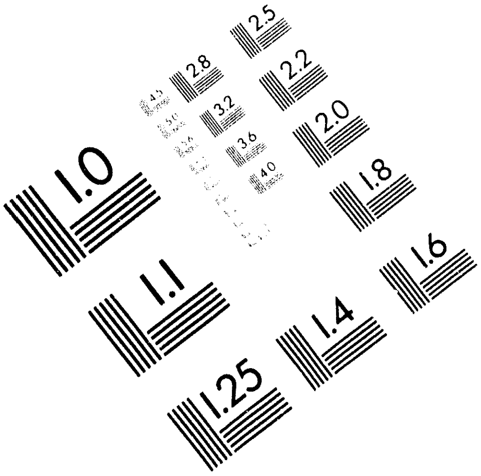
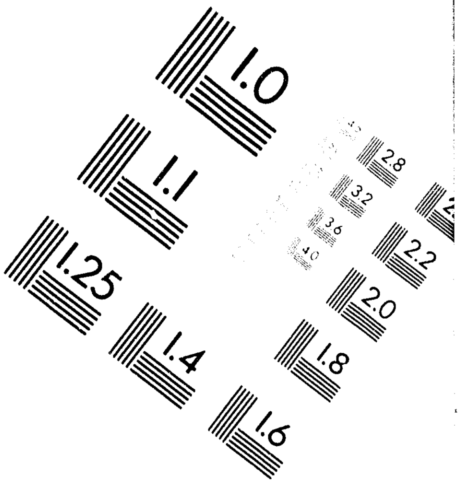


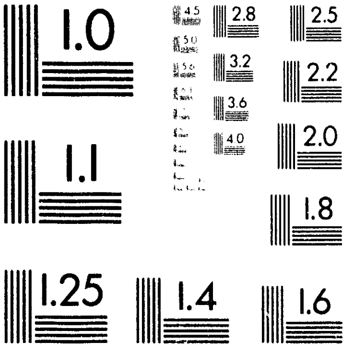
AIIM

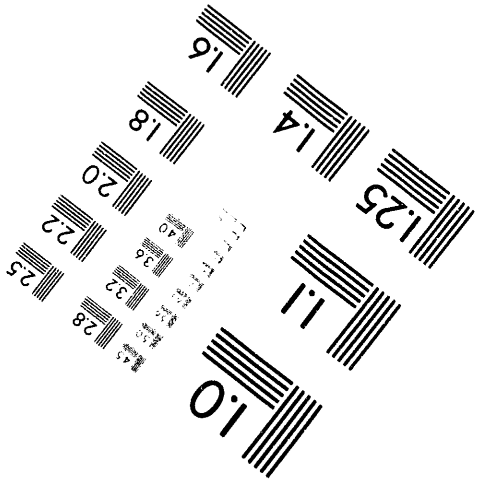
Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

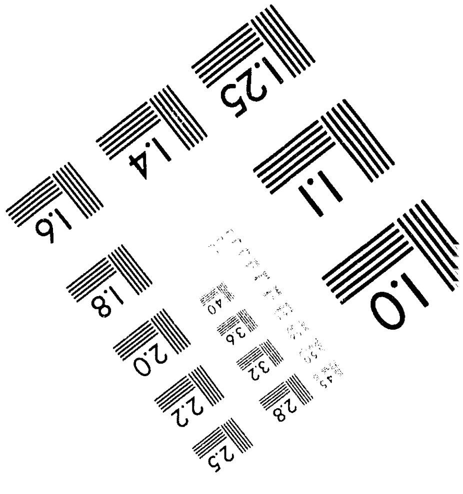
301/587-8202







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

DOE/PC/92521--T147

TECHNICAL REPORT
December 1 1993 through February 28th, 1994

Project title: **ANALYZING ORGANIC SULFUR IN COAL/CHAR: INTEGRATED MILD DEGRADATION/XANES METHODS**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/6.1A-1P
Principal Investigator:	Dr. Stephen R. Palmer, Department of Mechanical Engineering and Energy Processes, Southern Illinois University at Carbondale, Carbondale IL 62901.
Other Investigator:	Dr. G. P. Huffman, Consortium for Fossil Fuel Liquefaction Science, 233 Mining and Mineral Resource Building, University of Kentucky, Lexington, KY 40506.
Project Manager:	Ken Ho, Illinois Clean Coal Institute

ABSTRACT

The cost effective removal of sulfur from coal has been very difficult to accomplish. Perhaps the single most important reason for this is the fact that the organic sulfur in coal remains very poorly characterized. The overall goal of this study is to improve our understanding of sulfur in coals/chars via the use of combined advanced non-destructive and advanced destructive methods of sulfur analysis. This study combines selective oxidation, analytical pyrolysis, and sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis.

Although insufficient data has been collected at this time to allow a direct comparison between destructive and non-destructive techniques, it is clear that the sulfur chemistry of gasification chars is significantly different from that of the original coals. Examination of samples that were oxidized with peroxyacetic acid using the analytical pyrolysis technique showed that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. Sulfur XANES spectra of treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid at 25°C) showed preferential oxidation of one or more sulfur-bearing phases in the original coal.

U.S. DOE Patent Clearance is <u>NOT</u> required prior to the publication of this document.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EXECUTIVE SUMMARY

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain. To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called 'destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called 'non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived form them. To achieve this overall objective a number of specific goals and objectives can be identified. These are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived form them.

2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.

3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.

4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.

5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.

6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

Although insufficient data has been collected at this time to allow a direct comparison between destructive and non-destructive techniques, it is clear that the sulfur chemistry of gasification chars is significantly different from that of the original coals. This can be seen from a comparison of the analytical pyrolysis chromatograms of the IBC coals and their gasification chars and from the preliminary XANES results. Using the analytical pyrolysis technique, it is clear that the gasification char does not yield the alkyl and benzothiophenes that are abundant before gasification. Although this result is not too surprising, it clearly demonstrates that the distribution of sulfur species changes as a result of mild gasification.

In addition, examination of IBC-101 samples that were oxidized with peroxyacetic acid using the analytical pyrolysis technique shows that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. This observation would support our earlier findings which suggested that peroxyacetic acid was oxidizing simple thiophenes to methyl sulfonic acid.

From the XANES experiments conducted so far, the four original coal samples (IBC 101,102,106 and 109) were found to contain most of the organic sulfur in the form of thiophene derivatives, with a minor to significant amount present as organic sulfide. This is in agreement with previous XANES studies on Illinois coals. However, all of the coals were oxidized to some extent as the sulfate contents of the coals were significant. This result was also confirmed by Mössbauer spectroscopy, which showed that a significant fraction of the pyrite in the coal was oxidized. In the extreme case (IBC-

102), sulfate sulfur constituted over 50% of the sulfur in the sample and over half the iron was also present as $FeSO_4 \cdot H_2O$ (szomolnokite). In comparison, the other coal samples examined showed less than 15% of the sulfur or iron in the form of sulfates. We are currently re-examining freshly prepared samples.

