TECHNICAL REPORT

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Project Title: **ANALYSIS OF ORGANIC SULFUR AND NITROGEN IN
COAL VIA TANDEM DEGRADATION METHODS**

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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. In our research, we apply chemical and thermal degradation techniques to render coal amenable to standard GC characterization.

N/C and S/C ratios show only minor differences between asphaltenes and coal. On this basis, the asphaltenes continue to appear to be good surrogates for the characterization of organic acid rain precursors in coal. Alkylmethoxythiophene carboxylic acids (ATCA) are detected in all dichromate oxidation products analyzed to date. Relative concentrations of ATCA compounds are directly proportional to the sample's bulk organic sulfur contents. Concentrations of ATCA compounds in oxidation products decrease upon repeated oxidation. This may indicate that the thiophenic groups tend to be located in external positions on the coal macromolecular structure and a high proportion of them can be stripped away with only one mild oxidation step. If true, this may make industrial-scale removal of organic sulfur easier than expected. Using analytical micropyrolysis-gas chromatography with a sulfur-selective flame photometric detector, it is possible to easily see a full distribution of organic sulfur forms in a one-step analysis. The predominance of alkylthiophenes in the pyrolyzates lends credence to the discovery of thiophenic compounds in the dichromate oxidation products. The thiophene concentrations in pyrolyzates are directly proportional to bulk organic sulfur values. However, thiophene distributions in IBCSP coals are remarkably similar, regardless of organic sulfur content. It is thus possible to distinguish Illinois Basin coals from foreign coals on the basis of thiophene "fingerprints". To examine rank effects, we have started analysis on a group of five Appalachian coals ranging from high-volatile C to medium-volatile bituminous rank.

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EXECUTIVE SUMMARY

With the recent increase in concern for the environment, understanding the nature of organic sulfur and nitrogen in coal has become a pressing issue, as they are among the precursors of acid rain. Essential to the development of successful clean coal 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 processes for their effective removal. Attempts to characterize organic sulfur in coal have included many different techniques but the necessary detailed information still eludes the scientific community. This is largely due to the immense task of characterization and to the fact that no one technique can provide all the answers. Degradative methods employing chemical and thermal processes can provide detailed molecular information, but they suffer from the inability to characterize all of the sulfur at one time, and the possibility of regressive and/or rearrangement reactions. On the other hand, bulk spectroscopic ("non-destructive") techniques can observe all of the forms of sulfur simultaneously and *in situ*. However, most non-destructive techniques are not readily available to the general scientific community and suffer from the inability to gather detailed molecular information. At best, sulfur compounds are resolved only into general types and hence information such as the nature of substituents and substitution patterns are not available. All information is needed for desulfurization strategies. The present study undertakes a combination of chemical and thermal degradation techniques for the enhanced characterization of organic sulfur and organic nitrogen in coal.

The specific objectives of Year 2 of this study are to:

- 1) apply oxidative degradation methods and subsequent chromatographic analysis to a variety of coals and coal derivatives as a means of elucidation of their chemical structure, with emphasis on their organic sulfur and nitrogen forms. During Year 1 of the project, two oxidation methods were determined to be the most useful. Oxidation by peroxyacetic acid is very thorough and can provide a picture of the overall coal structure. Oxidation by sodium dichromate is milder, preserving details of the structure of organic sulfur compounds in particular.
- 2) apply analytical micropyrolysis techniques, in tandem with the two oxidative methods, to the same suite of samples. This approach will provide a second line of evidence to support findings of the oxidation experiments.
- 3) analyze all relevant samples from the Illinois Basin Coal Sample Program bank to ascertain the extent of variation in organic sulfur structures in the region.
- 4) analyze a series of Appalachian coals a) to compare organic sulfur structures with those in Illinois and b) to examine the effect of coal rank on organic sulfur type.
- 5) analyze several coals of extraordinarily high organic

sulfur content, which will make 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. 6) 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. 7) develop a routine methodology for the assessment of the nature of organic sulfur in any coal sample.

