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ABSTRACT

With the recent increase in concern for environmental issues and the implication of sulfur and nitrogen in coal combustion products as prime causes of acid rain, it has become clear that there is an urgent need for alternative methods for determining the nature of organic sulfur and nitrogen compounds in coal. The present study couples mild oxidative and reductive procedures to enhance the depolymerization of coal and its constituent macerals and the quantities of products amenable to analysis. The study also seeks to apply the degradative techniques to coal asphaltenes, since they are polymeric structures similar to the whole coal, but smaller and more readily analyzed.

During the last quarter sporinite, vitrinite and semi-fusinite single macerals were separated from the IBC 101 coal by the density gradient technique. In addition, a gel permeation chromatography (GPC) system was assembled and the GPC column calibrated with four polystyrene molecular weight standards.

A variety of sulfur compounds were identified in the dichromate oxidation products of the IBC101 coal, including a thiazole and isomers of C2-, C3- and C4-alkyl thiophene carboxylic acids. Precise agreement between GC-MS and FPD chromatograms were obtained for these compounds. These compounds probably originated as short alkyl chains on exterior portions of the original peat macromolecular structures and were sulfurized by H_2S shortly after burial. Thus the dichromate oxidation appears useful for the characterization of sulfur compounds. Unfortunately, this treatment yields only small amounts of products, but the reaction is relatively mild. On the other hand the peroxyacetic acid gives a very good yield in only a single step, but seems to be very degradative.

It was difficult to isolate the products after lithium aluminum hydride reduction of oxidation products. It is believed that this is due to the formation of polyalcohols from polycarboxyl compounds. However polyalcohols were successfully converted to their parent hydrocarbons by the LAH reduction of tosylate intermediates. This allows for much easier separation and characterization and leads to enhanced elucidation of coal structures.

To test the hypothesis that asphaltenes are similar in structure to their parent coal, IBC101 asphaltenes and the extracted coal were subjected to PAA oxidation and analytical pyrolysis. The PAA products as well as the pyrolysates show very good correlation. This indicates a very strong relationship between the organic structure of the coal and that of the asphaltenes derived from them.

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EXECUTIVE SUMMARY

With the recent increase in concern for environmental issues, there has been a shift in emphasis away from the determination of carbon structures in fossil fuels to the characterization of heteroatom structures, especially those containing organic sulfur and nitrogen. This has resulted in the development of a number of analytical techniques selective for sulfur and nitrogen. However, these techniques often produce conflicting data and consequently they are not universally accepted within the scientific community. Thus, there is an urgent need for alternative methods for characterizing organic sulfur and nitrogen compounds in coal. The present study undertakes a combination of oxidation and reduction techniques for the enhanced depolymerization of coal while increasing the quantities of products amenable to gas chromatographic techniques. In particular, the goal is to simplify oxidation/reduction products by reducing COOH and OH groups back to the hydrocarbon backbone. In addition to enhancing the quantities of GC amenable products, this would allow for liquid chromatographic separation of degradation products and allow for more compound identification via mass spectral computer library searches. This study also seeks to apply the degradative techniques developed on whole coal and macerals, to coal asphaltenes which are believed to be polymeric structure similar to the whole coal but smaller and more readily analyzed.

Three high sulfur coals have been obtained for investigation in this study. However, the majority of the research effort will concentrate on a sample of Herrin No.6, (IBC 101) coal, obtained from the Illinois Geological Survey Sample Bank. The other coal samples under investigation are the Rasa Coal from Pakistan and a Spanish lignite (Lignito De Mequinenza). These latter two coals have a much higher organic sulfur content than the Illinois coal. This makes for much easier detection and characterization of organic sulfur structures. Thus, it is anticipated that by comparing the degradation products of the Illinois coal with those of the higher sulfur coals, a much better understanding of the sulfur chemistry of the Illinois coal will be obtained.

Maceral separation of the IBC 101 coal led to the accumulation of 9 grams of liptinite concentrate, 150 grams of vitrinite concentrate and 25 grams of inertinite concentrate. From these concentrates sporinite, vitrinite and semi-fusinite single macerals were separated. A gel permeation chromatography (GPC) system was assembled from purchased units and the GPC column calibrated with four polystyrene molecular weight standards. The calibration curve obtained by plotting the elution time against the log of the molecular weight is virtually identical to that specified by the manufacturers of the GPC column.

Methylated dichromate and peroxyacetic acid oxidation products of IBC101 floated coal and Spanish lignite were analyzed by GCMS and GC-FPD to determine the distribution of their sulfur compounds. To identify the sulfur compounds by mass spectrometry, retention time equivalency had to be established between GCMS and the GC-FPD. The resulting GC-FPD analysis indicated that the three samples have two common sulfur products : methylsulfonic acid and ethylsulfonic acid.

A variety of more complex sulfur compounds were identified in the di-chromate oxidation products of the IBC101 coal, including a thiazole and, most interestingly, a series of a homologues and isomers of thiophenecarboxylic acid. The thiazole was probably trapped in the coal matrix, protecting it from oxidation. Three principal peaks with strong m/z 169 ions closely match the corresponding three peaks on the FPD trace. These are identified as the methyl esters of ethylthiophene carboxylic acid, methyl ether. Similarly, two principal

peaks having strong m/z 183 also correspond to two peaks on the FPD trace. These are identified as higher homologues, having a C3-alkylthiophene core. Peaks having a m/z 197 ion are much weaker and it was difficult to find their match on the FPD chromatogram. Nonetheless, they represent a continuation of the homologous series to compounds with a C4-alkylthiophene core. This group may collectively be termed the alkylthiophene carboxylic acids (ATCA). The discovery of the ATCA compounds is significant, as for the first time a sulfur compound can be recognized on a total ion chromatogram (TIC) of oxidation products. The ATCA compounds probably originated as short alkyl chains on exterior portions of the original peat macromolecular structures and were sulfurized by H_2S shortly after burial of the peat.

The dichromate oxidation seems to be an interesting reaction for the characterization of sulfur compounds. Unfortunately this treatment yields only small amounts of products in each step and the procedure must be repeated multiple times until all the reactive organic matter is consumed. However, the reaction is relatively mild. On the other hand the peroxyacetic acid gives a very good yield in only a single step, but this method seems to be very degradative. The GC-FPD and GCMS data for peroxyacetic acid oxidation products do not indicate the presence of the ATCA compounds identified in the dichromate products. Since the peroxyacetic acid is a very strong oxidant, the thiophenes may have been destroyed.

As reported previously it was difficult to separate part of the reduced organic matter from the inorganic products derived from the lithium aluminum hydride (LAH). It is anticipated that the reasons for the poor recoveries of organic matter concern the polycarboxyl groups present in the oxidation products. When these functional groups are reduced by LAH they form polyalcohols. Such compounds are readily soluble in both water and organic solvents and can transport inorganic ions between organic and aqueous phases.

To address this problem the polyalcohols were converted to their tosylated derivatives and then reduced with lithium aluminum hydride. Although detailed analysis of the products has not yet been completed, a homologous series of alkanes and some alkyl aromatic compounds have been detected. The only way that these compound could have been formed is via the successful reduction of the tosylates intermediates back to the parent hydrocarbon structure. Thus it appears possible to convert the polycarboxyl compounds often found in oxidation products into their parent hydrocarbon structure. This allows for much easier separation and characterization which should lead to enhanced elucidation of coal structures.

To test the hypothesis that asphaltenes are similar in structure to their parent coal, we subjected IBC101 asphaltenes (from a THF extract) and floated, THF-extracted coal to peroxyacetic acid (PAA) oxidation and analytical pyrolysis. The total ion chromatograms of the methylated PAA products show a very good correspondence in short chain compounds as well as with benzenetri- and benzenetetracarboxylic acids. In addition, the pyrolyzates are remarkably similar for the two samples, indicating a close structural correspondence. The salient features include 1) similar quantities of gas (methane-butane), 2) similar amounts of aromatic hydrocarbons, 3) dominance by phenols and 4) similar distributions of longer chain hydrocarbons (C14-C22).

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OBJECTIVES

The overall objective of this study is to continue the characterization of organic sulfur and nitrogen compounds in coal with greater thoroughness than has previously been attempted. The specific goals are:

1. To couple mild oxidative and reductive procedures to enhance the mild depolymerization of coal and improve the quantities of products amenable to gas chromatography techniques.
2. To study three oxidative and three reductive techniques separately and then as combined oxidative/reductive strategies.
3. To concentrate the analysis on the Herrin No.6 (IBC 101) coal and its component macerals.
4. To compare sulfur and nitrogen compounds identified with those detected in the oxidation products from peroxyacetic acid oxidation.
5. To simplify oxidation/reduction products by reducing COOH and OH groups back to the hydrocarbon backbone. This would enhance the quantities of GC amenable products, allow for liquid chromatography separation of degradation products and allow for more compound identification via computer library searches.
6. To apply the degradative techniques developed on whole coal and macerals to coal asphaltenes, since they are believed to be polymeric structures similar to the whole coal, but smaller and more readily analyzed.

