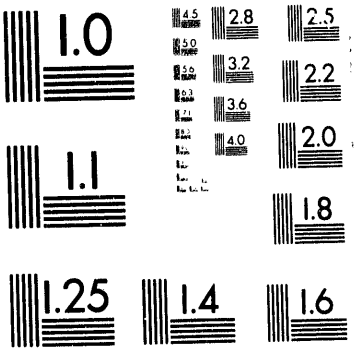
1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

1 of 1

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TECHNICAL REPORT
September 1, 1993 through November 30, 1993

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

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
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Principal Investigator: Dr. David H. Buchanan, EIU
Other Investigators: Ms. Mandy Amin, EIU
Mr. Richard Cunningham, EIU
Ms. Janette Galyen, EIU
Mr. Yungsong Tong, EIU
Project Manager: Dr. Ken K. Ho, ICCI

ABSTRACT

This project seeks to determine the identity of representative organosulfur compounds which are removed by coal desulfurization reactions. Demineralized coals from the Illinois Basin Coal Sample Program are solvent extracted and the extracts fractionated to separate and concentrate the organosulfur compounds for analysis by Gas Chromatography / Mass Spectroscopy. After the sulfur compounds are characterized, the parent extracts will be subjected to reactions previously shown to reduce the organic sulfur content of Illinois coals. The treated extracts will be fractionated and analyzed for organosulfur content by the same method to determine which compounds reacted during the chemical treatment. Finally, the original coal will be subjected to chemical desulfurization, extraction, fractionation and analysis in order to correlate changes in organic sulfur content of the coal with reactions of specific sulfur compounds. These compounds can thus be reliably considered as target molecules for the next generation of desulfurization processes.

Work during this quarter included studies to increase the amount of soluble material extracted from coal by several solvents and development of standard chromatographic methods for fractionation and analysis of soluble coal fractions. Pyridine solubility of several coals is enhanced by removal of mineral matter prior to extraction. The effect is modest (12% relative increase) for Illinois No. 6 coal and greater for lower rank coal. Ultrasound and swelling agents cause a large increase in pyridine solubility. Although toluene extracts much less material from Illinois coals than pyridine, removal of mineral matter prior to extraction causes a relatively larger increase in extraction yield (60 - 80% relative increase). Expected aromatic sulfur compounds such as dibenzothiophene have been detected by GC/MS analysis of non-polar fractions of Illinois No. 6 extracts and several oxidized thiophenes (such as diphenylthiophene sulfone) were detected in extracts of weathered IBC-105 coal.

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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 shown to be present in the feed coal. Reagent testing will be preceded by identification of a representative group of organosulfur compounds which can be extracted from coal with good solvents, such as pyridine, and then separated and concentrated by chromatography and selective chemical reactions. Analytical methods such as Gas Chromatography/Mass Spectroscopy will be used to determine which sulfur compounds are converted to sulfur-free products during the course of the desulfurization reactions.

Current and pending regulations on the burning of high-sulfur coal will require either pre-combustion removal of at least 90% of the sulfur in the coal or the use of post-combustion stack gas scrubbing for most Illinois coal. Pre-combustion desulfurization of Illinois coal must remove both mineral and organic sulfur to achieve the necessary degree of cleaning. Organic sulfur, which often makes up half of the sulfur in Illinois coal, cannot be removed by physical methods and its' removal from coal remains a major challenge, both scientifically and technologically.

Previous work at Eastern Illinois University and elsewhere has shown that solvent extraction methods can mobilize from 50% to 70% of the organic material in some bituminous coals and that the material so solublized contains a fraction of the total organic sulfur in the coal close to the weight fraction of material isolated. Of the sulfur compounds separated, some are so large or complex that complete identification is beyond the capability of current instrumentation. However, a set of the smaller and non-polar compounds in the extracts can potentially be identified *via* GC/MS analysis if they can be separated and concentrated prior to analysis. The identification of those extractable organosulfur compounds which can be fractionated and concentrated by various chromatographic methods forms the first portion of this project.

The overall idea is to extract several IBCSP coals with a good solvent such as pyridine, perhaps modified by the addition of quaternary ammonium salts under the influence of ultrasound irradiation, to solublize as much of the organic material in the coal as possible. Since the concentrations of individual compounds in coal extracts are low, the total extract will then be fractionated by solubility in less polar solvents and chromatographically separated into subfractions which can be analyzed by GC/MS. Additional analyses of fractions by Size Exclusion Chromatography, and FT-IR and FT-NMR spectroscopy may be used to assist in compound characterization. Soluble material of high mass or polarity

which cannot be analyzed by the GC/MS method will need further chemical modification for analysis. Complete identification of large and/or polar molecules remains beyond the scope of single-lab, single-year projects such as this. However, success with this project will demonstrate the feasibility of further studies in which macromolecules are selectively depolymerized and analyzed by the methods developed on this project.

The sulfur compounds thus identified will form a set of target molecules for chemical desulfurization reactions in the second portion of the project. The reactions will be first applied to sub-fractions of coal extracts, rich in identified organosulfur compounds and the products will be analyzed by the same methods used to identify the original organosulfur compounds. Loss of or conversion of target molecules to hydrocarbons will be measured. These reactions will then be applied to the unseparated coal extracts which will then be fractionated and analyzed as before. Loss and/or conversion of target molecules will again be measured. Finally, the demineralized coals will be treated with selected desulfurization reagents, solvent extracted, extracts fractionated and the sub-fractions analyzed as before. In each case the amount of measured desulfurization which can be attributed to reactions of identified compounds will be determined and used to evaluate and characterize the desulfurization method. If patterns of desulfurization activity are observed, chemical modifications of the reagents to increase their reactivity toward the target compounds will be attempted.

Work this quarter included studies of ultrasonically stimulated pyridine extractions of coal, investigation of the effect of mineral matter removal on solvent extraction, calibration of our GC/MS for coal derived mixtures and initial fractionation and analysis of non-polar coal extracts by column chromatography followed by GC/MS analysis.