Sulfur XANES spectra of the treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid at 25°C) showed preferential oxidation of one or more sulfur-bearing phases in the original coal. For example, the peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur, whereas the steam treatment appeared to largely alter the pyrite to pyrrhotite, along with some reduction of organic sulfide as well.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBJECTIVES

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived form them.

Specific Objectives

The specific goals and objectives of this study are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived form them.
2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.
3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.
4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.
5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.
6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

To achieve these goals a series of tasks were scheduled for completion within the contract period. These tasks include:

Task 1. Sample selection and preparation.

Four coals, IBC-101, IBC-102, IBC-106 and IBC-109 are to be obtained from the Illinois Basin Coal Sample Program. Aliquots of each are to be micronized, sink/floated and solvent extracted. Aliquots of these samples are then to be selectively oxidized, mildly gasified and chemically desulfurized.

In addition, a mild gasification reactor is to be designed and constructed and used for the preparation of mild gasification chars. The object of task 1 is to provide a variety of samples with different sulfur contents and distributions.

Task 2. Analytical pyrolysis.

The first sulfur characterization technique to be applied to the samples prepared in task 1 is analytical pyrolysis. Both py-GC-FPD and py-GCMS is to be used to characterized organic sulfur species present in the pyrolysis products.

Task 3. Coal/char oxidation with sodium dichromate.

The samples prepared in task 1 are to be characterized by selective oxidation with sodium dichromate. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 4. Coal/char oxidation with peroxyacetic acid.

The samples prepared in task 1 are to be characterized by selective oxidation with peroxyacetic acid. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using CG-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 5. Sulfur XANES and Mössbauer analysis.

Samples prepared in task 1 and selected samples produced in tasks 3 and 4 are to be examined by sulfur K-edge XANES and W-Band EPR. By analyzing the samples before and after selective oxidation, mild gasification and desulfurization, it will be possible to determine which sulfur forms are released from the coal, those which remain and transformations between sulfur forms resulting from the various treatments.

Task 6. ASTM methods of coal/char analysis.

Selected samples from tasks 1-5 are to be analyzed by standard ASTM methods of analysis such as proximate, ultimate, sulfur forms and BTU analysis.

INTRODUCTION AND BACKGROUND

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain.(1) To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite) (2,3), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

There have been many attempts to characterize the organic sulfur in coal and some important progress has been made.(4) However, a universally excepted method for organic sulfur characterization has yet to be provided. The problem is due to the extreme complexity of the chemistry of coal, a fact that prevents any single characterization technique from providing all of the necessary information. The solution to this problem would therefore appear to be the use of a combination of several techniques such that the combined information would be sufficient for complete sulfur characterization. This idea serves as the basis for this current research program.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called 'destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called 'non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The current study combines selective oxidation strategies, analytical pyrolysis with subsequent GC-FPD and GC-MS analysis, and Sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis of Illinois Basin coals and mild gasification chars derived from them for the complete characterization of organic sulfur.

It is anticipated that this characterization approach will provide both the detailed molecular structure, and the overall quantitative distribution, of organic sulfur thereby leading to a more complete analysis of organic sulfur structures in coals and chars.

EXPERIMENTAL PROCEDURES

Sample Preparation

Typical coal preparation includes coal micronization, coal demineralization, coal flotation and solvent extraction. Micronization is achieved using a nitrogen powered fluid energy mill and is necessary to liberate the mineral component of coal from the organic component. Approximately 200 grams of each coal were micronized. To remove minerals from the coal acid treatments with HCl and HF, and a subsequent sink/float procedure are required. The acid treatment is performed by dispersing 100grams of the micronized coal in a 500mL mixture of HF and HCl (3:1). After the mixture has been stirred for 3 hours the coal is recovered by filtration and the residual acid washed away with hot distilled water until the filtrate is neutral.

To remove minerals such as pyrite that are insoluble in the HF/HCl mixture the sink/float procedure was employed. This involves dispersing the acid treated coal in a cesium chloride solution of specific density 1.6g/mL. This coal slurry is then centrifuged so that the mineral sinks and the organic coal floats. The mineral free coal (approximately 1-1.5% ash) is collected by filtration, washed sequentially with dil. HCl and hot distilled water and finally dried. Solvent extraction was performed on aliquots of the demineralized coal using an azeotropic mixture of methanol and chloroform. Soxhlet apparatus was used.

Coal Oxidation

Two selective oxidation procedures have been used. The first is a relatively mild oxidation which results in little coal dissolution. This is used to provide samples for subsequent XANES, W-Band EPR and analytical pyrolysis analysis. The second procedure is more extensive and results in almost complete dissolution of the coal. This procedure is used for sulfur characterization by GC-FPD and GCMS.

Typical mild selective oxidation with peroxyacetic acid involves dispersing 2 grams of the solvent extracted coal sample in a mixture of 50mLs glacial acetic acid and 50mLs 30% (wt/v) hydrogen peroxide. The mixture is then stirred at room temperature for six hours. After this time the oxidation product is recovered at the filter largely as undissolved coal solids. This material is washed with distilled water and dried.

The procedure used for subsequent GC-FPD and GCMS analysis used the same quantities of coal and reagents but this time the reaction is carried out under reflux for 24 hours. After this time the coal is almost completely in solution. The solubilized oxidation products are recovered by first removing any residual undissolved material by filtration. Any excess peroxides in the oxidation products solution are then destroyed by the addition of 10mg of platinum on carbon (1% wt Pt). The peroxide free solution is the rotary evaporated to recover the soluble coal products. For GC-FPD and GCMS analysis these oxidation products are first methylated with diazomethane.

Coal Gasification

A preliminary mild gasification experiment was performed by sealing 2g of the IBC-101 micronized sample in a 10mL stainless steel micro-reactor with 2 mL of water. After purging the reaction with nitrogen it was sealed and heated to 450°C in a fluidized sand bath for 1 hour. After this time the reactor was cooled and the product recovered at the filter where it was washed with distilled water and dried.

Using the mild gasification unit constructed in the previous quarter, six gasification chars have been prepared. These experiments have been performed on 2 grams coal aliquots at a temperature of 450°C and 550°C using a 10mL per minute flow of nitrogen gas. Other chars will be prepared using hydrogen and steam as reactive gases.

Coal Desulfurization

The method of coal desulfurization used incorporates an oxidative pretreatment step followed by an alcohol/base desulfurization reaction. The pretreatment step involved dispersing coal (50g) in glacial acetic acid (200mL) and adding 50mL of 30% (wt/v) hydrogen peroxide solution. After stirring this mixture for 6 hours at room temperature the oxidized coal is recovered by vacuum filtration, washed with distilled water and finally dried at 110°C. The oxidized coal (2g) is then dispersed in a suspension of 0.2g NaOH in 5mL methanol. This mixture is placed in a 10 mL stainless steel micro-reactor, purged with nitrogen, sealed and then heated to 350°C for 1 hour. The resulting desulfurized coal is then collected at the filter, washed with distilled water and finally dried.