INTRODUCTION AND BACKGROUND

Essential to the development of successful sulfur and nitrogen removal technologies is the need to characterize the different forms of organic sulfur and nitrogen that occur in coal. Only when this has been done will it be possible to design the required technologies for their effective removal. Research in this area has brought a good understanding of the lighter sulfur and nitrogen species in coal extracts and oils but those species identified only account for a very small percentage of the total organic sulfur and nitrogen in the coals. Several new techniques have been used to investigate the total organic sulfur/nitrogen in coal, but these methods often rely on rather harsh pyrolysis conditions leading to the possibility of erroneous assignments. Consequently reliable methods for the characterization of organic sulfur/nitrogen in coal are severely lacking.

Oxidative and reductive techniques have been used extensively in attempts to elucidate the organic structure of complex organic solids such as coals, kerogens, humic acids and many other fossil fuel materials. In the vast majority of these studies the emphasis was to determine the carbon backbone of these materials and as a result very little information regarding the structures of heteroatom components was provided. This is especially true for organic sulfur and organic nitrogen species which are typically in low concentrations when compared to hydrocarbon structures.

With the recent increase in concern for environmental issues, there has been a shift in emphasis away from the determination of carbon structures in fossil fuels to the characterization of heteroatom structures, especially those containing organic sulfur and nitrogen. This has resulted in the development of a number of analytical techniques selective for sulfur and

nitrogen. However, these techniques often produce conflicting data and consequently they are not universally accepted within the scientific community. Thus, there is an urgent need for alternative methods for characterizing organic sulfur and nitrogen compounds in coal. The present study undertakes a combination of oxidation and reduction techniques for the enhanced characterization of organic sulfur and organic nitrogen in coal.

RESULTS AND DISCUSSION FOR THIS QUARTER

Samples

Three high sulfur coals have been obtained for investigation in this study. The majority of the research effort will concentrate on a sample of Herrin No.6, (IBC 101) coal, obtained from the Illinois Geological Survey Sample Bank. The other coal samples under investigation are the Rasa Coal from Pakistan and a Spanish lignite (Lignito De Mequinenza). These latter two coals have a much higher organic sulfur content than the Illinois coal. This makes for much easier detection and characterization of organic sulfur structures. Thus, it is anticipated that by comparing the degradation products of the Illinois coal with those of the higher sulfur coals, a much better understanding of the sulfur chemistry of the Illinois coal will be obtained.

Sample Preparation

Demineralization of Spanish Lignite:- Insufficient demineralization of the Spanish Lignite sample was obtained using standard procedures with the acid treated sample still containing over 30% ash. To demineralize the sample further additional HF and HCl treatments were employed using longer contact times and periods of ultrasonic agitation. TGA ash and moisture analysis of the product treated in this way gave a dry ash content of 2.61% indicating successful demineralization had been obtained.

Maceral Separation.:- The separation of the demineralized and micronized IBC 101 coal into liptinite, vitrinite and inertinite maceral groups was completed during the last quarter. The demineralization was performed on 200g of coal using HF and HCl. The yield of demineralized coal was 189.5g, this corresponding to a loss of 5.3% on a weight basis. The density cut points for the maceral group separations were identified from the density gradient profile as shown in the previous quarterly report. The liptinite/vitrinite cut point was taken at a density of 1.2350 g/mL and the vitrinite/inertinite cut point was taken at a density of 1.3200g/mL. This separation led to the accumulation of 9 grams of liptinite concentrate, 150 grams of vitrinite concentrate and 25 grams of inertinite concentrate. The inertinite concentrate contained pyrite and other acid insoluble minerals. This mineral matter was separated from the inertinites by centrifugation at a density of 1.6g/mL.

The liptinite, vitrinite and inertinite maceral concentrates where then examined individually by the DGC technique using a narrower density range. The increased resolution obtained, enabled the identification of individual macerals on the density profile. Using this information, new cut points were established for the separation of sporinite, vitrinite and semi-fusinite from

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the corresponding concentrates. The single macerals obtained have been submitted for elemental, ash and moisture analysis. Task 1, sample preparation, is complete.

Gel permeation chromatography.

A gel permeation chromatography (GPC) system was assembled from purchased units. The units concerned are a Scientific Systems Inc. LC pump model 330, a Scientific Systems Inc. Lo-Pulse pulse dampener, model LP-21, a Supelco mixed bed gel permeation column of type GMH6 and a Supelco mixed bed guard column of the same type. These units have been integrated with a Perkin Elmer uv/vis spectrophotometer model LC-55B. The GPC column was calibrated with four polystyrene molecular weight standards. The chromatograms obtained and the resulting calibration curve are shown in Figures 1 and 2 respectively. The GMH6 column has a particularly wide molecular weight range over which separations are obtained. This is necessary for the analysis of samples with unknown molecular weight distributions. However, resolution is sacrificed at the expense of the wide operating range. It is anticipated that once the molecular weight ranges that are typical to our samples have been established, other GPC columns with narrower ranges will be used to improve separation.

The polystyrene molecular weight standards were prepared as 1% (wt%) solutions in HPLC grade THF. Chromatographic conditions used for the separation of the standards include: 1ml per minute flow rate of degassed HPLC grade THF, column at room temperature and uv detector set at 254 nm. It is possible that the 1% (wt%) concentration was slightly too high for ideal separation since some of the peaks appear unusually broad. This is especially true for the very high molecular weight standards. Nevertheless the calibration curve obtained by plotting the elution time against the log of the molecular weight is virtually identical to that specified by the manufacturers of the GPC column.

Oxidation with Sodium Dichromate

2g of IBC 101 floated, THF-extracted coal was carefully oxidized stepwise with 3.5g $Na_2Cr_2O_7$ in 80 ml glacial CH_3COOH. The temperature of the reaction was 50^oC and the mixture was stirred magnetically for 22 hrs. At the end of the reaction the mixture was acidified with concentrated HCl to pH:1. 100 ml of water was added and stirred from about 1 hour, then filtered off. The solid was rinsed with distilled warm water and with $CHCl_3$. The filtrate was extracted with 3 x 50 ml of diethyl ether and 2 x 50 ml of chloroform. The combined total extracts were washed with 40 ml of water and dried over Na_2SO_4. The solvent was removed by rotary evaporation. A second step was carried out with the remaining coal residue using the same conditions as above. The combined organic extracts from the two steps were methylated with diazomethane in diethyl ether, then analyzed by GC-FPD and GCMS.

Table 1. Yields of sodium dichromate oxidation

Step No.	Soluble acids (SA) (mg)
1	21
2	72

GC-FPD and GCMS Analysis of Oxidation Products

The methylated dichromate and peroxyacetic acid oxidation products of IBC101 floated coal and Spanish lignite were analyzed by GCMS and GC-FPD to determine the distribution of their sulfur compounds. To identify the sulfur compounds by mass spectrometry, retention time equivalency had to be established between GCMS and the GC-FPD. The resulting GC-FPD (Figures 3, 4 and 5) indicate that the three samples have two common sulfur products : methylsulfonic acid (GC-FPD retention time about 3.7) and ethylsulfonic acid (GC-FPD retention time 4.55).

A variety of more complex sulfur compounds were identified in the dichromate oxidation products of the IBC101 coal, including a thiazole and, most interestingly, a series of a homologues and isomers of thiophenecarboxylic acid. In Figure 6, the right peak in the pair at 8.2 min. is identified as a thiazole, which is a compound containing both sulfur and nitrogen. A thiazole was also identified in the permanganate oxidation products, as described in the previous Quarterly Report. The thiazole was probably trapped in the coal matrix, protecting it from oxidation. The three principal peaks on the m/z 169 mass chromatogram closely match the corresponding three peaks on the FPD trace, as shown by arrows. These are identified as the methyl esters of ethylthiophene carboxylic acid, methyl ether. Similarly, the two principal peaks on the m/z 183 mass chromatogram also correspond to two peaks on the FPD trace. These are identified as higher homologues, having a C3-alkylthiophene core. The peaks on the m/z 197 trace are much weaker (note that the GCMS data in Figure 6 are normalized) and it is difficult to find their match on the FPD chromatogram. Nonetheless, they represent a continuation of the homologous series to compounds with a C4-alkylthiophene core. This group may collectively be termed the alkylthiophene carboxylic acids (ATCA). The mass spectra of the three strongest members of the pseudohomologuous series and a closely matching spectrum from the National Bureau of Standards spectral library are shown in Figure 7. The discovery of the ATCA compounds is significant, as for the first time a sulfur compound can be recognized on a total ion chromatogram of oxidation products (peak 31 on Figure 3 is the strongest C2-ATCA). The ATCA compounds probably originated as short alkyl chains on exterior portions of the original peat macromolecular structures and were sulfurized by H_2S shortly after burial of the peat. GCMS peak identification for the dichromate oxidation products are reported in Table 2.

The dichromate oxidation seems to be an interesting reaction for the characterization of sulfur compounds. Unfortunately this treatment yields only small amounts of products in each step and the procedure must be repeated multiple times until all the reactive organic matter is consumed. However, the reaction is relatively mild. The peroxyacetic acid gives a very good yield in only a single step, but this method seems to be very degradative. The GC-FPD and GCMS data for peroxyacetic acid oxidation products do not indicate the presence of the ATCA compounds identified in dichromate. Since the peroxyacetic acid is a very strong oxidant, the thiophenes are may be destroyed.

