the μPorasil column with all the dimethyl sulfoxide–carbon tetrachloride mobile phases (Table IV and Fig. 3).

The second type of hydroxyl aromatic which would appear in a nitrogen heterocycle fraction would be a polysubstituted compound which is capable of intramolecular hydrogen bonding. An example is 1,4,9,10-tetrahydroxyanthracene which is *para*-substituted twice and is able to form two intramolecular hydrogen bonds. Even though this compound has four hydroxyl groups, it is retained very weakly and overlaps with the nitrogen fraction with both the Nucleosil NO_2 and μPorasil columns (Tables III and IV).

It was found that diaza nitrogen heterocycles which are substituted opposite one another in the same ring (*i.e.* phenazine, Table I) retain very weakly compared to other diaza nitrogen compounds in which the nitrogen atoms are not opposite to one another. If one compares the retention data for phenazine in either the Nucleosil NO_2–chloroform–*n*-heptane or μPorasil–carbon tetrachloride–dimethyl sulfoxide systems it is evident that when two nitrogen atoms are opposite one another in a ring, the retention of the heterocycle is greatly reduced. This type of substitution appears to greatly reduce the polarity of the two nitrogen atoms thus reducing their interaction with the stationary phase. The apparent reduction in polarity can be large

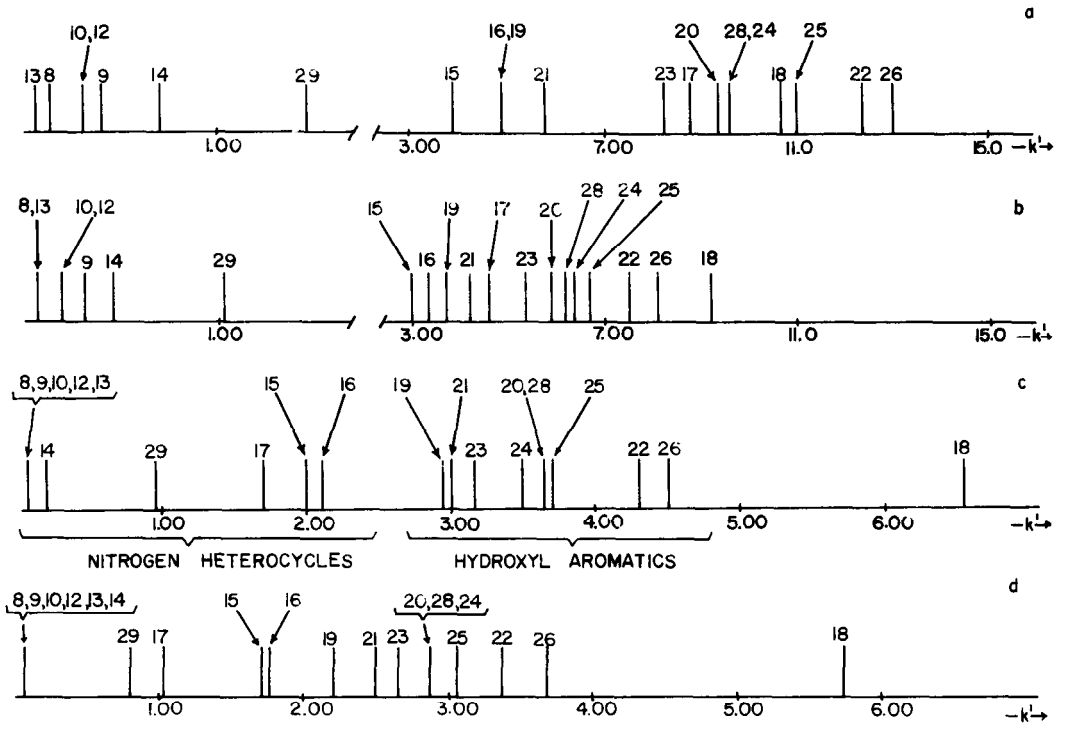


Fig. 3. Migration behavior of model compounds in Table IV on μPorasil with carbon tetrachloride–dimethyl sulfoxide mobile phases. (a) 99.75:0.25. (b) 99.50:0.50, (c) 99.00:1.00, (d) 98.75:1.25.