We have investigated the possibility that mineral matter in pores blocks access by the extraction solvent to potentially soluble material by comparing the total pyridine extraction yield of three Argonne Premium Coals, APC 201 - Wyodak subbituminous, APC 301, Illinois No.6 and APC 401 - Pittsburgh No. 8, with and without demineralization. Pyridine extractability increased for all three coals: 201 from 8 to 17.5%; 301 from 26 to 29% and 401 from 31 to 35%. The large increase for the sub-bituminous coal may be primarily the effect of converting insoluble salts of carboxylic acids into pyridine soluble form. The extract increase for the two bituminous coals is small, indicating that mineral pore blockage is not an important constraint on pyridine extract yield in these coals. However, preliminary results from toluene extraction of APC 301 before and after demineralization show a much larger relative increase in extract yield

as the result of demineralization. This suggests that pyridine which is a good swelling solvent for the insoluble coal matrix can remove soluble material around blocked pores while the poor swelling solvent toluene cannot. We propose to use demineralized coals for the desulfurization studies in this project.

Increasing the yield of solvent extracts and reducing extraction time using ultrasound has been reported by several groups. We have duplicated the 50% pyridine extract yield from APC 301 reported by Liotta on the small scale which he used, but have not been able to scale up the method to the 10-20g range, probably due to limitations in power output from the ultrasonic probe. Small scale extractions of coal using toluene or toluene/chloroform in test tubes in an ultrasonic cleaning bath showed little if any improvement in yield over Soxhlet extractions using the same solvents but were quicker and easier to carry out. The coal fractions so isolated have been used for GC/MS method development while the pyridine studies were in progress.

Method development for the fractionation and GC/MS analysis of coal extracts is in progress and a database of GC retention times of marker compounds is being prepared. Extracts must be fractionated by column chromatography and concentrated before GC/MS analysis in order to obtain reliable compound identification. Aromatic sulfur compounds have been found in several extract fractions as expected from the work of Lee and others. Several substituted thiophene sulfones have been found in extracts of air oxidized IBC-105 coal.

The highest yield method for isolating solvent extracts from Illinois coal for fractionation and GC/MS identification of sulfur compounds appears to be ultrasonic irradiation in the presence of n-Bu_4NOH during pyridine extraction. Demineralization prior to extraction increases the yield by a small amount at the risk of decreasing the yield due to air oxidation. In the next quarter this extraction method will be applied to IBC-101 and -108 coals in order to accumulate extracts for study. The work will emphasize detection of additional sulfur compounds and demonstration of the repeatability and reliability of the extraction - fractionation - GC/MS detection method for assessing the presence or absence of particular organosulfur compounds in coal.

OBJECTIVES

The primary objective of this project is 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 are treated with known coal desulfurization chemical reactions.
Specific goals of this project are to:

1. Maximize the organic material extracted from IBC-101 and -108 using pyridine/nBu_4NOH/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 <u>nature</u> 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.

The benefits from identification of organic sulfur species in coal transcend improvement of an existing process. By identifying specific target molecules for desulfurization, more chemists will be encouraged to work on the necessary new chemistry since they will no longer be shooting at unknown targets. The new detailed structural information on coal and coal extracts available from this work will also be of use to groups seeking to isolate or prepare high-value products from coal. The advances in selective solubilization and fractionation processes which will be further

developed and refined during this project will also be of value as analytical tools for other workers in coal research.

EXPERIMENTAL PROCEDURES

Coals studied this quarter include IBC-105 and Argonne Premium Coal Samples 201 (Wyodak subbituminous), 301 (Illinois #6, the parent of IBC-105) and 401 (Pittsburgh #8). The Argonne coals were included in the study to maximize pyridine extraction yield since they offer a range of volatile and mineral matter contents. Solvent extraction and product purification and isolation follow our published procedures.*(3)* Coals, extracts and residues are dried at 100°C, 0.1 Torr for several hours before weights are recorded for mass balance calculations. Solvents are HPLC grade, often distilled from a drying agent before use. Elemental analyses of coal fractions were done by Galbraith Laboratories, Knoxville, TN.

Acid demineralization uses a modification of standard methods developed in our lab.*(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 HNO_3 treatment as in ASTM D-2492 or by lithium aluminum hydride reduction using the method of Kuhn, *et al.(5)*

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-Bu_4NOH 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 ($AgNO_3$ test). Finally the extract was washed with 80% methanol/water, filtered (0.45 m Nylon membrane) and vacuum dried. The residue was isolated and washed in a similar manner.

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. 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 0.25 m 5% phenyl methyl silicone. Total ion chromatographs of the GC effluent are collected every half second and stored on the computer disk. Data analysis using the HP software matches 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 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.

RESULTS AND DISCUSSION

Compounds extractable from Illinois coal which can be analyzed using the EIU system are those which will elute from the GC column below 320°C with mass less than 660 daltons (the upper limit of the HP 5971 quadrupole detector). These compounds occur primarily in non-polar fractions of the extracts and may be isolated either by extraction with toluene or by fractionating the pyridine extracts into toluene soluble and insoluble portions. During this quarter we have used toluene extraction of IBC-105 coal followed by silica gel chromatography to isolate a suitable fraction of extract for GC/MS method development. This is a quick and efficient method to prepare realistic coal extract samples so that the GC portion of the project could be started before the new pyridine extraction methods were ready in their final form. Our pyridine extraction studies, which are nearly complete, will be discussed first.

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. The effect of removing mineral matter on pyridine extraction of three Argonne coals was studied. These results are presented in Tables 1, 2, 3 and summarized in Figure 1. Preliminary studies had shown that separate treatments with 25% HCl followed by 48% HF removed the same amount of mineral matter and produced the same increase in subsequent pyridine extract yield. Thus the mixed HCl/HF method is shown in Tables 1-3. For these studies, pyrite was removed by the LAH reduction method. The relative increase in pyridine extract yield after demineralization are seen to be: APCSP 201 (Wyodak) = + 109%; APCSP 301 (Ill No. 6) = + 12%; APCSP 401 (Pittsburgh 8) = + 12%. Material balances are very good in all cases. There two possible explanations for the large increase in extract after acid demineralization for the Wyodak subbituminous coal and much smaller effects for the higher rank coals: The higher mineral matter content of the Wyodak blocks more soluble material than in the Illinois or Pittsburgh coal in the pores which can become accesible after demineralization or; Metal salts of carboxylic acids known to be present in Wyodak coal are pyridine insoluble but after acidification the free acids are extracted. Although we cannot rule out the first possibility, the recent demonstration by Vorres *(6)* that large amounts of alkali and alkaline earth cations can be washed from Wyodak coal by dilute acid is consistent with the second explanation.