While the elemental analysis data set is still incomplete, new results confirm that asphaltenes show increases in H/C and decreases in O/C atomic ratios over the demineralized, floated parent coal. N/C and S/C ratios show only minor differences between asphaltenes and coal. On this basis, the asphaltenes continue to appear to be good surrogates for the characterization of organic acid rain precursors in coal.

We have analyzed dichromate oxidation products of additional IBCSP samples. Alkylmethoxythiophene carboxylic acids (ATCA) are detected in all samples. Relative concentrations of ATCA compounds are directly proportional to the bulk organic sulfur contents. As reported in the previous quarter, concentrations of ATCA compounds in oxidation products decrease upon repeated oxidation. This may indicate that the thiophenic groups tend to be located in external positions on the coal macromolecular structure and a high proportion of them can be stripped away with only one mild oxidation step. If true, this may make industrial-scale removal of organic sulfur easier than expected.

Using analytical micropyrolysis-gas chromatography with a sulfur-selective flame photometric detector, it is possible to easily see a full distribution of organic sulfur forms in a one-step analysis. The dominant products are H_2S and other simple gases, a complex distribution of alkylthiophenes and, to a lesser extent, alkylbenzothiophenes. The predominance of alkylthiophenes in the pyrolyzates helps to confirm the discovery of thiophenic compounds in the dichromate oxidation products.

The thiophene concentrations in pyrolyzates are directly proportional to bulk organic sulfur values. However, internal thiophene distributions in IBCSP coals are remarkably similar, regardless of organic sulfur content. It is therefore possible to distinguish Illinois Basin coals from foreign coals on the basis of the thiophene distributions. The thiophenes in IBCSP asphaltenes differ from those in their parent coals, but in an apparently consistent fashion. IBCSP exinite macerals are minority constituents of their coal but are very distinctive in their thiophene distributions. They must have a very different macromolecular structure than the dominant vitrinite maceral, which resembles the coal as a whole.

It is not known what effect coal rank has on the nature of organic sulfur in coal, since there is not much variation in rank amongst IBCSP samples. To examine rank effects, we have started analysis on a group of five Appalachian coals of the Lower Kittanning seam, ranging from high-volatile C to medium-volatile bituminous rank.

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 for the second year are:

1. To apply oxidative degradation methods and subsequent chromatographic analysis to a variety of coals and coal derivatives as a means of elucidation of their chemical structure, with emphasis on their organic sulfur and nitrogen forms. During Year 1 of the project, two oxidation methods were determined to be the most useful. Oxidation by peroxyacetic acid is very thorough and can provide a picture of the overall coal structure. Oxidation by sodium dichromate is milder, preserving details of the structure of organic sulfur compounds in particular.
2. In tandem with the two oxidative methods, to apply analytical micropyrolysis techniques to the same suite of samples. This approach will provide a second line of evidence to support findings of the oxidation experiments.
3. To analyze all relevant samples from the Illinois Basin Coal Sample Program bank, to ascertain the extent of variation in organic sulfur structures in the region.
4. To analyze a series of Appalachian coals a) to compare organic sulfur structures with those in Illinois and b) to examine the effect of coal rank on organic sulfur type.
5. To analyze several coals of extraordinarily high organic sulfur content, which will make 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.
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.
7. To develop a routine methodology for the assessment of the nature of organic sulfur in any coal sample.

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. Attempts to characterize organic sulfur in coal have included many different techniques but the necessary detailed information still eludes the scientific community. This is

largely due to the immense task of characterization and to the fact that no one technique can provide all the answers. Degradative methods employing chemical and thermal processes can provide detailed molecular information, but they suffer from the inability to characterize all of the sulfur at one time, and the possibility of regressive and/or rearrangement reactions. On the other hand, bulk spectroscopic ("non-destructive") techniques can observe all of the forms of sulfur simultaneously and in situ. However, most non-destructive techniques are not readily available to the general scientific community and suffer from the inability to resolve detailed molecular information. At best, sulfur compounds are resolved only into general types and hence detailed information such as the nature of substituents and substitution patterns are not available. All information is needed for desulfurization strategies.

