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HETEROATOM SPECIATION IN COAL LIQUEFACTION
VIA FTIR COUPLED WITH LIQUID CHROMATOGRAPHY

Quarterly Progress Report for the Period
October 1–December 31, 1983

By
L. T. Taylor

Date Published
May 1984

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Virginia Polytechnic Institute and State University
Blacksburg, Virginia

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RESEARCH OBJECTIVES

The objectives of the research are (1) evaluate the potential of FT-IR for qualitative functional group detection in chromatographic fractions of highly polar materials, (2) develop separation techniques with the aid of FT-IR detection for concentration of oxygen, nitrogen and sulfur functionalities in synfuels, (3) describe and quantify the various heteroatom functionalities in selected solvent refined coal fractions, (4) place speciation techniques on-line with chromatographic separations, (5) compare quantitative speciation information obtained from LC-FTIR with established "fluorine tagging" techniques regarding model compounds and synfuels.

SAMPLES STUDIED

The coal-derived samples employed in this study were received from the Kerr McGee Corporation. Liquefaction conditions were as follows:

Wyodak #3 feed coal
100% THQ; S:C, 2:1
1100 psi H₂, 30 minutes, 785°F

After the reaction was terminated, gases were vented from the reactor and the reaction vessel was emptied of its contents. Some residue and process solvent remained in the vessel. This material was removed by washing the vessel with tetrahydrofuran (THF). Material which was solubilized was designated THF solubles. Material remaining after distillation of the emptied vessel contents was denoted residue (+850°F). Residue and THF solubles were chosen for analysis.

Prior to detailed analysis both samples were preparatively fractionated in hopes of providing a simpler mixture for analysis. For the THF solubles sample, four preliminary fractions were generated by successive elution with one volume of hexane and two volumes each of carbon tetrachloride, chloroform and methanol (Figure 1). Fractions 2 and 3 were selected for detailed study. For the residue sample the elution schedule was slightly altered as shown in Figure 1. Fractions 3,4 and 5 were chosen for further analysis.

ANALYSIS OF FRACTIONS OF THF SOLUBLES

A preliminary preparative separation was performed in order to remove the relatively large amount of 1,2,3,4-tetrahydroquinoline (THQ) known to be present in the THF solubles sample. Fraction 1, eluted with hexane, was indeed found to contain almost exclusively THQ. Fractions 2 and 3 contained only a small amount of THQ. Their analysis is described below. Fraction 4 was not analyzed.

The static IR spectra of THF solubles fractions 2 and 3 (dissolved in CDCl₃) ratioed to CDCl₃ are shown in Figure 2. Both samples exhibit

Figure 1: Scheme for the preparative scale separations of the samples "THF Solubles" and "Residue".

Figure 2: Static infrared spectra of THF Solubles samples in CDCl_3 , 0.2 mm pathlength cell. A=Fraction 2; B=Fraction 3.

relatively intense aliphatic CH stretching. In both fractions there is considerably more methylene CH stretching (2928 cm^{-1} and 2855 cm^{-1}) than methyl CH stretching. This indicates either the presence of long aliphatic chains and/or ring aliphatics. An NH stretch at 3406 cm^{-1} appears in the spectrum of fraction 3. The band at approximately 3660 cm^{-1} in fraction 3 is due to water, present either in the sample or the solvent. Both fractions have weak aromatic CH stretching bands with these bands being much more intense in fraction 3. Both samples also exhibit multiple carbonyl stretching modes in the region $1700\text{--}1640\text{ cm}^{-1}$. Fraction 3 also exhibits an OH stretch at 3601 cm^{-1} typical of phenols which is absent in fraction 2. From these static spectra alone it appears that these two fractions are appreciably different.

FRACTION 2

A microbore scale chromatographic separation of fraction 2 with UV and FTIR detection is shown in Figure 3. Upon examination of the UV trace, it is seen that most peaks elute in the same region as previously found for simple basic nitrogen model compounds. On the basis of retention time comparisons alone, fraction 2 would seem to contain THQ (peak a) and quinoline (peak b) although most of these two compounds were found in fraction 1.

A greater amount of information is afforded by FTIR detection. The numbers over the peaks in Figure 3 correspond to individual spectra obtained throughout the μ HPLC-FTIR run. There is a large amount of saturation reflected in each file spectrum as evidenced by the relatively intense CH stretching modes between 2800 and 3000 cm^{-1} . This is perhaps an indication of alkyl side chains on an aromatic ring. Two major components in this fraction (as also predicted from the UV trace) are THQ (File 203, Figure 4) and quinoline (File 225, Figure 5). File 201 indicates the presence of N-methylaniline as shown by its comparison with the spectrum of the model

Figure 3: Separation of THF Solubles fraction 2. NH_2 column, 100 cm x 1 mm i.d.; 70:30 $\text{CDCl}_3:\text{CCl}_4$ + 0.02% TEA; 30 $\mu\text{L}/\text{min}$; A=UV detection (254 nm); B=FTIR detection.

Figure 4: Comparison of file 203 (from μ HPLC-FTIR analysis of THF Solubles fraction 2) with a static spectrum of 1,2,3,4-tetrahydroquinoline.