The data in Table 2 show that demineralization prior to a single pyridine extraction gives the same amount of pyridine extract as pyridine extraction, followed by demineralization followed by a second pyridine extraction. In terms of developing an efficient method for removing the maximum of soluble material this is good news. Results in Table 3 show that increasing LAH reaction times from 6 to 36 hours gives a small increase in the subsequent pyridine extract yield. To summarize: Demineralization of Illinois No. 6 coal (acid and LAH) followed by pyridine extraction gives about 30% of the dry coal as soluble material. This is 36% of the organic material (DAF) in the original coal. Elemental analyses of the feed coal and selected extracts are shown in Table 4. All extracts examined had sulfur contents close to the organic sulfur content of the feed coal, consistent with our previous work.[1] It is also important to note that the nitrogen contents of the extracts have not increased by a large amount, consistent with our claim that 80% methanol/water washing of extracts and residues removes residual pyridine.[3]

Because pyridine is a good swelling solvent for coals, it seems likely that it can effectively penetrate the insoluble coal matrix and, given enough time for mass transport, remove soluble material through the matrix - around any blocked pores which may be present. This is consistent with

small increases in pyridine extraction yields following mineral matter removal, as seen for the two coals which do not contain salts of carboxylic acids. In order to test this possibility, the effect of mineral matter removal on toluene extraction yields of Illinois coals is being studied. Toluene is a poor swelling solvent for Illinois coal and might not extract material blocked by mineral matter in pores. Preliminary results are shown in Table 5. Although the amount extracted is quite small when compared to pyridine, the amount extracted after dimeralization is nearly as large as that from toluene extraction of the original coal, a result consistent with at least some potentially soluble material being blocked behind mineral matter in pores. This study should be finished early in the second quarter.

Liotta has reported(7) that up to 50% by weight of Illinois No. 6 coal can be extracted by pyridine using ultrasonic irradiation with n-Bu_4NOH added to swell the coal. This contrasts to the 28% yield by conventional pyridine extraction. In our hands, ultrasonic irradiation during pyridine extraction gave little improvement in yield in the absence of added base. Results of our ultrasonic experiments with added n-BU_4NOH are given in Table 6. We are apparently seeing an effect of sample size in these experiments. With the equipment we have available, it is difficult to carry out ultrasonic extraction under an inert atmosphere and our previous work[3] has clearly shown that air oxidation leads to decreased yields in pyridine extraction of pristine coals. It is also possible that our ultrasonic probe is unable to generate sufficient power for large volumes of extraction solvents. This is not a major problem but means that accumulating large amounts of extract for further study would require multiple small extractions.

These problems in our method development for ultrasonic extraction should not overshadow the real improvement in extraction yield shown in column I of Table 5. In a single pyridine extraction using ultrasound and the swelling agent, 50% by weight of the dry coal can be made soluble, 59% on a DAF basis. Acid and LAH demineralization of the pyridine insoluble residue followed by pyridine extraction produce only a 3% increase in extract yield. At this point we can solublize 63% of the organic material originally present in the Argonne 301 coal. Our results to date on increasing the pyridine extraction yield of Illinois No. 6 coal are summarized in Figure 2.

To date, our attempts to carry out small scale extractions using test tubes of coal and solvent in a standard laboratory ultrasonic cleaning bath have resulted in only slightly increased yields of extract, which however is useful in GC/MS method development.

In Figures 3 and 4, GC/MS traces of fractionated toluene

extracts of IBC-105 coal are shown. For the sample in Figure 3, the toluene extract was chromatographed on dry-packed silica gel and eluted with hexane followed by toluene. A portion of the total ion chromatogram of the fraction eluting with toluene is shown at the top and the mass spectrum of peak 2551 (29.3 min) is shown below. This mass spectrum matches #127204 in the Wiley MS Library which is dibenzothiophene, the most common organosulfur compound found in solvent extracts of bituminous coals. Figure 4 shows the same type of data for a toluene chromatographic fraction from a toluene/chloroform (1:1) extract of IBC-105. The mass spectrum of peak 2575 (29.8 min) shown on the bottom matches that of #53300 in the Wiley MS Library - 2,3-diphenylthiirene 1,1-dioxide. It is significant that this sulfone was found in a more polar extract of an oxidized coal and illustrates the need for using polar extracting solvents such as pyridine to find all sulfur compounds. That this compound was formed during air oxidation over several months on a laboratory bench shows the complexity of organosulfur compounds which may be present in coal during large scale commercial processing.

CONCLUSIONS AND RECOMMENDATIONS

The most efficient method for isolating solvent extracts from Illinois coal for fractionation and GC/MS identification of sulfur compounds appears to be ultrasonic irradiation in the presence of n-Bu_4NOH during pyridine extraction. Demineralization prior to extraction might increase the yield by a small amount at the risk of decreasing the yield due to air oxidation. In the next quarter this method will be applied to IBC-101 and -108 coals in order to accumulate extracts for study.

Method development for the fractionation and GC/MS analysis of coal extracts is in progress and a database of GC retention times of marker compounds is being prepared. Aromatic sulfur compounds have been found in extracts as expected from the work of Lee and others and an diphenylthiophene sulfone has been found in the extract of oxidized IBC-105 coal. Work during the next quarter will emphasize detection of additional sulfur compounds and demonstration of the repeatability and reliability of the extraction - fractionation - GC/MS detection method for assessing presence or absence of particular organosulfur compounds in coal.

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Table 1 Multiple Extraction of Argonne Premium Coals (Standard Treatment)

		#2 COAL	#3 COAL	#4 COAL
	INITIAL WT g	16.4100	24.8549	19.3942
a	PY EXTRACT #1 g	1.3730	6.4093	5.9622
	WT % EXTRACT #1 %	8.37	25.79	30.74
b	PY RESIDUE #1 g	14.7989	18.8579	12.2690
	WT % RESIDUE #1 %	90.18	75.87	63.26
	MATERIAL BALANCE %	98.55	101.66	94.00
	PY RESIDUE #1 g	5.0560	7.8396	9.7851
	WT AFTER HCl/HF g	4.2158	6.1283	8.2116
	WT RECOVERY %	83.38	78.17	83.92
c	PY EXTRACT #2 g	0.4207	0.1500	0.0967
	WT % EXTRACT #2 %	9.98	2.45	1.18
d	PY RESIDUE #2 g	3.3850	6.0610	8.2699
	WT % RESIDUE #2 %	90.97	98.90	100.71
e	MATERIAL BALANCE %	100.95	-101.35	101.89
	WT % EXTRACT #1+#2 %	15.87	27.24	31.37
	PY RESIDUE #2 g	1.2465	2.1663	1.9880
	WT AFTER LAH RXN g	1.0891	1.9485	1.7817
	WT RECOVERY %	87.37	89.95	89.49
f	PY EXTRACT #3 g	0.0300	0.0624	0.1191
	WT % EXTRACT #3 %	2.75	3.20	6.68
g	PY RESIDUE #3 g	1.0667	1.8649	1.6240
	WT % RESIDUE #3 %	97.94	95.71	91.15
	MATERIAL BALANCE %	100.69	98.91	97.83
	TOTAL WT % EXTRACT %	17.52	28.93	34.57