XANES Analysis

The sulfur XANES spectra are measured at beam-line X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. This beam line is well suited for soft X-ray measurements because the X-rays are in vacuum right up to the sample and are therefore minimally absorbed before interacting with the sample. Spectra are collected in fluorescence geometry and stored in a MicroVAX II computer at NSLS before being transferred to a similar computer at the University of Kentucky. Standard computerized methods are used to separate the XANES region from the XAFS spectrum. A least-squares fitting program (EDGFIT) is then applied to the XANES spectrum to determine the contribution of different sulfur forms to the spectrum. The areas under the peaks in the fitted spectrum are then converted to wt% sulfur in the various forms.

RESULTS AND DISCUSSION

Sample Preparation

During the previous quarter six gasification chars have been prepared for analysis. The char yields and gasification conditions are given in Table 1.

Table. 1. Mild gasification yields and conditions.

Coal	101M	102M	106M	109M	101F	106F
Code	101MG2	102MG1	106MG1	109MG1	101MG3	106MG2
Conditions N2	450°C	450°C	450°C	450°C	550°C	550°C
Char yield	64.0	70.8	70.5	77.5	62.5	60.0
Tar yield	8.8	5.4	4.0	5.4	13.0	
weight loss	27.2	23.8	25.5	17.1	24.5	

M = micronized coal, F = floated coal

Aliquots of these samples plus those currently being prepared are to be delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES analysis during the March/April Brookhaven session. Aliquots will also be sent to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these same samples are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques. The available ultimate and proximate data for these new samples plus that for the ten samples prepared in the first quarter are listed in Table 2. (The data is reported on a dry basis.)

Table 2. Ultimate and proximate composition data.

Sample	Elemental Composition				Ash
	%C	%H	%N	%S	wt%
101M	72.41	4.51	1.30	4.40	10.82
102M	73.71	4.33	1.44	3.27	10.73
106M	79.41	4.94	1.79	3.90	9.06
109M	74.90	3.78	1.70	1.10	8.30
101FE	65.49	4.68	1.25	3.22	2.63
106FE	70.43	4.88	1.64	2.68	3.71
101SO	63.07	4.64	1.21	2.84	7.84
106SO	66.07	4.46	1.47	1.95	6.55
101MG1	74.50	3.09	1.36	3.16	9.23
101MG2	71.00	2.98	1.30	3.09	15.32
101MG3	87.16	2.55	1.68	2.28	2.29
102MG1	74.53	3.52	1.91	3.09	10.33
106MG1	71.61	2.94	1.98	2.67	13.29
109MG1	78.94	3.49	2.19	1.21	10.38
101DES1	75.38	5.08	1.17	0.77	13.98

M = micronized, FE = floated + extracted, SO = selectively oxidized, MG = mild gasification char (Table 1), DES = desulfurized.

As can be seen from the data in Table 2 samples have been prepared which have a wide variety of sulfur contents. (0.77% to 4.40%) In addition, since the methods of preparation vary, it is likely that the sulfur compound distributions in each sample will vary also. This sample set should therefore provide a good test for the various sulfur characterization techniques employed in this study.

It is clear that the demineralization procedures (acid treatment and sink/float) reduce the sulfur content of the samples considerably. This is due to the removal of mineral forms of sulfur, especially pyrite. However, the sulfur contents for the floated coals is not as low as predicted from the sulfur forms data provided by the IBCSP and it is suspected that some pyrite remains in these samples. This situation is probably due to the incomplete liberation of the pyrite during the micronization of the coals.

The oxidation treatment with peroxyacetic acid lowers the sulfur content of the coals further, primarily by the dissolution of any remaining pyrite but also by reaction with the organic sulfur. Previous investigations showed that between 10 and 20% of the organic sulfur in these coals was removed by peroxyacetic acid oxidation. (5)

With the exception of the micronized IBC-109 sample, all mild gasification chars show reductions in their sulfur contents when compared to their parent coal. For the IBC 101 and 106 samples the reduction in sulfur content is quite large (around 30%) but for the IBC-102 a sulfur content reduction of only 5% is observed. The 109 sample show an increase in its sulfur content of around 10% when treated under similar conditions. The reason for the difference in behavior of the samples is probably due to variations in the distribution of their sulfur forms and other structures in the coals.

Analytical Pyrolysis

Each of the samples prepared has or is being examined by analytical pyrolysis GCMS. From the total ion chromatogram (TIC) for each pyrolysate single ion chromatograms (SIC) are constructed for ions that are representative of sulfur containing compounds. Figure 1 shows the SICs for the sum of the ions (m/e) 98, 112, 126 and 140 for selected samples. These ions are characteristic of C_1, C_2, C_3 and C_4 substituted thiophenes respectively.

From Figure 1 it can be seen that substituted thiophenes can be detected in all samples. However, their abundance varies considerably. Indeed, it can be seen that as the level of selective oxidation increases so the abundance of the substituted thiophenes decreases. This finding supports our previous observation that peroxyacetic acid oxidizes simple thiophene structures to methylsulfonic acid. The mild gasification char prepared by a steam treatment at 450°C for 1 hour also has a low abundance of substituted thiophenes. Presumably these structures were removed from the coal during gasification or converted into other sulfur forms. The reduction in the sulfur content supports the removal theory but a conversion to another sulfur form cannot be ruled out.

Sulfur K-edge XANES Results

The sulfur K-edge XANES results for the ten sample submitted during the first quarter are summarized in Table 3. The XANES spectra for the four raw coals together with their Mössbauer spectra are shown in figures 2-5. It should be noted that these results are preliminary and that further analysis is needed to confirm many of the sulfur forms assignments.

Raw coals

All four coals show some oxidation of the sulfur forms. In the worst case, IBC-102 coal, the analysis shows that 52% of sulfur is in the sulfate form and that substantial sulfur

(8%) is present as elemental sulfur, generated as a product of pyrite oxidation. To accurately determine the original distributions of sulfur forms it will be necessary to analyze a new pristine set of coals.

Chemically treated coals

1. <u>Demineralized, floated and solvent extracted coals.</u> This mild treatment to remove mineral matter and the mobile phase from coal does not have much impact on the distribution of various sulfur forms in coals. The IBC-101 floated and extracted coal shows some oxidation during this treatment as the concentration of the oxidized forms (sulfoxide and sulfate) have increased and the sulfide and thiophene concentrations have decreased. As expected, the XANES peak due to pyrite is eliminated by this treatment.

2. <u>Desulfurized coal.</u> The desulfurization treatment (mild oxidation followed by alcohol/base treatment at 350°C) apparently removes all sulfide forms of sulfur from coal. The concentration of the oxidized forms of sulfur do not appear to have increased significantly during this process. Since the sulfur content of this particular sample is only 0.77% then thiophene types of sulfur must also have been removed since the original sulfur content assigned to thiophenes for this coal is approximately 1.7-2.0%.