Figure 5: Comparison of file 225 (from μ HPLC-FTIR analysis of THF Solubles fraction 2) with a static spectrum of quinoline.

compound in Figure 6. Obviously, another component(s) is also represented in File 201 since the two spectra do not perfectly agree. Some of the other files have not been identified; these contain bands consistent with nitrogen heterocyclic compounds but a match with model compound spectra has not been made. The spectrum corresponding to File 235 (Figure 6) is interesting. The component represented in this file elutes after quinoline but it is not resolved from quinoline. This spectrum contains a weak NH stretch. There are rather intense C=C and C=N bands at 1598 cm^{-1} and 1500 cm^{-1} in addition to two bands at 1324 cm^{-1} and 1296 cm^{-1} . This spectrum is suspected to be due to a THQ dimer compound whose structure is shown in Figure 6. This component will be examined in further detail when the fraction's mass spectrum is discussed.

A survey of all the files also indicated the presence of several different carbonyl species. Figure 7 shows the carbonyl stretching region ($1800\text{-}1600\text{ cm}^{-1}$) for selected spectra taken throughout the entire run. The band at 1600 cm^{-1} which is present in every file is due to an aromatic C=C ring stretch. Early in the run (File 190), before elution of THQ, bands at 1677 and 1690 cm^{-1} are observed. These bands are seen in all files up to 201. After THQ elutes (File 203) an unique band at 1660 cm^{-1} is seen in File 217 prior to elution of quinoline (File 225). Finally, compounds elute between Files 244-250 with a characteristic FTIR absorbance at 1774 cm^{-1} .

File 190 exhibits bands at 1690 and 1677 cm^{-1} ; whereas, by the time we get to File 217 only a single band at 1661 cm^{-1} is exhibited. A tertiary amide exhibits a band near 1650 cm^{-1} . This could correspond to the band in File 217 but not File 190. A type of ketone is also possible. Aryl ketones give higher energy bands like those in File 190; whereas, an α,β -unsaturated ketone exhibits lower energy bands as in File 217. Our preferred assignment

Figure 6: File spectra 201 and 235 (from μ HPLC-FTIR analysis of THF Solubles fraction 2) and a static spectrum of N-methylaniline.

Figure 7: Carbonyl stretching region ($1800\text{--}1600\text{ cm}^{-1}$) for selected spectra obtained during the $\mu\text{HPLC-FTIR}$ run of THF Solubles fraction 2. Taken from files 190-255/

is that hydroxypyridine or a similar compound could be responsible for the IR absorbance in this region. Many of these types of compounds exist exclusively in the keto form. Enanmines such as tetrahydropyridine are known to be susceptible to reaction with oxygen as follows

A similar kind of reaction could well be occurring with THQ during liquefaction. Single injections of 2-hydroxypyridine and 4-hydroxypyridine support this assignment in that these results show that the compounds elute with retention times similar to those of compounds found in Files 190-217. Figure 8 shows the IR spectrum of 2-hydroxypyridine and 4-hydroxypyridine for comparison with File spectra 190 and 217.

The 1774 cm^{-1} band in Files 244-250 is higher in frequency than is seen in many types of carbonyl compounds and is therefore more easily assigned. Carbonylic materials expected to exhibit absorption in this region would include anhydrides, lactones, acid peroxides, and vinyl and phenyl esters. Anhydrides and acid peroxides have a second band around 1800 cm^{-1} . Both vinyl and phenyl esters have a band near 1210 cm^{-1} which these file spectra do not exhibit. A five-membered γ -lactone has a band at 1770 cm^{-1} . The presence of such a species is likely since THF was used to isolate the original sample. It is known that in the presence of coal-derived material THF adducts readily to the coal material and can be converted to γ -butyrolactone under rather mild conditions. A static IR spectrum of γ -butyrolactone is compared with File

Figure 8: Static IR spectrum of 2-hydroxypyridine and 4-hydroxypyridine and file spectra 190 and 217 from the μ EPLC-FTIR analysis of THF Solubles fraction 2.

spectrum 250 in Figure 9. Obviously, some of the extra IR bands in File 250 are due to another compound(s) eluting in the vicinity of the lactone. Additional support for this assignment comes from the observation that γ -butyrolactone exhibits, under the same chromatographic conditions, a chromatographic retention time that is consistent with the material giving rise to File 250.

To confirm assignments made on the basis of μ HPLC-FTIR as well as to gain additional information fraction 2 was subjected to field ionization mass spectrometry (FIMS). The sample was 100% volatile in the spectrometer in the temperature range employed (48-451°C). Spectra were collected over eight temperature ranges and these were then summed into one over-all spectrum. This composite spectrum is shown in Figure 10. FIMS produces unfragmented molecular ions and their isotopic peaks; therefore, a peak should represent one or more compounds having that particular molecular mass. The number average molecular weight is 328 for this fraction and the weight average molecular weight is 396. An overall ratio of odd to even mass peaks at 0.84 was calculated for this sample. It appears from this O/E ratio that almost half the material in fraction 2 contains an odd number of nitrogen atoms.

Table I presents the most intense mass peaks (counts > 20) for this fraction and their possible assignments. Some masses have several compound possibilities, but only reasonable assignments have been listed in the Table.

Examining the individual temperature ranges affords more information than an examination of the summed spectrum alone. Each temperature gives rise to a spectrum that is simpler than the composite spectrum since all the compounds are not present in each range. The first temperature range examined (48-83°C) has an O/E ratio of 4.36. Obviously, compounds having an odd number of nitrogen atoms dominate. The most intense peaks are THQ ($m/e = 133$) and

Figure 9: Comparison of file 250 (from μ HPLC-FTIR analysis of THF Solubles fraction 2 with γ -butyrolactone (static spectrum).

Figure 10: Summed FIMS spectrum of THF Solubles fraction 2.

