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Project Title: Characterization of Illinois Coal: Correlation of  
Chemistry with Petrography

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**ABSTRACT**

This project sought to improve the chemical and physical characterization of Illinois coal. The relationship between organo-sulfur compounds and oxygen containing functional groups in extracts, plus the correlation of chemical with petrographic changes were the primary goals of the project.

Quantitative and qualitative changes in the visual physical characteristics of individual macerals in oxidized and un-oxidized samples of coals were correlated with changes brought about by sequential solvent extraction. Specific macerals yield extracts at different points in sequential solvent extractions. Petrographic analyses of Illinois coals and sequential extraction residues indicate little alteration of any maceral group by toluene or THF. DMF and pyridine extraction residues show extensive surface alteration of liptinitic macerals, particularly resinite, decreases in resinite fluorescence intensity, and decreased vitrinite reflectance. Extracts of weathered coals show the same petrographic changes, but to a smaller degree, consistent with the lower extract yields of these coals.

Methylation or butylation of coals prior to sequential solvent extraction increased total extract yields and shifted the distribution such that most of the extract was removed by toluene. Alkylation produced extensive surface erosion of all macerals except inertinite and dramatically changed reflectance and fluorescence characteristics of vitrinite and liptinite macerals before extraction. Petrographic changes in alkylated resinite after toluene extraction were similar to changes seen in raw coals only after pyridine extraction.

Chemical and petrographic data are consistent with the view that toluene and THF extract material mainly from pore spaces with little effect on coal structural components while DMF and pyridine extract additional material with physical changes in macerals due to extensive swelling and/or selective removal of structural components. Air oxidation of coals decreased overall extract yields of Illinois, but not of higher rank, coals and usually lowered the sulfur contents of the extracts 10-20% from the un-oxidized values. Sulfur contents were usually higher in the more polar extracts. Taken together, the lower yield and reduced sulfur contents indicates that organic sulfur in weathered Illinois coals is more difficult to mobilize than that in fresh coals.

## EXECUTIVE SUMMARY

The primary goal of this project was improvement of the chemical and physical characterization of Illinois coals through an investigation of the visual physical changes in individual maceral groups and subgroups which occur when whole coals are sequentially extracted with a series of increasingly better solvents for coal material. Since macerals, which can be identified visually, can be considered to be 'building blocks' for the organic portion of the coal, studies which relate behavior such as solubility to specific macerals serve to unify petrographic and chemical information obtained by diverse research groups.

### Chemical Analyses

Low-temperature air oxidation (artificial weathering) changes the yield, molecular weight profile, and FT-IR spectra of material extracted from Illinois coals in a manner consistent with the oxidative coupling of phenols and further oxidation induced transformations of phenols and ethers. If organic sulfur is associated with these phenols and ethers, which is chemically reasonable, the mobility of organic sulfur and reagents which might remove it will be influenced by the oxidation history of the coal. The sequential solvent extraction technique has the ability to probe the mobility (solubility) of both polar and non-polar materials in fresh and oxidized coals. By use of Size Exclusion Chromatography (SEC), molecular weight profiles of each extract can be compared and changes resulting from chemical reactions of the coal noted. Solvent swelling behavior and phenol contents of the remaining insoluble coal residues can also be related to the chemical reactions. If quantitative petrographic analysis of fresh and oxidized coals before and after extraction reveals changes in specific maceral groups or subgroups, it also may be possible to identify the macerals responsible for a particular behavior. Such maceral specific information is difficult to obtain at present.

Sequential solvent extractions (toluene < THF < DMF < pyridine) of both fresh and weathered versions of the Argonne Premium Sample coals were completed to provide a basis for comparison with sequential extractions of the Illinois Basin Coal Samples. Total extract yield as a function of rank reached a maximum at 78-79% C (daf) as expected from previous work, however individual solvent yields show more variation with rank than does total yield. SEC analysis of all extracts in pyridine showed that, for each coal, average molecular size of extracts increased in the order toluene, THF, DMF, pyridine. For any given solvent, molecular size varied as the yield of extract from coal to coal. Higher yields correlated with larger molecular size, although the variation in size with rank for a single solvent was less than the variation in size with solvent for a single coal.

Elemental analyses of sequential extracts from Illinois coals showed a decrease in the atomic H/C ratio and an increase in the atomic O/C ratio from toluene to THF to DMF. Both percent sulfur and atomic S/C ratios for these extracts increased about 20% from sequential toluene extract to sequential DMF or pyridine extracts. IBCSP coal 2 (Colchester) was unique in that the toluene extract was highest in sulfur content and that the yield of toluene extract was low compared to other coals. For the

original coals, organic S/C ratios were 0.012-0.015 and S/C ratios of the extracts ranged from 0.003 to 0.016. Variation in S/C ratio for each sequential extract correlated with percent organic sulfur, rather than total sulfur in the original coal, as expected. The sequential pyridine extracts of these coals generally are low in yield (< 2%), since the coals have been exhaustively extracted with the previous three solvents, and show more variation in H/C and O/C ratios. Elemental analytical, SEC, and FT-IR data are consistent with the idea that the sequential pyridine extracts contain material similar to toluene and THF extracts which has been released due to the superior swelling behavior of the pyridine, in addition to material soluble only in pyridine. Atomic S/O ratios varied widely for the extract fractions, perhaps an artifact of the difference method of determining oxygen.