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 chemical and thermal degradation techniques for the enhanced characterization of organic sulfur and organic nitrogen in coal.

EXPERIMENTAL METHODS

Samples

Eight coals from the Illinois Basin Coal Sample Program (nos. 101, 102, 104, 105, 106, 109, 110 and 111) have been obtained for investigation in Year 2 of this study. These samples will be referred to as IBC101, IBC102, etc. for purposes of these reports. The IBC101 coal was separated into concentrates of its constituent macerals during Year 1 and these macerals will be analyzed during this year. The other coal samples under investigation are the Rasa Coal from

Pakistan and a Spanish lignite (Lignito De Mequinenza), both of which have extraordinarily high organic sulfur contents. A series of coals from the Lower Kittanning seam of Pennsylvania will also be studied.

Other Methods

Other methods were described in detail in the November 1992 quarterly report. We describe here the few small changes or additions that were made. The dichromate oxidation procedure was modified to handle smaller sample sizes (0.25 to 2.0 g) than the 4.0 g described in the previous report by proportionately decreasing the amounts of reagents. For pyrolysis-gas chromatography-mass spectrometry the GC temperature program was modified slightly (initial temperature of 0° C for 5 min., instead of -20° for 1 min.). The mass spectrometer was in full scan mode (40-450 Da).

Py-GC peaks identifications are confirmed by re-analysis by py-GC-MS and by reference to literature. Conveniently, py-GC results for the Rasa and Spanish samples have been published during the past year [1,2]. This further emphasizes the interest of the scientific community in the characterization of organosulfur compounds in coals and confirms our strategy that the task can be most readily done if materials of extraordinarily high sulfur content are chosen.

RESULTS AND DISCUSSION FOR THIS QUARTER

Elemental Analysis

During the previous quarter further elemental analysis was performed on each coal sample as its preparation was completed (Tables 1 and 2). Although the data is incomplete at this time it is clear that good agreement between the IBCSP data and that from our laboratories is obtained. The exceptionally high organic sulfur content (sulfur determination performed after mineral removal) of the Spanish lignite and the Rasa coal should be noted. In general the sulfur contents of the extracted floated coals are lower than that of the raw coals but not as low as might have been expected from the IBCSP data for organic sulfur content. The difference is probably explained by the incomplete liberation and subsequent removal of very fine pyrite during the grinding, demineralization and sink/float procedures. Nevertheless significant removal of inorganic sulfur forms is achieved by these processes.

Generally the asphaltenes have higher carbon and hydrogen contents and H/C ratios than the extracted floated coals from which they were derived. The most significant difference is the hydrogen content. From the elemental analysis alone the asphaltenes appear less aromatic than the parent coals.

Table 1 - Elemental analysis results (dry, ash free basis)

SAMPLE	%C	%H	%N	%S	%O
101R	81.08	5.08	1.47	4.93	7.45
101EF	65.49	4.68	1.25	3.22	25.37
101ASP	76.25	6.25	0.99	3.03	13.48
101CP	—	—	—	—	—
101ECP	75.57	7.88	1.00	3.63	11.92
101SP	72.49	6.32	0.99	4.08	16.12
101ESP	73.89	6.46	1.14	4.17	14.34
101VP	71.58	5.33	1.34	3.07	18.68
101EVP	71.10	5.17	1.43	3.17	19.14
102R	78.87	4.64	1.53	3.52	11.44
102EF	70.94	4.95	1.48	1.41	21.23
102ASP	75.44	6.20	1.25	2.18	14.94
104R	80.08	4.30	1.47	6.78	7.37
104EF	—	—	—	4.11	—
104ASP	74.58	6.12	0.99	3.45	14.87
105R	78.00	4.08	1.47	5.53	10.92
105EF	—	—	—	3.57	—
105ASP	77.42	6.06	1.30	2.15	13.07
106R	87.31	5.45	1.96	4.29	0.98
106EF	70.43	4.88	1.64	2.68	20.38
106ASP	75.09	6.06	1.29	2.21	15.35
109R	81.68	4.12	1.85	1.20	11.15
109EF	72.70	4.93	1.83	0.76	19.78
109ASP	74.99	5.92	1.38	0.44	17.27
110R	78.60	4.28	1.55	5.21	10.36
110EF	—	—	—	4.71	—
110ASP	78.75	6.30	1.44	2.01	11.50
111R	80.52	3.44	1.69	2.25	12.10
111EF	—	—	—	—	—
111ASP	80.59	6.60	1.40	0.75	10.67
SL	72.09	0.73	1.40	6.33	19.45
SLEF	—	—	—	—	—
SLASP	66.73	6.46	0.90	10.53	15.39
RC	81.97	6.07	1.38	10.60	0.0
RCEF	69.92	5.09	1.27	10.35	13.38
RCASP	72.29	5.67	1.48	10.58	9.98