TABLE I

Compound Identifications by FIMS for THF Solubles Fraction 2

Mass	Ion Counts	Identification
107	77	o-toluidine, lutidine, ethylpyridine, N-methylaniline
117	12	indole, propylpiperidine
121	28	ethylaniline, homologue of mass 107
129	131	quinoline
131	26	dihydroquinoline, 117 homologue
133	661	1,2,3,4-tetrahydroquinoline
134	72	indanol, C ₄ -alkylbenzene, 1,2,3,4-tetrahydroquinoxaline
135	30	homologue of mass 107
143	47	methylquinoline
145	28	hydroxyquinoline, 117 homologue
147	52	homologue of mass 133
149	11	homologue of mass 107
157	88	C ₂ -alkylquinoline
158	14	hexahydroacenaphthylene
159	11	homologue of mass 117
161	79	C ₂ -tetrahydroquinoline
162	13	C ₆ -alkylbenzene
171	15	C ₃ -alkylquinoline
175	18	C ₃ -tetrahydroquinoline
185	14	C ₄ -alkylquinoline
220	19	di-t-butylbenzoquinone
234	56	C ₄ -homologue of phenanthrene
248	37	homologue of mass 134
256	146	biquinolyl
260	1009

261	228
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Table I (continued)

Mass	Ion Counts	Identification
262	182
263	50
264	108
266	255
270	29	C ₁ -alkylbiquinolyl
274	104	homologue of mass 260 diphenylbenzoquinone
275	35	homologue of mass 261
276	58	homologue of mass 262
278	33	homologue of mass 264
280	59	homologue of mass 266
284	56	C ₂ -alkylbiquinolyl
288	151	C ₂ -homologue of mass 260
289	48	C ₂ -homologue of mass 261
290	61	C ₂ -homologue of mass 262
292	284	C ₂ -homologue of mass 264
294	66	C ₂ -homologue of mass 266
320	62	homologue of mass 264

quinoline ($m/e = 129$). These compound assignments can be confidently made (as opposed to the isomers 1,2,3,4-tetrahydroisoquinoline and isoquinoline) because of the information obtained from μ HPLC-FTIR. Also, from the FTIR analysis, N-methylaniline can be at least in part responsible for the peak at 107. The other possible isomers of $m/e = 107$ were not observed by FTIR.

FIMS on the other hand suggests the presence of compounds not indicated by FTIR. These include indole or propylpiperidine (m/e 117) and their homologues ($m/e = 131$), ethylaniline or a C_1 homologue of mass 107 ($m/e = 121$) and indanol ($m/e = 134$). Some compounds indicated by FIMS may also have been indicated in the FTIR analysis but a lack of model compounds and/or spectral library prevented exact assignment. For example, these might include homologues of THQ and quinoline ($m/e = 143, 147, 157, 161$). A hydroxyquinoline is suggested at mass 145 which supports an earlier assignment made via μ HPLC-FTIR.

In the second temperature range (87-110°C), in addition to compounds seen in the first temperature range, compounds of higher molecular weight are detected. The O/E ratio changes dramatically due to the nature of the compounds being volatilized during this temperature range. The O/E ratio is now 0.96. In the third temperature range (110-122°C) the O/E ratio decreases even further to 0.49. The mass peaks increasing most in intensity during the second and third temperature ranges are $m/e = 260-266$. With the exception of THQ, these peaks are the most intense ones in the FIMS summed spectrum. The suggested compounds for $m/e = 260-266$ are dimers of THQ and phenylquinoline-type compounds.

The presence of such compounds in coal liquefaction products has been previously speculated. It has been noted that nitrogen-containing

liquefaction solvents, while enhancing the liquefaction process by increasing the amount of soluble product, also produced non-distillable products and resulted in severe solvent loss. The suggestion was made that the liquefaction solvent was being incorporated into the coal structure or otherwise reacting to produce higher molecular weight materials. Various reactions have been postulated to produce compounds with molecular weights corresponding to the intense peaks in the FIMS spectra. For example a dihydroquinoline molecule, acting as an electrophile, may attack a THQ molecule, which acts as a nucleophile. The result is a dimer of THQ less two hydrogens (Figure 11A). Hydrogenated, dehydrogenated, and alkylated products of this dimer may also appear. It should be noted that a mass peak corresponding to dihydroquinoline appears in the mass spectrum. The reaction shown in Figure 11B illustrates nucleophilic attack by THQ on a hydroxyquinoline (keto form) to produce a biquinoline and a carbonyl compound. Reactions such as this may be one source of carbonyl compounds in this coal-derived fraction.

Unidentified IR spectra obtained by μ HPLC-FTIR can be associated with compounds of $m/e = 260-266$ found in the FIMS spectra. Model compounds are unavailable for exact assignment by either method. As mentioned previously, the alkylated homologues of "quinoline-like" dimers are also believed to be present in the FIMS spectra. This assignment is preferred for peaks at $m/e = 274, 276, 288, 289, 290, 292, 294, 302, 306, 320$.

In the higher temperature ranges, the O/E ratio approaches 1.00. This suggests that each high molecular weight species has been "tagged" with THQ. As seen from the summed spectrum in Figure 10, these high mass peaks ($> m/l = 320$) are not very intense. Such high mass peaks could be due to trimers of THQ and related compounds.

Figure 11: Possible reactions taking place during liquefaction with THQ as solvent.

A limited gas chromatography-mass spectrometry study was performed on this fraction. No new information was obtained since few compounds were detected due to non-volatility and irreversible adsorption of the basic nitrogen compounds to the GC column.