3. <u>Peroxyacetic acid oxidation.</u> Examination of the XANES data indicated that sulfide forms of sulfur are converted to their sulfones by peroxyacetic acid. This is supported by the oxidation of sulfide model compounds to their sulfones under similar conditions. The thiophenic sulfur forms however appear to be unchanged by the oxidation. This is surprising because previous mild degradation and analytical pyrolysis results suggest that simple thiophenes are oxidized by this treatment. It is expected that the discrepancy is due to the differences in the sensitivity of the different analytical methods to minor changes in sulfur form distributions, and from the fact that the sample that was analyzed by XANES received only a very mild oxidative treatment. It is anticipated that stronger oxidation conditions will reveal changes in the thiophene content as determined by XANES analysis. This will be examined later in this study.

4. <u>Steam treatment at 450°C.</u> This treatment converts pyrite to pyrrhotite. Since the pyrrhotite peak is better isolated from the sulfide and thiophene peaks than the pyrite peak (at -0.5 eV), it is easier to deconvolute it from the sulfur XANES spectra. Thus, although both pyrite and pyrrhotite have similar calibration constants, the pyrrhotite percentages are usually more accurate than the pyrite percentages in XANES analysis. The steam treatment does not appear to induce any additional oxidation of the sample.

Table 3. Sulfur K-edge XANES edgefit results.

XAFS file	Sample #	%s	Pyrrhotite	Pyrite	Elem. S	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
spalmer.655	IBC-101	100				29	62	5		4
spalmer.656	IBC-102	100			8	12	27			52
spalmer.657	IBC-106	100		28		16	42	1		13
spalmer.658	IBC-109	100		25		9	56			10
spalm.814	FE6	100				12	67	5		16
spalm.815	FE1	100				22	53	8		17
spalm.817	MG1	100	33			9	49	3		7
spalm.821	D1	100					88	6	2	4
spalm.822	SO1	100					64	6	20	11
spalm.824	SO6	100					57	4	21	18

^{57}Fe Mössbauer Spectroscopy

As mentioned earlier, because of lower calibration constants, XANES analysis has poorer sensitivity for pyrite and pyrrhotite forms than other forms of sulfur. Fortunately, Mössbauer spectroscopy is an excellent technique for identifying and quantifying these forms of iron in coal. We have carried out room temperature Mössbauer spectroscopy on all of the raw coal samples to further quantify these forms. The following table shows the distribution of iron into various forms as identified by Mössbauer spectroscopy. Also listed in the table are the values of weight percent pyritic sulfur as determined by Mössbauer spectroscopy.

Table 4. ^{57}Fe Mössbauer results.

Mössbauer File	Sample #	Pyrite	Jaro site	Szomol nokite	Clay	wt% Pyritic Sulfur
MK1724	IBC101	87	13	0	0	0.26
MK1721	IBC102	29	25	46	0	0.46
MK1722	IBC106	73	16	11	0	1.24
MK1725	IBC109	72	13	0	15	0.37

Mössbauer spectroscopy confirms the XANES data in that oxidation of the coals is observed. Jarsonite and szomolnokite are iron sulfate forms produced as a product of pyrite oxidation. They compromise the sulfate peaks in the sulfur K-edge XANES spectra of these coals.

CONCLUSIONS AND RECOMMENDATIONS

Although insufficient data has been collected at this time to allow a direct comparison between destructive and non-destructive techniques, it is clear that the sulfur chemistry of gasification chars is significantly different from that of the original coals. This can be seen from a comparison of the analytical pyrolysis chromatograms of the IBC coals and their gasification chars and from the preliminary XANES results discussed earlier. Using the analytical pyrolysis technique, it is clear that the gasification char does not yield the alkyl and benzothiophenes that are abundant before gasification. Although this result is not too surprising, it clearly demonstrates that the distribution of sulfur species changes as a result of mild gasification.

In addition, examination of IBC-101 samples that were oxidized with peroxyacetic acid using the analytical pyrolysis technique shows that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. This observation would support our earlier findings which suggested that peroxyacetic acid was oxidizing simple thiophenes to methyl sulfonic acid.

From the XANES experiments conducted so far, the four original coal samples (IBC 101,102,106 and 109) were found to contain most of the organic sulfur in the form of thiophene derivatives, with a minor to significant amount present as organic sulfide. This is in agreement with previous XANES studies on Illinois coals. However, all of the coals were oxidized to some extent as the sulfate contents of the coals were significant. This result was also confirmed by Mössbauer spectroscopy, which showed that a significant fraction of the pyrite in the coal was oxidized. In the extreme case (IBC-102), sulfate sulfur constituted over 50% of the sulfur in the sample and over half the iron was also present as $FeSO_4 \cdot H_2O$ (szomolnokite). In comparison, the other coal samples examined showed less than 15% of the sulfur or iron in the form of sulfates. We are currently re-examining freshly prepared samples.

XANES spectra of the treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid) showed preferential oxidation of one or more sulfur-bearing phases in the original coal. For example, the peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur, whereas the steam treatment appeared to largely alter the pyrite to pyrrhotite, along with some reduction of organic sulfide as well.

REFERENCES

1. Record, F., Bebenick, D. and Kindya, R.J. 1982. Acid Rain Information Book; Noyes Data Corp., Park Ridge, NJ.

2. Aplan, F.F., 1977. In Coal Desulfurization. Chemical and Physical Methods. (Wheelock T.D (Ed)), ACS Symp. Ser. No.64, American Chemical Society, Washington DC, p70.

3. Chugh, Y.P and Caudle, R.D. 1987, Processing of High Sulfur Coal II. Elsevier, NY.

4. Orr, W.L. and White, C.M. (Eds). 1990, Geochemistry of sulfur in fossil Fuels. ACS Symp. Ser. No. 429, American Chemical Society, Washington DC.

5. Palmer, S.R., Hippo, E.J., Kruge, M.A. and Crelling J.C. 1992, "Characterization and selective removal of organic sulfur from Illinois Basin coals." Coal Preparation, 10, p93-106.