R = Raw coal   EF = extracted float   ASP = asphaltenes
 SL = Spanish Lignite   RC = Rasa Coal
 CP = cutinite peak   SP = sporinite peak   VP = vitrinite peak

Table 2 - Atomic ratios computed from values in Table 1.

SAMPLE	H/C	S/C	N/C	O/C	N/S
101R	0.7519	0.0228	0.0155	0.0689	0.6805
101EF	0.8566	0.0184	0.0164	0.2905	0.8885
101ASP	0.9836	0.0149	0.0111	0.1326	0.7494
101CP	—	—	—	—	—
101ECP	1.2513	0.0180	0.0113	0.1183	0.6293
101SP	1.0462	0.0211	0.0117	0.1668	0.5543
101ESP	1.0491	0.0211	0.0132	0.1456	0.6235
101VP	0.8935	0.0161	0.0160	0.1957	0.9969
101EVP	0.8726	0.0167	0.0172	0.2019	1.0286
102R	0.7057	0.0167	0.0166	0.1088	0.9958
102EF	0.8373	0.0074	0.0178	0.2244	2.3977
102ASP	0.9854	0.0108	0.0142	0.1485	1.3124
104R	0.6442	0.0317	0.0157	0.0690	0.4944
104EF	—	—	—	—	—
104ASP	0.9849	0.0173	0.0113	0.1495	0.6554
105R	0.6279	0.0265	0.0161	0.1050	0.6074
105EF	—	—	—	—	—
105ASP	0.9393	0.0104	0.0144	0.1266	1.3840
106R	0.7492	0.0184	0.0193	0.0084	1.0467
106EF	0.8315	0.0142	0.0199	0.2170	1.3993
106ASP	0.9683	0.0110	0.0147	0.1533	1.3361
109R	0.6048	0.0055	0.0194	0.1024	3.5320
109EF	0.8138	0.0039	0.0215	0.2041	5.4778
109ASP	0.9473	0.0022	0.0157	0.1728	7.1766
110R	0.6541	0.0248	0.0169	0.0988	0.6817
110EF	—	—	—	—	—
110ASP	0.9600	0.0096	0.0157	0.1095	1.6398
111R	0.5126	0.0105	0.0180	0.1127	1.7180
111EF	—	—	—	—	—
111ASP	0.9822	0.0035	0.0149	0.0993	4.2783
SL	0.1213	0.0328	0.0166	0.2024	0.5067
SLEF	—	—	—	—	—
SLASP	1.1613	0.0591	0.0115	0.1729	0.1945
RC	0.8890	0.0484	0.0145	0.000	0.2986
RCEF	0.8727	0.0554	0.0155	0.1435	0.2798
RCASP	0.9412	0.0548	0.0175	0.1036	0.3200

The sulfur contents of the asphaltenes and more importantly the S/C ratios are usually slightly lower than those of the parent extracted floated coals. The only exception to this found so far is the IBC 102 sample where

the asphaltenes have a much higher S/C values. It is not known why the IBC 102 sample behaves differently but it demonstrates that at least part of the organic sulfur in this coal can be removed by solvent extraction alone.