Table 2 Effect of Demineralization Before First Pyridine Extraction of #3 Coal Sample

	ACID DEMI + PY EXTRACTION	PY EXT + DEMI + 2nd PY EXT
FRESH COAL (g)	3.3683	---------
PY RESIDUE #1 (g)	---------	7.8396
WT AFTER HCl/HF (g)	2.8219	6.1283
WT RECOVERY (%)	83.78	78.17
PY EXTRACT (g)	0.7884	0.1500
WT % EXTRACT (g)	27.94	2.45
PY RESIDUE (g)	1.9364	6.0610
WT % RESIDUE (%)	68.61	98.90
TOTAL WT % EXT (%)	27.94	27.24*

*: including first pyridine extract (see Entry a in Table 1)

Table 3 Methods Used to Increase Pyridine Extract of #3 Coal

	Standard Treatment	LAH Rxn 36 h	Mixed Acid & LAH Rxn 36 h
PY RESIDUE #1* g	7.8396		3.3433
WT AFTER HCl/HF g	6.1283		2.5670
WT RECOVERY %	78.17		76.78
PY EXTRACT #2 g	0.1500		0.0456
WT % EXTRACT #2 %	2.45		1.78
PY RESIDUE #2 g	6.0610		2.5357
WT % RESIDUE #2 %	98.90		98.78
MATERIAL BALANCE %	101.35		100.56
WT % EXTRACT #1+#2 %	27.24		26.82
PY RESIDUE #2 g	2.1663	2.0150	2.0964
WT AFTER LAH RXN g	1.9485	1.8106	1.8935
WT RECOVERY %	89.95	89.86	90.32
PY EXTRACT #3 g	0.0624	0.1177	0.0670
WT % EXTRACT #3 %	3.20	6.50	3.54
PY RESIDUE #3 g	1.8649	1.6890	1.7842
WT % RESIDUE #3 %	95.71	93.28	94.23
MATERIAL BALANCE %	98.91	99.78	97.77
TOTAL EXTRACT %	28.93	30.67	28.66

*: the same as Entry b in Table 1

Table 4 Elemental Analysis of #3 Coal Fraction and Extracts (Illinois No. 6 Coal)

	% C	% H	% N	% S	% O[1]	% ash	C/H[2]	S/C[2]
A	77.67	5.00	1.37	2.38[3]	13.51	15.48	1.30	.0115
B	80.01	6.00	1.58	2.47	9.94	0	1.12	.0116
C	78.91	6.26	1.57	2.44	10.82	0	1.06	.0116
D	73.78	6.94	1.80	2.12	15.36	0	.892	.0108
E	75.77	6.16	1.48	2.20	14.39	0	1.03	.0109
F	76.69	6.41	1.60	2.50	12.80	0	1.00	.0122

A: moisture and ash free coal sample
data from User Handbook for the Argonne Premium Coal Sample Program (October 1, 1989 U.S. Dept. of Energy)
B: pyridine extract #1 (Standard Treatment, see Entry a in Table 1)
C: pyridine extract after demineralization and LAH reaction (Standard Treatment, see Entry f in Table 1)
D: extract after ultrasonic treatment I (see Entry a in Table 6)
E: extract after ultrasonic treatment II (see Entry a in Table 6)
F: pyridine extract after LAH reaction in ultrasonic treatment II (see Entry c in Table 6)
[1]: by difference
[2]: mole ratio
[3]: organic sulfur (total S=4.83%)

Table 5 Toluene Extraction of Oxidized IBC-105 Coal

	Dry Coal	Demineralized Toluene Residue
Initial Wt g	9.2215	7.9230
Toluene Extract Wt g	0.0640	0.0433
Toluene Extract Wt %	0.69%	0.55%
Toluene Residue Wt g	9.3529	8.1081
Material Balance %	102.1	102.9

Table 6 Ultrasonically Enhanced Coal Extraction

		I	II	III
	DRY #3 COAL (g)	2.5256	15.0020	7.5331
a	EXT AFTER ULTRA (g)	1.2585	3.8663	2.1233
	RES AFTER ULTRA (g)	1.0518	10.3178	5.4551
	WT % EXTRACT (%)	50.03	25.77	28.19
	RESIDUE (g)	0.9015	9.1772	
	WT AFT HCl/HF (g)	0.6290	7.5619	
b	PY EXTRACT (g)	0.0429	0.4673	
	PY RESIDUE (g)	0.6092	7.1090	
	WT % EXTRACT (%)	6.82	6.18	
	EXTRACT 2 STEPS (%)	52.02	29.27	
	RESIDUE (g)	0.5757	5.0011	
	WT AFT LAH (g)	0.4780	4.2924	
c	PY EXTRACT (g)	0.0197	0.1515	
	PY RESIDUE (g)	0.4780	4.2720	
	WT % EXTRACT (%)	4.12	3.53	
	TOTAL EXTRACT (%)	52.98	30.89	

Figure 1

MULTIPLE EXTRACTION OF ARGONNE PREMIUM COALS

(Standard Treatment)

