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Project Title: **REACTIVITY OF TARGET COMPOUNDS FOR CHEMICAL
COAL DESULFURIZATION**

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ABSTRACT

The goal of this project is identification of organosulfur compounds which are removed from Illinois coal by chemical desulfurization reactions. IBC-101, -105 and -108 coals from the Illinois Basin Coal Sample Program and demineralized Argonne Premium Coal 301 were extracted with pyridine and the extracts split into fractions for analysis and desulfurization reactions. THF soluble fractions of the extracts were separated by chromatography and analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS). Extracts and THF-soluble/pyridine-insoluble extract fractions were treated with K/naphthalene/THF or with Nickel boride respectively. Organosulfur contents were reduced 22 - 49% by these reactions depending upon the coal and method used. Treated extracts were analyzed by GC/MS in order to determine which sulfur compounds reacted.

In model compound studies, K/naphthalene/THF (Single Electron Transfer reagent) reduced dibenzothiophene (DBT) to a mixture of 52% biphenyl and 30% 2-phenylthiophenol, even in the presence of excess reagent. Nickel boride produced only biphenyl from DBT in 49% yield. Although GC/MS is a sensitive method for analysis of complex mixtures, relatively few organosulfur compounds were unambiguously identified in the coal extract fractions studied. DBT was identified in untreated coals along with of isomers of benzthiazoles and related aromatic compounds, although the small amounts detected cannot be reliably quantified. These compounds were absent in the products. No aliphatic sulfur compounds were found although other evidence suggests their presence. IBC-105 extract contains elemental sulfur and sulfones of several substituted thiophenes - oxidation products formed during storage and handling. IBC-101 and -108 extracts contain sulfones but not elemental sulfur, consistent with the low pyrite content of these coals.

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EXECUTIVE SUMMARY

The goal of this project is improved chemical coal cleaning by determination of the reactivity of several desulfurization reagents with specific organosulfur compounds present in the feed coal. Reagent testing was preceded by identification of a representative group of organosulfur compounds which can be extracted from coal with good solvents and then separated and concentrated by chromatography. GC/MS was used to determine which sulfur compounds were lost during the course of the desulfurization reactions.

Although GC/MS is limited to volatile compounds which may be extracted from the whole coal in a low-boiling solvent, previous work in this and other laboratories has shown that a good solvent such as pyridine extracts up to 30% of the coal by weight and that the elemental composition of the solvent-free extract is close to that of the feed coal reported on a mineral-matter free basis. However, many compounds extracted by pyridine are too non-volatile for GC/MS analysis. Nearly all compounds extracted by less polar solvents such as toluene may be analyzed by GC/MS, however the amounts extracted are very small, typically 1 - 2% by weight. This project has shown that fractionation of pyridine extracts to isolate suitable samples for GC/MS analysis, although more time-consuming, is better than direct toluene extraction for providing a representative set of compounds for analysis. It was shown that mineral matter in coal prevents toluene from dissolving soluble material even after long-term extraction. Demineralization of toluene extracted coals followed by additional toluene extraction yields additional soluble material. In contrast, demineralization of pyridine-extracted coals yields little additional material upon subsequent extraction with fresh pyridine. We believe this is due to the ability of pyridine to swell coal and carry soluble material around any mineral matter blocked pores.

For this work, coals were extracted with pyridine and the extracts separated into fractions suitable for GC/MS analysis by chromatography on alumina. Additional fractions studied were the tetrahydrofuran (THF) soluble portions of the pyridine extracts. Pyridine extracts were isolated from IBC-101, -105 and -108 coals and from Argonne-301 coal (parent of IBC-105) which we demineralized before extraction. All operations were carried out with minimum exposure of coal and extracts to air using standard methods previously developed in our laboratory.

The toluene extracts and non-polar fractions of pyridine extracts of IBC-105 coal contain significant amounts of elemental sulfur. The pristine version of IBC-105, Argonne-301, does not contain elemental sulfur, which arises from oxidation of pyrite during storage and handling. In con-

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trast, the non-polar fractions of IBC-101 extracts contain little elemental sulfur. We believe this is significant in that both IBC-101 and -105 are Herrin Illinois No. 6 coals. IBC-101 was obtained from a commercial preparation plant in 1983 and has one of the lowest pyritic sulfur values for a conventionally-washed coal. Since elemental sulfur can be slowly incorporated into the coal as organic sulfur, removal of pyrite before storage appears to have the additional benefit of preventing conversion of easily removed mineral sulfur into difficult to remove organic sulfur via oxidation to elemental sulfur.

Previously studied desulfurization reactions using the single electron transfer (SET) reagent, K/THF/naphthalene, and the reactive nickel boride reagent were repeated on dibenzothiophene. The reaction mixtures were purified by column chromatography as planned for the coal extracts and analyzed by GC/MS. Both reagents reduced DBT to biphenyl, although neither was quantitative and the SET reagent left 30% of the product as 2-phenylthiophenol, the compound formed by cleavage of only one of the two C-S bonds in DBT.

Duplicate SET and nickel boride reactions with the pyridine extracts and their THF-soluble sub-fractions from IBC-101, -108 and demineralized Argonne-301 coals gave from 22 - 49% reductions in sulfur content. In all cases, the H/C atomic ratios are higher and the S/C atomic ratios are lower in the product fractions than in the feed fractions. Since these are mineral matter-free extracts, all of the sulfur removed would be counted as organic sulfur in the original coal. GC/MS analyses of extract fractions before and after desulfurization show that substituted thiophenes present before reaction are absent or in lower concentration in the products. Sulfones present in fractions of oxidized coals are absent in product fractions. Products from SET reactions have increased concentrations of hydroaromatic hydrocarbons. Product fractions are more soluble than their feed fractions in several polar and non-polar solvents, suggesting lower molecular weights although this was not studied further.

In general, this project has shown that it is possible to identify several organosulfur compounds in coal extracts that are removed by the desulfurization reactions studied. However, the limitations of the GC/MS instrument available and the low concentrations of the sulfur compounds present precluded more than a qualitative demonstration of the power of the proposed method for developing new desulfurization reagents. A particular disappointment was the failure to detect aliphatic sulfur compounds in any coal extract and points out the limits of using only low-resolution GC/MS for these analyses. Future work along these lines should involve several laboratories with complimentary analytical abilities.

OBJECTIVES

The primary objective of this project was to identify as many as possible of those organosulfur compounds which may be extracted from coal by simple solvent treatment below 150°C and to determine their fate when the coal fractions in which they are found were treated with known coal desulfurization chemical reactions.

Specific goals of this project were to:

1. Maximize the organic material extracted from IBC-101 and -108 using pyridine/nBu₄NOH/ultrasound.
2. Demineralize Argonne Premium Coal Sample 301 (parent of IBC-105) and extract as in 1.
3. Fractionate pyridine extracts into sub-fractions using solubility in hexane and toluene for further analysis.
4. Separate and concentrate sub-fractions containing sulfur compounds using preparative chromatography and/or extrography.
5. Analyze sulfur-containing sub-fractions by GC/MS correlated with SEC, FT-IR and FT-NMR analyses to identify as many organosulfur compounds as possible.
6. Correlate analytical data with extraction and fractionation yields to develop mass balances for identified sulfur species.
7. Desulfurize characterized sub-fractions and total pyridine extracts by several methods such as: Dissolving metals, Nickel boride, Ni/Al alloy, and Lochmann's BASE.
8. Repeat goals number 3-6 on the desulfurized sub-fractions and extracts.
9. Use the best methods from goal 7 on demineralized coals and repeat goals 1-6 on the coal product.
10. Correlate and summarize the data to determine which organosulfur compounds react in the desulfurization methods and determine how much of the observed desulfurization can be accounted for in the reactions of identified compounds.