enough for these diaza compounds to be retained less than a mono aza species. It can be seen in Table IV and Fig. 3 that the μPorasil–carbon tetrachloride–dimethyl sulfoxide system elutes phenazine before most of the mono aza compounds. This effect is not as pronounced in the Nucleosil NO_2–chloroform–*n*-heptane system. The data also shows that the μPorasil–carbon tetrachloride–dimethyl sulfoxide systems studied retained 3-aminofluoranthene substantially longer than the Nucleosil NO_2–chloroform–*n*-heptane systems investigated. Fig. 3 illustrates that 3-aminofluoranthene is retained longer than the hydroxyl aromatic compounds in the μPorasil–carbon tetrachloride–dimethyl sulfoxide (98.75:1.25) system. The elution characteristics of amino substituted compounds allowed a clean separation of our standards into three compound classes. The order of elution from the μPorasil–carbon tetrachloride–dimethyl sulfoxide system can be written as nitrogen heterocycle < hydroxyl aromatic < amino substituted. Although 3-aminofluoranthene was the only amino compound studied, it is reasonable to assume that similar compounds would behave in an analogous manner.

As seen from Table II and Fig. 1, no overlap of nitrogen compounds into the PAH fraction was observed with the μPorasil column employing the carbon tetrachloride–chloroform (95:5) eluent.

Migration behavior of model compounds under increasing organic modifier concentrations

The model compounds in Tables III and IV were chromatographed with mobile phases of increasing strength to investigate the migration behavior of the functional classes and determine which binary solvent mixture gave the best selectivity. The Nucleosil NO_2 column yielded the best functional group separation with a chloroform–*n*-heptane (40:60) mobile phase (Table III and Fig. 2). Although the retention of the larger hydroxyl aromatics is very long with this mobile phase, smaller species such as 1-naphthol and 4-phenylphenol are eluted with k' values of 15.1 and 18.3, respectively. While a relatively good separation of these model compounds could be achieved with the stronger chloroform–*n*-heptane (60:40 or 70:30) mobile phases, a very complex sample such as a coal-derived liquid would require more separation between the functional classes due to the large number of nitrogen compounds present. The analysis time could be shortened, however, by using a gradient elution step to elute the hydroxyl aromatics more rapidly after the nitrogen compounds had been collected.

In Table III and Fig. 2 it is evident that for the Nucleosil NO_2 column, as the amount of chloroform in the mobile phase increases, the relative elution order of some of the hydroxyl aromatic compounds switches. This is in contrast to the μPorasil column which generally displayed a global shift of the hydroxyl standards to lower k' values as the amount of dimethyl sulfoxide in the mobile phase increased (Table IV and Fig. 3).

As we have discussed, the μPorasil stationary phase was able to separate the model nitrogen heterocycles from hydroxyl aromatics more effectively than the Nucleosil NO_2 column. All the model compounds eluted more quickly with the μPorasil chromatographic systems which demonstrated that the functional classes rapidly eluted in two relatively narrow bands. In Fig. 3 it can be seen that a difference of less than one k' unit separates these functional classes with the carbon tetrachloride–dimethyl sulfoxide (99:1) mobile phase. For a mixture of fifteen or twenty hydroxyl aromatics and nitrogen heterocycles, a μPorasil system similar to the one described would be an excellent choice for a compound class separation because of the selectivity and speed of the chromatographic system. The application of such a μPorasil system to a highly complex coal-liquid sample may present problems due to the approximate continuum of molecular structures and various polar functional groups present for heteroatom compounds[34]. The μPorasil system with the carbon tetrachloride–dimethyl sulfoxide mobile phases investigated in this report eluted the nitrogen heterocycles relatively close to the hydroxyl aromatics so that these functional classes may not be adequately resolved in a coal-liquid sample. Other weaker organic modifiers, such as chloroform, could yield a binary mobile phase of intermediate strength and may prove useful in increasing the selectivity of the system. Present work in this laboratory involves investigating such a mobile phase for the separation of nitrogen heterocycles from hydroxyl aromatics on μPorasil.

CONCLUSIONS

In general, PAHs are best separated from nitrogen heterocycles on the μPorasil column utilizing chloroform–carbon tetrachloride mobile phases (see Table II). Nu-

cleosil NO_2 does not resolve these functional classes sufficiently and yields an inferior separation. The chloroform–carbon tetrachloride mobile phases are attractive because of the high solubility of coal-derived liquids in such solvents. For separating the nitrogen heterocycles from hydroxyl aromatic standards, the μPorasil column utilizing dimethyl sulfoxide–carbon tetrachloride mobile phases yielded a superior separation due to the rapid elution of the nitrogen heterocycles and the stronger retention of sterically hindered hydroxyl aromatic compounds. The results of these studies demonstrate the potential for separating coal derived liquids into compound class fractions. These fractions would then provide a basis for evaluating the PAH, nitrogen heterocycle and hydroxyl aromatic character of these highly complex samples.

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