Artificial weathering lowered the total extract yield for all the Illinois coals studied to date, but this behavior was not characteristic of coals of either lower or higher rank from the Argonne Premium Sample program. For the Illinois coals, the decrease in yield generally was due to loss of THF, DMF, and pyridine fractions of which the DMF was often the most significant in terms of total mass of extract. SEC results show that the correlation of extract yield and molecular size also holds for changes due to oxidation as well as those due to rank. FT-IR spectra revealed increases in carbonyl containing functional groups for coals of all ranks upon artificial weathering and these groups were concentrated and partially fractionated in the sequential solvent extracts. Evidence for both ester and quinone groups is readily apparent in the spectra of extracts, even when FT-IR difference spectra of oxidized minus fresh coal show only broad, unresolved bands in the  $1700\text{ cm}^{-1}$  region.

For the Illinois coals studied in detail, changes in atomic H/C, and O/C ratios of sequential extracts brought about by weathering showed no obvious trends from solvent to solvent. Artificial weathering decreased the amount of organic sulfur extracted by each solvent in the sequence and the atomic S/C ratios of the extracts by 6-20%.

#### Petrographic Analyses

Petrographic analyses of fresh, weathered, methylated, and butylated coals plus their residues from sequential solvent extraction indicate significant solvent specific maceral alteration.

Analyses of raw coals and residues indicate little or no alteration of any maceral group through toluene and THF extraction. However, DMF and pyridine extraction residues show extensive alteration of some liptinitic macerals, in particular resinite. This alteration is shown by extensive chemical erosion, that results in lowered reflective characteristics of resinite particles; and a marked decrease in fluorescence intensity and color. DMF and pyridine residues also exhibit a trend of lowered vitrinite reflectance values.

Analyses of oxidized coals and residues from sequential solvent extraction show similar trends to those observed from raw coals, however the severity of chemical erosion and degree of change in fluorescence intensity and color is less significant. Percent reflectance of

vitritinite particles continues the trend toward lower values.

Analyses of butylated and methylated coals and their extraction residues yielded a quite different alteration process. Both alkylations produced extensive surface erosion of all macerals except inertinite. An attempt to view the alkylated coals under fluorescent light showed that the vitritinite had significantly increased both the intensity and color of fluorescence. The epoxy mounting medium had absorbed so much fluorescing material from the coal particles that further fluorescence qualification was meaningless. Further petrographic analyses of extraction residues showed that toluene was the major solvent affecting alteration of the liptinitic macerals, again mainly resinite. Reflectance analyses of both alkylated samples have become problematical due to a severe photochemical interaction of sample with the microscope immersion oil while using the mercury light source for fluorescence and reflectance observations.

### Conclusions

It was shown that chemical modifications of coals such as solvent extraction or alkylation can be correlated with changes in visual physical characteristics in specific maceral groups or subgroups in un-separated coal samples. Such techniques, if developed further, will enable maceral specific chemical behavior of coals to be investigated without expensive and difficult maceral separation and concentration techniques.

The petrographic analyses performed during this study have produced many new and intriguing questions that require further investigation. The conclusions from this part of the study indicate that un-oxidized and oxidized coals subjected to toluene, THF, DMF, and pyridine extraction yield products from solvent specific macerals - in these analyses resinite. The study also indicates that toluene and THF are extracting soluble materials from pore spaces and are not altering the coal structure. DMF and pyridine, however, are further extracting larger molecules from pore spaces accessible due to the extensive swelling capacity of these solvents, and/or are chemically removing components of the coal structure from resinite maceral particles of microscopic and disseminated sub-microscopic sizes.

It was shown that sequential solvent extraction in the order toluene, THF, DMF, pyridine removes progressively larger and more polar material from Illinois coals. Both the yield and molecular size of extracts are decreased by artificial weathering at ambient temperature for several months. Removal of toluene and THF extracts from the coals causes little visual change to any macerals but DMF and pyridine cause extensive modification of resinite surfaces and reflectance properties. Vitritinite reflectance also decreases after extraction with these solvents. Sulfur contents are higher in the more polar extracts except for Colchester coal and decrease by 10-20% in extracts of weathered coals. Since yields are also decreasing, the amount easily mobilized organic sulfur (as measured by solvent extraction) is seen to be significantly reduced by weathering.

## OBJECTIVES

The primary goal of this project was improvement of the chemical and physical characterization of Illinois coals through an investigation of the visual physical changes in individual maceral groups and subgroups which occur when whole coals are extracted with a variety of solvents of different polarity. Since macerals, which can be identified visually, can be considered to be 'building blocks' for the organic portion of the coal, studies which relate well-defined chemical behavior to specific macerals are very useful. For example, if a particular maceral was the primary source of a particular soluble component of known sulfur content, then petrographic analysis of untested coals should allow the prediction of the sulfur contents of their extracts without lengthy chemical processing.

The primary objective of the chemical study was to extend the solvent extraction studies already underway to the determination of how the organic sulfur compounds of Illinois coal are partitioned when the coal was extracted at low temperatures with a selection of solvents of varying polarities. The goal was fundamental knowledge of how the various organosulfur compounds in coal are bound in the macromolecular network and their association with various polar groups. The solvents chosen for this study were not being evaluated as candidates for an actual desulfurization process, they were used to obtain information on the chemical environment of organic sulfur compounds in the coal matrix. Such improved characterization of organosulfur compounds should also improve future technology, developed by other groups, for the removal of sulfur from Illinois coal.

An additional objective of the chemical portion of the study was to correlate the extractability of organic sulfur compounds at low temperature with the degree of oxidation of the coal. Oxidation induced changes in swelling ratios as a function of rank and maceral content would also be determined for coals whose liquefaction and gasification behaviors were known or currently under investigation. This information should be of value in the design and improvement of coal process chemistry and may also lead to more convenient and rapid methods of predicting the storage, coking and liquefaction behavior of Illinois coals. A final chemical objective was to correlate SEC molecular size distributions and the sulfur content of coal fractions soluble in pyridine, DMF, THF, and toluene with one another. Such information could provide the basis for more complete characterization of coals and their liquefaction products.