Although slight variations in the elemental composition of the coals and the asphaltenes derived from them do exist, this fact alone does not eliminate the asphaltenes as being considered as suitable models for the organic sulfur chemistry of the whole coal. This determination can only be made by examining the sulfur chemistry of the asphaltenes and the coals using the techniques employed in this as well as other studies.

Reasons for Examining Kittanning Coals.

The Illinois Basin coals provided by the Illinois Basin coal sample program do not encompass a wide range of coal ranks. To study how coal rank influences organic sulfur distribution it is necessary to examine non sample bank coals. One of the most important and well characterized rank series of coals is from the Lower Kittanning seam of Pennsylvania and Ohio. These coals all come from the same seam and hence have the same or very similar source of vegetative matter, but due to geologic forces certain portions of the seam attained different rank. Study of this series of coals will therefore allow for the effects of varying rank on the distribution of organic sulfur species to be investigated. It will also help to establish whether certain organic sulfur species are unique to the Illinois Basin coals and therefore, whether different desulfurization strategies may be needed for Illinois versus non-Illinois coals.

Five Kittanning coals have been selected. Important selection criteria were rank and organic sulfur content. Generally the coal sample with the highest organic sulfur content for that particular rank range was selected. Using this approach the five coals have vitrinite reflectance ranging from 0.65 to 1.42 % and organic sulfur contents from 0.75 to 2.25%. The inclusion of these samples, plus the very high organic sulfur foreign coal samples, along with the series of Illinois Basin coals, provides an extensive test of the characterization methods employed in this study.

Oxidation by Sodium Dichromate

The previous Quarterly Report focused on the 5-step successive dichromate oxidation of a single large (4 g) sample of IBC101 floated coal. We noted progressive increase in aromaticity (indicated by relative concentrations of benzene and methylbenzene polycarboxylic acids) and decrease in aliphatic and alkylthiophenic carboxylic acids with each new oxidation step. In the second quarter, we proceeded with one or two step dichromate oxidation of smaller quantities of the remainder of the IBC and foreign coals and asphaltenes,

as well as the IBC101 coal macerals. Most of the oxidation work is completed and we are now engaged in GC-MS analysis.

Figure 1 - Partial total ion current chromatograms of methylated dichromate oxidation products showing benzene and methylbenzene dicarboxylic acids ($\beta 2$ and $m\beta 2$) and ethyl- and propylmethoxythiophene carboxylic acids ($\theta 2$ and $\theta 3$) as methyl esters. A) IBC106 coal, 1st oxidation step, B) IBC106 coal, 2nd step, C) IBC102 coal, 1st step and D) IBC101 sporinite, 1st step.

In the new oxidation products analyzed thus far, the long-chain *n*-alkyldioic acids (C_8 - C_{13}) were much less abundant than in the large-scale 4 g experiment of the first quarter. This seems to indicate that the smaller scale oxidation is more efficient, i.e., a product of greater aromaticity can be produced in fewer steps. Thus, simple linear reduction in

reagent quantities may not be adequate when scaling down the oxidation to handle the smaller sample sizes. The alkylthiophene carboxylic acid derivatives (ATCA) noted in the November 1992 Quarterly Report are still present (02 and 03 in Fig. 1). The relative concentrations of these peaks

Figure 2 - Plots of peak ratios from GC-MS data collected on the methylated dichromate oxidation products of a) IBC101 asphaltenes, 1st oxidation step, b) IBC101 sporinite, 1st step, c) IBC101 coal, 1.5 g run, 1st step, d1-d5) IBC101 coal, 4.0 g run, 5 steps, e1-e2) IBC102 coal, 2 steps, and f1-f2) IBC106 coal, 2 steps.

decrease with decreasing S/C ratios, as can most readily be seen by monitoring peak 03, which is large in the sporinite (Fig. 1D), less in IBC106 coal (Fig. 1A) and lesser still in IBC102 coal (Fig. 1C). Also ATCA peaks are still seen to

diminish after repeated oxidation. Peak 03 is weaker in the products of the second oxidation step of IBC106 coal (Fig. 1B) than after the first step (Fig. 1A). This is expressed graphically in Figs. 2A and 2B, which also include data from the 5-step procedure performed on IBC101 coal, for which the trends are the clearest. In Fig. 2B, it can also be seen that thiophene contents diminish after the repeated oxidation of IBC102 coal. It is interesting that the behavior of this sulfur-lean coal is similar to the richer samples.