INTRODUCTION AND BACKGROUND

The need to understand sulfur chemistry in Illinois coals is central to our need to protect both the environment and the

job base in the Illinois coal fields. Even if all mineral sulfur were removed, most Illinois coals could not meet existing or scheduled sulfur emission standards. Organic sulfur must be removed and this will involve selective chemical reactions. Previous work at EIU has shown that simple processes such as solvent extraction do not selectively remove sulfur from coal - that is, during solvent extractions sulfur compounds were removed by both polar and non-polar solvents in approximately the same concentration as they were found in the original solid coal.¹ One impediment to the development of effective pre-combustion desulfurization technology is that the actual target compounds are not known. Although there have been many recent studies of organic sulfur in coal, including those sponsored by ICCI, few sulfur compounds have been identified as existing in whole coal. Non-destructive spectroscopic methods such as XANES and very high field ESR show great promise for determining the major classes of organosulfur functional groups present in coal or coal products. However, at the resolution available now or in the next few years, even these very expensive and sophisticated methods are not able to identify individual compounds.

It is unreasonable to expect advanced coal cleaning or utilization processes to develop if the actual target compounds in sulfur removal schemes are unknown. Knowing the nature of sulfur species present (ie relative amounts of aliphatic sulfides, aromatic sulfides, thiophenes, etc.) is important, but even more important is knowing the identity and amount present of the actual compounds. A simple example will illustrate the problem. Oxidation of sulfide to sulfoxide is the necessary first step in any oxidative desulfurization process. Dibutyl sulfide and dioctyl sulfide are very similar aliphatic sulfides, yet oxidation of sulfide sulfur to the sulfoxide by air in the presence of hydroaromatic promoter compounds is much faster for the butyl than for the octyl case and both react slower than dibenzylsulfide.² Because all three of these compounds involve $-S-CH_2-$ bonds, they would be measured as aliphatic S in the XANES analysis and the first two would not be observed by any current ESR technique. Design of desulfurization processes would be greatly improved by better information on the identity and reactivity of the target molecules in coal.

EXPERIMENTAL PROCEDURES

Coals studied include IBC-101, -105 -108 and Argonne Premium Coal Samples 301 (Illinois No. 6, parent of IBC-105), 201 (Wyodak) and 401 (Pittsburgh #8). The Argonne coals were included in the initial study to maximize pyridine extraction yield since they offer a range of volatile and mineral matter contents and have not suffered air oxidation in storage and handling. Solvent extraction and product puri-

fication and isolation follow our published procedures.³ Coals, extracts and residues were dried at 100°C, 0.1 Torr for several hours before weights were recorded for mass balance calculations. Direct toluene extractions of coal on a 1-2 g scale were conducted as described in previous Quarterly Reports. Solvents were HPLC grade, often distilled from a drying agent before use. Elemental analyses of coal fractions were done by Galbraith Laboratories, Knoxville, TN.

The acid demineralization used was a modification of standard methods.⁴ Coal or solvent insoluble residue (10g) was placed in a 250 mL RB flask containing a magnetic stirring bar along with 50 mL of 25% HCl. An ice-filled cold finger condenser was connected to the flask and the exit attached to a nitrogen gas system. The stirred reaction mixture was heated to 100°C for two hours, cooled, filtered and washed with deionized water until the wash water pH was above 5.5, and dried overnight under a slow flow of nitrogen. The sample was then placed in a 500 mL heavy polyethylene tube containing 50 mL of 48% HF and heated to 70°C for two hours. After cooling the product was collected by vacuum filtration and washed with deionized water until the pH of the wash water was above 5.5 after which the product was vacuum dried in the usual manner. A variation used 25% HCl and 48% HF mixed 1:1 in a single acid demineralization. Pyrite was removed either by HNO₃ treatment as in ASTM D-2492 or by lithium aluminum hydride reduction using the method of Kuhn, et al.⁵

In the early phase of the study, ultrasonic irradiation to increase extraction yield used a Biosonik III generator at 85% intensity. The solvent swollen coal was put in a suitable beaker cooled with an ice bath to maintain a temperature of 30±6°C. A 2.5g sample of dry coal in 40 mL pyridine and 13 mL of 1.0 M n-Bu₄NOH in methanol was irradiated for 3 hours in a 100 mL beaker. A slow flow of argon gas over the surface was used to minimize the effects of air oxidation. After sonication, the slurry was transferred to a centrifuge tube with 3 mL of methanol and spun at 2500 rpm for 30 minutes in an IEC Centra-7 centrifuge to separate extract and residue. Solvent was removed from the extract with a rotary evaporator followed by washing with 3M HCl and up to 7 L of deionized water - until no Cl⁻ was present in the filtrate (AgNO₃ test). Finally the extract was washed with 80% methanol/water, filtered (0.45 um Nylon membrane) and vacuum dried. The residue was isolated and washed in a similar manner. We were unable to scale up this method to the larger amounts of coal needed for isolation of detectable quantities of organosulfur compounds and the method was not used further.

Toluene soluble coal extract fractions were chromatographed through a short column of dry packed silica gel to remove

high boiling compounds which would not elute from the gas chromatograph although later work showed that the small amounts present were not a problem provided a suitable inlet liner was used in the GC injector port. Pyridine extracts or THF soluble portions of these extracts were similarly chromatographed on neutral alumina to prepare samples for GC analysis. Fractions were eluted with hexane followed by toluene. Each fraction was reduced in volume with a flowing stream of nitrogen and capped in a sample vial for GC/MS analysis. GC/MS analyses were carried out on an Hewlett Packard 5890B chromatograph interfaced with a model 5971 mass selective detector and equipped with an autoinjector and electronic pressure programming. The column was a 30 m x 0.25 mm HP-5 MS column coated with a 0.25 μ m film of 5% phenyl methyl silicone. Total ion chromatographs of the GC effluent were collected every half second and stored on computer disk. Data analysis using the HP software matched the mass spectrum of GC peaks of interest with the Wiley MS library of over 130,000 pure compounds.

Several different GC temperature programs have been evaluated for coal extract analysis. Standard mixtures of n-alkanes and polycyclic aromatic hydrocarbons were purchased and used to calibrate the analytical methods. * Mixtures of organosulfur compounds available from previous projects were also used to help define regions of the GC traces in which to search for sulfur containing compounds.

All coal extracts were fractionated and purified by column chromatography before GC/MS analysis. Best results were obtained by stirring overnight a pyridine extract with 10-20 times its weight of distilled THF, separating the insoluble residue and concentrating the THF soluble portion by rotary evaporation followed by chromatography on a neutral alumina column packed in hexane. Elution with hexane and toluene gave aliphatic and aromatic hydrocarbon fractions containing non-polar organosulfur compounds. The toluene fractions also contained heterocyclic sulfur compounds containing oxygen and/or nitrogen.