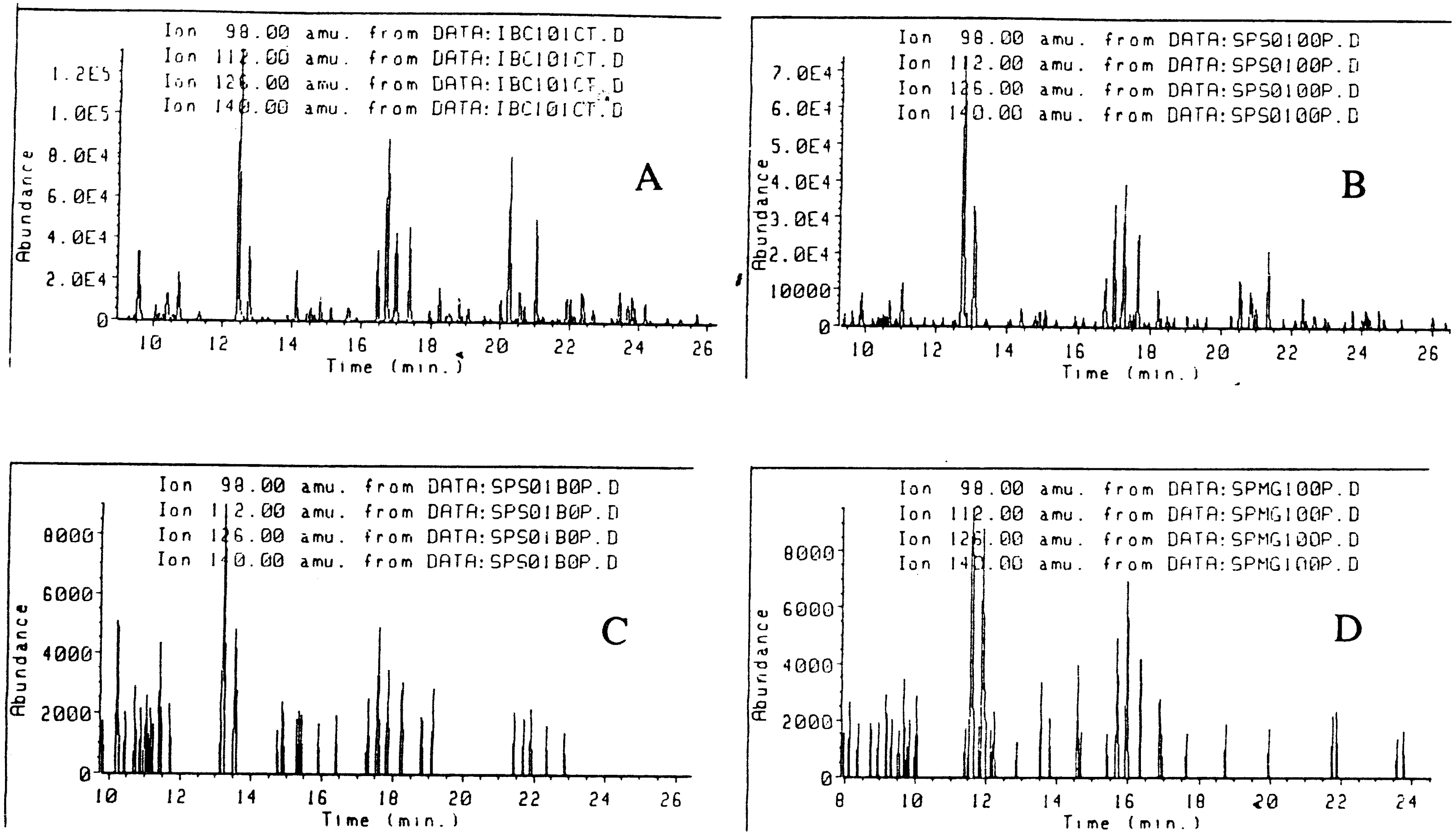


Figure 1. Single ion chromatograms for C1, C2, C3 and C4 substituted thiophenes derived from analytical pyrolysis-GCMS. A = IBC101 coal, B = selectively oxidized IBC101 (room temp 6hrs), C = selectively oxidized IBC101 (104°, 15mins), D = Mild gas. char (IBC101, steam 450°C 1hr).

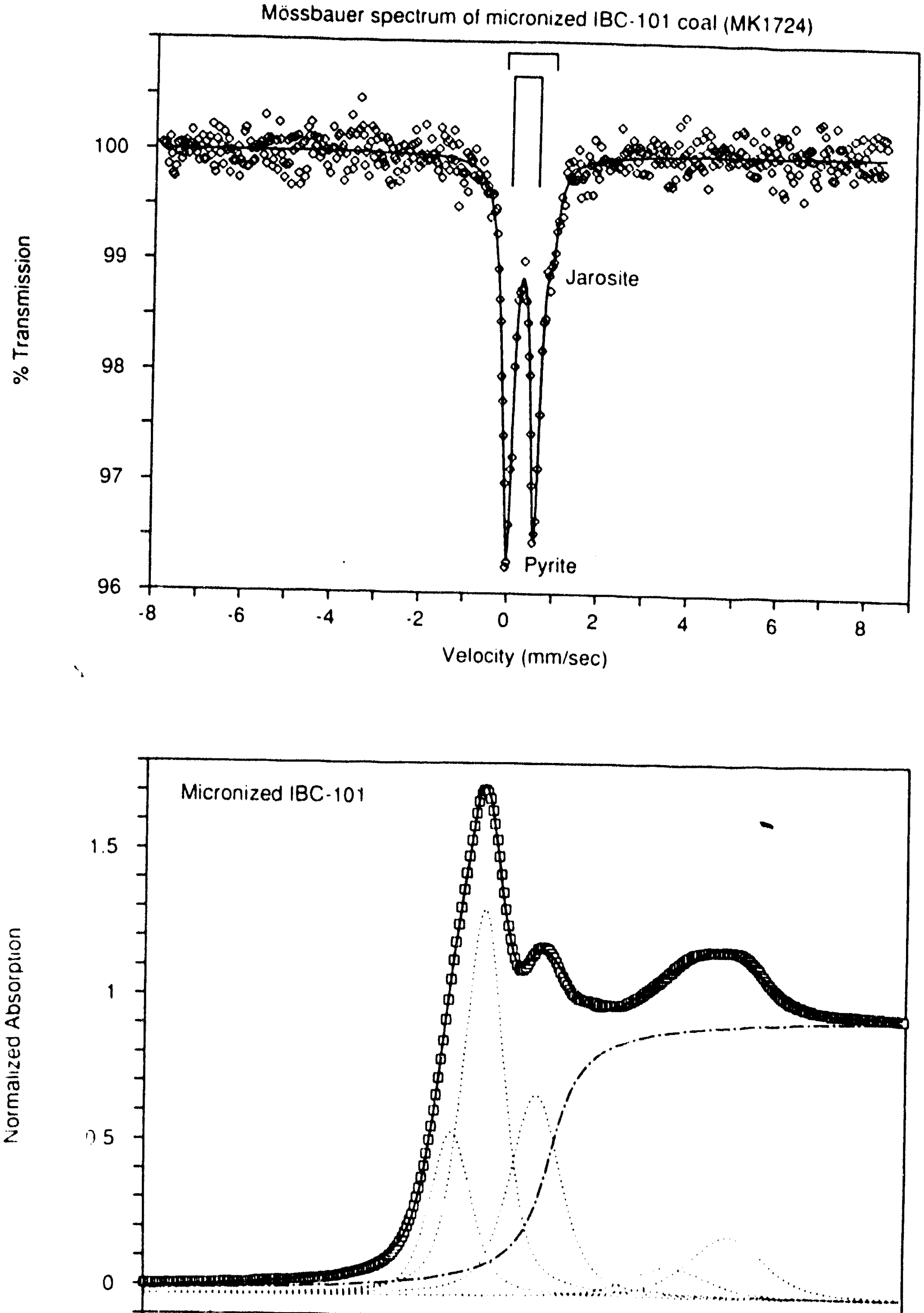


Figure 2. XANES and Mössbauer spectra for Micronized IBC 101 coal.