The distribution of the sulfur compounds in the peroxyacetic acid oxidation products of the demineralized and THF extracted Spanish lignite are shown in Figure 4. Many of the sulfur compounds detected in the IBC101 coal are also present in the Spanish Lignite but the distribution between them is

Table 2 GCMS peak identifications for dichromate oxidation products.

Peak	Compound Name	Base Peak (m/z)
1	unknown	73
2	unknown	87
3	unknown	101
4	butanoic acid, dimethyl ester	115
5	unknown	118
6	butanoic acid, methyl-,dimethyl ester	59
7	benzoic acid, methyl ester	105
8	unknown	87
9	pentanoic acid dimethyl ester	59
10	pentanoic acid, methyl-, dimethyl ester	55
11	pentanoic acid, methyl-, dimethyl ester	59
12	butanoic acid, dimethyl-, dimethyl ester	55
13	benzoic acid, hydroxy-, methyl ester	120
14	benzoic acid, methyl-, methyl ester	119
15	pentenoic acid, trimethyl ester	97
16	hexanoic acid, methyl-,dimethyl ester	59
17	hexanoic acid, dimethyl ester	59
18	pentanoic acid, dimethyl-,dimethylester	69
19	butanoic acid, ethyl, methyl-, dimethyl ester	59
20	unknown	104
21	hexanedioic acid, methyl-, dimethyl ester	73
22	benzaldehyde, dimethyl-	134
23	heptanedioic acid, dimethyl ester	74
24	benzoic acid, methoxy-, methyl ester	135
25	unknown	163
26	unknown	161
27	undecanoic acid, methyl ester	74
28	octanedioic acid, dimethyl ester	74
29	benzenedicarboxylic acid dimethyl ester	163
30	unknown	131
31	ethylthiophene carboxylic acid,methyl ether,me ester	169
32	benzene dicarboxylic acid, dimethyl ester	163
33	benzenedicarboxylic acide, dimethyl ester	163
34	benzenedicarboxylic acid, methyl-, dimethyl ester	176
35	dodecanoic acid, methyl ester	74
36	nonanedioic acid, dimethyl ester	55
37	benzenedicarboxylic acid, methyl-, dimethyl ester	177
38	unknown	147
39	unknown	183
40	unknown	132
41	2-propenoic acid, hydroxyphenyl-,methyl ester	178
42	benzenedicarboxylic acid, dimethyl ester	178
43	unknown	91
44	dodecanoic acid, methyl ester	74
45	unknown	55
46	unknown	73
47	unknown	191
48	unknown	147
49	unknown	190
50	unknown	191
51	tetradecanoic acid, methyl ester	74
52	undecanoic acid, dimethyl ester	55
53	unknown	193
54	unknown	169
55	unknown	205
56	benzenetricarboxylic acid, trimethyl ester	221
57	unknown	202
58	undecanoic acic, monomethyl ester	55
59	benzenetricarboxylic acid, methyl, trimethyl ester	235
60	hexadecanoic acid, methyl ester	74
61	unknown	73
62	unknown	57
63	unknown	57
64	undecanedioic acid, methyl-, dimethyl ester	55
65	heptadecanoic acid, methyl-, methyl ester	74
66	unknown	59
67	hexanedioic acid, dioctyl ester	129

Table 4 GCMS identifications for peroxyacetic acid oxidation products of IBC1 floated coal and asphaltenes.

Peak	Compound Name	Base Peak m/z
1	propanoic acid dimethyl ester	101
2	butanoic acid, dimethyl ester	99
3	unknown	113
4	butanedioic acid, dimethyl ester	59
5	butanedioic acid, dimethyl ester	115
6	butanedioic acid, methyl-, dimethyl ester	59
7	butanedioic acid, hydroxy-, dimethyl ester	103
8	pentanedioic acid, dimethyl ester	59
9	pentanedioic acid, methyl-, dimethyl ester	59
10	pentanedioic acid, methyl-, dimethyl ester	55
11	benzoic acid, hydroxy-, methyl ester	120
12	hexanedioic acid, dimethyl ester	59
13	pentanedioic acid, oxo-,dimethyl ester	115
14	butanoic acid, methylene-, dimethyl ester	127
15	benzenedicarboxylic acid dimethyl ester	163
16	hexane dioic acid dicyclohexyl ester	129
17	benzenedicarboxylic acid, methyl- dimethyl ester	177
18	benzenetricarboxylic acid, trimethyl ester	221
19	benzenetricarboxylic acid, trimethyl ester	221
20	benzenetricarboxylic acid, methyl, trimethyl ester	235
21	unknown	105
22	unknown	105
23	unknown	105
24	unknown	269
25	unknown	205
26	benzenedicarboxylic acid, butyl, methyl ester	149
27	benzenetetracarboxylic acid, tetramethyl ester	279
28	benzenetetracarboxylic acid, tetramethyl ester	279
29	benzenetetracarboxylic acid, tetramethyl ester	279
30	unknown	293
31	unknown	249
32	unknown	290
33	benzenepentacarboxylic acid, pentamethyl ester	337
34	hexaneoioic acid, octyl ester	129
35	unknown	319
36	phthalate	149
37	benzenehexacarboxylic acid, hexamethyl ester	395

Table 3 GCMS peak identications for peroxyacetic acid oxidation products of "Spanish Lignite" (float).

Peak	Compound Name	Base Peak m/z
1	butanoic acid, -ol, methyl ester	59
2	unknown	95
3	unknown	59
4	propanedioic acid, dimethyl ester	101
5	butanedioic acid, dimethyl ester	99
6	propanedioic acid, dimethyl ester	101
7	butanedioic acid, dimethyl ester	113
8	butanedioic acid, dimethyl ester	115
9	butanedioic acid, methyl-, dimethyl ester	59
10	butanedioic acid, ethyl methyl ester	115
11	butanedioic acid, hydroxy-, dimethyl ester	103
12	pentanedioic acid, dimethyl ester	59
13	butanoic acid, dimethyl, methyl ester	73
14	hexanedioic acid, monomethyl ester	59
15	pentanoic acid, methoxy-, methyl ester	85
16	hexanedioic acid, dimethyl ester	59
17	unknown	101
18	unknown	55
19	unknown	115
20	butanedioic acid, methylene-, dimethyl ester	127
21	unknown	115
22	cyclobutane dicarboxylic acid, dimethyl ester	59
23	cyclobutane dicarboxylic acid, dimethyl ester	55
24	dodecanedioic acid, dimethyl ester	227
25	benzoic acid, cyclohexyl ester	105
26	butanol, methyl-, benzoate	105
27	pentadecane dicarboxylic acid dimethyl ester	269
28	pentadecanoic acid, methyl-, methyl ester	74
29	phthalate	149
30	unknown	285
31	benzenetetracarboxylic acid, tetramethyl ester	279
32	benzenetetracarboxylic acid, tetramethyl ester	279
33	octadecanoic acid, methyl ester	74
34	benzenetetracarboxylic acid, tetramethyl ester	279
35	unknown	349
36	benzenepentacarboxylic acid, pentamethyl ester	337
37	dimethyl phtalate	149
38	benzenehexacarboxylic acid, hexamethyl ester	395

different. GC-MS analysis of the oxidation products from the Spanish sample is shown in Figure 4 and peak identifications reported in Table 4.

Direct Reduction of IBCl Floated Coal with Sodium Metal

1g of IBC101 floated and THF extracted coal was dispersed in 80 ml of ethyl alcohol. 10g of sodium was added slowly in small pieces at room temperature and under a nitrogen stream. The mixture was left stirring for 12 hrs. After the reaction, a saturated solution of ammonium chloride was slowly added to consume the excess sodium. The solid residue was then collected by filtration and washed with distilled water. The filtrate was extracted with diethyl ether, then chloroform. The extract was dried over sodium sulfate and concentrated using the rotary evaporator. The product yield was 9mg.

The reduction products were solubilized in excess acetic anhydride. A catalytic quantity of pyridine was added (3 drops). The solution was heated to 50 ^{o}C for 30 minutes, then hydrolyzed with ice and stirred for 2 hours. The organic extract (2 x 20 $CHCl_3$, 1 x 20 ml Et_2O) was neutralized by a saturated solution of $NaHCO_3$ and then a saturated solution of NaCl. The organic extract was dried over sodium sulfate and concentrated with a rotary evaporator.

GCMS Analysis of Direct Reduction Products

GCMS analysis revealed the presence of polychlorinated compounds in the reduction products, the source of which is at present unknown. The preparation may have to be redone.

Tandem Oxidation/Reduction Reactions

Lithium aluminum hydride reduction of oxidation products.:- As reported previously it was difficult to separate part of the reduced organic matter from the inorganic products derived from the lithium aluminum hydride. Initially the reaction was quenched, and excess hydride destroyed, by adding a 1:1 mixture of methanol and distilled water. Concentrated HCl was then added dropwise until a pH of 1 was obtained. In the second LAH reduction the reaction was quenched with a 15% aqueous solution of sodium hydroxide. However, in either case some of the reduced organic matter could not be isolated from the inorganic material produced during the quenching of the excess hydride.