The first objective of the petrographic study was quantitation of the changes in percent reflectance of vitrinite as a function of chemical reaction or solvent extraction. The second objective was observation and recording of changes in fluorescence intensity and color caused by chemical treatment for fluorescent maceral groups and subgroups. Finally, changes occurring in visual physical characteristics such as fracturing of the coal particles due to exposure to the reagents used in this study was recorded. Since the Petrographic Microscope in the Geology Department was not equipped for the quantitative or fluorescence portions of this study, the first task for the geologist was upgrading and calibration of the microscope.

## INTRODUCTION AND BACKGROUND

The organic fraction of coal has long been recognized to be a heterogeneous mixture of optically distinct units designated macerals by Stopes, but only recently have techniques been developed to investigate possible chemical differences between these units. Two distinct approaches to studies of maceral chemistry have evolved: in situ analyses of elemental maceral composition by various microprobes, and the physical separation of pure maceral concentrates. A complete characterization of the organic portion of coal demands that the chemistry specific to each maceral group or subgroup be identified and quantified, both as pure macerals and in contact with one another and with minerals, as found in native coal.

The organosulfur content is known to differ among the various macerals of Illinois coals. We have previously observed that the sulfur contents of total pyridine soluble fractions of some IBCSP coals differ from the organic sulfur contents of the parent coals. For example, Coal 1 (Illinois No. 6) from the sample bank has 2.59% DAF organic sulfur but the toluene insoluble, pyridine soluble (TIPS) fraction of that coal contains only 1.08% sulfur and 0.85% ash. Solvent swelling behavior and other evidence suggests that this coal was oxidized before being added to the sample bank. An un-oxidized Illinois No. 6 coal containing 3.08% organic sulfur gave a TIPS fraction containing 3.05% sulfur and 0.35% ash. If organic sulfur is associated with phenol rich material, the extractability of sulfur compounds should decrease with air oxidation of the coal, as is observed for the phenols themselves. On the other hand, if organic sulfur occurs mainly as monofunctional compounds, oxidation may not play a major role in its extraction behavior. A correlation of the solvent extractability, sulfur content of extracts and residues, and petrographically observable changes in macerals caused by extraction can potentially yield information on the nature of organic sulfur compounds in coal macerals which are still part of the original coal. This technique cannot replace work on pure macerals, but can perhaps extend it and permit rapid analysis of other coals which have not yet been subjected to maceral separation.

Both the information obtained from extraction studies and the chemical characterization of macerals would be enhanced by careful extractions of pure maceral concentrates. This would be a time and labor intensive task since extractions require multi-gram quantities of starting solids if usable amounts of soluble fractions are to be isolated and characterized. As an adjunct or alternative to such studies, extraction studies on whole coal, when coupled with careful petrographic analysis of changes in individual macerals in those coals can potentially provide useful information concerning which macerals are most affected by a particular extracting solvent. The latter approach was the focus of this study.

## EXPERIMENTAL PROCEDURES

Detailed procedures for the sequential extractions, molecular size profiles by size exclusion chromatography, and coal alkylations are given in the Experimental sections of the reprints and manuscripts attached to

this report as Appendices A, B, C, and D.

Petrographic mounts of coals and extraction residues were prepared by the following method. A plastic mold having a 10mm diameter x 1mm deep well was attached to a 25 x 75 mm glass microscope slide by epoxy resin. Coal or residue samples, which have been vacuum dried at 60° C, were dispersed in an epoxy resin/hardener mixture and poured into the sample well on the microscope slide until a meniscus extends approximately 0.5 mm above the mold. The resin was cured in an oven at 60° C for at least two hours and the mount was then placed in a slide holder and coarse ground on 600 grit silicon carbide paper. Final polishing was accomplished on a covered bronze polishing lap wheel, set at 175 rpm, using a 0.3 micron alumina suspended polishing medium. For some samples a 0.05 micron alumina suspended polishing medium was used. After polishing, the mount was cleaned of polishing media with distilled water in an ultrasonic bath. After inspection to verify preparation of a satisfactory surface, the mount was stored in a desiccator for several hours to remove surface moisture prior to microscopic examination.

## RESULTS AND DISCUSSION

### Part A - Chemical Analyses

Table 1 summarizes the analyses of the coals studied during this project. The Argonne premium coals are listed in order of increasing rank in both Tables 1 and 2. Table 2 lists the sequential extraction yields for the Argonne premium coals, three IBCSP coals, and two other ISGS coals used to develop the sequential extraction method. Total and individual extract yields as a function of rank (%C) are plotted in Figure 1 for the IBCSP and APCSP coals. In general, the ISGS coals give lower total extract yields than sample bank coals of the same rank. This is probably due to oxidation which occurred in the processing of the ISGS coals since all Illinois coals examined have shown decreased total extract yields upon weathering. Swelling ability of the solvent correlates directly with the yield of extract in that solvent, even after weathering.

Elemental analyses of sequential extracts from Illinois coals (Table 3) showed a decrease in the atomic H/C ratios and an increase in the atomic O/C ratios from toluene to THF to DMF. Both percent sulfur and atomic S/C ratios for these extracts increased about 20% from sequential toluene extract to sequential DMF or pyridine extracts. IBCSP coal 2 (Colchester) was unique in that the toluene extract was highest in sulfur content and that the yield of toluene extract was low compared to other coals. For the original coals, organic S/C ratios were 0.012-0.015 and S/C ratios of the extracts ranged from 0.003 to 0.016. Variation in S/C ratio for each sequential extract correlated with percent organic sulfur, rather than total sulfur in the original coal, as expected. The sequential pyridine extracts of these coals generally are low in yield (< 2%), since the coals have been exhaustively extracted with the previous three solvents, and show more variation in H/C and O/C ratios. Elemental analytical, SEC, and FT-IR data are consistent with the idea that the sequential pyridine extracts contain material similar to toluene and THF extracts which has been released due to the superior swelling behavior of the pyridine plus material soluble only in pyridine. Atomic S/O ratios

varied widely for the extract fractions, perhaps an artifact of the difference method of determining oxygen.