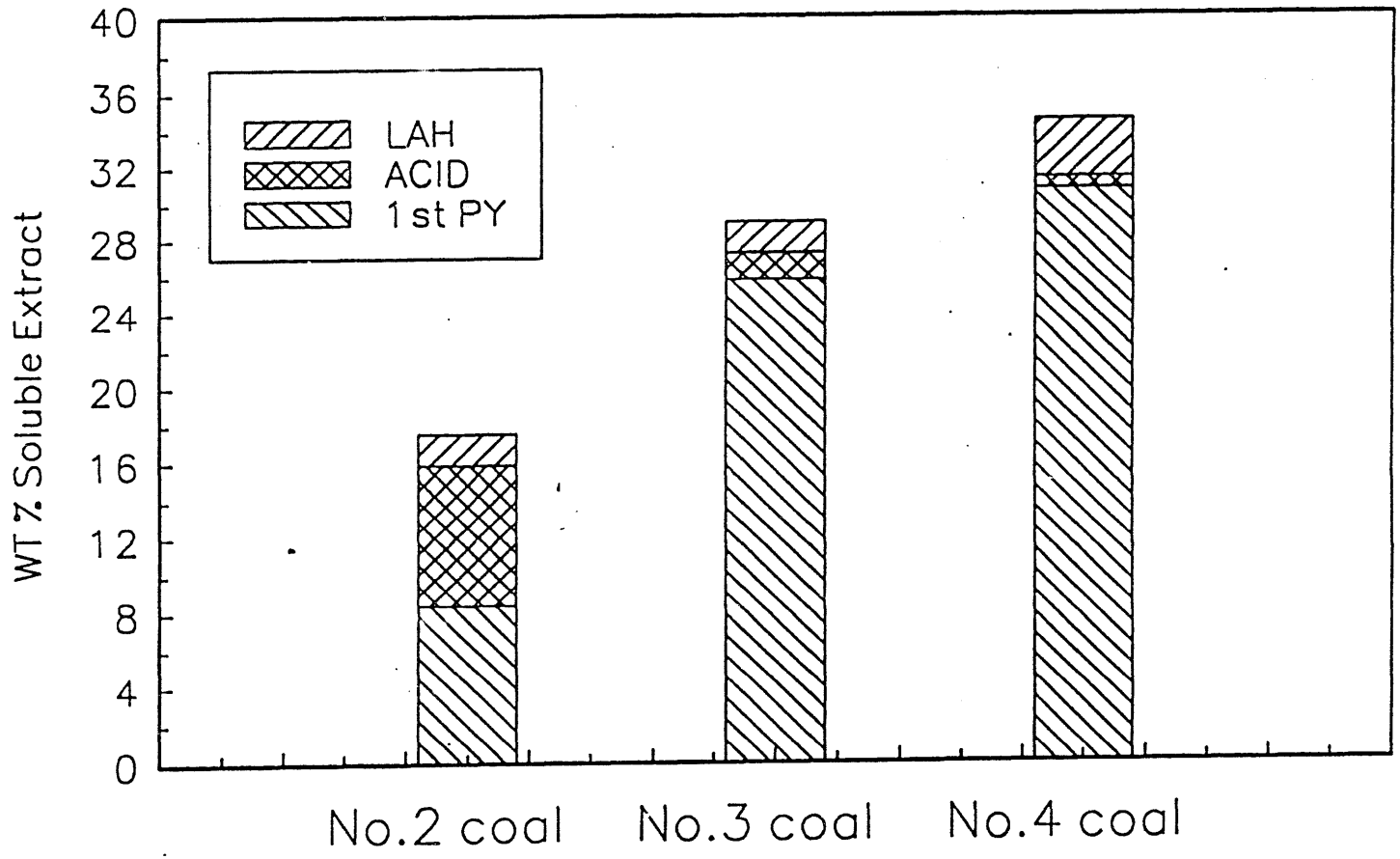


Figure 2

METHODS USED TO INCREASE PY EXTRACT OF NO.3 COAL