It is anticipated that the reasons for the poor recoveries of organic matter concern the nature of the reduction products. From FTIR, NMR and GC-MS analysis, the oxidation products are known to contain abundant carboxylic acid and other carbonyl groups. When these functional groups are reduced by LAH they form alcohols. Since many polycarboxylated products are found in the oxidation products it is very likely that many poly alcohol structures result after reduction. If this is the case it is not surprising that difficulties in separation are observed. Such compounds are usually readily soluble in both water and organic solvents and actively transport inorganic ions between organic and aqueous phases. An example of this behavior is the phase transfer properties of glycol and its derivatives (crown ethers).

To address the problem of complete product isolation after LAH reduction, the organic/inorganic mixture was derivatized without the attempted separation of the organic material. In this way the alcoholic groups are

converted to other functional groups which do not hinder the separation process. The derivatization method used was that outlined in the original work plan, that is forming the hydrocarbon from the alcohol via the LAH reduction of tosylate intermediates. In this way very little deviation from the original work proposed has been necessary. It was aniticipated that once the alcohols have been converted to their parent hydrocarbon molecules, they could then be extracted into such organic solvents as hexane and methylene chloride and very clean separations of the organic and inorganic components obtained. The following section describes the tosylation/reduction sequence in more detail.

Tosylation of LAH reduction products:- To test the tosylation/LAH reduction reaction sequence, the material isolated from the original aqueous methanol quench of the tandem PAA/LAH oxidation/reduction, was used. This initial test was performed to established if the tosylates could be formed and then subsequently reduced, and to establish the conditions necessary for reaction.

0.5 grams of the isolated PAA/LAH oxidized/reduced material was dissolved in 30mls of dry pyridine. This solution was then cooled to $0^{o}C$ and 6 grams of *p*-toluene sulfonyl chloride (tosyl chloride) added. The reaction vessel was then shaken before being placed in the refrigerator at $1\text{-}2^{o}C$ for 1.5 days. The formation of needle-like crystals of pyridinium chloride during this time indicated that the tosylation reaction had proceeded. The reaction products were isolated by pouring them into 100 mL of stirred ice water. After stirring for 1 hour the precipitate was filtered at the pump, washed with 50mL cold distilled water, and finally dried in a vacuum desiccator.

The aqueous filtrate appeared to contain some organic material and was therefore extracted with two 30 ml portions of diethyl ether. The ether extracts were then extracted with 1N HCl to remove pyridine. The resulting ethereal solution was dried over magnesium sulfate.

The ether extract and the precipitate were combined and reduced with 0.4 grams of lithium aluminum hydride in 40 mLs dry THF. After refluxing for 1 day and standing for 3 days the excess LAH was quenched with the dropwise addition of 0.4 mL water, 0.4 mL 15% aqueous sodium hydroxide and finally 1.2 mL water. The resulting precipitate was filtered off, washed with THF and the washings added to the filtrate. The THF solvent was evaporated and replaced with methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate before chromatographic analysis.

The GC-FPD and GCMS analysis of this material revealed the presence of tosylate derivatives in relatively high concentration. Thus it appeared that the tosylation reaction was successful but that the subsequent LAH reduction failed to remove at least some of the tosyl groups. For this reason the LAH reduction was repeated on this sample for a longer period of time (four days at reflux). The material was the analyzed again. This time the strong tosylate peaks were absent from the chromatogram. The GC-FPD and GCMS TIC chromatograms for the sample are shown in Figure 8.

Although detailed analysis of the products has not been completed, a homologous series of alkanes and some alkyl aromatic compounds have been detected. The only way that these compound could have been formed is via the successful reduction of the tosylates intermediates back to the parent hydrocarbon structure. Thus it appears possible to convert the polycarboxyl compounds often found in oxidation products into their parent hydrocarbon structure. This allows for much easier separation and characterization which

should lead to enhanced elucidation of coal structures.

Comparison of IBC1 Asphaltenes and Floated Coal.

To test the hypothesis that asphaltenes are similar in structure to their parent coal, we subjected IBC101 asphaltenes (from a THF extract) and floated, THF-extracted coal to peroxyacetic acid (PAA) oxidation and analytical pyrolysis. We have shown in the previous Quarterly Report that the bulk organic sulfur content is close to that of the coal and if the asphaltenes are structurally similar, then it may be advantageous for future studies to use coal asphaltenes as convenient, easy to prepare analogs for the larger, more cumbersome solid coal structures.

The total ion chromatograms of the methylated PAA products show a very good correspondence in short chain compounds such as peaks 5 and 8 (Figure 8 and Table 4), as well as with benzenetri- and benzenetetracarboxylic acids. As might be expected, the coal shows greater prominence of the benzenepenta- and benzenehexacarboxylic acids (peaks 33 and 37), as these have been ripped from heavily condensed regions of the coal structure during oxidation. However, as suggested by the recognition of ATCA sulfur compounds discussed above, a good portion of the organic sulfur may be in exterior positions, to which the asphaltenes as a starting material might provide better access. The GC-FPD data from these two PAA oxidation products (Figure 5) has not as yet been fully evaluated, but visual examination of the chromatograms shows that many of the peaks correspond closely.

As a rapid alternative to the oxidation techniques, we attempted analytical pyrolysis-gas chromatography (py-GC) of the asphaltene and floated coal samples. A CDS 120 Pyroprobe was employed, coupled to a Hewlett Packard 5890A GC, equipped with flame ionization (FID) and flame photometric detectors (FPD). As of this writing, only FID experiments have been run. A 25 m HP-1 capillary column was used and the GC was held at -20°C for one minute, then ramped to 300° at 5°/min., where it was held for 15 min. Pyrolysis was at 610°C for 20 sec. The pyrolyzates are remarkably similar (Figure 9) for the two samples, indicating a close structural correspondence. The salient features include 1) similar quantities of gas (methane-butane), eluting at 2-3 min., 2) similar amounts of aromatic hydrocarbons (e.g., toluene and xylenes, which are the tall peaks at 14 and 16 min., respectively), 3) dominance by phenols (tall peaks between 22 and 29 min.) and 4) similar distributions of longer chain hydrocarbons (C14-C22, which are apparent as a distinct series of peaks beginning at 36 min.). Detection of sulfur compounds will require re-analysis using the sulfur-selective FPD.

CONCLUSIONS AND RECOMMENDATIONS

1. Maceral separation of the IBC 101 coal led to the accumulation of 9 grams of liptinite concentrate, 150 grams of vitrinite concentrate and 25 grams of inertinite concentrate. From these concentrates sporinite, vitrinite and semi-fusinite single macerals were separated.
2. A gel permeation chromatography (GPC) system was assembled from purchased units and the GPC column calibrated with four polystyrene molecular weight standards. The calibration curve obtained by plotting

the elution time against the log of the molecular weight is virtually identical to that specified by the manufacturers of the GPC column.

3. A variety of sulfur compounds were identified in the dichromate oxidation products of the IBC 101 coal, including a thiazole and, most interestingly, a series of homologues and isomers of thiophenecarboxylic acid. GCMS analysis gave strong ions at m/z 169, 183 and 197 which were identified as the methyl esters of C2-, C3- and C4- alkyl thiophene carboxylic acids respectively. The peaks on the GCMS single ion chromatogram for these ions matched precisely with peaks on the FPD chromatogram.

4. The discovery of the thiophene carboxylic acids is significant, as for the first time sulfur compounds can be recognized on a total ion chromatogram of oxidation products. These compounds probably originated as short alkyl chains on exterior portions of the original peat macromolecular structures and were sulfurized by H_2S shortly after burial.

5. The dichromate oxidation seems to be an interesting reaction for the characterization of sulfur compounds. Unfortunately this treatment yields only small amounts of products in each step and the procedure must be repeated multiple times until all the reactive organic matter is consumed. However, the reaction is relatively mild. The peroxyacetic acid gives a very good yield in only a single step, but this method seems to be very degradative.

6. It was difficult to separate part of the reduced organic matter from the inorganic products derived from the lithium aluminum hydride. It is anticipated that the reasons for the poor recoveries of organic matter concern the polycarboxyl groups present in the oxidation products which when reduced form polyalcohols.

7. Polyalcohols were successfully converted to their parent hydrocarbon structures by the LAH reduction of tosylate intermediates. This allows for much easier separation and characterization which should lead to enhanced elucidation of coal structures.

8. To test the hypothesis that asphaltenes are similar in structure to their parent coal, we subjected IBC101 asphaltenes and floated, THF-extracted coal to PAA oxidation and analytical pyrolysis. The TIC's of the methylated PAA products show a very good correspondence in short chain compounds as well as with benzenetri- and benzenetetracarboxylic acids. In addition, the pyrolyzates are remarkably similar for the two samples, indicating a close structural correspondence.

