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SEPARATION AND CHARACTERIZATION OF COAL DERIVED COMPONENTS

Quarterly Report for the Period October 1—December 31, 1983

By
R. J. Hurtubise
H. F. Silver

January 16, 1984

Work Performed Under Contract No. AC22-83PC60015

University of Wyoming
Laramie, Wyoming

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Separation and Characterization of Coal Derived Components

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Laramie, Wyoming 82071

Quarterly Report

Prepared for

Pittsburgh Energy Technology Center
Department of Energy
Pittsburgh, Pennsylvania

Highlights

1. Elemental analyses were obtained on preasphaltenes-1 and preasphaltenes-2 from F-45 and F-51.
2. It was shown that Chromasorb T is an acceptable substitute for Fluoropak in the Fluoropak-basic alumina procedure.
3. The optimum mobile phases have been obtained for the separation of monohydroxyl aromatics and dihydroxyl aromatics by reversed-phase chromatography.
4. It appears a new way of predicting retention in normal-phase chromatography has been developed.
5. Several manuscripts are in the process of being written.

Abstract

No new field-ionization data was obtained this quarter. For preasphaltenes, elemental analysis data was obtained on Kentucky and Wyodak preasphaltene samples. In conjunction with the preasphaltene work, solubility and thin-layer chromatography experiments were performed. The results indicated that basic alumina would not be useful as a general stationary phase for the separation of preasphaltenes. Several experiments were carried out with Chromasorb T, and the results showed it would be an adequate substitute for Fluoropak. The hydrocarbons in a sample from Pittsburgh Energy Technology Center were separated by the number of double bonds. The optimum mobile phases for the separation of monohydroxyl aromatics and dihydroxyl aromatics by reversed-phase liquid chromatography were obtained. In addition, a means of predicting retention in normal-phase chromatography was considered, and a NO_2 high-performance chromatographic column showed promise for the separation of compound classes.

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A. Field-Ionization Mass Spectrometry (FIMS)

No new FIMS data was obtained this quarter. However, hydrocarbon mole % FIMS data obtained under the previous DOE contract (DE-AC22-79ET14874) was converted from mole% to wt%. The data was converted for samples F-30 (mildly hydrogenated F-45) and F-31 (severely hydrogenated F-45). The F-45 sample is Wyodak coal-derived SRC from Wilsonville. With the wt% data a manuscript is being written in which hydrocarbon double bond fractions from F-45, F-30, and F-31 will be compared. The manuscript is being written in conjunction with Dr. Mietek Boduszynski of Chevron Research Company. Dr. Boduszynski worked under the previous DOE contract at the University of Wyoming.

B. Preasphaltenes

Preasphaltenes-1 (chloroform soluble) and preasphaltenes-2 (pyridine soluble) from F-45 and F-51 (Kentucky 9/14 coal-derived SRC) were submitted to Huffman Laboratories, Inc. for elemental analysis. Table 1 shows the results obtained. Based on the H/C atomic ratio, the F-45 preasphaltenes-1 are more aromatic than the F-51 preasphaltenes-1. However, the preasphaltenes-2 in F-45 and F-51 have similar H/C atomic ratios. The preasphaltenes-1 oxygen content in F-45 and F-51 are essentially the same, but the oxygen content of F-51 preasphaltenes-2 is greater than the oxygen content in F-45 preasphaltenes-2. In comparing the corresponding preasphaltenes-1 and preasphaltenes-2 fractions in F-45 and F-51, F-51 shows a greater N and S content than the fractions from F-45. The elemental analysis data will be used with future FIMS and chromatographic data.

In conjunction with the characterization work on preasphaltenes, the solubility of seven more model compounds were tested in $CHCl_3$, $CHCl_3$:CH_3OH(4:1, v/v), tetrahydrofuran, and pyridine. To date, the solubility of eighteen

Table 1. Elemental Analysis Data for Preasphaltenes from F-45 and F-51.[1]

	Fraction			
	F-45		F-51	
Element	Preasphaltenes-1	Preasphaltenes-2	Preasphaltenes-1	Preasphaltenes-2
C	85.69	85.86	84.99	83.86
H	5.51	5.33	5.80	5.07
O	5.77	4.79	5.78	5.36
N	2.07	3.13	2.54	3.86
S	0.20	0.14	0.71	0.63
Total	99.24	99.25	99.82	98.78
H/C atomic ratio	0.772	0.745	0.819	0.725

[1] Average of duplicate results.