One method of qualitative analysis in liquid chromatograph is to compare the retention time of a component via two different LC methods. This has been called the retention-time cross-check technique. The two methods should involve two different separation mechanisms. If the retention time of a model compound on two different LC columns matches with the retention time of an unknown peak on those two systems, the chances of correctly identifying the unknown as that model compound is increased over the chances if only one LC method has been utilized.

Nitrogen model compounds were chromatographed on a normal phase system (NH_2 column with $\text{CDCl}_3:\text{CCl}_4 + 0.02\% \text{ TEA}$). Retention was found to be influenced by basicity and steric hindrance. These same model compounds were then chromatographed on a reversed phase system (250 mm x 4.6 mm IBM C_{18} column employing a mobile phase of 60:40 $\text{CH}_3\text{CN}:\text{H}_2\text{O} + 0.02\% \text{ TEA}$). Detection was by UV at 254 nm. Acetonitrile (CH_3CN) was chosen over methanol because of greater sample solubility in CH_3CN . Also, as in the normal phase system, triethylamine (TEA) was added to the mobile phase to prevent tailing. The retention-time cross-check technique was applied to the model compounds so that this method could then be used for coal-derived samples.

Reversed-phase chromatography is useful in this retention-time cross-check due to the fact that the retention mechanism in the reversed phase mode is very different from that in the normal phase mode. The separation of the thirteen model compounds on this reversed phase system is shown in Figure 12. The order of retention of the model compounds on this C_{18} column is

AZA-ARENE AND AMINE MODELS

Figure 12: Reversed phase separation of basic nitrogen compounds. C_{18} (250 x 4.5 mm) column; 60:40 $CH_3CN:H_2O$ + 0.02% TEA; 1 mL/min; UV detection (254 nm)

essentially reversed from the order on the NH_2 column.

Structural retention parameters which have previously been calculated in our laboratory for a C₁₈ column with MeOH:H₂O may be applied to obtain an idea of the mechanism at work here. The parameters must be applied with caution since they have not been verified with a mobile phase of CH₃CN:H₂O. The order of retention of the model nitrogen compounds can be predicted by this retention equation. Table II presents the predicted and actual retention times of the nitrogen models. Because the retention parameter equation was derived for a different system, the retention times do not agree exactly. However, the predicted order agrees essentially with the actual with some exceptions. Quinaldine and quinoline elute earlier than predicted while N-methylaniline and THQ elute later than predicted. The general agreement suggests that the same factors are at work in this chromatographic system as in the one discussed previously (MeOH:H₂O) from which the retention equation was derived. Compounds with a greater amount of hydrocarbon character (aromatic rings, aliphatic carbons) elute after compounds with a smaller amount of hydrocarbon character. The fact that 5,6- and 7,8-benzoquinoline have different retention times; whereas, the equation predicts identical times indicates the importance of steric hindrance in the overall separation mechanism (i.e. the unhindered nitrogen in 5,6-benzoquinoline is "free" to influence retention to a greater extent than the hindered nitrogen in 7,8-benzoquinoline).

Several other model compounds were singly injected in order to gain more information concerning retention on the reversed phase system (Table III). As is to be expected, retention increases as the number of aromatic rings increases. One ring nitrogen heterocyclic compounds eluted before 5 minutes, two ring nitrogen heterocyclic compounds eluted at (or a short time after) 5

TABLE II

Predicted^a vs Actual Retention Behavior of Basic Nitrogen Models on a Reversed Phase Chromatographic System

Model ^b	Actual R.T. ^c	Predicted R.T. ^c
13. Pyridine	3.10	3.26
11. Aniline	3.42	3.30
12. 3-Picoline	3.51	3.62
8. Quinoline	3.79	5.62
4. o-Toluidine	4.05	3.69
6. Quinaldine	4.12	6.89
10. 2,3-Cyclohexenopyridine	4.31	5.78
7. 4-Azafluorene	4.69	6.89
1. N-Methylaniline	4.79	3.69
5. 2-Benzylpyridine	4.80	6.89
9. 5,6-Benzoquinoline	5.42	7.33
3. 1,2,3,4-tetrahydroquinoline	5.60	4.82
2. 7,8-Benzoquinoline	7.65	7.33

^aPredicted values calculated with the structural parameter equation

^bListed in order of increasing retention

^cRetention Time, Minutes

TABLE III

Retention Behavior of Representative Basic Nitrogen
Compounds and Phenols on a Reversed Phase System

Compound	Retention Time, Minutes
<u>One ring azaarenes</u>	
2,7-Dimethylquinoline	4.89
4-Ethyl-3-methylpyridine	4.50
2,6-Lutidine	3.50
2-Ethylpyridine	3.80
8-Methylquinoline	5.18
<u>Two ring azaarenes</u>	
3-Phenylpyridine	4.65
2-Phenylpyridine	5.15
4-Phenylpyridine	4.80
<u>Other azaarenes</u>	
Acridine (3 rings)	5.48
1,10-Phenanthroline (3 rings, 2 N atoms)	4.78
4-Piperidinopyridine (2 rings, 2 N atoms)	7.75
Dibenzacridine (5 rings)	19.10
<u>Indoles</u>	
Indole	4.82
2-Methylindole	5.5
<u>Phenols</u>	
Phenol	3.28
o-Cresol	4.00
β -naphthol	4.03
1-Indanol	3.65
4-t-butylphenol	5.73
2,4-Di-t-butylphenol	Not eluted
2,6-Di-t-butylphenol	Not eluted
2-t-butyl-4-methylphenol	Not eluted
Hydroxypyridine	2.48
8-Hydroxyquinoline	4.0
Anthraquinone	8.00

minutes and a nitrogen heterocycle with 5 aromatic rings eluted at 19 minutes. Weakly basic nitrogen compounds, indoles, also eluted around 5 minutes. Simple phenols eluted early (<4 minutes) while hindered phenols (e.g. 2,6-di-*t*-butylphenol) would not elute from the column. Hydroxypyridine eluted very early (2.5 minutes) while hydroxyquinoline eluted at 4 minutes and tailed significantly. A quinone eluted at 8 minutes. These guidelines have been useful in gaining information concerning components in the THF solubles and residue samples.