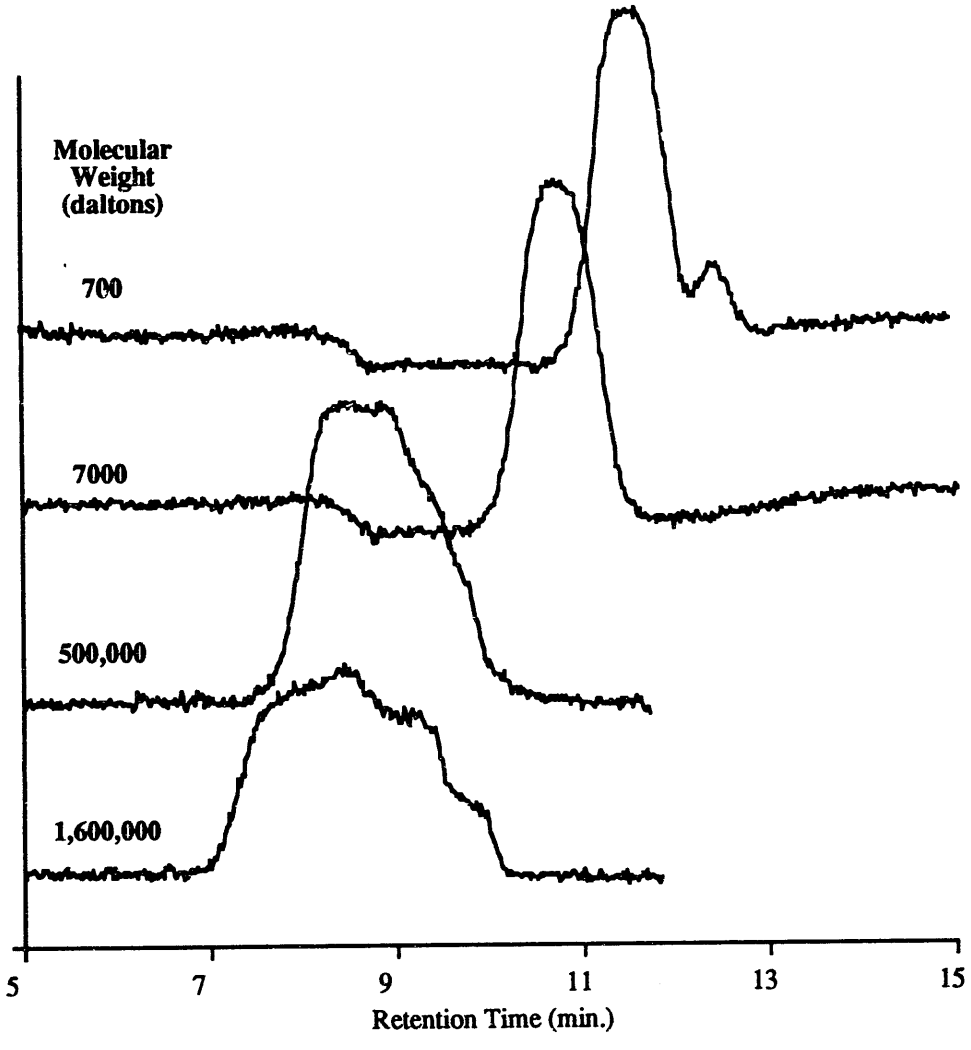

Figure 1 Gel permeation chromatograms of four standards.

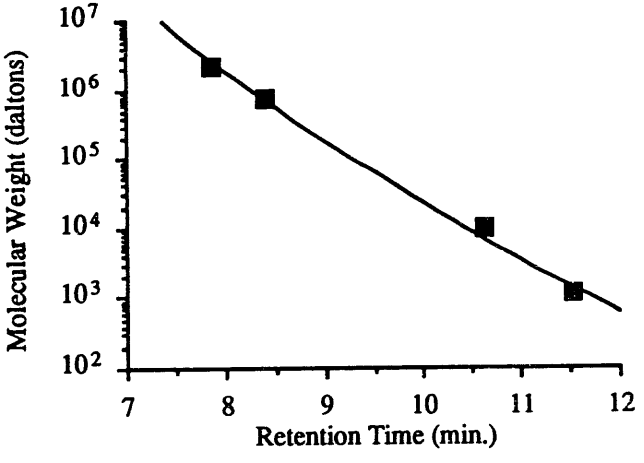

Figure 2 Correlation between GPC retention time and molecular weight of standards.