multifunctional compounds has been tested. Seven were insoluble or only partially soluble in chloroform. Only one compound was insoluble in $CHCl_3:CH_3OH$(4:1, v/v), and two were insoluble or only partially soluble in tetrahydrofuran. In addition, the eighteen model compounds used in the solubility studies were characterized by silica gel and basic aluminum oxide thin-layer chromatography. The thin-layer chromatography experiments were carried out to determine qualitatively how these compounds would behave in a Chromasorb T-basic aluminum oxide or Chromasorb T-silica gel separation procedure. Table 2 shows the thin-layer chromatography results obtained. The results with silica gel show that four compounds had R_f values greater than 0.2 with chloroform as a mobile phase, but with $CHCl_3:CH_3OH$ (4:1, v/v) as a mobile phase all the compounds have R_f values greater than 0.4. The previous results suggest that the $CHCl_3:CH_3OH$(4:1, v/v) mobile phase should be useful as a solvent for exploratory work in the separation of preasphaltenes. Chloroform was not a useful solvent with basic aluminum oxide as indicated in Table 2. Most of the compounds did not migrate and also streaked. On basic alumina with $CHCl_3:CH_3OH$(4:1, v/v) as a mobile phase, all the compounds in Table 2 which contained only basic nitrogen migrated to the solvent front (compound numbers 5, 6, 15, 16, 17, and 18). Compound number 13, 4-(p-nitrophenylazo)-resorcinol, also migrated to the solvent front. Two compounds did not migrate and the remaining compounds migrated to various extents but exhibited excessive streaking. Generally, from the results in Table 2, it appears basic aluminum oxide will not be useful as a stationary phase for the separation of multifunctional compounds. However, it may be possible to isolate a "clean" basic nitrogen fraction with the stationary phase.

In the future, some dipolar aprotic solvents will be tested as mobile

Table 2. R_f Values for Model Compounds on Silica Gel and Basic Aluminum Oxide

		R_f			
		Silica Gel		Basic Aluminum Oxide	
Compound Number	Name	$CHCl_3$	$CHCl_3$:MeOH (4:1, v/v)	$CHCl_3$	$CHCl_3$:MeOH (4:1, v/v)
1	5-hydroxyquinoline	0.02	0.84	0.0	0.0 →[1] 0.8
2	2-hydroxycarbazole	0.06	0.83	0.0 (0.4)	0.0 → 0.6
3	1,7-dihydroxynaphthalene	0.02	0.81	0.0	0.0 → 0.3
4	2,4-quinolinediol	0.00	~0.6		
5	phenazine	0.23	0.94	(0.0) 0.77	0.97
6	3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine	0.05	0.94	0.14	0.97
7	1,4,9,10-tetrahydroxyanthracene	0.48	0.93	0.0	0.0 → 0.4
8	2,3-dihydroxypyridine	0.00	~0.64	0.0	0.0
9	1-hydroxy-9-fluorenone	0.67	0.79	0.0	0.0 → 0.1
10	1,8-dihydroxyanthraquinone	0.72	0.94	0.0	0.0 → 0.1
11	1,3-dihydroxynaphthalene	0.03	0.65	0.0	0.0 → 0.3
12	2,4-dihydroxybenzophenone	0.09	0.77	0.0	0.0 → 0.2
13	4-(p-nitrophenazo)-resorcinol	0.04	0.77	0.0 → 0.4	0.02, 0.96
14	4',5,7-trihydroxyflavanone	0.00	0.87	0.0	0.0
15	4-azabenzimidazole	0.00	0.45	0.0	1.0
16	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline	~0.09	0.83	0.0 → 0.6	1.0
17	6,7-dimethyl-2,3-di-(2-pyridyl)-quinoxaline	0.03	0.79	→ 0.3	1.0
18	pyrrolo[1,2-a]quinoxaline	0.14	0.77	0.0 → 0.6	0.99

[1] → = streaking

phases with silica gel (1).

C. Replacement of Fluoropak with Chromasorb T in the Fluoropak-Basic Alumina Procedure

As discussed in the previous quarterly report, Chromasorb T was investigated as a substitute for Fluoropak in the Fluoropak-basic alumina procedure because Fluoropak is no longer available. The Fluoropak-basic alumina procedure employed has been described in the literature (2,3). There were two procedures described in the references cited, namely, Variant I and Variant II. In this work, Variant I has been used. It was concluded in the last quarterly report that Chromasorb T is an adequate substitute for Fluoropak. However, additional experiments were to be run to check the results. In Table 3, the results from several earlier runs for F-45 using the Fluoropak-basic alumina procedure are compared with results obtained from F-45 using the Chromasorb T-basic alumina procedure. The results from the Fluoropak-basic alumina procedure are based on thirteen runs. However, 5 data points were rejected out of 125 data points after applying the Q-test. The Chromasorb T results are based on five runs and no data points were rejected. As Table 3 indicates, the standard deviation and 95% confidence limits values are good for both the Fluoropak and Chromasorb T results. The differences between the average values for Fluoropak and Chromasorb T results in the last row in Table 3 show that the maximum difference was +2.0% and the minimum difference was +0.4%. Based on the standard deviation values, 95% confidence limits values, the difference values, and the individual data in Table 3, it is concluded that comparable results are obtained with Fluoropak and Chromasorb T, and that Chromasorb T is an acceptable substitute for Fluoropak.