As a control useful in monitoring the effects of scaling down the oxidation procedure, a one-step oxidation of 1.5 g of fresh IBC101 floated coal was performed. The thiophene/benzene ratio from the oxidation products of this experiment is comparable with that from the second step of the 4 g experiment (bars c and d2 in Fig. 2B), seeming to confirm that the scaled-down oxidations are more efficient. Also of interest is the internal distributions of ATCA compounds, exemplified in Fig. 2C by a ratio of the 02 and 03 peaks. The C₃-substituted variety diminishes with successive oxidation steps, but is slightly favored in the sporinite and asphaltene over the coal.

Pyrolysis-Gas Chromatography

Work on pyrolysis-gas chromatography continued during the second quarter primarily using the sulfur-selective flame photometric detector (py-GC-FPD). Fig. 3 shows examples of results from Illinois Basin and foreign coals and asphaltenes. The IBC and Spanish samples are dominated by H₂S and thiophene and its simple alkyl derivatives (C₁-C₃). The Rasa coal is distinctive in that it has a much greater proportion of benzothiophene and C₁-C₃ alkylbenzothiophenes. For all samples, the relative prominence of the benzothiophene series is slightly higher in the asphaltenes than in the parent coal, perhaps due to a great efficiency of pyrolysis. Except for such systematic shifts, the asphaltenes show an overall similarity to their coals.

The thiophenes can be examined in detail by studying the distributions of C₂ and C₃ alkylthiophene and alkylbenzothiophene isomers (Figs. 4 and 5). As examples, the two foreign coals are compared with two from the Illinois Basin coals - IBC101 from the Illinois No. 6 seam and IBC106 from the Indiana V seam. Except for the slightly higher amount of 2,4-dimethylthiophene (peak f in Fig. 4) in IBC106 asphaltenes, the two IBC samples are virtually identical. This is remarkable since they are from different seams mined in widely separated parts of the basin. The C₃-alkylthiophenes are the most effective in distinguishing the foreign coals from the IBC. The Rasa coal and asphaltene shows more of peaks h, j and l, while the Spanish samples show more of peak i. All asphaltenes are subtly different from their parent coals, usually with lesser amounts for peaks e and i. The distributions of C₂ and C₃

Figure 3- Py-GC-FPD traces showing organosulfur compound distribution in floated and extracted IBC106 coal (A) and Rasa coal (B), as well as IBC106 (C) and Rasa (D) asphaltenes. See Table 3 for peak identification.

Figure 4- Partial Py-GC-FPD traces showing C1- and C2-alkylthiophenes in IBC101 floated coal (A) and asphaltenes (B), IBC106 floated coal (C) and asphaltenes (D), Rasa floated coal (E) and asphaltenes (F) and Spanish lignite whole coal (G) and asphaltenes (H). See Table 3 for peak identifications.

Figure 5- Partial Py-GC-FPD traces showing C2- and C3-alkylbenzothiophenes in IBC101 floated coal (A) and asphaltenes (B), IBC106 floated coal (C) and asphaltenes (D), Rasa floated coal (E) and asphaltenes (F) and Spanish lignite whole coal (G) and asphaltenes (H).

alkylbenzothiophenes are more complex since more isomers are possible (Fig. 5), and this should make their chromatograms good for "fingerprinting" purposes. The two IBC coals are again very similar (Figs. 5A and 5C), but the IBC106 asphaltene shows more of peaks 8, 13 and 15 than does IBC101 (Figs. 5B and 5D). The Rasa coal and asphaltene differ from the IBC in a prominence of peak 6 and a lack of peaks 12 and 14 (Figs. 5E and 5F). The Spanish samples have simpler distributions, with a predominance of peaks 1, 4, 11 and 12 (Figs. 5G and 5H).