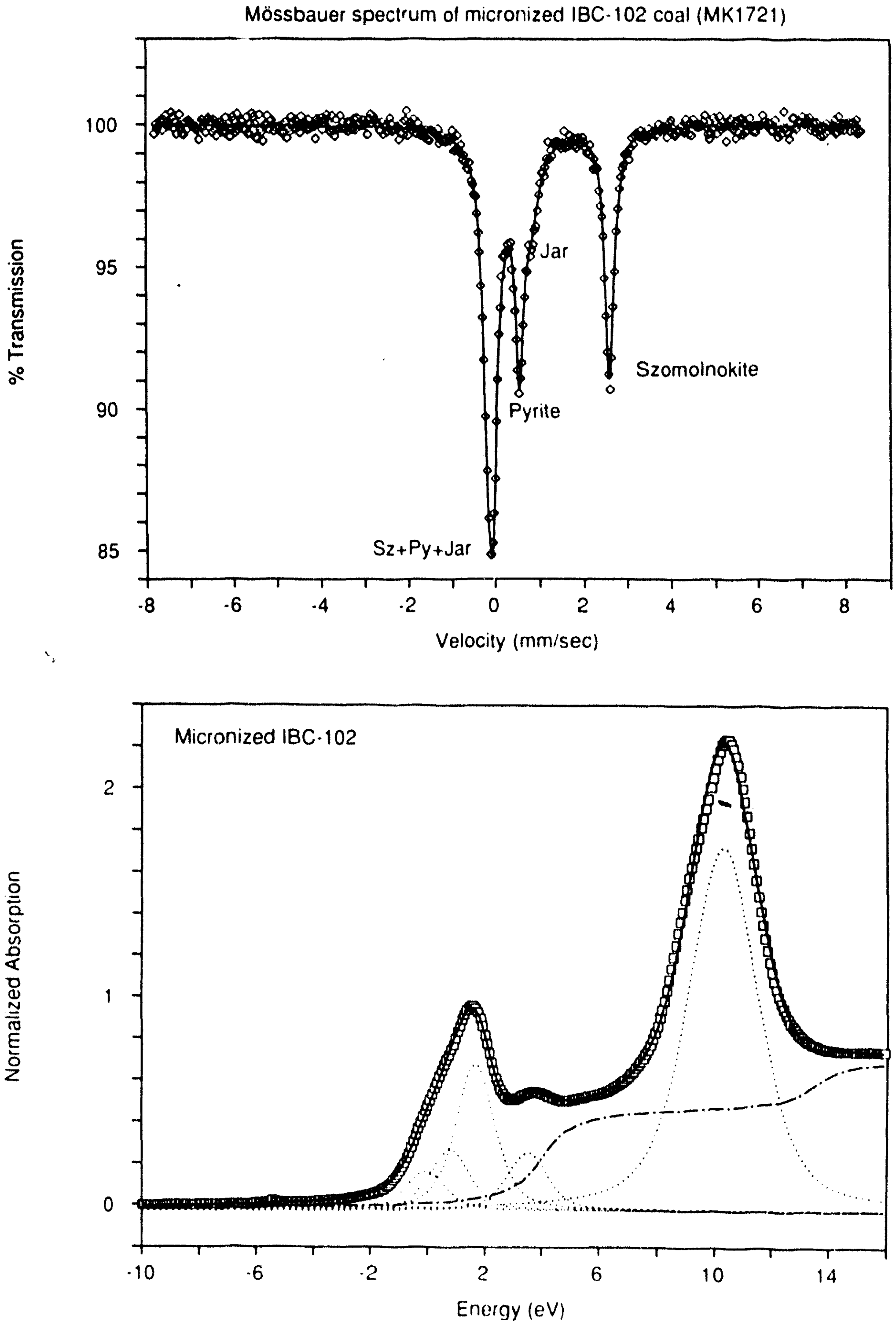


Figure 3. XANES and Mössbauer spectra for Micronized IBC 102 coal.