Table 3. Comparison of Results (%) Obtained with Fluoropak and Chromasorb T Using F-45[1]

				Oils			Asphaltenes		Preasphaltenes	
Column Packing	Oils[2]	Asph.[3]	Preasph.[4]	HC	N	OH	HC+N	OH	chloroform soluble	pyridine[5] soluble
Fluoropak	19.0	38.0	44.2	9.9	4.1	4.5	14.7	23.1	12.6	32.0
Standard Deviation	1.6	1.8	3.1	1.2	0.56	1.3	1.4	0.90	2.1	2.4
95% Confidence Limits	±1.1	±1.1	±1.9	±0.8	±0.3	±0.8	±0.9	±0.5	±1.5	±1.7
Chromasorb T	18.2	36.9	44.9	8.3	4.2	5.7	12.7	24.2	12.2	32.7
Standard Deviation	1.1	0.51	1.2	0.58	0.63	0.30	0.33	0.37	0.36	0.92
95% Confidence Limits	±1.4	±0.6	±1.5	±0.7	±0.8	±0.4	±0.4	±0.5	±0.5	±1.1
Differences between the average values for Fluoropak and Chromasorb T, $X_F - X_C$	+0.8	+1.1	-0.7	+1.6	-0.1	-1.2	+2.0	-1.1	+0.4	-0.7

[1] Fluoropak results are the average of thirteen runs. Chromasorb T are the average of five runs. Asph = asphaltenes, Preasph = preasphaltenes, HC = hydrocarbons, N = nitrogen compounds.

[2] Oils = HC(Oils) + N(Oils) + OH(Oils)

[3] Asph = HC + N(Asph) + OH (Asph)

[4] Preasph = chloroform soluble + pyridine soluble(pyridine soluble obtained by difference)

[5] Average values obtained by difference

D. Sample from Pittsburgh Energy Technology Center

A neutral fraction from a 650°F(-) product made at Wilsonville PDU (BT-4-120-3) was received from Chuck Schmidt. The hydrocarbons in the fraction were separated by the number of double bonds. In addition oils, asphaltenes, and preasphaltenes were isolated; however, there were essentially no preasphaltenes in the neutral fraction. Mr. Schmidt plans to carry out low-voltage high-resolution mass spectrometry experiments with the fractions. Tables 4 and 5 give the wt% values and the descriptions of the fractions sent to Mr. Schmidt.

E. High-Performance Liquid Chromatography

1. Hydroxyl Aromatics

In the last quarterly report, it was mentioned that thirty-six hydroxyl aromatic standards were investigated by reversed-phase chromatography with a C-18 column and with several ternary mobile phases. Table 6 lists several additional ternary mobile phases that have been investigated. Work is also continuing with mobile phases for use with normal-phase chromatography. The main emphasis in this part of the research has been to find the optimum mobile phases for both reversed-phase and normal-phase chromatography. In the remaining part of this section, one of the important approaches used to optimize the mobile phases in the reversed-phase work will be considered.

The solvent optimization approach centers around the recent work of Billiet et al. (4-6). In the optimization approach, the solubility parameter theory and ternary phase diagrams are used. It is assumed that binary and ternary mobile phases offer the possibility of specific chromatographic effects and thus would allow enhanced chromatographic resolution of a multicomponent mixture. One can consider exploiting specific mobile phase effects as follows. With two binary

Table 4. Compound Class, Oils and Asphaltenes wt% Values for the BT-4-120-3 Sample[1]

n-hexane solubles			n-hexane insoluble toluene soluble					
hydrocarbons	nitrogen compounds	hydroxyl compounds	nitrogen compounds	hydroxy compounds	chloroform soluble	recovery[2]	oils[3]	asphaltenes[4]
85.5	4.9	4.8	0.3	0.9	0.0	96.4	95.2	1.2

[1] Average of duplicate runs.
[2] Based on 295.7 mg sample size for run 1, and 289.4 mg sample size for run 2.
[3] Sum of n-hexane soluble fractions.
[4] Sum of toluene soluble fractions.