Table 3 - Py-GC-FPD peak identification for Figs. 3-5.

θ	thiophene
θ1	methylthiophenes
θ2	C ₂ -alkylthiophenes, specified in Fig. 4 as follows:
	d 2-ethylthiophene
	e 2,5-dimethylthiophene
	f 2,4-dimethylthiophene
	g 2,3-dimethylthiophene
θ3	C ₃ -alkylthiophenes, specified in Fig. 4 as follows:
	h 2-propylthiophene
	i 2-ethyl-5-methylthiophene
	j 2-ethyl-4-methylthiophene
	k 2,3,5-trimethylthiophene
	l 2,3,4-trimethylthiophene
Bθ	benzothiophene
Bθ1	methylbenzothiophenes
Bθ2	C ₂ -alkylbenzothiophenes (also peaks 1-8, Fig. 5)
Bθ3	C ₃ -alkylbenzothiophenes (also peaks 9-15, Fig. 5)

As the number of samples increase, it becomes no longer practical to show all the chromatograms. Instead chromatographic peaks must be quantitated and expressed in ratio form. We have now completed py-GC-FPD analysis of 22 coal, asphaltene and maceral samples. Fig. 6 plots the peak areas of prominent thiophenes (two methylthiophenes, an ethylthiophene and three dimethylthiophenes, labeled as θ1 and θ2 in Fig. 3) as a function of bulk organic sulfur content for all samples. The thiophene content increases predictably for the IBC coals, asphaltenes and vitrinite as the S_{org} content rises. This points to a consistent style of incorporation of sulfur in their macromolecular structure, regardless of the amount of sulfur present. The Spanish asphaltene is also on this trend. The Spanish coal appears enriched in thiophenes, but this point is only provisionally plotted using the value from the whole coal (we are still waiting for sulfur analysis on the floated coal). The Rasa samples appear depleted in thiophenes, but as discussed above, benzothiophenes take up much of their organic sulfur and these compounds are not included in this ratio. The IBC101 exinites (sporinite and cutinite macerals) appear enriched in thiophenes and we believe that this corresponds

to a real difference in their macromolecular structure, clearly distinguishing them from their parent coal and its vitrinite and asphaltene.

Figure 6 - Log-log plot of thiophene content from py-GC-FPD data as a function of bulk organic sulfur content.

In an effort to begin to classify the samples by the kind of organic sulfur present, rather than simply the amount, two simple ratios are proposed. The change in concentration of methylthiophenes and C₂-alkylthiophenes (collectively designated θ_1 and θ_2 in Fig. 3) leads to one ratio. The variable amounts of 2,5-dimethylthiophene (peak e in Fig. 4) when compared to the other dimethylthiophenes (peaks f and g) form the basis for another. The two ratios are cross-plotted and the samples are readily grouped (Fig. 7). IBC coals and vitrinite form a distinctive cluster, especially interesting since the samples come from different seams and mines and have widely varying sulfur content. Their asphaltenes also form another tight cluster, showing that the asphaltenes, while different in detail from their parent coals, differ in a consistent fashion. The IBC exinites, as in Fig. 6, are shown to be structurally distinctive from coal, vitrinite and asphaltene. Finally, the foreign coals are clearly differentiated from the IBC.

Figure 7 - Cross-plot of thiophene ratios from py-GC-FPD data.

CONCLUSIONS AND RECOMMENDATIONS

1) While the elemental analysis data set is still incomplete, new results confirm that asphaltenes show increases in H/C and decreases in O/C atomic ratios over the demineralized, floated parent coal. N/C and S/C ratios show only minor differences between asphaltenes and coal. On this basis, the asphaltenes continue to appear to be good surrogates for the characterization of organic acid rain precursors in coal.

2) We have analyzed dichromate oxidation products of additional IBCSP samples. Alkylmethoxythiophene carboxylic acids (ATCA) are detected in all samples. Relative concentrations of ATCA compounds are directly proportional to the bulk organic sulfur contents of the samples. As reported in the previous quarter, concentrations of ATCA compounds in oxidation products decrease upon repeated oxidation. This may indicate that the thiophenic groups tend to be located in external positions on the coal macromolecular structure and a high proportion of them can be stripped away with only one mild oxidation step. If true, this may make industrial-scale removal of organic sulfur easier than expected.