Model compound desulfurization reactions were carried out following published procedures. Nickel boride desulfurization of dibenzothiophene duplicated our previously reported method⁴ with the addition of GC/MS in place of GC analysis. Single electron transfer (SET) reactions using potassium in THF used our modification⁴ of Stock's method⁶, also with GC/MS analysis.

RESULTS AND DISCUSSION

Because mineral matter in coal is often found within the pores in the coal, it is possible that potentially soluble material is not being extracted due to blockage by the

minerals. Our study of the effect of demineralization on solvent extraction using both toluene and pyridine was reported previously and is summarized in Figure 1. Toluene yields after demineralization represent a significantly larger fraction of the initial extract yields than is the case for pyridine yields following demineralization. Previous work by the PI has shown that the toluene soluble fractions of pyridine extracts of Illinois No. 6 coal account for a small amount of the material extracted by pyridine.⁷ Taken together this suggests that the presence of mineral matter prevents toluene from removing material which is toluene-soluble. A working hypothesis is that minerals block pores such that toluene cannot reach potentially soluble material, which can be removed by pyridine which swells Illinois coals to more than two and one half times the original volume. Diffusion through the matrix or through pathways opened around mineral grains during swelling are possible routes for removal of this material.

Compounds extractable from Illinois coal which can be analyzed using the EIU system are those which will elute from the GC column below 290°C with mass less than 660 daltons (the upper limit of the HP 5971 quadrupole detector). These are generally those compounds which are found in hexane or toluene coal extracts. During the first two quarters, we attempted to develop a short method for obtaining representative solvent extract fractions without using pyridine. Although direct toluene extraction can work for some samples of some coals, in our hands it did not prove to be reliable. While we could duplicate the high pyridine extraction yields (up to 60%) using ultrasound plus a quaternary ammonium hydroxide on the 1 - 2g scale reported in the literature, this did not produce enough material for GC/MS analysis using our instrument. Our attempts to scale up ultrasonic extraction to the 10 - 20g scale needed were unsuccessful (Goal 1). We now believe that the best method for isolating a representative sample of organosulfur compounds from coal is to fractionate a pyridine soluble extract (long term Soxhlet extraction method⁴) into a THF soluble fraction (usually about 40-60%) of the pyridine extract and to chromatograph the THF fraction on neutral alumina. The hexane and toluene fractions eluting from the column are then concentrated by rotary evaporation before GC/MS analysis. This method is longer and more tedious than other methods but was the only one which gave reliable results on both pristine and oxidized coals from several seams. This method was used in the desulfurization studies reported below.

At the top of Figure 2 is the total ion chromatogram (TIC) of the hexane fraction from the column chromatography of the pyridine extract of IBC-101 coal. The small peak at 24.45 minutes was identified by the mass spectrum shown at the bottom of Figure 2 to be dibenzothiophene (DBT). Most of the chromatographic peaks are hydrocarbons. Normal alkanes

are seen in a regular pattern of peaks approximately 0.6 minutes apart on top of which is superimposed a more random collection of peaks due to aromatic hydrocarbons and the relatively few organosulfur compounds identified.

Previous desulfurization work at EIU involved both model compounds and coal fractions. Since both the personnel and analytical instrumentation changed since that project, we repeated the several reactions on the model compound dibenzothiothiophene (DBT), which is also a component of the solvent extracts of Illinois coal. The results are shown in Table 1. The SET reaction did not completely reduce DBT even though the green color of the active K^+ /naphthalide⁻ radical ion species was present at the end of the reaction and excess un-reduced naphthalene (electron transfer agent) was detected in the quenched reaction mixture by GC/MS. In agreement with our previous work, not all of the "missing" DBT has been desulfurized to biphenyl. We found 30% of the DBT converted to 2-phenylthiophenol, the product of cleavage of only one of the two C-S bonds in DBT. Thus, SET was only 52% effective in removing the sulfur from DBT during this reaction.

In agreement with our previous work⁴, Nickel boride, produced by the $NaBH_4$ reduction of nickel chloride, gave only biphenyl from DBT, in up to 49% yield under reverse addition conditions. Since this reaction involves an insoluble reagent it is limited to soluble coal fractions but provides a good alternative to SET reagents in mode of reaction for these studies.

The yields for pyridine extractions and separation of portions of these extracts into THF soluble/pyridine insoluble fractions for use in the nickel boride reactions are reported in Table 2. These results are consistent with previous studies in this laboratory in that the pristine Argonne coal gave the highest and the oxidized IBC-108 gave the lowest extraction yields. Elemental analyses of the extracts and THF soluble fractions are listed in Tables 3 and 4 and illustrate the point that elemental analyses of these fractions are similar to the DMMF analyses of the whole coals from which they are derived.

Tables 3 and 4 also summarize the results of the desulfurization reactions of these fractions with the SET and the nickel boride reagents. Atomic H/C and S/100C ratios are also reported for both the starting fractions and isolated product fractions from the desulfurization reactions in order to highlight the chemical changes going on. H/C ratios increase in all cases (chemical reduction) with the SET reaction giving relatively larger increases than the nickel boride reagent. This is consistent with the ability of the SET reagent to reduce aromatic hydrocarbons in the presence of a hydrogen ion donor. Although all solvents,

reagents and glassware are pre-dried, the coal fraction itself contains transferable hydrogen (phenols, tightly bound water and other forms). During the product isolation step for both solvent extraction and desulfurization, the coal fractions are washed free of reagents and inorganic products with water and finally 50% water/methanol. The water/methanol wash solution becomes more highly colored after the desulfurization reactions than after the original solvent extraction and fractionation. This probably indicates that some large, insoluble coal molecules are being cleaved by the desulfurization reagent rendering them more soluble in the polar washing solvent. Indeed, during the workup of the nickel boride reactions up to 40% by weight of the original coal fraction is lost as water soluble material. This aspect of the desulfurization has not been studied in detail.

The data in Tables 3 and 4 also show that these reagents are removing sulfur from the coal fractions. In each case the S/100C atomic ratios of the products are lower than those of the starting fractions. The Desulfurization section in each Table lists the percent decrease in the S/100C ratio for each fraction due to the chemical reaction. Since the amount of sulfur is scaled to the carbon content, this calculation is independent of the loss or gain of any other element present and focuses attention on the number of C-S bonds in the starting material and products. The key step in chemical desulfurization is cleavage of C-S bonds. For the three coals studied, the SET reaction produces more desulfurization than the nickel boride approach.

We had hoped to further differentiate these two reagents in terms of the actual sulfur compounds removed, consistent with prior model compounds studies.^{4, 6} However, the small number and low concentration of the sulfur compounds identified did not allow this degree of quantitative analysis. We had originally proposed to also study the sulfur compounds removed by Lochmann's base, a mixture of n-butyl lithium and potassium t-butoxide in THF, which Stock has shown to be effective in reducing the aliphatic sulfur content in Illinois coals⁶ (part of Goal #7). However our failure to detect any aliphatic sulfur compounds using the GC/MS method rendered this impossible to study.