Table 5. Label Description, Weight of Fractions, and Contents of Vials[1]

Labels	Weight, mg	Description
BT-4-120-3 (01)	210.4[2]	hydrocarbons (oils)
BT-4-120-3 (02)	16.1	nitrogen compounds (oils)
BT-4-120-3 (03)	12.2	hydroxyl compounds (oils)
BT-4-120-3 (A2)	0.5	nitrogen compounds (asphaltenes)
BT-4-120-3 (A3)	2.5	hydroxyl compounds (asphaltenes)
BT-4-120-3 (P1)[3]	0.1	chloroform soluble (preasphaltenes-1)
BT-4-120-3 (01) saturates	6.4	saturates
BT-4-120-3 (01) 3 d.b.	9.4	three double bond hydrocarbons
BT-4-120-3 (01) 5 d.b.	5.1	five double bond hydrocarbons
BT-4-120-3 (01) 6 d.b.	3.2	six double bond hydrocarbons
BT-4-120-3 (01) 7 d.b.	2.6	seven double bond hydrocarbons
BT-4-120-3 (01) 8 d.b.	2.0	eight double bond hydrocarbons
BT-4-120-3 (01) 9 d.b.	1.0	nine double bond hydrocarbons
BT-4-120-3 (01) $\geq$ 10 d.b.	2.3	ten and greater double bond hydrocarbons

[1] Results fom a single run.

[2] Amount remaining of this fraction after separation of a portion of the fraction on µ-Bondapak NH_2. The portion separated on µ-Bondapak NH_2 was separated by the number of hydrocarbon double bonds.

[3] Run 1 gave no preasphaltenes-1, but Run 2 gave 0.1 mg of preasphaltenes-1.

Table 6. Additional Reversed-Phase High Performance Liquid Chromatography Mobile Phases Investigated for Hydroxyl Aromatics with a C-18 Column

1. Ternary mobile phases investigated for monohydroxyl compounds

methanol:tetrahydrofuran:water (v/v/v)	acetonitrile:tetrahydrofuran:water (v/v/v)
30.0:21.5:48.5	19.2:24.7:56.1
13.1:31.9:55.0	9.4:32.5:58.1
	14.6:28.3:57.1
	16.9:26.5:56.6

2. Ternary mobile phases investigated for dihydroxyl compounds

methanol:tetrahydrofuran:water (v/v/v)
13.1:16.8:70.1
8.5:19.7:71.8
8.0:20.0:72.0

mobile phases such as methanol-water and tetrahydrofuran-water, it can be assumed that the polarities of both mobile phases are the same. This means that the solubility parameters of both mobile phases is assumed to be the same. However, in reality each mobile phase most likely shows various specific interactions with solutes, and different chromatograms could result for a given set of solutes with the two mobile phases. The same general concepts apply to ternary mobile phases. In this case, it is assumed that the ternary mobile phase has the same polarity as a reference binary mobile phase. It can be shown theoretically that all ternary mixtures of water, methanol and a second organic modifier that possess a given polarity follow a straight line between two limiting binary compositions (4). The dashed lines in Figure 1 (iso-eluotropic diagram) represent the theoretical straight lines between the limiting binary compositions. The term ϕ_m^* represents the volume fraction of methanol. The iso-eluotropic lines connect solvents of equal eluotropic strength. Specific solvent-solute effects are defined as variations in retention for a particular solute, using solvents of equal eluotropic strength. The specific solute effects are manifested by deviations from the theoretical iso-eluotropic lines. This is illustrated by the solid experimental lines in Figure 1. The specific solute effects are essentially the basis on which mobile phase optimization depends.

Below is outlined the general approach used to obtain optimum mobile phases for the reversed-phased chromatography work. The references cited can be consulted for details (4-6). Two optimization criteria have been used and these are defined by Equations 1 and 2. In addition, iso-eluotropic mobile phases are used in the optimization approach.

$$\Pi R_S = \prod_{i=1}^{n-1} \frac{k_{i+1} - k_i}{k_{i+1} + k_i + 2} \tag{1}$$

$$r = \prod_{i=1}^{n-1} Rs_{i+1,i} \Bigg/ \left[\left(\sum_{i=1}^{n-1} Rs_{i+1,i} \right) \Big/ (n-1) \right]^{n-1} \qquad (2)$$

R_S is chromatographic resolution; k is the capacity factor, πR_S is the product of the resolution values for each pair of adjacent peaks in a chromatogram. The optimization criterion defined by Equation 2 is generally more reliable than the one defined by Equation 1, but both optimization criteria were used in this work. One attempts to obtain the highest possible value for πR_S or an r value as close to unity as possible. To achieve these goals the following steps are used.

(a) The sample is subjected to a gradient elution run usually running from pure water to pure organic modifier. This allows a decision to be made if the isocratic k' values are between 1 and 10. In addition, it allows one to decide on a starting mobile phase for the optimization scheme.

(b) Next one runs a possibly useful mobile phase determined by the above gradient elution run in the isocratic mode in addition to other binary mobile phases of the same strength. Normally, methanol-water, tetrahydrofuran-water, and acetonitrile-water are used.