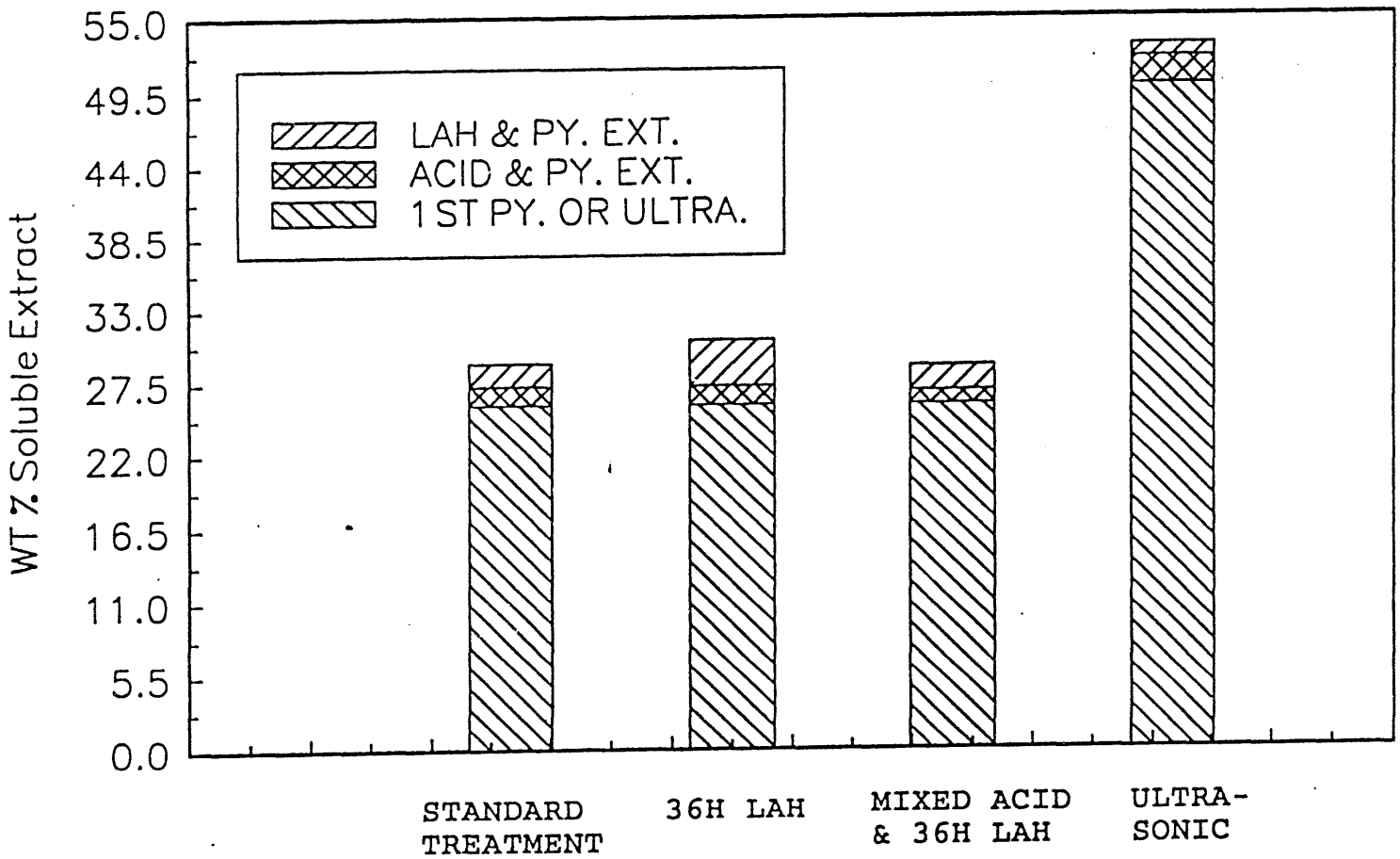
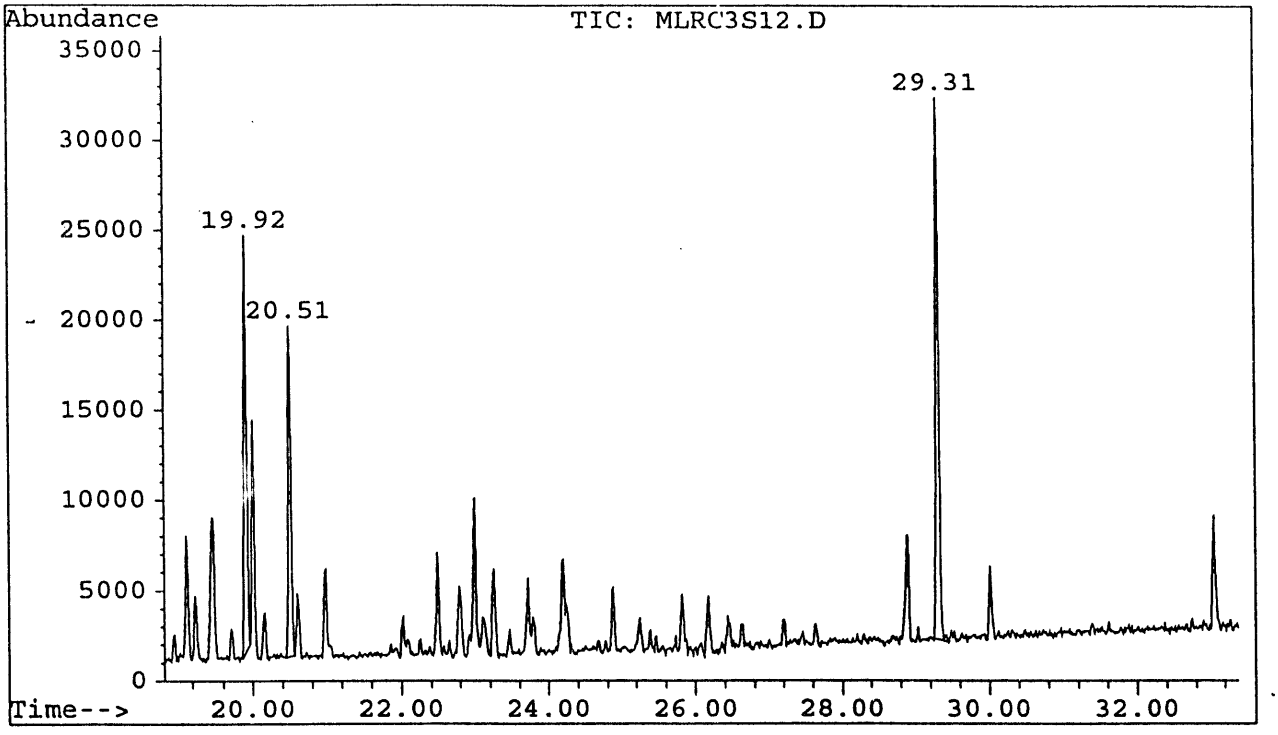