Table 5 lists organosulfur compounds positively identified in one or more of the coal extracts. The number of positive identifications is small and the relative amount of any compound present in any coal fraction is too low to quantify reliably. In general, the Argonne coal extract had more DBT than the other coals. The fact that Argonne 301 extract did not contain sulfones and that the extracts of both IBC-101 and -108 had thiophene sulfones as prominent sulfur containing species suggests that the sulfones are formed from the thiophenes during storage and handling. Any proposed desul-

furization method must then be able to deal with variable amounts of these components, whose concentrations are expected to vary with the individual history of each batch of coal treated. In this study, no product mixture contained sulfones which is not surprising for the strong chemical reducing agents employed.

Figure 3 is an expanded region of the total ion chromatogram (TIC) of the hexane fraction from column chromatography of the pyridine extract of Argonne 301 coal before desulfurization. The mass spectrum of the 24.45 minute peak is shown below the TIC, confirming the identification as DBT. Figure 4 is the same expanded region of the hexane fraction from column chromatography of the product after SET reduction. A variety of new peaks have appeared and others have been lost. There is a very small peak at 24.45 minutes but examination of the mass spectrum for this peak shown at the bottom of Figure 4 reveals that it is not DBT. The characteristic fragment ions at 92, 139 and 152 mass units are missing and the relative intensities of the low mass ions differ from that of DBT. The library search routine could find no match for this mass spectrum. Based on the pattern of peaks below 100, it appears to be an alkane perhaps co-eluting with a trace of DBT. Figures 3 plus 4 are typical of the results of analyses of both the hexane and toluene chromatographic fractions from all three coals studied using both desulfurization reagents. Small peaks for organosulfur compounds present in the feed fractions are missing or lower in peak area compared with nearby n-alkanes which are expected to be inert to the reaction conditions.

Although the identified sulfur compounds in the feed fractions are missing in the products, it is important to note that the identified compounds are in such low abundance that their loss accounts for only a very small fraction of the total sulfur lost during the desulfurization reactions. Nearly all of the lost sulfur is present in compounds yet to be identified.

CONCLUSIONS AND RECOMMENDATIONS

A reproducible method for isolating and purifying coal extracts for use in desulfurization studies was developed and used with two desulfurization reagents - K/naphthalene/THF and $\text{NiCl}_2/\text{NaBH}_4/\text{ethanol}/\text{THF}$. Extracts of IBC-101 and -108 and demineralized Argonne-301 coals had their organosulfur contents reduced 22 - 49% by these reagents. A few aromatic organosulfur compounds were identified by GC/MS analyses of the starting extracts and were shown to be absent in the products. The number and concentrations of the identified sulfur compounds lost during the desulfurization reactions account for less than 1% of the

sulfur lost as measured by elemental analyses. The failure to detect additional sulfur compounds, including the absence of identified aliphatic sulfur compounds in any extract is disappointing and points out the limits of using low resolution GC/MS for these analyses.

During the method development phase of the project, fractionation of pyridine extracts to isolate suitable samples for GC/MS analysis of coal extracts, although more time-consuming, was found to be better than direct toluene extraction in terms of providing a representative set of compounds for analysis due to the superior ability of pyridine to swell coal and hence to remove soluble material blocked by mineral matter in pores. The non-swelling solvent toluene was shown to leave toluene-soluble material in coal which became accessible after demineralization.

IBC-101 coal has less elemental sulfur in the non-polar extract fraction than IBC-105 and other IBC coals studied on previous projects. Both IBC-101 and -105 are Illinois No. 6 coals from the Herrin seam. Extracts of IBC-108 also show no elemental sulfur. Apparently early removal of at least some of the pyrite by conventional coal cleaning of IBC-101 and by deep cleaning of IBC-108 has stopped elemental sulfur production by the previously documented pyrite oxidation route. Since elemental sulfur slowly reacts with the organic material in coal to form organosulfur compounds, this suggests that early pyrite removal is better than later, even if additional cleaning steps will be used at a later time.

This project has demonstrated the feasibility of identifying and tracking sulfur compounds in coal extracts during desulfurization studies if sensitive analytical methods are available. Any future work should combine laboratories with experience and equipment for coal extraction and fractionation with those having very high resolution mass spectrometers with solid inlet probes and gas chromatographs with sulfur specific detectors.

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TABLE 1

DIBENZOTHIOPHENE (DBT) DESULFURIZATION

Method:	<u>K/Naphthalene</u> ^a	<u>Ni Boride</u> ^b	
		<u>Normal Addn</u>	<u>Reverse Addn</u>
Product Mixture			
mol % DBT	18.3	74.0	50.9
mol % BP ^c	51.6	26.0	49.1
mol % PTP ^d	30.1	0 ^e	0
% desulfurization	51.6	26.0	49.1

a References 4 and 6 b Reference 4
c Biphenyl d 2-Phenylthiophenol
e None detected, less than 0.1 %

TABLE 2

SOLVENT EXTRACTION/FRACTIONATION
OF ILLINOIS COALS
PERCENT BY WEIGHT OF DRY COAL

	<u>IBC-101</u>		<u>DEMINERALIZED ARGONNE 301</u>		<u>IBC-108</u>	
	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>
PYRIDINE SOLUBLE						
	22.5	18.9	32.9	36.8	15.4	14.7
THF SOLUBLE FRACTION OF PYRIDINE SOLUBLE						
	49.9	65.7	41.9	50.4	51.6	-----

Material balances of solvent-free extracts plus residues were generally 95 - 102%

TABLE 3

DESULFURIZATION RESULTS

K/THF/Naphthalene Desulfurization
Pyridine Extracts of Indicated Coals
Elemental Composition

	<u>IBC-101</u>		<u>DEMINERALIZED ARGONNE 301</u>		<u>IBC-108</u>	
	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>
<u>EXTRACT BEFORE REACTION</u>						
% C	76.19	76.18	77.17	77.94	77.88	77.88
% H	5.93	6.25	5.85	5.90	5.85	5.85
H/C	0.928	0.978	0.903	0.902	0.895	0.895
% S	3.22	3.14	2.26	2.19	2.24	2.24
S/100C	1.58	1.54	1.10	1.05	1.08	1.08
<u>EXTRACT AFTER REACTION</u>						
% C	74.77	73.34	73.42	73.19	71.11	74.31
% H	7.21	7.07	7.22	7.05	6.83	6.75
H/C	1.149	1.149	1.172	1.148	1.145	1.082
% S	1.84	2.04	0.92	1.21	1.11	1.41
S/100C	0.92	1.04	0.47	0.62	0.58	0.71
<u>% DESULFURIZATION</u>						
	42%	33%	57%	41%	46%	34%
AVERAGE	38%		49%		40%	

TABLE 4

DESULFURIZATION RESULTS

NiCl₂/NaBH₄/Ethanol/THF Desulfurization
 THF Soluble Fractions of Pyridine Extracts of Indicated Coals
 Elemental Composition