(c) One then constructs iso-eluotropic diagrams as shown in Figure 1 or assumes such diagrams are valid and proceeds with the next step.

(d) Phase-selection diagrams are then constructed based on the optimization criteria and chromatographic retention data of standards. Figure 2 shows a phase selection diagram obtained from twenty-one monohydroxyl aromatic compounds. The maximum values for πR_S and r are very close to one another. In this particular case with the maximum r value, the predicted ternary mobile phase has a composition of acetonitrile:tetrahydrofuran:water (44.8:4.2:51.0, v:v:v).

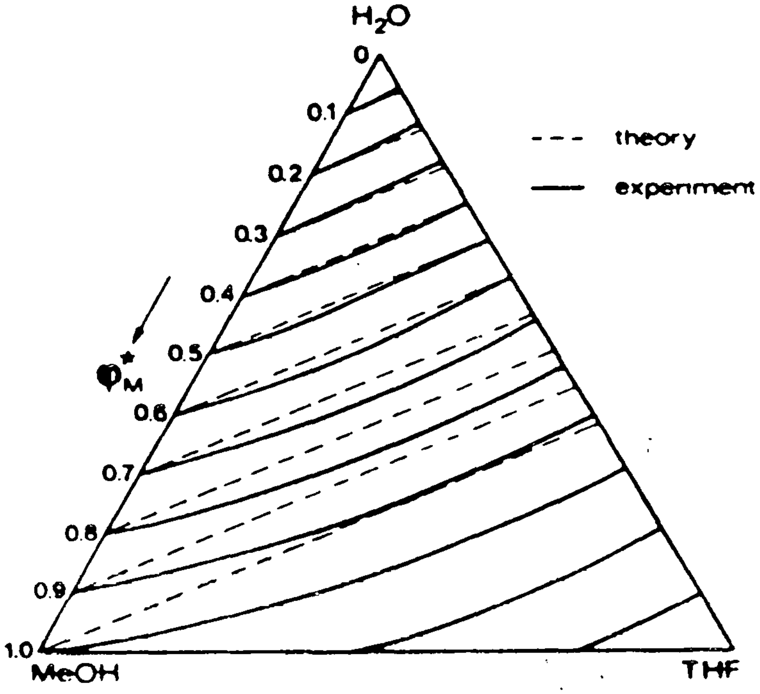

Figure 1. Iso-eluotropic diagram for the methanol-tetrahydrofuran-water system (taken from Reference 4).

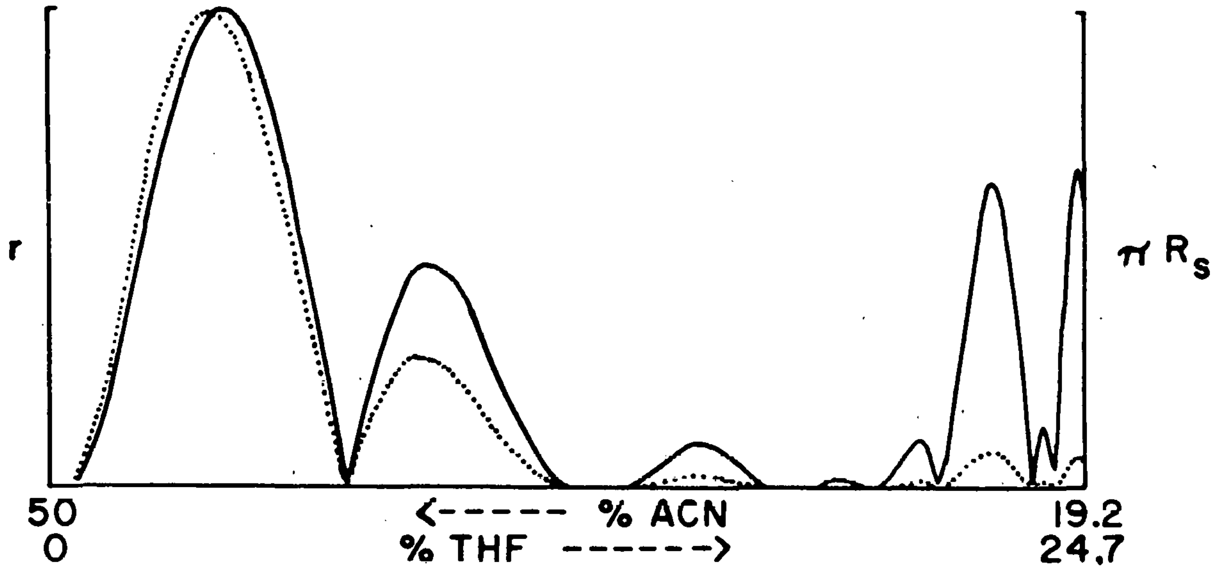

Figure 2. Phase-selection diagram for twenty-one monohydroxyl aromatic compounds using water, acetonitrile, and tetrahydrofuran mobile phases.