y = 5.6297e+23 * x^-19.603 R^2 = 0.992

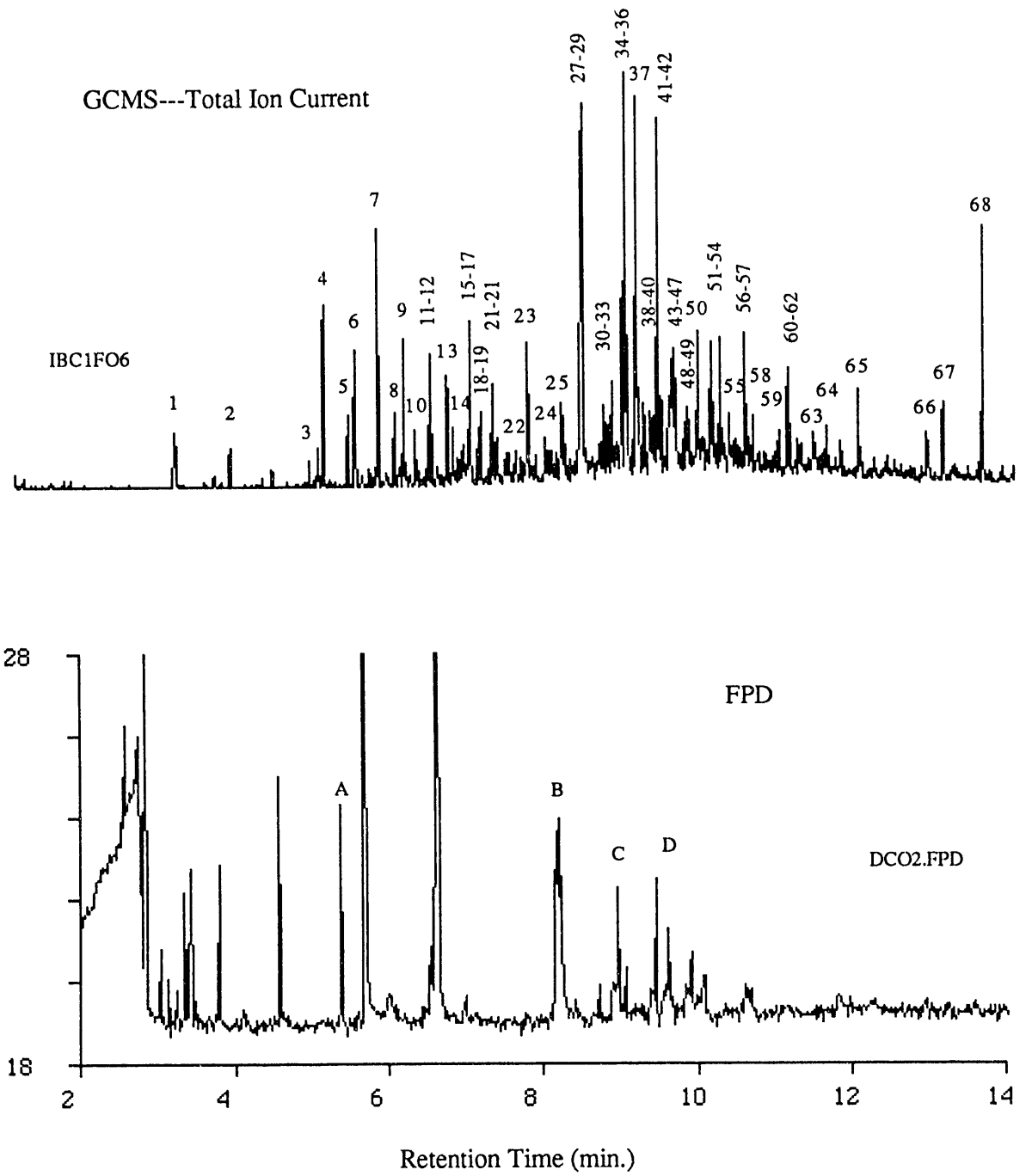

Figure 3 --- Chromatograms of methylated dichromate oxidation products

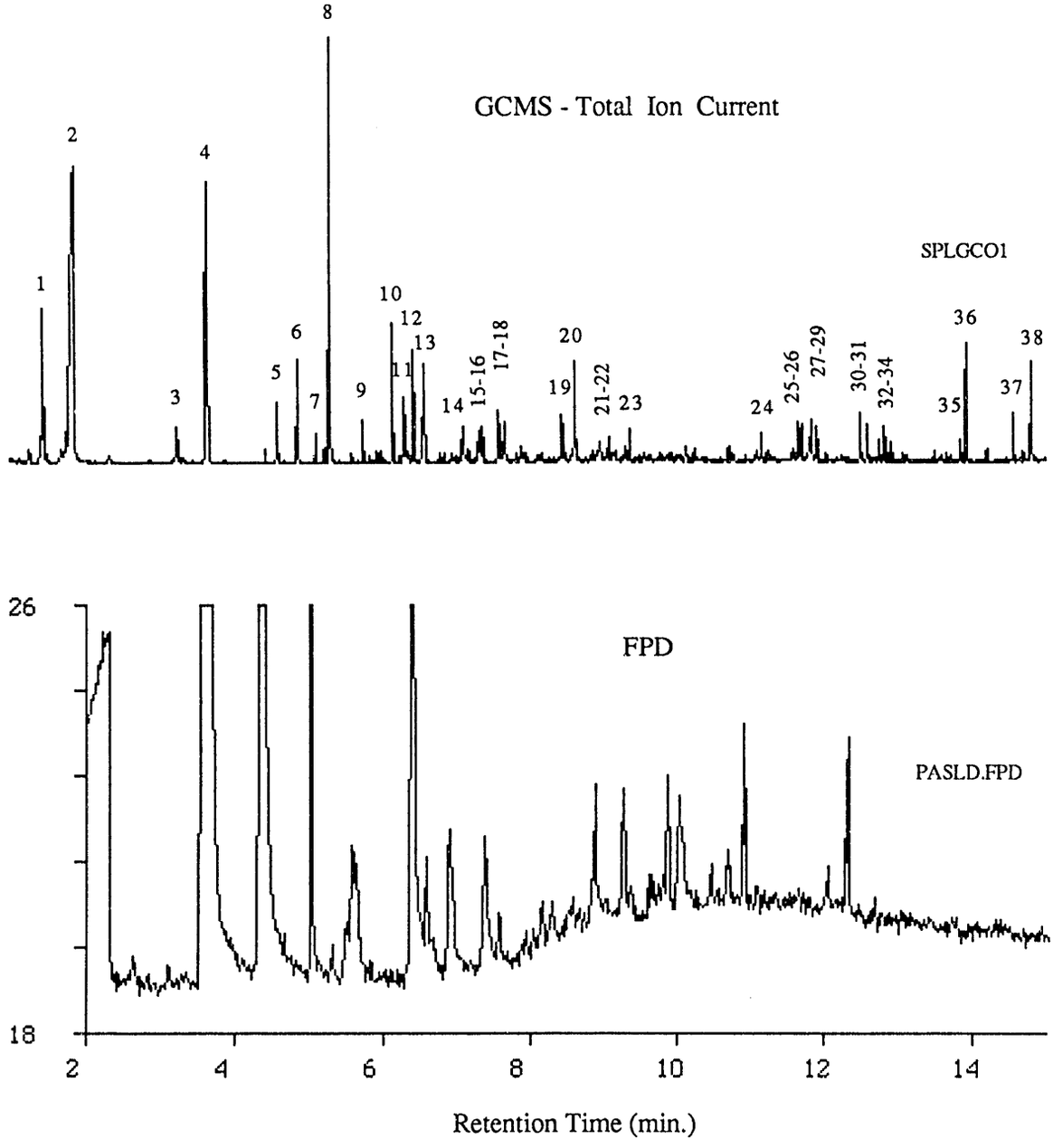

Figure 4 --- Chromatograms of the methylated peroxyacetic acid oxidation products of the "Spanish lignite"

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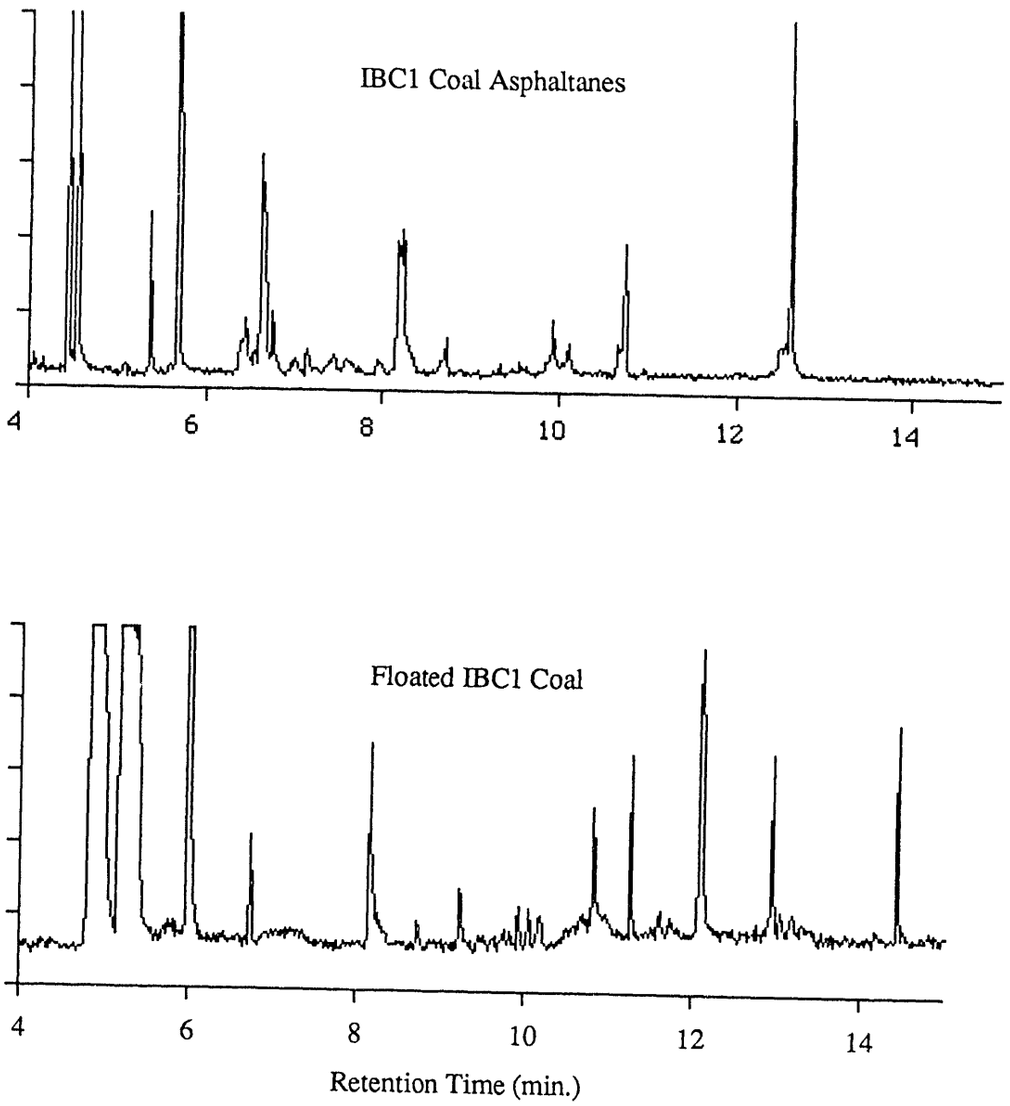

Figure 5 --- GC-FPD chromatograms of methylated peroxyacetic acid oxidation products

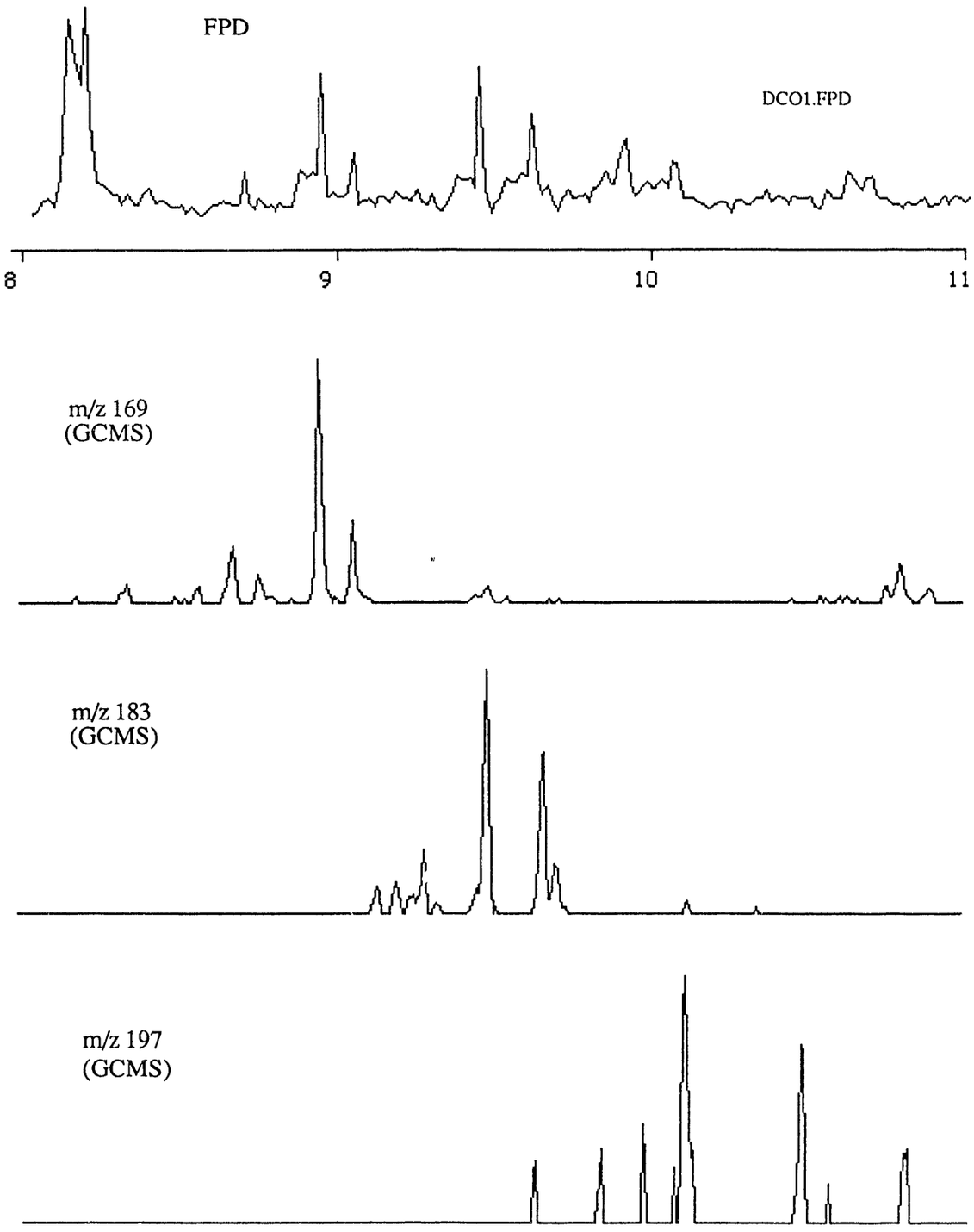

Figure 6 ---- Normalized chromatograms of dichromate oxidation products (methylated)