	<u>IBC-101</u>		<u>DEMINERALIZED ARGONNE 301</u>		<u>IBC-108</u>	
	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>	<u>Expt 1</u>	<u>Expt 2</u>
<u>THF FRACTION BEFORE REACTION</u>						
% C	78.78	79.40	79.13	79.88	80.01	80.01
% H	6.60	6.91	6.34	5.99	6.36	6.36
H/C	0.998	1.037	0.955	0.894	0.947	0.947
% S	3.06	2.83	2.08	2.05	1.98	1.98
S/100C	1.46	1.34	0.98	0.96	0.93	0.93
<u>THF FRACTION AFTER REACTION</u>						
% C	65.72	74.96	79.37	80.49	80.91	80.60
% H	6.54	7.56	6.99	6.63	7.26	6.95
H/C	1.186	1.209	1.050	0.982	1.069	1.028
% S	1.87	2.18	1.57	1.34	1.24	1.34
S/100C	1.07	1.09	0.74	0.62	0.57	0.62
<u>% DESULFURIZATION</u>						
	27%	18%	25%	35%	39%	33%
AVERAGE	22%		30%		36%	

TABLE 5

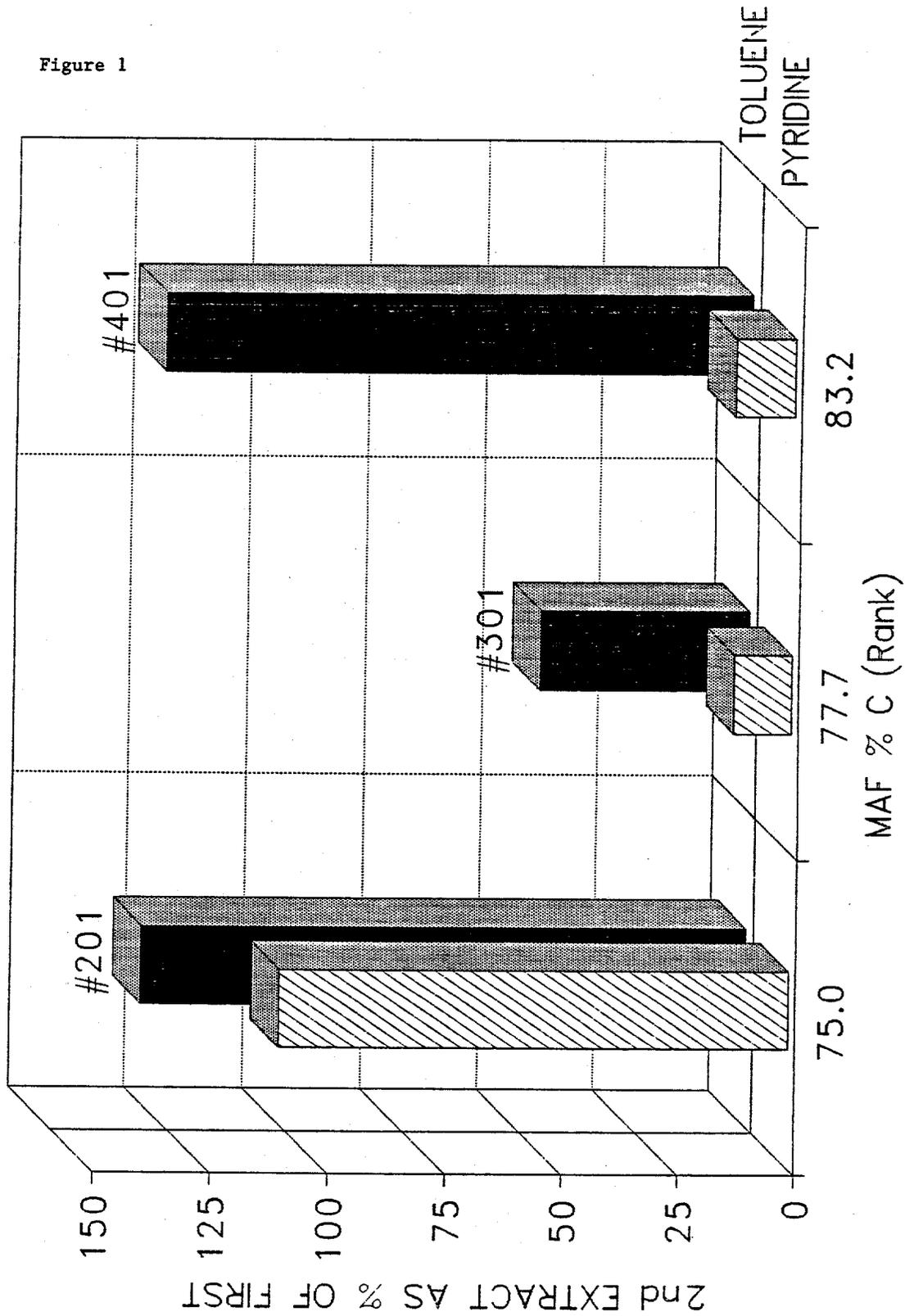
SULFUR CONTAINING COMPOUNDS IDENTIFIED BY GC/MS IN FRACTIONS OF PYRIDINE EXTRACTS OF ARGONNE #301 COAL

COMPOUND	FORMULA	QUALITY OF MS LIBRARY MATCH ^a
Benzothiazole	C ₇ H ₅ NS	87
2-Methylthiobenzothiazole	C ₈ H ₇ NS	98
Dibenzothiophene	C ₁₂ H ₈ S	94
2(3H)-Benzothiazolethione	C ₇ H ₅ NS ₂	46
3-Ethyl-1,2,3,4-tetra- hydrodibenzothiophene	C ₁₄ H ₁₆ S	90
(this co-elutes with: Dibenzothiophene sulfone	C ₁₂ H ₈ O ₂ S	53
2,3-Diphenylthirene 1,1-dioxide	C ₁₄ H ₁₀ O ₂ S	90