Fraction 2 was chromatographed on a reversed phase system under identical conditions as the nitrogen model compounds (Figure 13). The sample was injected onto the column in 100% CH₃CN. The sharp peaks at 1.85 and 2.00 minutes are solvent peaks instead of peaks due to sample components. The peaks labeled "a" and "b" are quinoline and THQ respectively. The peak labeled "c" has the retention time of both *N*-methylaniline and indole. FTIR indicated the presence of *N*-methylaniline; while, the presence of indole was suggested by mass spectral methods. The peak labeled "d" has a retention time near both *o*-toluidine and quinaldine. FIMS indicated the presence of a methylquinoline (e.g. quinaldine). Other model nitrogen compounds eluted with retention times similar to the peaks observed in Figure 13; however, it is difficult to make assignments on the basis of retention time alone. The nitrogen models in Figure 12 eluted before a retention time of 8 minutes; fraction 2 has several peaks eluting after this time. The late eluting (after 10 minutes) compounds in fraction 2 are obviously large ring systems similar to dibenzacridine, a five ring heterocycle which eluted at 19 minutes. No doubt some of the late peaks are due to the THQ dimer and related compounds which were indicated from FIMS. Table IV lists the predicted retention times of the compounds which have been suggested for *m/e* = 260-264 and 266. These

Figure 13: Reversed phase separation of THF Solubles fraction 2.

TABLE IV

Retention Times of Compounds with Masses 260-266

Compound (Mass)	Predicted R.T. ^a
(260)	15.8
(261)	24.0
(262)	11.6
(263)	29.6
(264)	12.5
(266)	13.0

^aRetention Time, minutes; predicted retention times calculated from structure parameter equation

predicted values are a result of applying the structural retention parameters alluded to earlier. While these values are approximate, it can be seen that THQ dimer-like compounds are predicted to elute in the region where several late peaks are seen in the chromatogram.

In summary, fraction 2 contains large amounts of THQ, quinoline and alkyl-substituted quinolines. Compounds such as N-methylaniline, indole and γ -butyrolactone were also found. Carbonyl species of the "hydroxypyridine-type" are believed to be present. Compounds corresponding to a THQ dimer and its various homologs are indicated by FTIR and FIMS.

FRACTION 3

THF soluble fraction 3 was eluted from the preparative column with chloroform. With the stronger solvent, phenolic compounds eluted as evidenced by the static spectrum (Figure 2). Fraction 3 was subjected to μ HPLC using a microbore NH_2 column with 100% CDCl_3 + 0.02% TEA. This mobile phase is stronger than the one used for fraction 2 and should be better able to elute strongly retained components. This anticipated result was not realized. The same compounds which were identified in fraction 2 were found in fraction 3. Even though an OH stretch at 3599 cm^{-1} is seen in the static IR of fraction 3, no OH stretching band was observed in the μ HPLC-FTIR run. Any OH containing compounds probably failed to elute from the column suggesting that the OH group in these materials is not highly hindered. Clearly a different type of chromatographic separation is needed here in order to detect other types of chemical species. The appearance of THQ and quinoline in fractions 2 and 3 is puzzling. Some carry-over from fraction 1 could account for this since the capacity of the preliminary column is low. Alternatively if most coal-derived products are adducted with basic nitrogen compounds, it seems conceivable

that dissolution in CDCl_3 and separation on an amino column could cause significant dissociation of some of the adduct.

Fraction 3 was also chromatographed on a reversed phase system as was fraction 2 (Figure 14). Both fractions appear to be quite similar. Comparing the two chromatograms, it is seen that fraction 2 is more complex than fraction 3. Fraction 2 has a greater number of components eluting throughout the entire chromatogram. Fraction 2 also appears to have more late eluting components (>10 mL) than fraction 3. FIMS was not performed on fraction 3. A good comparison of the various preparative fractions insofar as FIMS is concerned can be found in the residue discussion (vide infra).

ANALYSIS OF FRACTIONS OF RESIDUE

The solubility of P-24 residue in CHCl_3 was 60%. In order to provide simpler fractions of the residue a preliminary preparative separation on a small NH_2 column was undertaken. Fractions 3, 4, and 5 which were eluted with 50:50 $\text{CHCl}_3:\text{CCl}_4$, CHCl_3 , and 50:50 $\text{CHCl}_3:\text{MeOH}$ respectively, were chosen for detail study.

FRACTION 3

The static infrared spectrum of fraction 3 in Figure 15 shows an OH stretch at 3603 cm^{-1} and a NH stretch at 3442 cm^{-1} . There are also carbonyl bands in the range $1690\text{--}1658\text{ cm}^{-1}$. There is an intense methylene aliphatic CH stretch which suggests the presence of alkyl side chains on aromatic rings.