(e) A chromatogram is run with the ternary mobile phase defined in step d. It is then determined whether to construct a new phase-selection diagram based on the retention data from the chromatograms previously run. Normally a new phase-selection diagram is obtained to decide if further mobile phase optimization is needed. In fact, several phase-selection diagrams may be constructed before the "best" mobile phase is found.

Using the approach outlined in steps a-e the optimum mobile phases for twenty-one monohydroxyl compounds and fourteen dihydroxyl compounds were determined separately. For the monohydroxyl aromatics, the optimum mobile phase was determined to be acetonitrile:tetrahydrofuran:water (14.6:28.2:57.1, v:v:v) for a C-18 column. The optimum mobile phase for the dihydroxyl compounds for a C-18 column was methanol:tetrahydrofuran:water (8.5:19.7:71.8, v:v:v). Figure 3 shows the chromatogram obtained for the twenty-one monohydroxyl aromatics with the optimum mobile phase acetonitrile:tetrahydrofuran:water, and Figure 4 shows the chromatogram for the fourteen dihydroxyl aromatics using the methanol:tetrahydrofuran:water mobile phase. As indicated in Figure 3, a Fisher Resolvex C-8 column was used. The resolution with this column is actually better than a μ-Bondapak C-18. In Figure 3, sixteen peaks were obtained out of a possible twenty-one peaks. In Figure 4, eleven peaks out of fourteen are indicated (two of the components are not shown in the Figure). It is also planned to use the Fisher Resolvex C-8 column for the dihydroxyl compounds to improve the resolution for these compounds. Table 7 lists the monohydroxyl aromatics and dihydroxyl aromatics used in the optimization work.

As Figures 3 and 4 show, not all monohydroxyl and dihydroxyl aromatics were resolved. However, it is important to realize that with the optimization procedure, the "best" mobile phases were obtained for the chromatographic

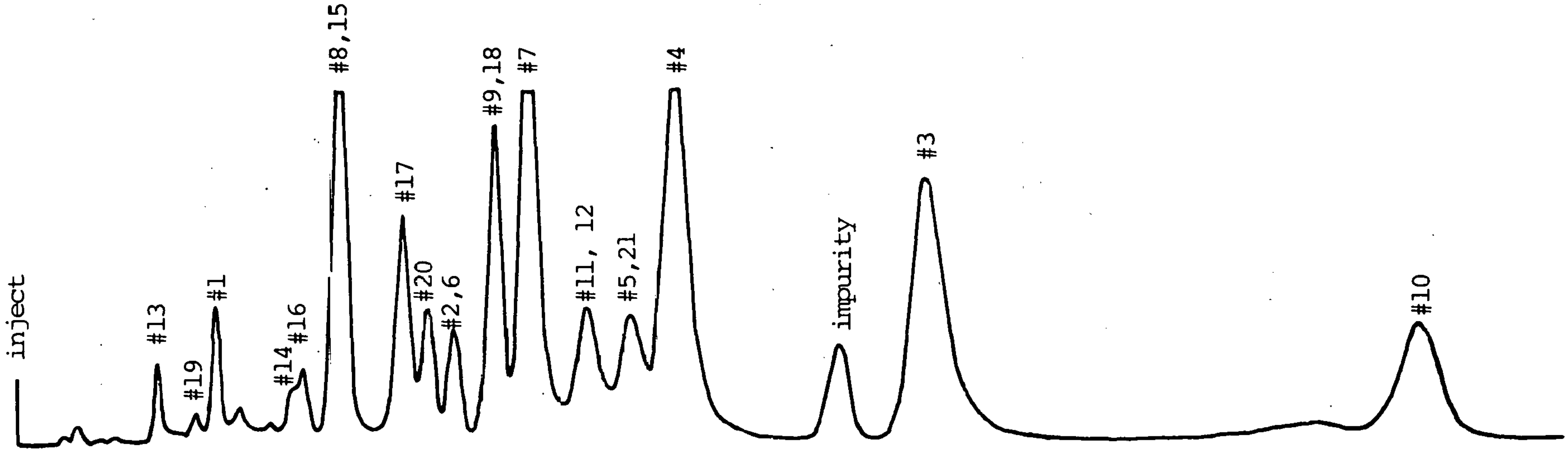

Figure 3. Separation of monohydroxy aromatic standards on a Fisher Resolvex C-8 column with an acetonitrile: tetrahydrofuran:water (14.6:28.3:57.1, v:v:v) mobile phase at 1.0 mL/min.