FIGURE 3

File : C:\HPCHEM\1\DATA\MLRC3S12.D
Operator : JMG
Acquired : 5 Nov 93 12:44 pm using AcqMethod MLEE.M
Instrument : 5971 - In
Sample Name: RICK SAMPLE 1 FRAC 2
Misc Info : TOLUENE EXT MAX SENSE METHOD
Vial Number: 1



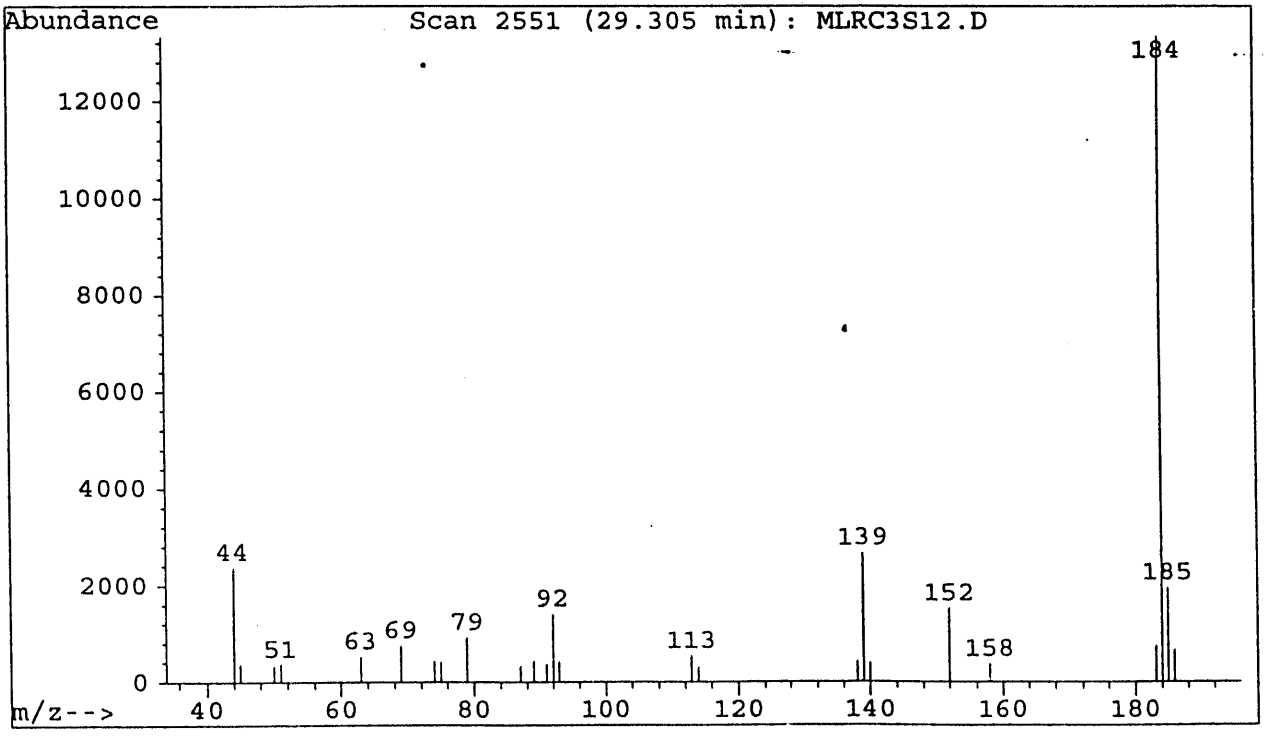
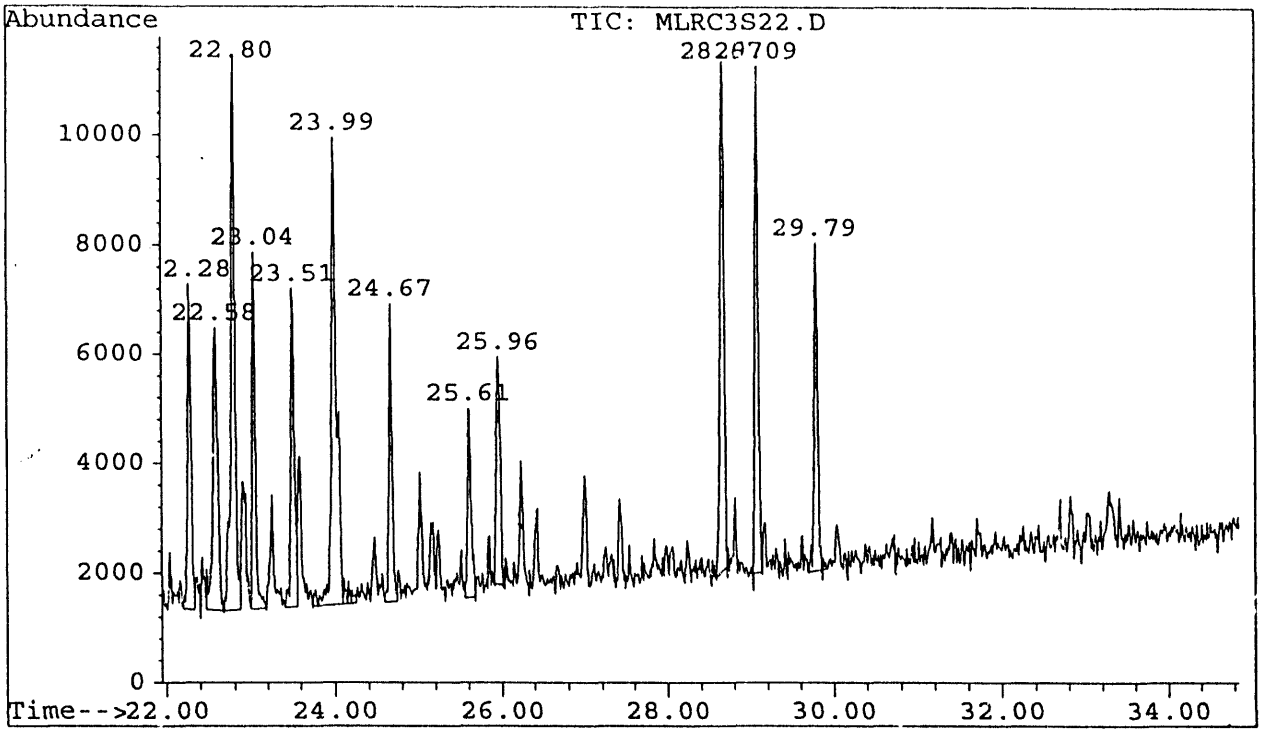
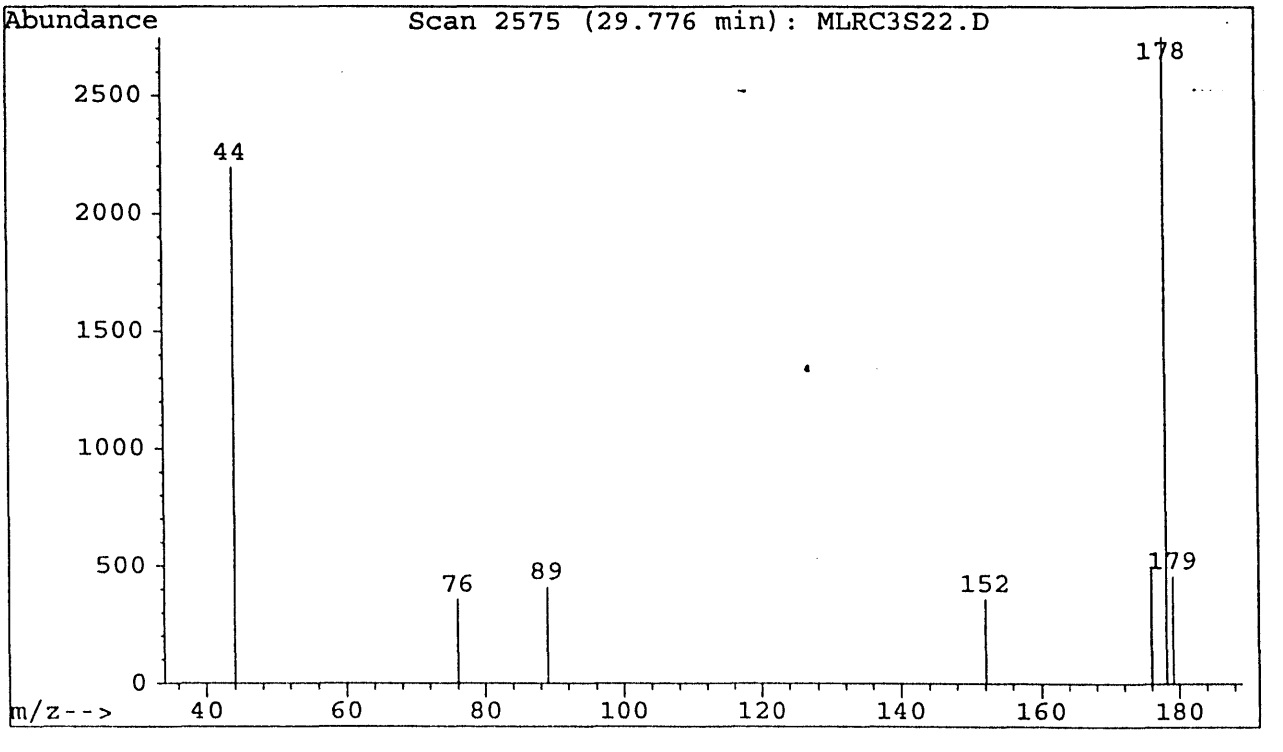