Artificial weathering lowers the total extract yield for all Illinois coals studied to date, but this behavior was not characteristic of coals of either lower or higher rank from the Argonne Premium Sample program. For the Illinois coals, the decrease in yield generally was due to loss of THF, DMF, and pyridine fractions of which the DMF was often the most significant in terms of total mass of extract. SEC results show that the correlation of extract yield and molecular size also holds for changes due to oxidation as well as those due to rank. FT-IR spectra reveal increases in carbonyl containing functional groups for coals of all ranks upon artificial weathering and these groups are concentrated and partially fractionated in the sequential solvent extracts. Evidence for both ester and quinone groups are readily apparent in difference spectra of extracts even when FT-IR difference spectra of oxidized - fresh whole coals show broad, unresolved bands in the  $1700\text{ cm}^{-1}$  region. Increases in a band near  $1720\text{ cm}^{-1}$  seen in many extracts of weathered coals were always accompanied by increases in bands near  $1260$  and  $1102\text{ cm}^{-1}$ , consistent with ester formation.

Spectra of coals, sequential solvent extracts, and insoluble residues for both fresh and weathered versions of IBCSP #5 (600 series) and Argonne #3 (930 series) coals were shown in Figures 2-13 of Quarterly Report #3 and in Appendix B. The spectra were similar, but not superimposable, and illustrate the increase in carbonyl bands and C-O stretching bands ( $1720, 1666, 1260, 1102\text{ cm}^{-1}$ ) caused by weathering. SEC analyses of sequential extracts from fresh and oxidized coals were summarized as Molecular Size Profiles in Figures 14-19 of Quarterly Report #3. The vertical bars in these plots show the fraction of total extract removed by the indicated solvent.

If SEC peaks are symmetrical and reasonably narrow, the retention volume corresponding to the peak maximum is the geometric mean of the number average and weight average molecular weights of the sample. (Appdx. 3) The SEC average molecular weights for the soluble extracts determined from this assumption are tabulated in Tables 4 and 5 and illustrate the correlation between extract yield and molecular size noted earlier. Samples marked \* have slightly asymmetric peaks and should be regarded with caution. Several samples marked -c- gave broad, double peaked curves which cannot be analyzed by this method.

Alkylation of raw coals prior to extraction increased total extract and shifted the distribution such that most material was removed by toluene. SEC analyses of these extracts showed a much broader distribution of molecular sizes than in toluene extracts of raw or weathered coals.

Artificial weathering decreased the amount of organic sulfur extracted by each solvent in the sequence and the atomic S/C ratios of the extracts by 10-20%.



TABLE 1. ELEMENTAL ANALYSES (DAF) AND SWELLING RATIOS OF COALS STUDIED

COAL#	TYPE	FROM	%C	%H	%N	%S	%O(Diff)	%Ash	Solvent Swelling <sup>a</sup>	
									Tol	Py
380	ILL 6	IBCSP-1 <sup>b</sup>	75.41	5.41	1.31	4.74	12.96	10.28	1.28	2.07
381	OXID <sup>c</sup>	380	73.01	5.72	1.47	4.79	15.01	9.04		
480	ILL 2	IBCSP-2	78.54	5.58	1.57	3.46	10.80	6.66	1.46	2.57
481	OXID	480	78.05	5.31	1.27	3.34	12.03	6.10	1.23	2.00
500	ILL 5	ISGS	79.29	6.06	1.32	5.74	7.37	28.27	1.33	1.93
501	OXID	500	78.70	6.12	1.47	5.86	7.82	29.46	1.38	1.97
600	ILL 6	IBCSP-5	77.14	5.36	1.50	5.64	10.23	18.00	1.58	2.20
601	OXID	600	76.65	5.91	1.38	5.36	10.67	18.90	1.52	1.97
6620	MeCOAL	600	81.23	5.99	1.13	5.53	6.12	24.67	1.39	1.79
6631	BuCOAL	600	78.16	6.92	1.07	4.17	9.68	20.43	2.11	2.41
700	ILL 6	ISGS	78.19	5.58	1.37	5.11	9.72	11.50	1.26	2.18
701	OXID	700	76.55	5.45	1.39	4.99	11.59	12.12	1.37	1.99
910	MVBit	APCSP-1 <sup>d</sup>	87 <sup>e</sup>	5.5	-	2.8	4	13	1.17	1.31
911	OXID	910	87.29	5.37	1.53	3.00	2.79	11.23	1.59	1.75
920	SUBit	APCSP-2	74 <sup>e</sup>	5.1	-	0.5	19	8	1.31	1.68
921	OXID	920	70.68	5.77	0.75	0.28	22.49	10.16	1.61	1.82
930	ILL 6	APCSP-3	77 <sup>e</sup>	5.7	-	5.4	10	16	1.64	2.31
931	OXID	930	78.09	5.99	1.39	5.52	8.98	16.90	1.51	2.51
940	PIT 8	APCSP-4	83 <sup>e</sup>	5.8	-	1.6	8	9	1.54	2.76
941	OXID	940	83.31	5.91	1.39	2.26	7.02	10.06	1.56	2.23
950	LVBit	APCSP-5	91 <sup>e</sup>	4.7	-	0.9	3	5	1.06	1.10
951	OXID	950	89.72	4.95	1.17	0.21	3.91	4.22	1.02	1.06
960	HVBit	APCSP-6	79 <sup>e</sup>	6.0	-	0.5	13	5	1.88	2.24
961	OXID	960							1.82	2.23
970	HVBit	APCSP-7	81 <sup>e</sup>	5.5	-	0.6	11	20	1.39	1.82
971	OXID	970								