3) Using analytical micropyrolysis-gas chromatography with a sulfur-selective flame photometric detector (py-GC-FPD), it is possible to easily see a full distribution of organic sulfur forms in a one-step analysis. The dominant products

are H₂S and other simple gases, a complex distribution of alkylthiophenes and, to a lesser extent, alkylbenzothiophenes. The predominance of alkylthiophenes in the pyrolyzates lends credence to the discovery of thiophenic compounds in the dichromate oxidation products.

4) The thiophene concentrations in pyrolyzates are directly proportional to bulk organic sulfur values. However, thiophene distributions in IBCSP coals are remarkably similar, regardless of organic sulfur content. It is possible to distinguish Illinois Basin coals from foreign coals on the basis of the thiophene distributions. IBCSP asphaltenes are also distinguishable from the parent coals by thiophene distributions, but are not radically different. IBCSP exinite macerals are minority constituents of their coal but are very distinctive in their thiophene distributions. They must have a very different macromolecular structure than the dominant vitrinite maceral, which resembles the coal as a whole.

5) It is not known what effect coal rank has on the nature of organic sulfur in coal, since there is not much variation in rank amongst IBCSP samples. To examine rank effects, we have started analysis on a group of five Appalachian coals of the Lower Kittanning seam, ranging from high-volatile C to medium-volatile bituminous rank.

REFERENCES

- 1) Sinninghe Damsté J.S., de las Heras F.X.C. and de Leeuw J.W. (1992). *J. Chrom.* **607**:361-376.
- 2) Sinninghe Damsté J.S. and de Leeuw J.W. (1992). *Fuel Process. Tech.* **30**:109-178.

PROJECT MANAGEMENT REPORT
1 December, 1992 through 28 February, 1993.

Project Title: **ANALYSIS OF ORGANIC SULFUR AND NITROGEN IN
COAL VIA TANDEM DEGRADATION METHODS**

Principal Investigator: Michael A. Kruge, Assoc. Professor,
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Project Monitor: Ken Ho, CRSC

The project is proceeding essentially on schedule and budget.
More time will be needed to complete the gel permeation
chromatography.

EXPENDITURES - EXHIBIT B

Cumulative Projected and Estimated Actual Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1992	Projected	13,219	2,500	500	0	3,750	1,997	21,966
to Nov. 30, 1992	Estimated Actual	16,871	697	0	0	490	1,806	19,863
Sept. 1, 1992	Projected	26,438	5,000	1,000	0	8,000	4,044	44,482
to Feb. 28, 1993	Estimated Actual	27,573	4,310	-0-	0	3,940	3,522	39,345
Sept. 1, 1992	Projected	39,658	7,500	1,000	0	15,750	6,391	70,299
to May 31, 1993	Estimated Actual							
Sept. 1, 1992	Projected	67,819	10,000	1,000	0	18,500	9,732	107,051
to Aug. 31, 1993	Estimated Actual							

*Cumulative by quarter.

CUMULATIVE COSTS BY QUARTER - EXHIBIT C

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

O = Projected Expenditures -----

Δ = Actual Expenditures _____

Total CRSC Award \$107,051

SCHEDULE OF PROJECT MILESTONES — YEAR 2

TASK	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
1. Sample Preparation (complete)												
2. Oxidation Alone (complete)												
3. Reduction Alone (complete)												
4. Tandem Oxidation/Reduction												
5. Chromatography and MS												
a. Gel Perm. Chromatography												
b. GC-FPD & GC-TSD												
c. GCMS												
d. Probe-High Res. MS												
e. py-GC-FID & FPD												
6. Interpretation												
Reporting												

Comments: Due to the concentration on the extensive gas chromatographic work, more time will be required to complete the gel permeation chromatography.

END

DATE
FILMED

6 / 17 / 93