FIGURE 4

File : C:\HPCHEM\1\DATA\MLRC3S22.D
Operator : JMG
Acquired : 5 Nov 93 2:16 pm using AcqMethod MLEE.M
Instrument : 5971 - In
Sample Name: RICK SAMPLE 2 FRAC 2
Misc Info : TOLUENE EXT MAX SENSE METHOD
Vial Number: 1





PROJECT MANAGEMENT REPORT
September 1, 1993 through November 30, 1993

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
	Mr. Richard Cunningham, EIU
	Ms. Janette Galyen, EIU
	Mr. Yungsong Tong, EIU
Project Manager:	Dr. Ken K. Ho, ICCI

COMMENTS

Technician Linda Warfel who had worked on coal research with PI Buchanan since 1984 resigned August 31, 1993 to accept a position with a nearby pharmaceutical laboratory. Following State of Illinois Civil Service regulations, the position was advertised and applicants were screened by the EIU Office of Human Resources. The top three candidates were interviewed in late September and Janette Galyen was hired to begin work on October 1, 1993. Ms. Galyen is an EIU BS Chemistry graduate (1990) with several years of industrial experience. The other investigators are graduate and undergraduate students at EIU.

SCHEDULE OF PROJECT MILESTONES

```
A    X------■-------------------------------------------------------X
B    X--------------------------------X
C    X-------------------X
D            X---------------------X
E                        X----------------------------------X
F                                                X-----------------X
G                                                          X-----------X
H            ----■            ----X            ----X            ----X
I            ----■            ----X            ----X            ----X
```

Begin	S	O	N	D	J	F	M	A	M	J	J	A
Sept. 1 1993												

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

EXPENDITURES - EXHIBIT B

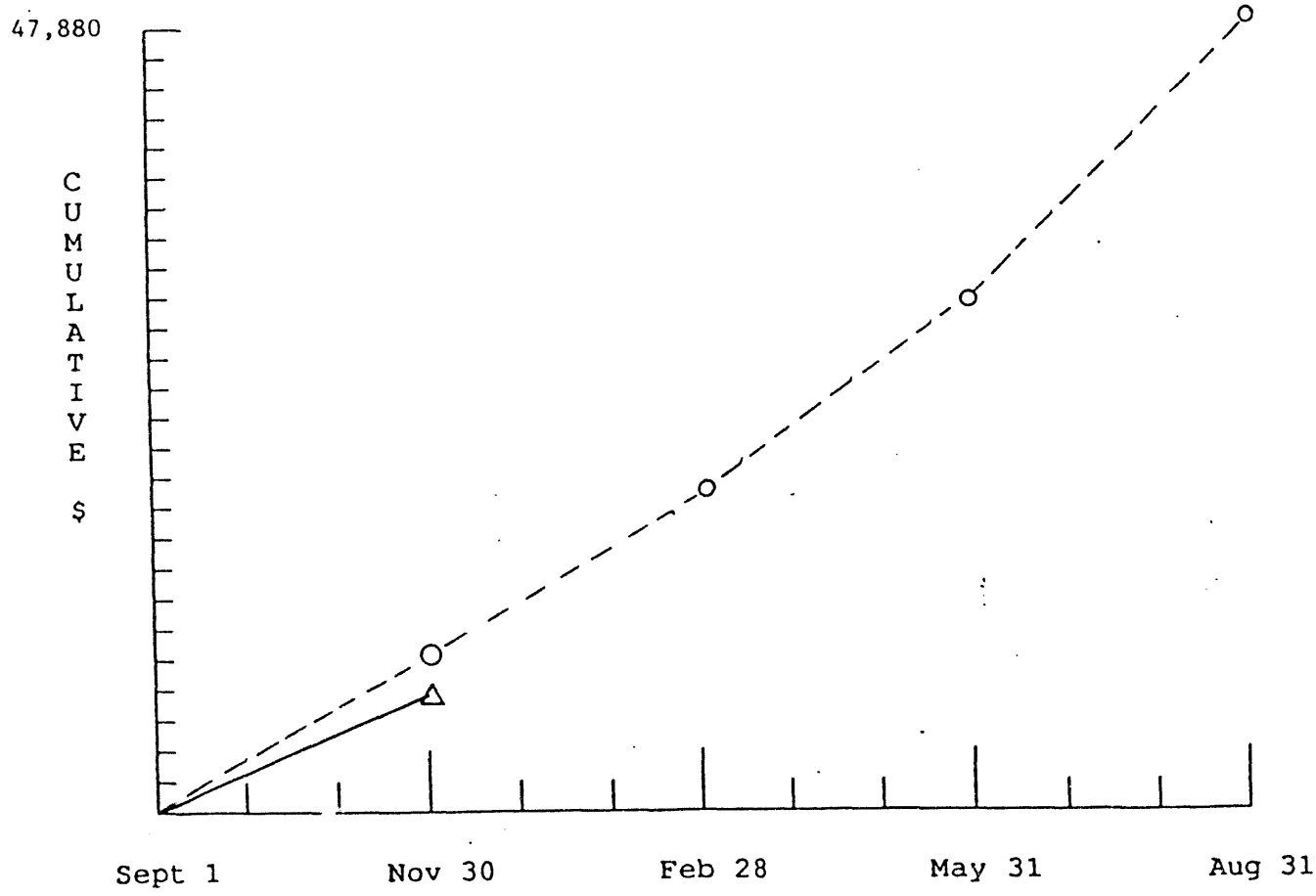
CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

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	6,860	635	600	25	-0-	700	882	9,702
	Estimated	4,514	268	448	-0-	-0-	20	525	5,775
Sept. 1, 1993 to Feb. 28, 1994	Projected	13,720	1,270	1,200	50	400	1,300	1,794	19,734
	Estimated								
Sept. 1, 1993 to May 31, 1994	Projected	20,580	1,905	1,800	50	850	1,900	2,708	29,793
	Estimated								
Sept. 1, 1993 to Aug. 31, 1994	Projected	34,591	3,247	2,400	139	850	2,300	4,353	47,880
	Estimated								

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER -- EXHIBIT C

Reactivity of Target Compounds for Chemical Coal Desulfurization



Months and Quarters

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

Δ = Actual Expenditures ————————

Total ICCI Award $ 47,880

DATE
FILMED
4/13/94

END