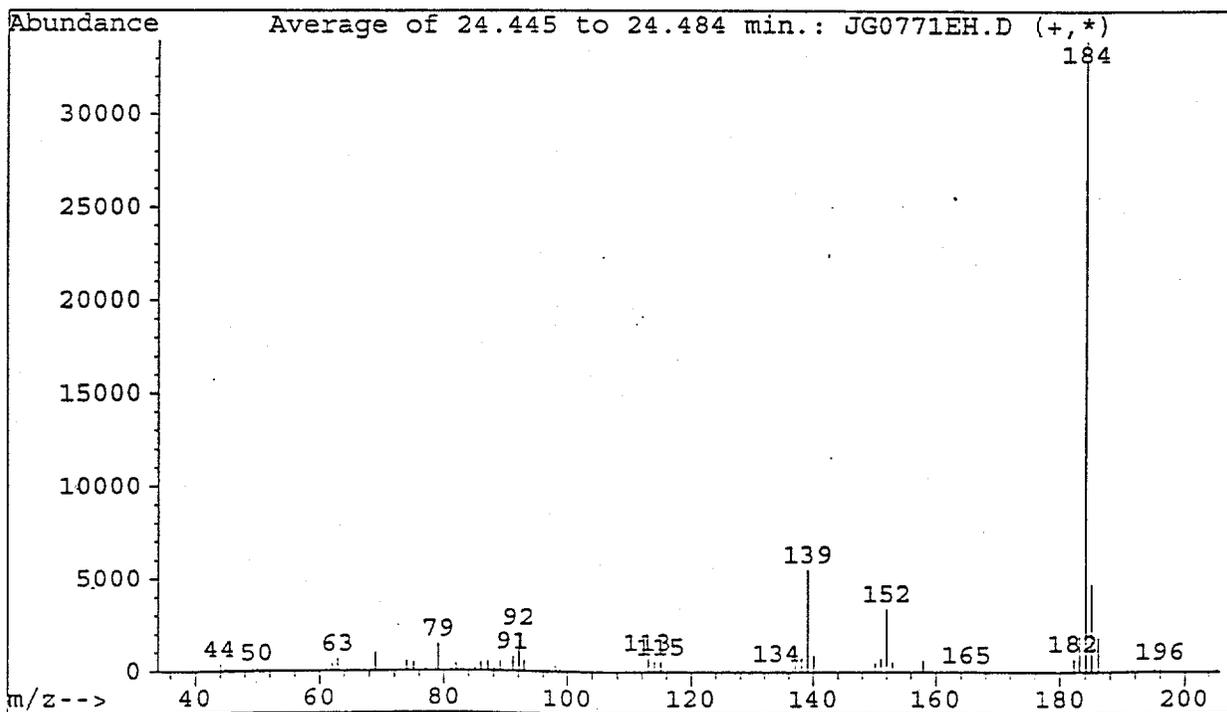
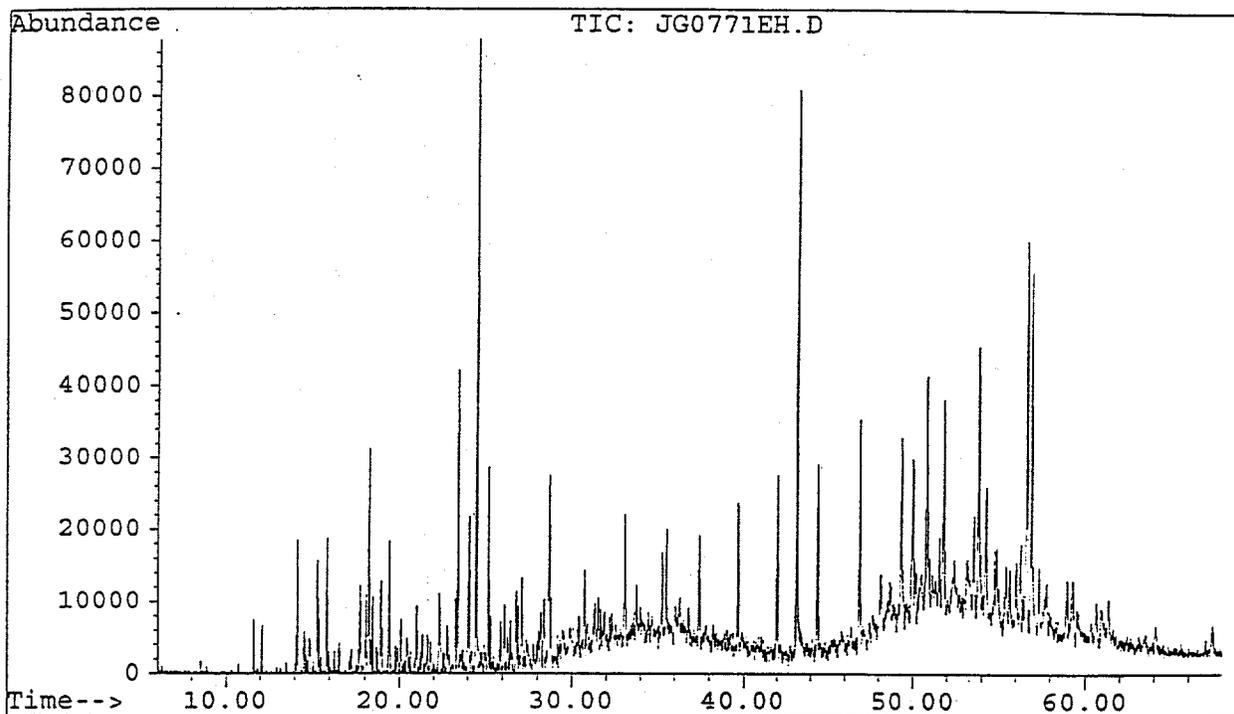
a McLafferty algorithm for judging goodness of match between MS of compound and Wiley Library of MS, Scale 0 - 100, matches below 50 are suspect.

A variety of other S-containing hetrocyclic compounds are detected with Quality Matches of 30 - 90, but because of their unusual structures, are not considered to be positively identified.