Fraction 3 has been chromatographed on an NH_2 column (Figure 16). For $\mu\text{HPLC-FTIR}$ analysis, the mobile phase was 100% CDCl_3 + 0.02% TEA. FTIR detection reveals only three peaks; whereas, more sensitive but less informative UV detection suggested numerous eluting materials. The first peak, whose maximum (File 170) has the IR spectrum shown in Figure 17. There

Figure 14: Reversed phase separation of THF Solubles fraction 3.

Figure 15: Static infrared spectra of Residue fractions 3, 4 and 5 in CDCl_3 , 0.2 mm pathlength cell.
A=Fraction 3; B=Fraction 4; C=Fraction 5.

Figure 16: Separation of Residue fraction 3. NH_2 column, 50 cm x 1 mm i.d.; 100% CDCl_3 + 0.02% TEA; 30 $\mu\text{L}/\text{min}$; A=UV detection (254 nm); B=FTIR detection.

Figure 17: File spectra (170, 195, 206) from the μ HPLC-FTIR analysis of Residue fraction 3.

are intense methylene CH stretching bands at 2931 cm^{-1} and 2857 cm^{-1} . There is a small amount of aromatic CH stretching and also a band at 1600 cm^{-1} which is indicative of an aromatic ring. Methyl CH stretches are weak; a band at 1379 cm^{-1} is attributable to a symmetric methyl bending vibration. A carbonyl band centered at 1702 cm^{-1} could be due to a ketone. The component(s) represented in this file spectrum elutes earlier than any of the basic nitrogen models. Figure 17 shows the spectrum corresponding to the next peak, File 195. This is a spectrum of THQ again. This spectrum also contains bands that are not due to THQ. The band at 1620 cm^{-1} is perhaps indicative of a quinoline compound. File spectrum 206 (Figure 17) corresponding to the third peak is quite intense, with sharp bands.

In order to gain more information on the components in these three peaks, fractions were collected from the column during a HPLC run and direct-probe electron impact mass spectra were obtained for these fractions. The fraction giving rise to the spectrum in File 206 shows peaks at $m/e = 256-260$. It would appear from these data that the spectrum in File 206 is that of the THQ dimer or a related compound. Unfortunately, lack of an authentic sample of the THQ dimer prevents a direct comparison of infrared spectra. Figure 18 presents a static spectrum of 4-piperidinopyridine for comparison to File 206. This model compound is similar in structure to the THQ dimer compound. Its FTIR spectrum also bears resemblance to the spectrum in File 206. The FTIR spectrum of the last peak (File 276) is presented in Figure 19 with the spectrum of o-ethylaniline which appears to be a reasonable visual match.

Although the static IR spectrum of fraction 3 has an OH stretch at 3603 cm^{-1} , such a band was not seen in any file spectrum from the μ HPLC-FTIR run suggesting that phenolic compounds did not elute from the column or they were too dilute to be detected by FTIR. We believe that they did not elute since

Figure 18: Comparison of file 206 (from μ HPLC-FTIR analysis of Residue fraction 3) with the static spectrum of 4-piperidinopyridine.

Figure 19: Comparison of file 276 (from μ HPLC-FTIR analysis of Residue fraction 3) with the static spectrum of o-ethylaniline.

the OH functionality would be adsorbed strongly by the column NH_2 functionality.

Residue fraction 3 was also analyzed by FIMS. The sample was 100% volatile at the operating temperatures of the instrument (57-450°C). The number average molecular weight was 467.5 and the weight average molecular weight was 520.5. These numbers are substantially higher than were seen for the THF solubles sample. The summed mass spectrum is presented in Figure 20. Compared to residue fractions 4 and 5, this spectrum is relatively simple (vide infra). The most intense peaks are centered around $m/e = 250-300$ and $m/e = 385-400$. The over-all ratio of odd to even mass peaks is 0.90 suggesting that almost half the material contains an odd number of nitrogen atoms.

Table V lists the most intense mass peaks and possible identifications. In general, the same components in THF solubles fraction 2 are also seen in residue fraction 3 but the proportions differ greatly. In the first temperature range scanned (57-121°C), the mass peaks below $m/e = 256$ are very weak in intensity. These include $m/e = 117, 129, 131, 133, 155, 156, 234$. Neither $m/e = 155$ (possibly phenylpyridine) or $m/e = 156$ (possibly dimethylnaphthalene or bipyridyl) was present in THF solubles fraction 2. The most intense peaks occur after $m/e = 255$. These include $m/e = 256, 257, 260, 261, 262, 263, 264, 266, 267, 274, 276, 284, 288, 289, \text{ and } 290$.

It is interesting to note that in residue fraction 3 there is 45 times more component of $m/e = 260$ than there is THQ ($m/e = 133$). In THF solubles fraction 2 there was only 2 times more component of $m/e = 260$ than of THQ. It appears therefore that the majority of the THQ has been incorporated into the residue. In the first temperature range, the ratio of odd to even mass peaks is 0.48; this is due to the fact that the most intense peaks ($m/e = 260, 262,$

Figure 20: Summed FIMS spectrum of Residue fraction 3.

TABLE V

Compound Identifications by FIMS for Residue Fractions 3, 4, and 5.