a Volumetric solvent swelling ratio (Q) of insoluble residue

b Illinois Basin Uniform Coal Sample Number, ISGS

c Air oxidized, -100 mesh coal, room temperature, 6 months

d Argonne Premium Coal Sample Number

e Preliminary values furnished by Dr. Karl Vorres

Table 2

Sequential Solvent Extraction Yields  
Weight %

Sample Number	Toluene Extract	THF Extract	DMF Extract	Py Extract	Total Extract	Insoluble Residue	Material Balance
Argonne Premium Coals (Increasing Rank)							
0920	2.16	1.38	1.76	0.34	6.1 <sup>a</sup>	91.8	97.9
0921	2.35	0.97	3.52 <sup>b</sup>	0.54	9.0 <sup>c</sup>	86.9	95.9
0930 <sup>d</sup>	7.08	7.76	11.40	0.86	27.1	75.5	102.6
0931	5.18	5.08	7.38	0.54	18.2	84.8	103.0
0960	3.72	11.00	14.29	0.35	29.4	74.9	104.2
0961	3.87	7.32	10.51	0.36	22.1	78.8	100.9
0970	0.46	4.65	6.62	0.62	12.4	88.0	100.3
0971	3.41	3.03					
0940	5.80	8.18	10.35	0.64	25.0	76.0	101.0
0941	5.72	7.78	10.97	1.18	25.6	73.7	99.3
0910 <sup>d</sup>	0.58	0.16	12.63	7.56	20.9	77.9	98.8
0911	1.12	0.19	17.37	1.45	20.1	76.3	96.4
0950	0.40	0.24	0.25	0.30	1.2	100.2	101.4
0951	0.37	0.37	0.48	0.28	1.5	96.3	97.8
Illinois Geological Survey Coals							
0380	6.17	9.79	9.87	0.24	26.1	76.0	102.1
0381	1.88	9.89	12.04	0.41	24.2	72.7	96.9
0480	1.15	12.29	11.57	0.50	25.5	74.8	100.3
0481	10.25	3.36					
0500	0.82	7.33	5.94	1.42	15.5	75.8	91.3
0501	3.57	3.72	4.23	2.18	13.7	86.2	99.9
0600	8.47	6.16	6.09	1.72	22.4	75.52	98.0
0601	4.75	4.15	6.52	0.24	15.7	83.17	98.8
R600 <sup>e</sup>	0.18	0.01	0.43	22.17	22.8	74.85	97.6
Me600	18.79	3.06	2.03	0.68	24.8	75.79	100.6
0660 <sup>f</sup>	0.65	9.53	7.19	0.25	17.6	80.5	96.7
Me660	16.99	1.78	1.57	0.59	20.9	80.0	100.3
Bu660	20.08	1.15	0.21	0.41	21.9	73.7	95.4
0700	3.30	6.73	7.32	2.10	19.4	71.96	91.4
0701	6.54	5.69	4.70	1.81	18.7	72.39	91.4

Coals are identified in Table 1. Extraction in order listed above.

- a Includes 0.44% material recovered from MeOH/H<sub>2</sub>O wash of residue.  
 b An additional 1.20% was recovered from MeOH/H<sub>2</sub>O wash of extract.  
 c Includes 0.37% material recovered from MeOH/H<sub>2</sub>O wash of residue.  
 d Average of duplicate extractions.  
 e Reversed extraction order: Pyridine, Toluene, THF, DMF.  
 f Dried at 65° rather than 100°.

TABLE 3 ELEMENTAL ANALYSES OF ILLINOIS No. 6 COALS AND EXTRACTS (DAF)