ADDITIONAL EXTRACT
AFTER DEMINERALIZATION

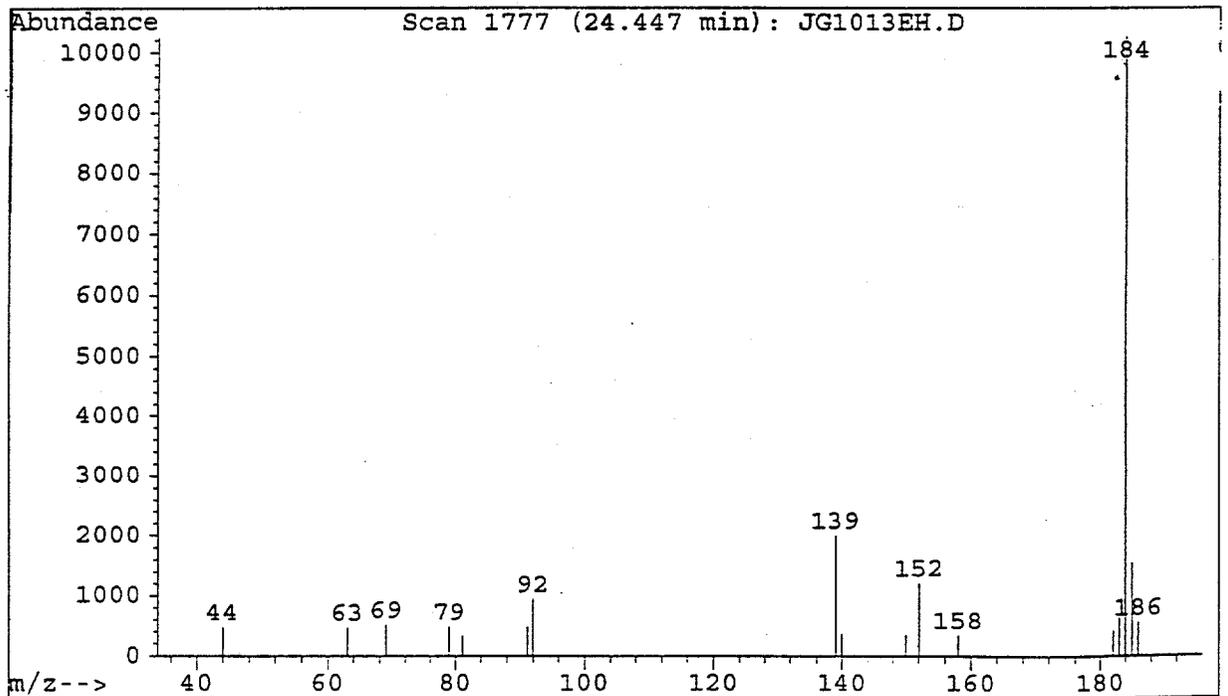
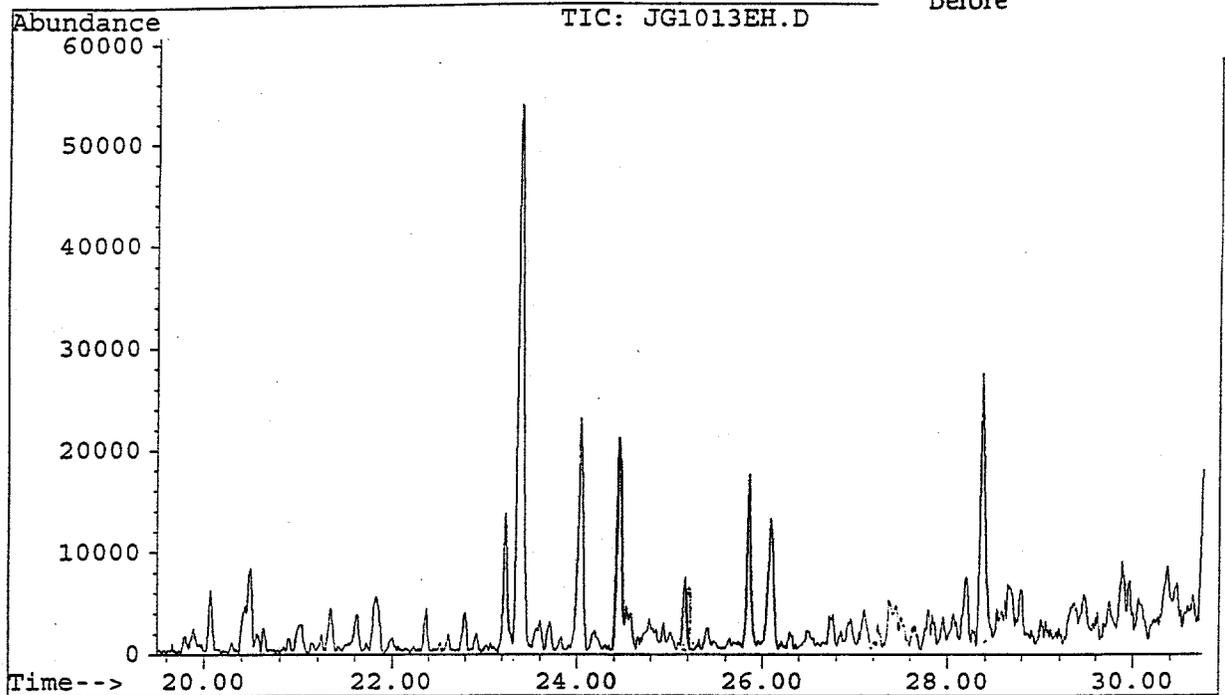


File : C:\HPCHEM\1\DATA\JG0771EH.D
Operator : jg
Acquired : 8 Jun 94 2:22 pm using AcqMethod MODHMLEE.M
Instrument : 5971 - In
Sample Name: exp 11 IBC101 hex frac before desulf
Misc Info : py ext dissolved in THF for Al Chrom
Vial Number: 2



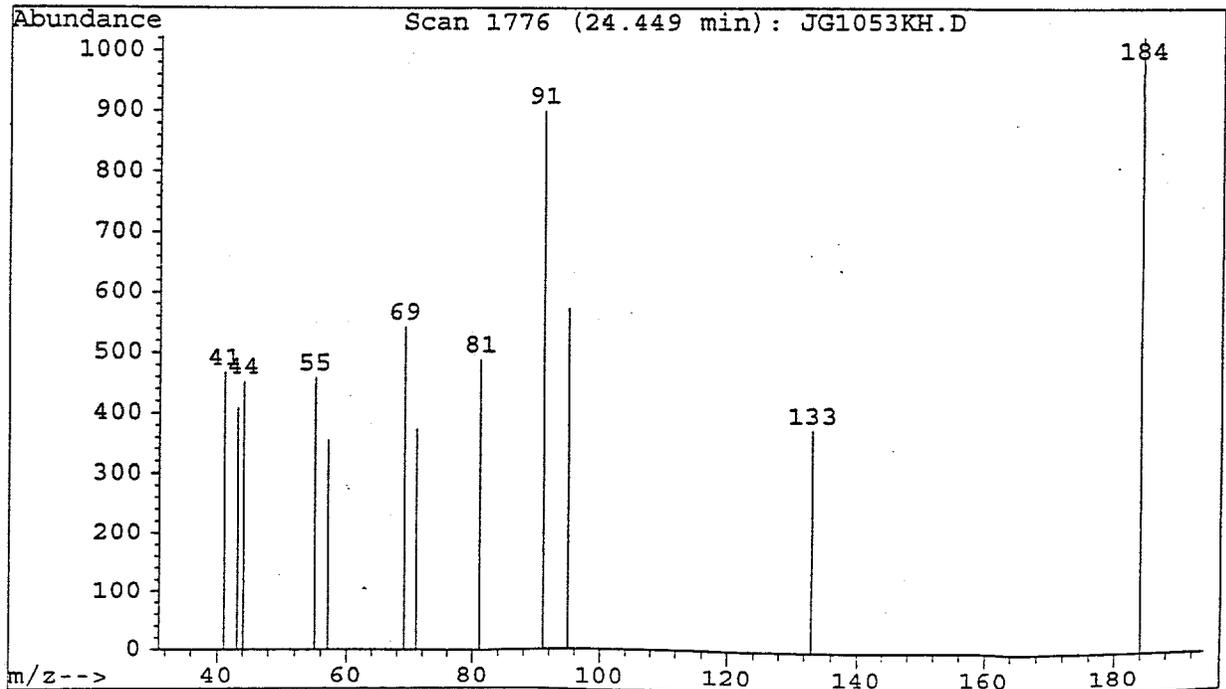
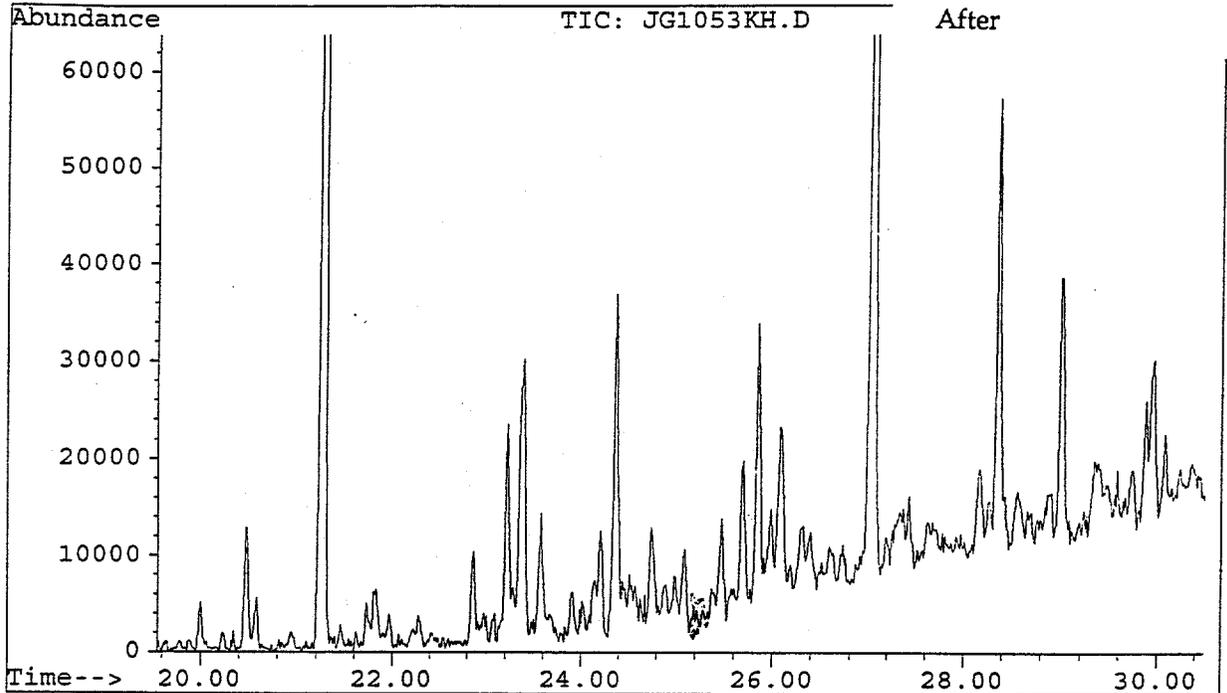
File : C:\HPCHEM\1\DATA\JG1013EH.D
Operator : JG
Acquired : 8 Jul 94 3:40 pm using AcqMethod MODHMLEE.M
Instrument : 5971 - In
Sample Name: py ext before desulf exp 13 hex frac
Misc Info : Alumina chrom Arg#301 Lab book p 101
Vial Number: 1