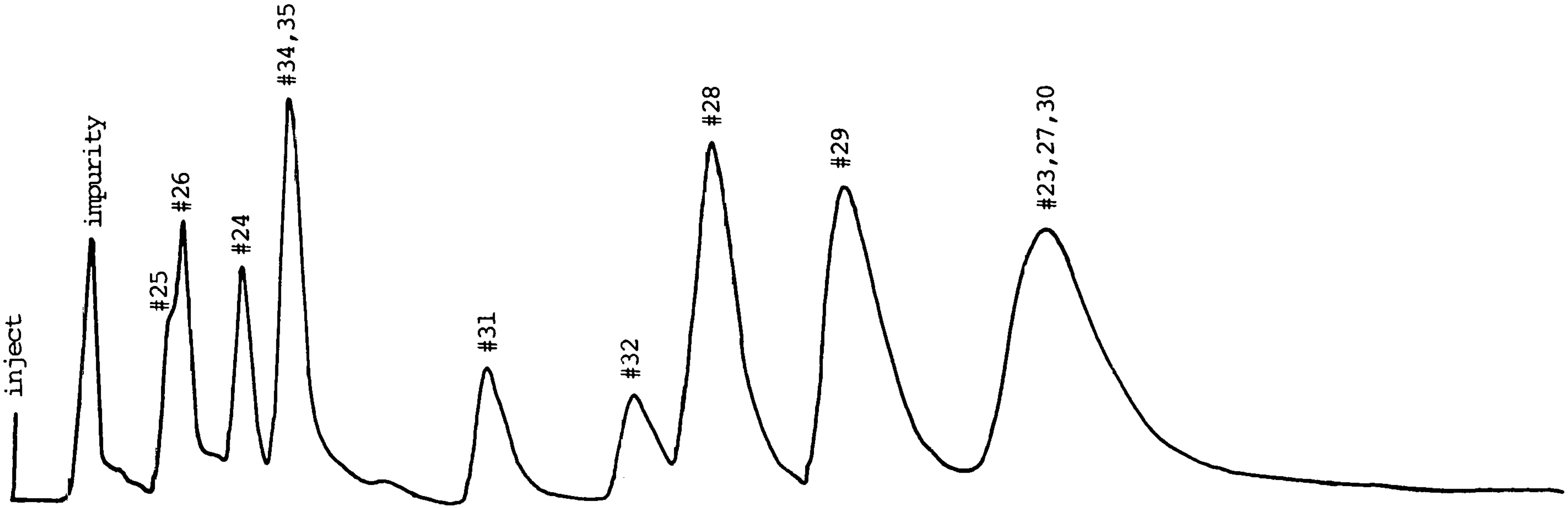

Figure 4. Separation of dihydroxyl aromatic standards on a μ-Bondapak C-18 column with a methanol:tetrahydrofuran: water (8.5:19.7:71.8, v:v:v) at 1.0 mL/min.

Table 7. Hydroxyl Aromatic Standards

1. 1-acenaphthenol
2. 5H-dibenzo(a,d)cycloheptene-5-ol
3. 7,12-Dimethyl-9-hydroxybenz(a)anthracene
4. 2-hydroxybenzo(c)phenanthrene
5. 3-hydroxybenzo(c)phenanthrene
6. 1-(1-hydroxyethyl)pyrene
7. 1-(hydroxymethyl)benz(a)pyrene
8. 4-hydroxymethylpyrene
9. 9-hydroxyphenanthrene
10. 13-hydroxypicene
11. 1-hydropyrene
12. 4-hydroxypyrene
13. 1-indanol
14. 5-indanol
15. 1-naphthol
16. 2-naphthol
17. 3-phenylphenol
18. 1,2,3,4-tetrahydro-4-hydroxy-4-methylphenanthrene
19. 1,2,3,4-tetrahydro-1-naphthol
20. 5,6,7,8-tetrahydro-1-naphthol
21. 5,6,7,8-tetrahydro-2-phenanthrol
22. o,o'-biphenol
23. p,p'-biphenol
24. 1,2-dihydroxybenzene
25. 1,3-dihydroxybenzene
26. 1,4-dihydroxybenzene
27. 1,3-dihydroxynaphthalene
28. 1,6-dihydroxynaphthalene
29. 1,7-dihydroxynaphthalene
30. 2,3-dihydroxynaphthalene
31. 2,6-dihydroxynaphthalene
32. 2,7-dihydroxynaphthalene
33. 2,5-dihydroxyphenanthrene
34. 2,6-dihydroxytoluene
35. 3,5-dihydroxytoluene
36. 1,2,3-trihydroxybenzene
37. 1,3,5-trihydroxybenzene

systems investigated. It is very unlikely that a greatly improved reversed-phase mobile phase system could be found from the ones investigated. In other words, the optimization procedure gives the "best" mobile phase, but it also reveals the limitations of the chromatographic systems.