Sequential Toluene, THF, DMF, Pyridine Extracts of Fresh and Oxidized Coals

NUMBER	SAMPLE	Wt %	% C	% H	% N	% S	% O	H/C	O/C	S/C
0380 <sup>a</sup>	COAL	----	75.41	5.42	1.32	4.75	12.96	.855	.129	.023
0480 <sup>b</sup>	COAL	----	78.54	5.58	1.57	3.46	10.82	.846	.103	.016
0600 <sup>c</sup>	COAL	----	77.12	5.36	1.50	5.64	10.25	.829	.099	.027
0930 <sup>d</sup>	COAL	----	77	5.7	-	5.4	10	.88	.097	.026
0700 <sup>e</sup>	COAL	----	78.19	5.58	1.38	5.11	9.72	.850	.093	.024
0381 <sup>a</sup>	OX-COAL	----	73.01	5.72	1.47	4.79	15.01	.934	.154	.024
0481 <sup>b</sup>	OX-COAL	----	78.05	5.31	1.27	3.34	12.03	.811	.116	.016
0601 <sup>c</sup>	OX-COAL	----	76.65	5.91	1.38	5.36	10.67	.919	.104	.026
0931 <sup>d</sup>	OX-COAL	----	78.09	5.99	1.39	5.52	8.98	.914	.086	.026
0701 <sup>e</sup>	OX-COAL	----	76.55	5.45	1.39	4.99	11.59	.848	.113	.024
3800	SEQ TOL	6.17	82.31	7.14	1.56	2.80	6.16	1.034	.056	.012
4800	SEQ TOL	1.15	87.23	8.45	0.44	2.22	1.65	1.154	.014	.009
7610	SEQ TOL	8.47	83.40	7.01	0.87	2.38	6.32	1.001	.056	.010
9310	SEQ TOL	7.08	84.64	7.37	1.66	2.05	4.26	1.038	.037	.009
7611	OXSEQ TOL	4.75	81.91	7.86	1.08	2.04	7.09	1.144	.064	.009
9311	OXSEQ TOL	5.18	84.21	7.34	1.39	1.69	5.34	1.039	.047	.007
3802	SEQ THF	9.79	78.96	5.98	3.12	3.03	8.88	.903	.084	.014
4802	SEQ THF	12.29	83.71	6.68	1.19	0.87	7.53	.951	.068	.003
7615	SEQ THF	6.16	79.61	5.96	1.83	2.35	10.22	.893	.096	.011
9315	SEQ THF	7.76	81.23	6.07	2.32	2.09	8.27	.891	.076	.009
4715	SEQ THF	6.73	80.69	6.08	1.59	2.79	8.83	.898	.082	.012
7616	OXSEQ THF	4.15	80.51	6.23	1.66	2.30	9.27	.923	.086	.010
9316	OXSEQ THF	5.08	80.96	5.93	2.17	2.25	8.68	.873	.080	.010
4717	OXSEQ THF	5.69	73.99	6.05	1.22	2.14	16.57	.974	.168	.010
3804	SEQ DMF	9.87	75.04	5.55	2.13	3.26	13.99	.882	.141	.016
4804	SEQ DMF	11.57	77.69	6.08	2.94	1.07	12.22	.932	.118	.005
7620	SEQ DMF	6.09	76.40	5.72	1.79	2.59	13.48	.892	.132	.012
9320	SEQ DMF	11.40	77.16	4.77	1.57	2.36	14.11	.737	.137	.011
4720	SEQ DMF	7.32	76.21	5.60	1.99	2.78	12.62	.876	.124	.013
7621	OXSEQ DMF	6.52	77.87	5.75	1.86	2.38	12.11	.881	.116	.011
9321	OXSEQ DMF	7.38	77.35	5.50	1.98	2.39	12.75	.848	.123	.011
7625	SEQ PY	1.72	76.75	5.59	1.89	2.49	13.25	.869	.129	.012
9325	SEQ PY	0.86	80.05	6.05	1.67	2.29	9.90	.901	.092	.010
4725	SEQ PY	2.10	74.63	5.26	1.80	3.10	14.81	.840	.149	.015
9326	OXSEQ PY	0.54	76.83	6.09	3.51	2.14	11.41	.945	.111	.010
4727	OXSEQ PY	1.81	75.37	5.46	2.13	2.87	14.14	.864	.140	.014
3809	SEQ RESID	76.0	75.41	5.17	2.41	4.93	12.05	.817	.120	.024
4808	SEQ RESID	74.8	76.89	5.21	1.70	4.11	12.09	.807	.118	.020
7631	SEQ RESID	75.2	66.86	5.46	1.47	6.29	19.89	.973	.223	.035
9331	SEQ RESID	75.5	76.71	5.84	1.68	6.85	8.90	.907	.087	.033
4726	SEQ RESID	72.0	68.61	5.46	1.74	4.80	19.37	.948	.211	.026
7632	OXSEQ RESID	83.2	70.59	4.88	1.55	6.34	16.62	.823	.176	.033
9332	OXSEQ RESID	84.8	76.89	5.55	2.32	6.24	8.97	.861	.087	.030
4728	OXSEQ RESID	72.2	70.00	5.84	1.87	4.64	17.62	.995	.188	.024

- a Coal #1 Illinois Basin Uniform Sample Program, Extracts = #38xx
- b Coal #2 Illinois Basin Uniform Sample Program, Extracts = #48xx
- c Coal #5 Illinois Basin Uniform Sample Program, Extracts = #76xx
- d Coal #3 Argonne Premium Coal Sample Program, Extracts = #93xx
- e River King coal from Illinois State Geological Survey, Extracts = #47xx

TABLE 4 SEC AVERAGE MOLECULAR WEIGHTS OF SEQUENTIAL EXTRACTS<sup>a</sup>

ILLINOIS GEOLOGICAL SURVEY COALS <sup>b</sup>												
EXTRACT	ILLINOIS 5		HVCB				ILLINOIS 6				HVB	
	HVB		HVCB	HVCB	HVCB	HVCB	HVCB	HVCB	R600	HVB	HVB	
	500	501	380	381	480	481	600	601	R600	700	701	
SEQ TOL	330	290	360	290	210	370	420	340	520	280	390	
SEQ THF	510	530	580	480	530	660	840	450	710	540	720	
SEQ DMF	3980	3110	960	4450*	-c-		4130*	940	930*	4060	4170	
SEQ PY	5050	4830	880	3880*	4804		3950*	1640*	-c-	4780	4490	

a Weight corresponding to  $V_r$  max on SEC curve

b Analytical data in Table I

c Calculation not meaningful, see text

\* Peak not symmetrical, see text

TABLE 5 SEC AVERAGE MOLECULAR WEIGHTS OF SEQUENTIAL EXTRACTS<sup>a</sup>

ARGONNE PREMIUM COALS INCREASING RANK ----->														
EXTRACT	920	921	930	931	960	961	970	971	940	941	910	911	950	951
SEQ TOL	340	320	340	310	220*	230	190	320	340	350	290	420	180	170
SEQ THF	440	500	610	490	400	450	300	490	490	450	530	400	270	320
SEQ DMF	620	510	2640*	780	3630*	3630*	-c-		1040	1310	530	410	390	360
SEQ PY	520	450	2730*	950	3080*	1420*	4530		2510*	1350	750	990	390	470