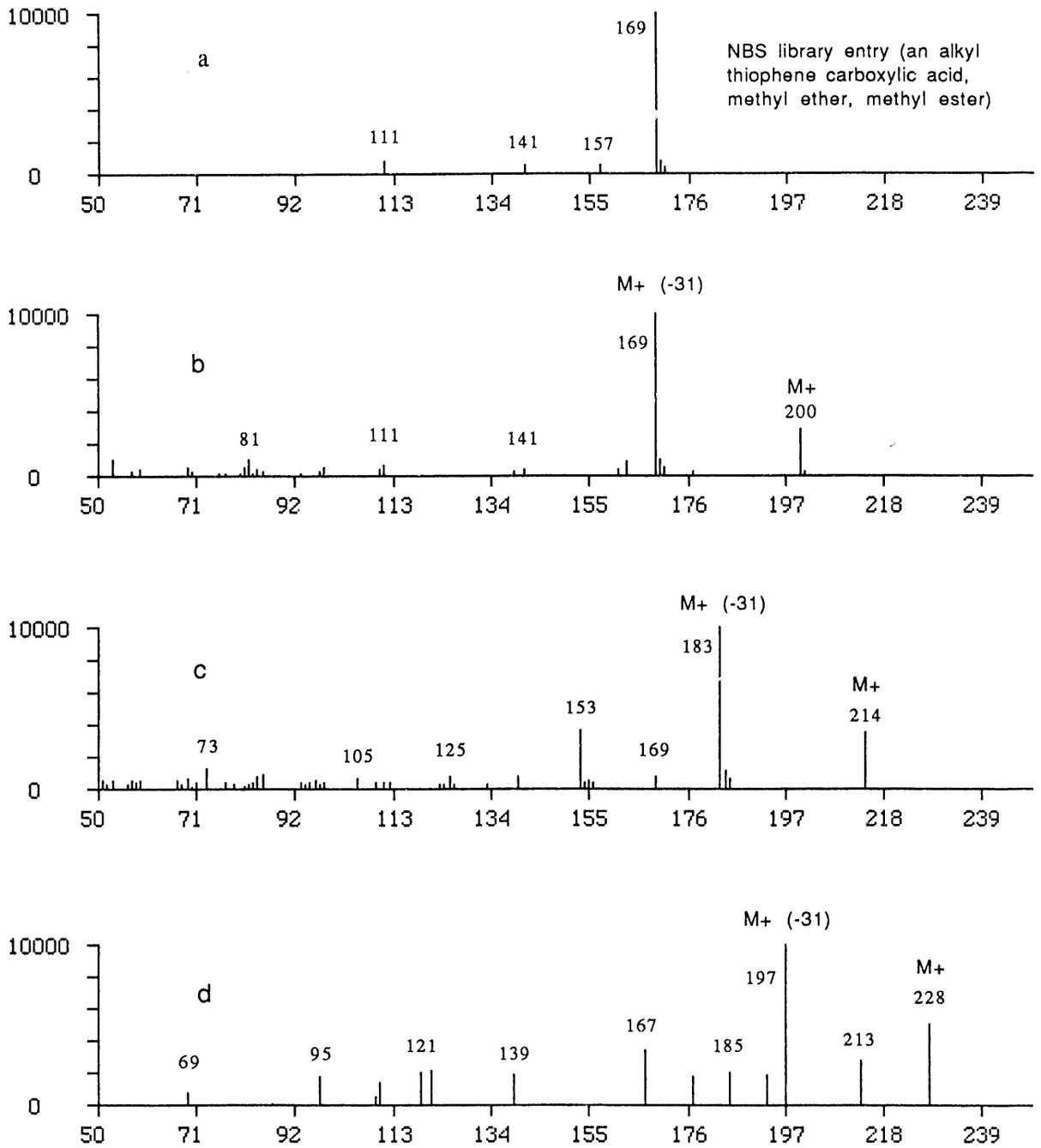

Figure 7 ---Mass spectra of three sulfur compounds found in the dichromate oxidation products and one NBS mass spectral library entry

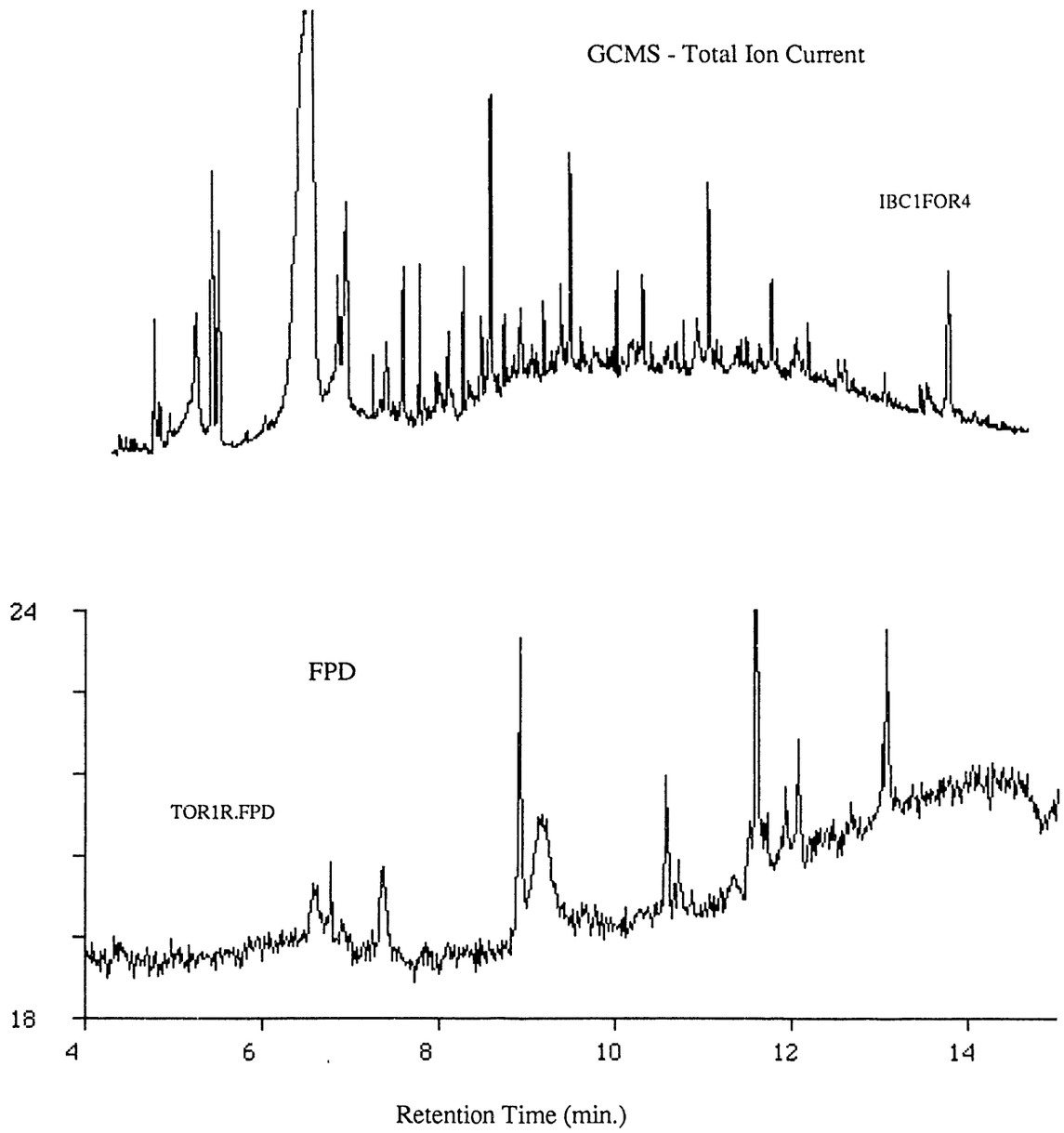

Figure 8 --- Chromatograms of Tandem PAA Ox/LAH red followed by Tosylate/LAH reduction. IBC 101 Extracted/Floated coal