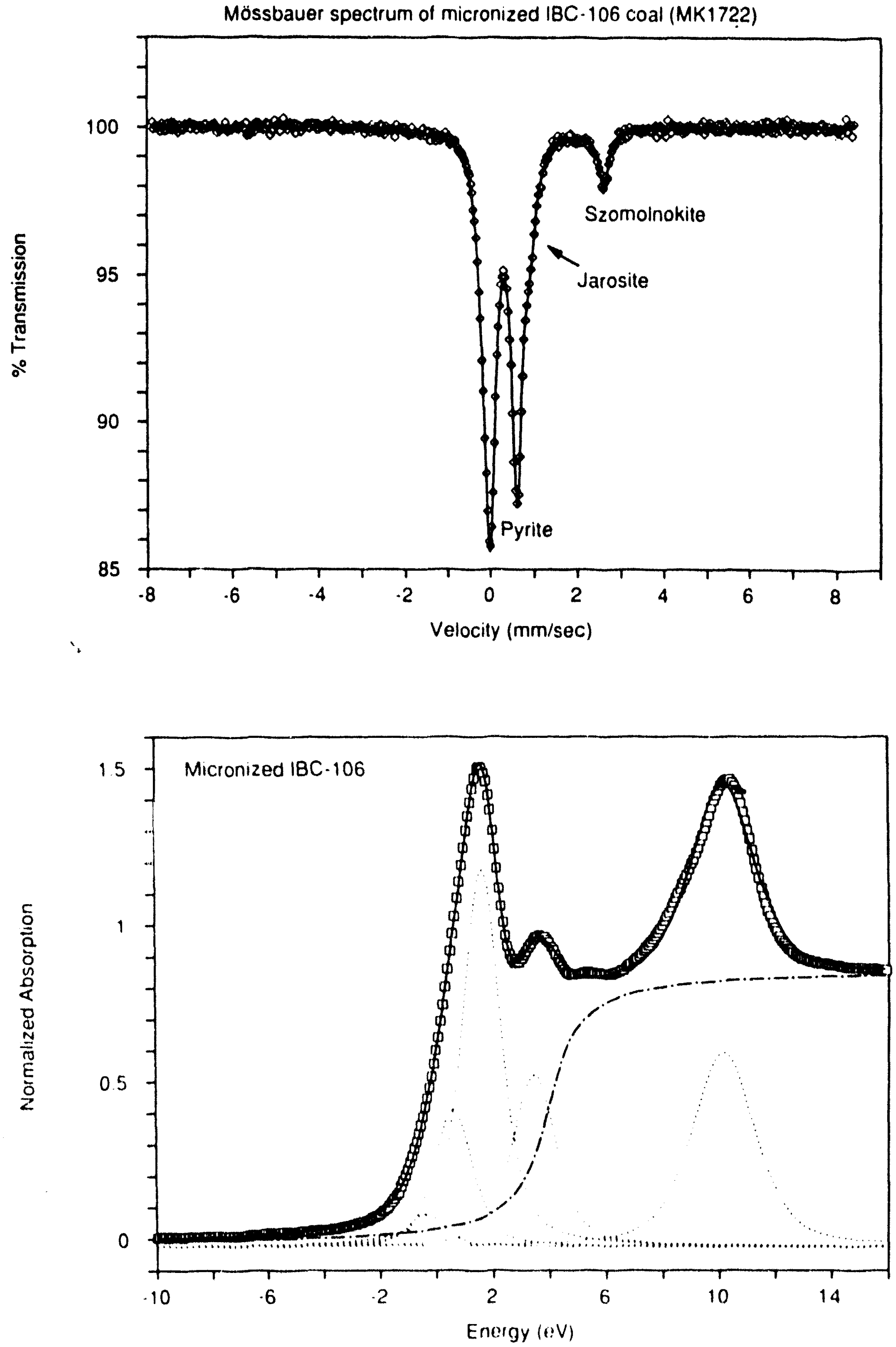
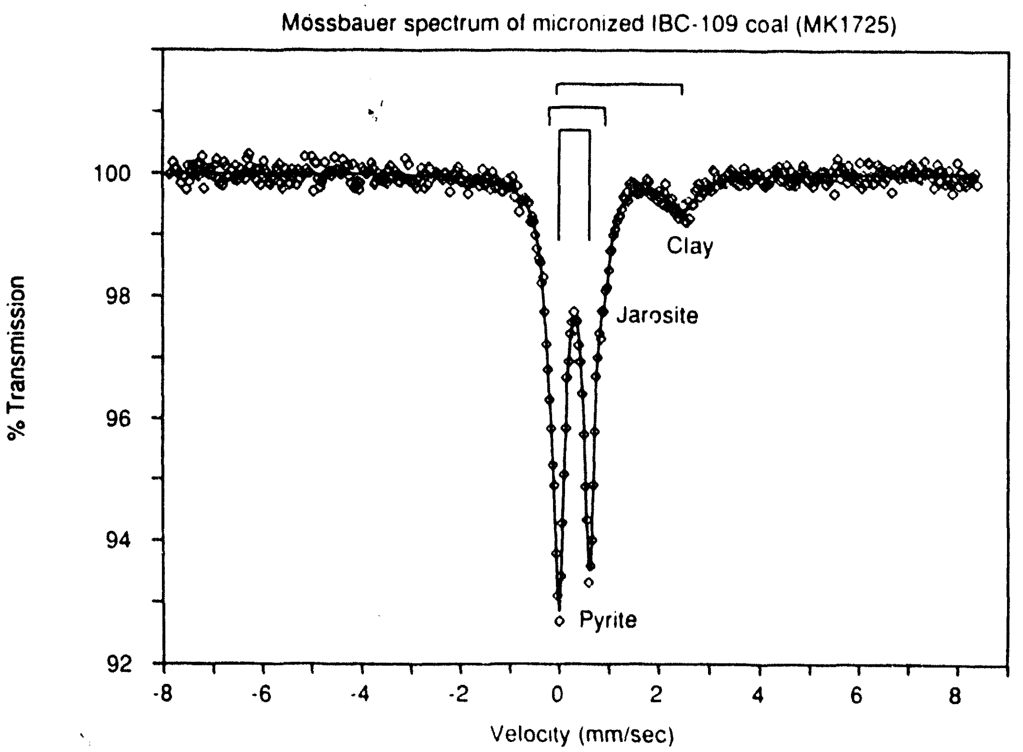


Figure 4. XANES and Mössbauer spectra for Micronized IBC 106 coal.



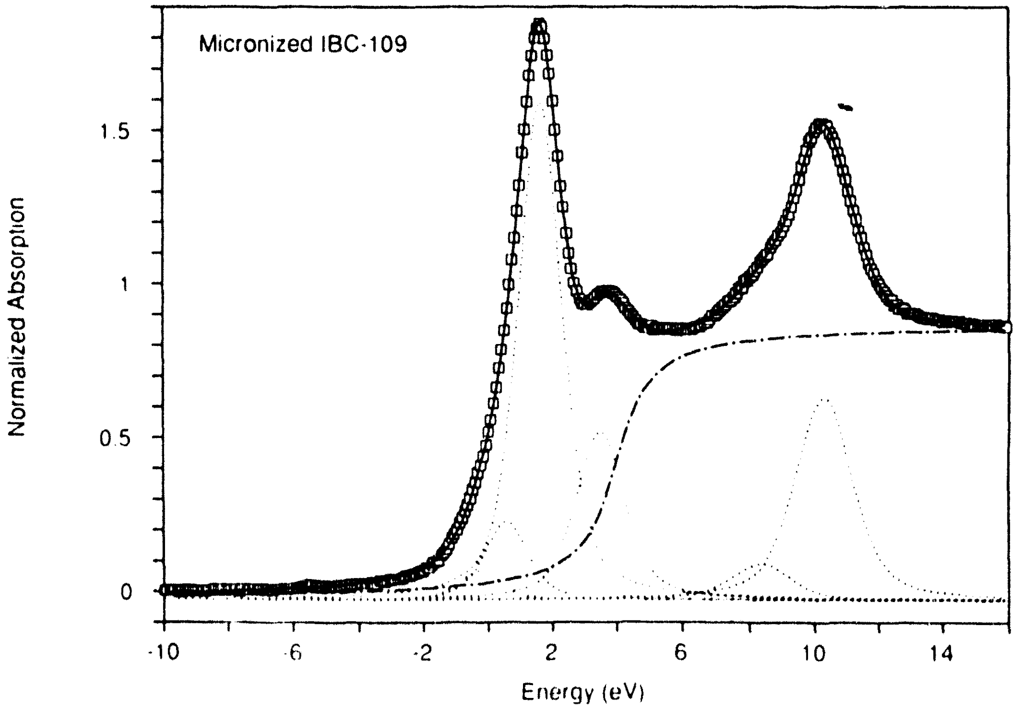


Figure 5. XANES and Mössbauer spectra for Micronized IBC 109 coal.

PROJECT MANAGEMENT REPORT
December 1, 1993 through February 28, 1994

Project Title: **Analyzing Organic Sulfur in Coal/Char: Integrated Mild Degradation/Xanes Methods**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/6.1A-1P
Principal Investigator:	Stephen Palmer Department of Geology Southern Illinois University at Carbondale
Project Manager:	Ken Ho, Illinois Clean Coal Institute

COMMENTS

Estimated and actual costs deviate because the subcontract to University of Kentucky hasn't gone through as yet. Costs for this subcontract will show up at a later date. Also personnel will take salary during last six months of project instead of throughout the whole year.