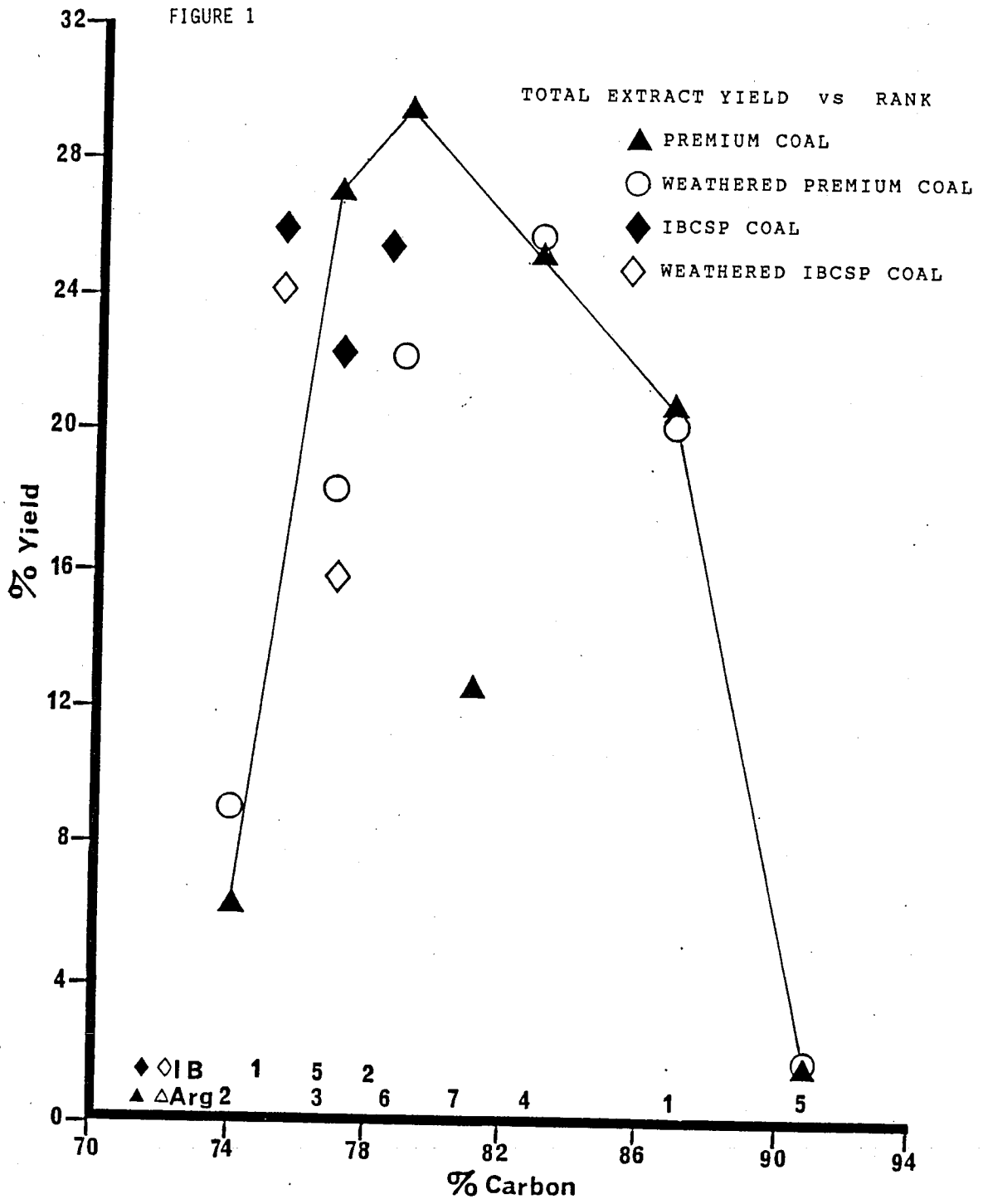
a Weight corresponding to  $V_r$  max on SEC curve

b Analytical data in Table I

c Complex curve; Calculation not meaningful, see text

\* Peak not symmetrical, see text

FIGURE 1



## Part B-Petrographic Analyses

Fluorescence, reflectance, and visual analyses of fresh (unoxidized), weathered (oxidized), methylated, and butylated coals plus their residues from sequential solvent extraction indicate solvent specific maceral alterations that greatly change individual petrographic characteristics. The maceral that show the most significant effect is resinite, a submaceral in the lipinite group. Sporinite and cutinite, both liptinites, show minor and unpredictable physical alterations. The maceral group vitrinite also shows some change that is predictable. The inertinite maceral group shows no observable alteration.

Petrographic analyses of fresh coals provide reference characteristics for comparison with weathered coals, alkylated coals, and extraction residues. In Figure 2, resinite from a fresh coal is compared with resinates from fresh coal toluene and THF residues. However, continuing the sequential extraction process through DMF and pyridine results in major alteration of the resinite particles. This alteration is shown by extensive chemical erosion (Figures 5 and 6) indicated by the graininess of the surface of the resinite particles, and a marked decrease in both fluorescence intensity and color. Throughout the entire sequential solvent extraction process, a trend toward lowered vitrinite reflectance values is observed (Table 6 and Figure 18) and usually accelerates at the THF or DMF stage. DMF and pyridine are extremely good swelling agents and can cause extensive fragmentation of the coal particles (Figure 7).

Analyses of weathered coals and extraction residues show similar trend as those described for fresh coals and residues. Figure 8 shows a resinite particle from the toluene residue that indicated little or no alteration. This suggests that weathering will not result in increased reactivity of liptinite macerals to extraction solvents. However, observing reflectance data for vitrinite (Table 6 and Figure 18) shows that weathering will significantly reduce the initial and residues reflectivity. In part, this probably results from an increase in pitting of the coal particles. All other petrographic properties appear to resemble those observed from fresh coals and residues but to a slightly lesser degree.