K/THF/Naph Reaction
Before



File : C:\HPCHEM\1\DATA\JG1053KH.D
Operator : JG
Acquired : 15 Jul 94 2:56 pm using AcqMethod MODHMLEE.M
Instrument : 5971 - In
Sample Name: py ext after desulf exp 13 hex frac
Misc Info : Alumina chrom Arg#301 Lab book p 105
Vial Number: 1

K/THF/Naph Reaction



REFERENCES

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PROJECT MANAGEMENT REPORT
June 1, 1994 through August 31, 1994

Project Title: **REACTIVITY OF TARGET COMPOUNDS FOR CHEMICAL
COAL DESULFURIZATION**

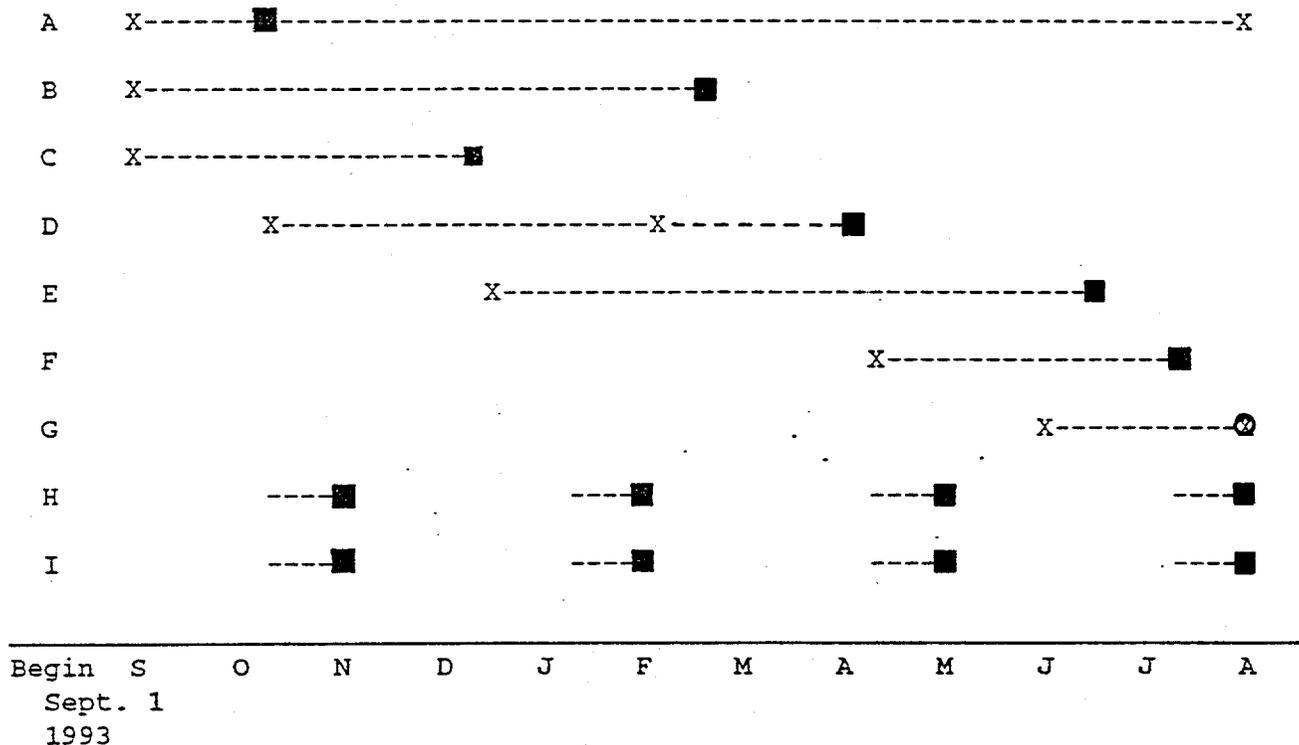
DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.3A-1P
Principal Investigator: Dr. David H. Buchanan, EIU
Other Investigators: Ms. Mandy Amin, EIU
Ms. Janette Galyen, EIU
Project Manager: Dr. Ken K. Ho, ICCI

COMMENTS

On August 1, 1994 PI, David H. Buchanan, began as the Dean of the College of Arts and Sciences at West Chester University, West Chester, PA 19383. Phone: (610) 436-3521. Final work on the project was completed at EIU by technician Janette Galyen and graduate student Mandy Amin. Buchanan remains the PI however, Dr. Ellen Keiter, Chair of Chemistry at EIU, has signature authority as an additional fiscal agent for the project.

Buchanan hosted and chaired the annual meeting of the Illinois Clean Coal Research Association (formerly ARSC) on July 21, 1994 at EIU. Janette Galyen presented a poster on this project at the Annual ICCI Contractors Conference in Champaign, August 3, 1994.

SCHEDULE OF PROJECT MILESTONES



Milestones:

- A. Personnel employed
- B. Sample acquisition and preparation
- C. Extraction of coal to maximize yield
- D. Fractionation of extract to concentrate sulfur compounds
- E. Analyses of fractions for sulfur compounds
- F. Desulfurization reactions of extract and analysis of products
- G. Desulfurization of coal, extraction and analysis of fractions
- H. Technical Reports Prepared and Submitted
- I. Project Management Reports prepared and submitted

Comment: D. Hardware and software problems with GC/MS has delayed completion of analysis of extracts used to develop the fractionation method.

G. Because the number of sulfur compounds identified was so small, whole coals were not used for desulfurization.