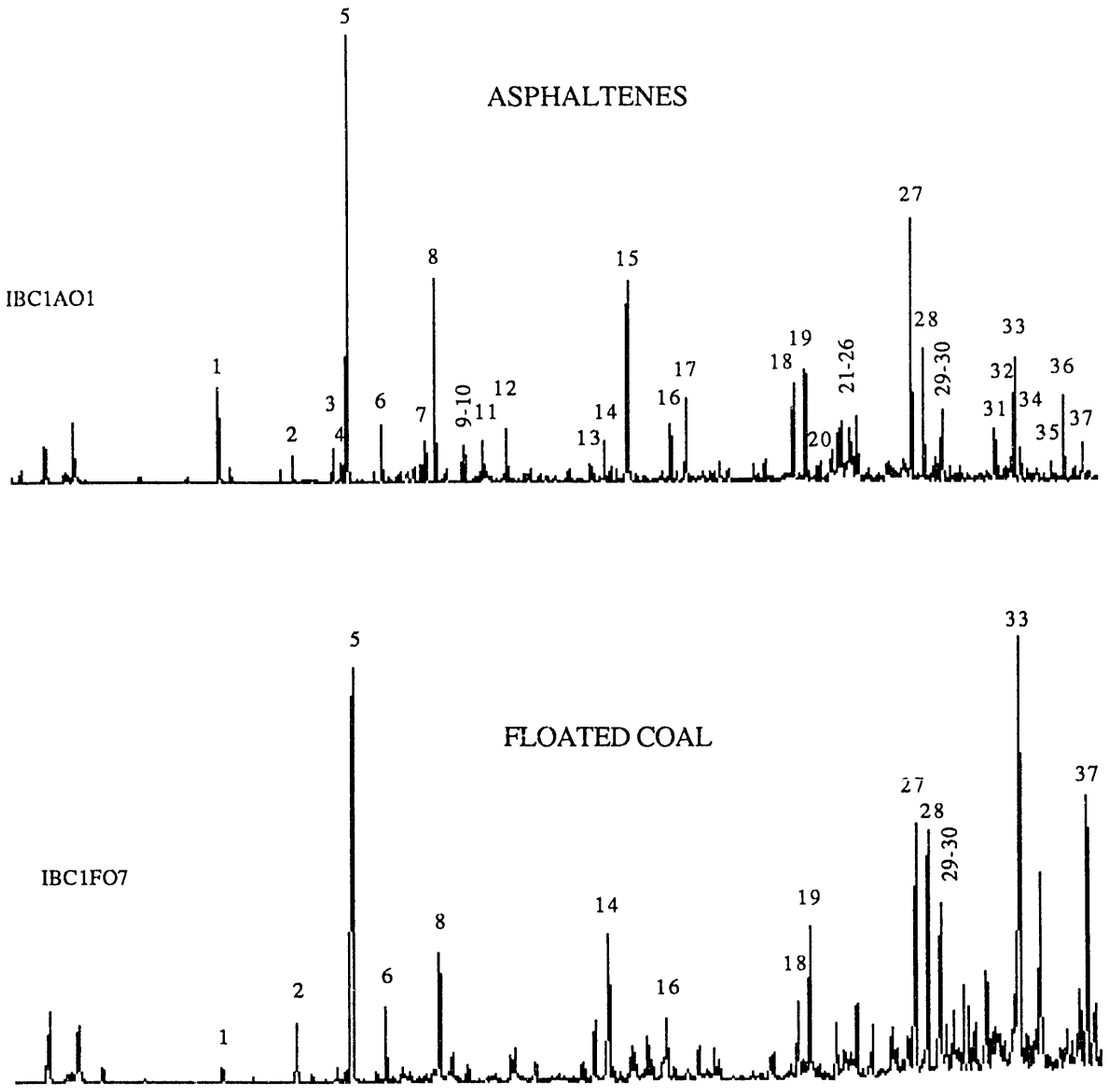

Figure 9 --- GCMS Total Ion Chromatograms of the methylated peroxyacetic acid oxridation products of IBC1 coal derivatives

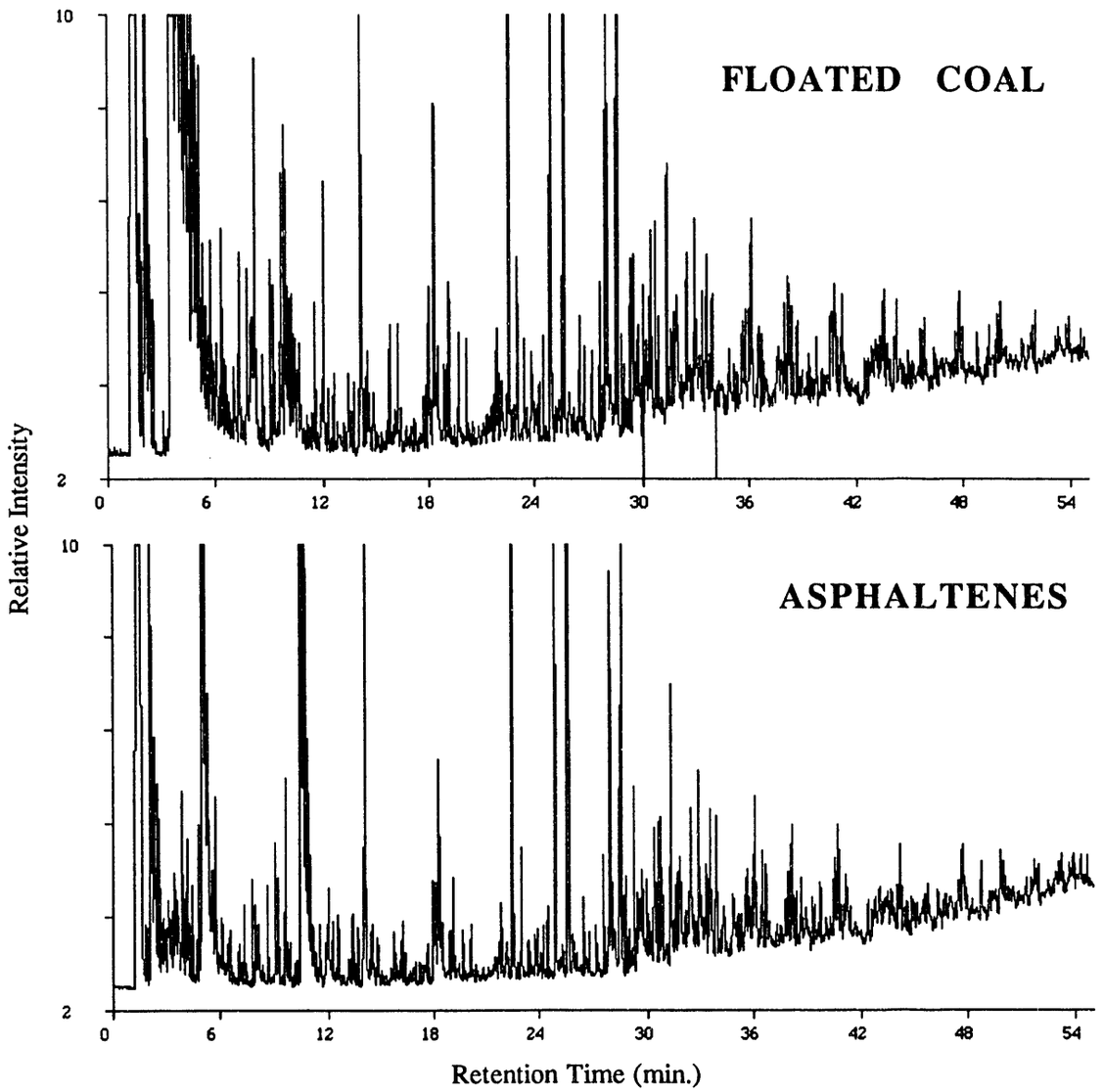

Figure 10 Pyrolysis-gas chromatograms (FID) of two IBC1 coal derivatives.

PROJECT MANAGEMENT REPORT
1 March through 31 May 1992.

Project Title: Analysis of Organic Sulfur and Nitrogen in Coal via Tandem Degradation Methods

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Project Monitor: Ken Ho, CRSC

COMMENTS

The project is proceding essentially on schedule and on budget.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared programs.

SCHEDULE OF PROJECT MILESTONES — YEAR 1

TASK	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
1. Sample Preparation	—	—	—	—	—	—	—	■				
2a. PAA Oxidation	—	—	—	■								
2b. Permanganate Oxidation					—	—	—	—	—	—	X	
2c. Chromate Oxidation											—	—
3a. LAH Reduction	—	—	—	—	—	—	—	■				
3b. Na/EtOH Reduction					—	—	—	—	—	—	—	X
3c. K/Glyme Reduction											—	—
4. Tandem Oxidation/Reduction				—	—	—	—	—	—	—	—	—
5. Asphaltene Degradation				— ■						—		
6. Chromatography and MS			—	—	—	—	—	—	—	—	—	—
7. Interpretation			—	—	—	—	—	—	—	—	—	—
Reporting			— ■			— ■			— ■			— X

END

DATE
FILMED
11/24/92