Mass	Ion 3	Counts 4 5		Identification
107	60	96	247	o-toluidine, lutidine, ethylpyridine, N-methylaniline
108	0	27	107	methylphenol
109	0	13	31	hydroxymethylpyridine
117	76	25	61	indole, C ₃ -piperidine
119	39	41	59	indoline, allylpyridine
121	28	36	109	ethylaniline, homologue of mass 107
122	0	19	88	C ₂ -alkylphenol
123	0	13	30	homologue of mass 109
127	0	14	88	C ₄ -piperidine
129	64	53	238	quinoline
131	66	58	75	dihydroquinoline or 117 homologue
133	54	42	68	1,2,3,4-tetrahydroquinoline
135	24	28	81	homologue of mass 107
136	0	18	67	C ₃ -alkylphenol
137	19	12	24	homologue of mass 109
143	67	53	180	methylquinoline
145	33	29	74	hydroxyquinoline, 117 homologue
147	23	23	51	C ₁ -tetrahydroquinoline
149	18	17	38	homologue of mass 107
150	0	13	47	C ₄ -alkylphenol
155	52	40	93	phenylpyridine
156	50	21	100	bipyridyl or dimethyl naphthalene
157	42	36	137	C ₂ -alkylquinoline
159	22	25	57	C ₂ -homologue of mass 117
161	25	20	42	C ₂ -tetrahydroquinoline
169	21	18	44	C ₁ -phenylpyridine
170	28	15	49	phenylphenol of 156 homologue
171	31	27	83	C ₃ -alkylquinoline
173	21	25	58	C ₃ -homologue of mass 117
175	20	19	49	C ₃ -tetrahydroquinoline
185	22	31	58	C ₄ -alkylquinoline
220	45	69	104	di-t-butylbenzoquinone, C ₉ -hydroxybenzene

Table V (continued)

Mass	Ion 3	Counts 4 5		Identification
221	32	37	97	hydroxyphenylquinoline
226	25	33	149	homologue of mass 170
234	134	58	111	homologue of mass 220
240	59	49	223	homologue of mass 170
248	110	77	195	homologue of mass 234
254	49	54	320	homologue of mass 170
256	682	186	275	biquinolyl
257	188	71	155	benzylcarbazole
260	2459	358	189
261	725	147	193
262	1977	385	486
263	493	193	269
264	325	111	282
266	624	130	373
268	104	89	391	homologue of mass 170
270	185	98	211	methylbiquinolyl
274	391	187	202	homologue of mass 260
275	145	138	188	homologue of mass 261
276	372	141	340	homologue of mass 262
277	138	140	225	homologue of mass 263
278	123	106	344	homologue of mass 264
280	130	122	412	homologue of mass 266

Table V (continued)

Mass	Ion 3	Counts 4	5	Identification
282	101	104	395	homologue of mass 170
284	360	135	253	C ₂ -alkylbiquinolyl
288	666	206	252	C ₂ -homologue of mass 260
289	247	181	215	C ₂ -homologue of mass 261
290	568	185	369	C ₂ -homologue of mass 262
291	201	152	231	C ₂ -homologue of mass 263
292	159	108	306	C ₂ -homologue of mass 264
294	158	106	387	C ₂ -homologue of mass 266
298	168	126	234	C ₃ -alkylbiquinolyl
387	379	258	397	Homologue of mass 261
389	565	373	410	homologue of mass 263
390	335	264	385	homologue of mass 264
395	405	322	355	THQ trimer

266) contain two nitrogen atoms. Above 121°C, there are no peaks detected below $m/e = 258$. Above 166°C, all the components in the range $m/e = 260-266$ have been volatilized. Peaks of moderate intensity are detected up to $m/e = 806$ as compared to $m/e = 320$ for THF solubles fraction 2. As the temperature increases further, higher mass peaks of moderate to weak intensity are detected.

The ratio of odd to even mass peaks increased from 0.48 in the first temperature range to 1.10 at 200°C and then decreased slightly to 0.97 by the end of the analysis (450°C). These values again indicate a high degree of nitrogen incorporation into the coal structure. The most intense high mass peaks are $m/e = 387, 389, 390, 391, 393, 394, 395$, and 420. Some of these species may be possible homologues of the components of mass 260-266 or a THQ trimer at mass 395.

Both methyl naphthalene and dimethyl naphthalene have been indicated from FIMS and GC-MS measurements as being present in fraction 3. The presence of such compounds in this sample is surprising in view of the fact that distillation (+825°F) was performed on the process solvent/residue mixture. It would be expected, therefore, that compounds such as these would have been lost during distillation. However, during the distillation, compounds apparently become "trapped" in the "tar-like" mixture and are not completely removed by distillation. It is also surprising to find nonpolar compounds in fraction 3 which were eluted from an NH_2 preparative column with 50:50 $CHCl_3:CCl_4$. A compound such as dimethyl naphthalene would be expected to appear in an earlier fraction. The appearance of such compounds in this fraction suggests either severe overload of the column or an adduction of these compounds to material which elutes in this fraction.

In summary, residue fraction 3 contains a small amount of THQ and

quinoline and a large amount of material in the range $m/e = 260-266$ which is suspected to be THQ dimer compounds. This fraction contains a greater amount of THQ dimer compounds than THF solubles fraction 2. Also in contrast to THF solubles fraction 2, residue fraction 3 contains compounds such as phenylpyridine, dimethyl naphthalene and a small amount of phenolic material in addition to alkyl quinolines.

FRACTIONS 4 AND 5

Fractions 4 and 5 were eluted from the preparative column with CHCl_3 and 50:50 CHCl_3 :MeOH, respectively. Figure 15 presents the static IR of these fractions which appear to be quite similar to each other. FIMS, however, shows that some fractionation of components has occurred. Fractions 4 and 5 both contain OH functionality. A weak NH stretch around 3400 cm^{-1} is suggested in fraction 4; this band appears to be absent in fraction 5. Both fractions have bands in the carbonyl region with fraction 5 exhibiting a sharp band at 1710 cm^{-1} .