In earlier work it was found that monohydroxyl aromatic standards could be completely separated from the dihydroxyl aromatic standards with a μ-Bondapak NH_2 column and a n-heptane:2-propanol mobile phase. In the future, it is planned to combine the Chromasorb T-basic alumina procedure and procedures developed from the reversed-phase and normal-phase chromatographic results to separate monohydroxyl and dihydroxyl aromatics from coal-liquid samples. The isolated hydroxyl aromatics will be characterized by field-ionization mass spectrometry.

2. Nitrogen Heterocycles and Aromatic Amines

In the last quarterly report it was mentioned that thirty-five nitrogen heterocycle and aromatic amine standards were investigated with several normal-phase chromatography systems. It has been found that a general nitrogen compound class separation can be achieved with a μ-Bondapak NH_2 column and a n-heptane:2-propanol (95:5 v:v) mobile phase. Aromatic amines, nonbasic nitrogen compounds, and basic compounds can be separated into classes. However, there is some overlap betwen the classes. Other mobile phases are being investigated to improve the separation of compound classes. These mobile phases are various volume ratios of n-heptane:ethyl acetate and n-heptane:chloroform.

In addition to mobile phase optimization as discussed in section E.1., it is important to predict the retention of solutes <u>a priori</u> to determine the overlap of compound classes and the retention characteristics of various coal derived components. Graphs were prepared of log k' versus log δ for nitrogen compounds from data obtained with a μ-Bondapak NH_2 column and several n-heptane:2-propanol mobile phases. The term k' is capacity factor, and the term δ is solubility parameter. The log k' versus log δ graphs were linear for the nitrogen standards investigated. The slopes and intercepts from the above linear relationships were next graphed and another linear relationship was obtained between the slope and intercept values. Similar slope-intercept relationships have been found by us for hydroxyl aromatics and other classes of compounds. It appears a new way has emerged for predicting retention in normal-phase chromatography with the slope-intercept correlations. More details on this approach will be given in future reports.

3. Compound Class Separation of Polycyclic Aromatic Hydrocarbons, Nitrogen Heterocycles, and Hydroxy Aromatics

In Table 9 of the previous quarterly report, several stationary phases and mobile phases were listed that have been investigated for compound class separation. Three additional high-performance columns have been investigated along with several additional mobile phases. The three columns are a NO_2 column (normal-phase), a CN column (reversed-phase), and a dimethylamino column (reversed-phase). Of the three columns, the NO_2 column shows the most promise in separating coal-derived components by compound class. Two of the mobile phases employed with the NO_2 column were n-heptane:2-propanol (99:1, v:v) and n-heptane:chloroform (80:20, v:v). With the NO_2 column and the previous two mobile phases basic nitrogen, nonbasic nitrogen, and amino compounds were separated from monohydroxyl aromatics. Additional mobile phases to be investigated with the NO_2 column are 25%, 30%, and 35% chloroform in n-heptane. Also, it is planned to investigate the ability of a μ-Porasil column and dimethylsulfoxide-carbon tetrachloride mobile phases to separate compounds by compound class (1).

F. Manuscripts

1. A manuscript entitled "Relationship between Solvent-Derived and Compound-Class Fractions in Coal-Derived Distillates and Vacuum Still Bottoms" was recently published in Fuel. Boduszynski, M. M.; Hurtubise, R. J.; Silver, H. F. Fuel 1984, 63, 93. The results described in this manuscript were obtained under the previous DOE contract (No. DE-AC22-79ET14874).
2. A manuscript entitled "Composition of Distillate Recycle Solvents Derived from Direct Coal Liquefaction in the SRC-1 Process" was submitted to Fuel for review. The results described in the manuscript were obtained under the previous DOE contract (No. DE-AC22-79ET14874).
3. A manuscript is being written in which the hydrocarbon composition of moderately and hydrogenated F-45 is compared. The data were obtained during the previous DOE contract period.
4. A rough draft of a manuscript was written in which the hydrocarbon composition of F-45 and F-51 are compared.

Literature Cited

1. Chmielowiec, J. Anal. Chem. 1983, 55, 2367.
2. Boduszynski, M. M., Hurtubise, R. J., Silver, H. F. Anal. Chem. 1982, 54, 372.
3. Boduszynski, M. M., Hurtubise, R. J., Silver, H. F. Anal. Chem. 1982, 54, 375.
4. Schoenmakers, P. J., Billiet, H. A. H., deGalan, L. J. Chromatogr. 1981, 218, 261.
5. Schoenmakers, P. J., Drouen, A. C. J. H., Billiet, H. A. H., deGalan, L., Chromatographia 1982, 15, 688.
6. Drouen, A. C. J. H., Billiet, H. A. H., Schoenmakers, P. J., deGalan, L., Chromatographia 1982, 16, 48.

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