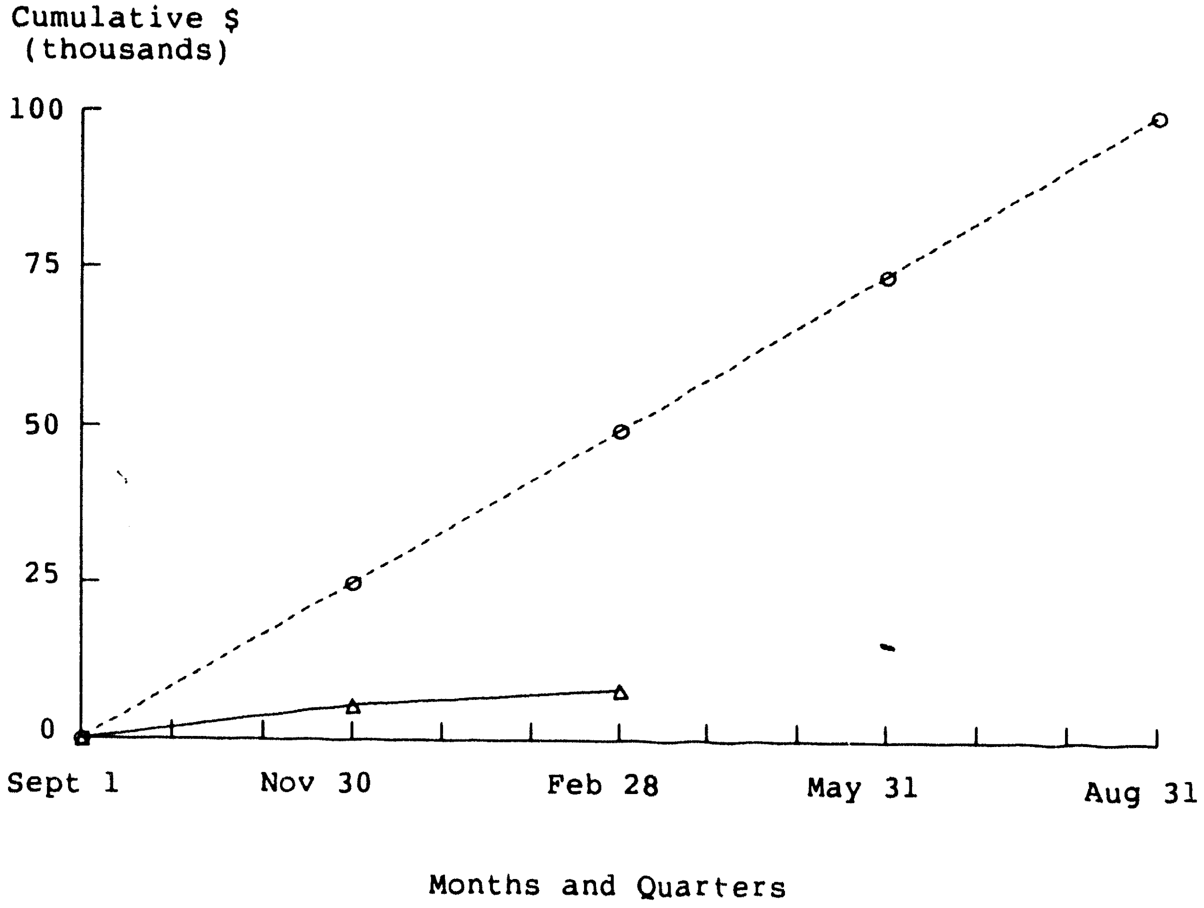
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	6,151	1,710	1,500	0	0	13,122	2,248	24,731
	Estimated	2,550	0	426	0	0	2,045	502	5,523
Sept. 1, 1993 to Feb. 28, 1994	Projected	12,302	3,421	3,000	0	0	26,244	4,497	49,464
	Estimated	2,772	0	1,475	0	0	3,102	735	8,084
Sept. 1, 1993 to May 31, 1994	Projected	18,545	5,132	4,500	0	0	39,366	6,754	74,297
	Estimated								
Sept. 1, 1993 to Aug. 31, 1994	Projected	24,606	6,842	6,000	1,000	0	52,489	9,094	100,031
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER

Analyzing Organic Sulfur in Coal/Char: Integrated Mild Degradation/Xanes Methods

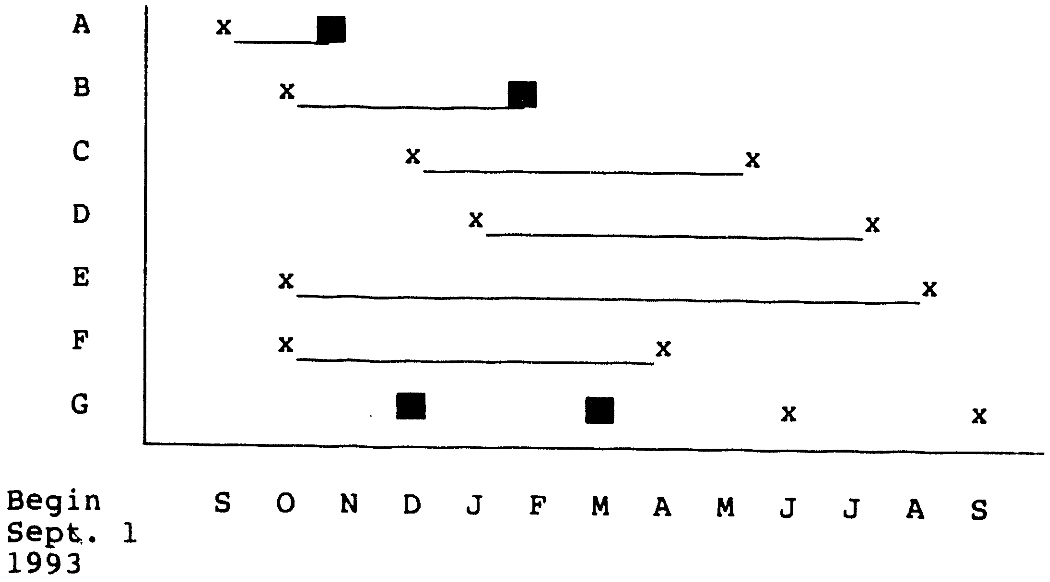


O = Projected Expenditures ---------

Δ = Estimated Actual Expenditures ________

Total Illinois Clean Coal Institute Award $100,031

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Task 1. Sample preparation.
B. Task 2. Analytical pyrolysis.
C. Task 3. Coal/char oxidation with sodium dichromate.
D. Task 4. Coal/char oxidation with peroxyacetic acid.
E. Task 5. Sulfur XANES analysis.
F. Task 6. ASTM methods of coal analysis.
G. Task 7. Reporting.

DATE FILMED

6/24/94

END