Fraction 4 is totally soluble in CHCl_3 while fraction 5 is not. Therefore only the soluble portion of each fraction was chromatographed and analyzed. Both fractions were chromatographed on a 50 cm microbore NH_2 column with a mobile phase of 100% CDCl_3 + 0.02% TEA. The chromatograms of fractions 4 and 5 reveal that only a small amount of material is eluting from the column since the UV detector was operated at its most sensitive setting. Both chromatograms are very similar to that found for fraction 3 (Figure 21). Obviously, some of the same components present in fraction 3 are also present in fractions 4 and 5, although in a very reduced amount. It will be seen (vide infra) that fractions 4 and 5 do contain some additional high molecular weight components although these components do not appear to be eluting from the chromatographic system employed here.

Figure 21: Separation of Residue fractions 4 and 5. NH_2
column, 50 cm x 1 mm i.d.; 100% CDCl_3 + 0.02%
TEA; 30 $\mu\text{L}/\text{min}$; UV detection (254 nm);
A=Fraction 4; B=Fraction 5.

Fractions 4 and 5 were then separated with FTIR detection on two chromatographic systems one of which was designed to separate basic nitrogen (see above) and the other to separate phenolic materials. Only a small amount of material eluted in each case therefore detection by FTIR was difficult due to a small signal to noise ratio. Unfortunately, the IR spectra obtained for either fraction did not contain much information. The FIMS spectra for fractions 4 and 5 are shown in Figures 22 and 23, respectively. Fraction 4 was 93% volatile at the probe temperatures employed for the experiment (64-450°C), while fraction 5 was only 58% volatile.

Fraction 4 has a number average molecular weight of 496 and a weight average molecular weight of 543. The overall ratio of odd to even mass peaks is 1.04 which is higher than for fraction 3. This ratio suggests that solvent nitrogen has been widely incorporated into the coal structure. In fraction 3, it was seen that components having masses in the range $m/e = 258-266$ were concentrated. In fraction 4, there is a more even distribution of components up to $m/e = 806$. Table V provides a list of the most intense mass peaks for fraction 4. Some of the components with $m/e = 258-266$ associated with the THQ dimer have been carried over into fraction 4. A rather intense peak is seen at 395 which may correspond to a THQ trimer.

The FIMS spectrum for fraction 5 is shown in Figure 23. The number average molecular weight is 399 and the weight average molecular weight is 440. The two summed spectra for fraction 4 and 5 are very similar except that fraction 4 has a greater amount of high molecular weight material (greater than $m/e = 500$). The overall ratio of odd to even mass peaks is 0.91. Fraction 5 has all the compounds that are listed in Table V for fraction 4. In addition there are peaks at the following masses: $m/e = 108$, methylphenol; $m/e = 122$, C₂-phenol; $m/e = 170$, phenylphenol.

Figure 22: Summed FIMS spectrum of Residue fraction 4.

Figure 23: Summed FIMS spectrum of Residue fraction 5.

Examination of the individual mass spectra from each temperature range revealed a very low ratio of odd to even mass peaks at the first two temperature ranges (74-127°C and 132-168°C). In previous samples, low O/E mass ratios have been postulated to be caused by high amounts of THQ dimer components which have two nitrogen atoms and therefore an even molecular weight. That is not the case here since in the first two temperature ranges the mass peaks for the THQ dimer and related components are low in intensity. Instead, the low O/E mass ratio is probably due to a wide range of even molecular weights. The identity of these even molecular weight components could be phenolic material.

In conclusion many compounds have been identified in residue fractions 3, 4 and 5 by employing both chromatographic and spectrometric methods. The major components in fraction 3 are the THQ dimer and related compounds and alkylated products of THQ. This sample also contains alkyl pyridines, quinolines, biquinolines, and tetrahydroquinolines. Fractions 4 and 5 appear to contain the same compounds as fraction 3, although in different amounts. Both these fractions have a greatly reduced amount of THQ dimer and related homologues. Both fractions also have a series of pyridines and quinolines.

It is interesting to note that fraction 5 has a greater amount of relatively low molecular weight compounds than fractions 3 and 4. For example, fraction 5 has a greater relative amount of ethylpyridine ($m/e = 07$), quinoline ($m/e = 129$), methylquinoline ($m/e = 143$) and C₂-quinoline ($m/e = 157$). Also, both FTIR and FIMS suggest a greater amount of phenolic content upon going from fraction 3 to fraction 5. FTIR spectra did not contain any OH stretching modes for fraction 3 or 4. FIMS indicated an absence of simple OH compounds in fraction 3 with the exception of hydroxypyridine ($m/e = 145$) and possibly phenylphenol ($m/e = 170$). However, indications from FIMS are that

both fractions 4 and 5 contain such phenols as cresol and phenylphenol with fraction 5 containing more phenolic material than fraction 4. HPLC-FTIR also indicated the presence of phenolic material in fraction 5.

Each method used in this work did not analyze the entire sample. Fractions 3 and 4 were totally soluble in the liquid chromatographic solvents but all components did not elute under the conditions employed. A portion of fraction 5 was not analyzed by HPLC-FTIR due to incomplete solubility in the mobile phase. High molecular weight material in fraction 3 (>200) was not successfully handled by the GC-MS analysis due to low volatility and a non-optimum column. Although fraction 3 was 100% volatilized during analysis by FIMS, fractions 4 and 5 were not.