Analyses of methylated and butylated coals and their residues from sequential solvent extraction yielded quite different alteration characteristics. Observing the pre-extracted coals under fluorescent light resulted in little useable information except to note that the level of fluorescence had increased drastically. The intensity was great enough to nearly mask all but the very bright fluorescing macerals. Vitrinite particles that prior to alkylation were a very dark chocolate brown color are altered by alkylation to a light to medium brown, a marked increase in both intensity and color. The mounting medium had absorbed enough fluorescing material that additional observation of the raw coal was not warranted. Both methylation and butylation produce severe erosion of the coal particles. This can be seen on the reflectance photograph in Figure 9. Notice the very dark color of the vitrinite and

liptinite under reflected light. This is the result of a photochemical reaction that almost instantaneously alters the coal particles exposed to a mercury light source. The exact nature of this effect is not yet understood but makes vitrinite reflectance analyses virtually impossible with a mercury source. This does not happen with a tungsten source. However, this photochemical alteration does not appear to modify fluorescence characteristics.

Fluorescence observations of coal particles (Figures 9 and 10) show brightly fluorescing vitrinite and liptinitemacerals. Figure 10 shows a large liptinite particle with a bright margin and dull greenish center. This effect of a marginal increase in fluorescence was observed only lightly at the DMF/Pyridine stage of extraction. With alkylation, the effect is pronounced at the toluene stage. In fact, alkylation has accelerated the extraction process so that from the toluene residues the characteristics of the DMF stage of extraction has been achieved. Figures 11, 12, and 13 show resinite particles that have been severely altered by toluene, based on extraction yields. Note that the fluorescence photograph in kFigure 12 shows the marginal effect of increased fluorescence. Alkylation does enhance structural detail, as shown by Figure 14. Note the bright fluorescing brown vitrinite.

Of the two alkylation processes, butylation is the most effective in promoting extraction. However, Figure 15 provides a caution. On this photograph, both fluorescence and reflectance show that this coal particle was not completely infiltrated. The bright area on the fluorescence and dark area on the reflectance photographs represent areas of butylation. The remaining area was untouched. One of two solutions must be considered, be sure the samples are ground smaller than 20 mesh or allow more time for alkylation. This particular coal particle would just pass through a 20 mesh screen.

The effectiveness of butylation is illustrated in Figure 16. These resinities are from the toluene extraction stage. Severe alteration is evident by the erosion shown by reflectance and marginal effect shown by fluorescence. Another excellent example of marginal increase in fluorescence is shown by the liptinite in Figure 17.

The petrographic analyses performed during this study have produced many new and intriguing questions that require further investigation. The data indicate that unoxidized and oxidized coals subjected to toluene, THF, DMF, and pyridine extraction yield products from solvent specific macerals, in particular resinite. The study also indicates that toluene and THF are extracting soluble materials from pore spaces; and are not altering the coal structure. DMF and pyridine, however, are further extracting larger molecules from pore spaces accessible due to the extensive swelling capacity of these solvents, or, are more probably chemically removing components of the coal structure from resinite maceral particles of microscopic and disseminated sub-microscopic sizes.

However, Alkylation accelerates the extraction process resulting in toluene as the major effective extraction solvent.



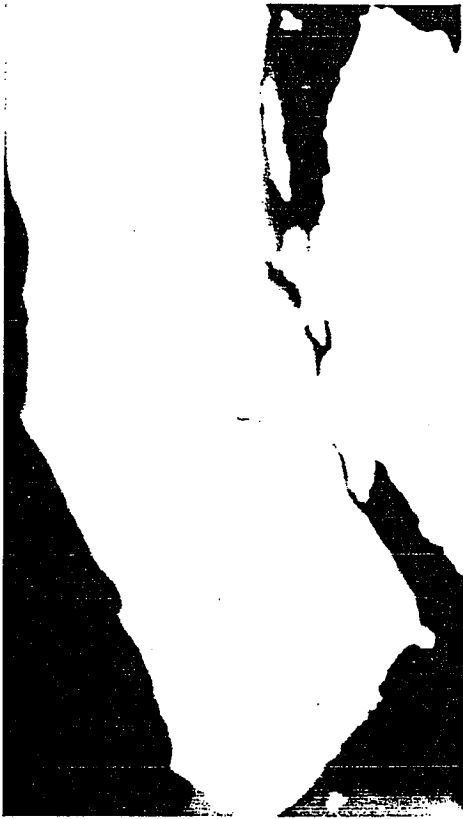


Fig. 2. Sample no. 0386, Illinois Coal No. 6, IBCSP-1; fresh, untreated. Left: reflectance of resinite with vitrinite above and inertinite below. Right: fluorescence of resinite with 546nm excitation.

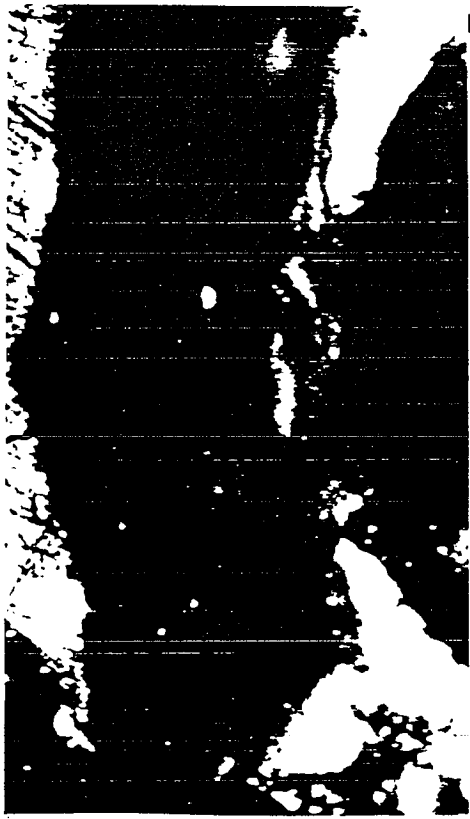


Fig. 3. Sample no. 3801, Illinois Coal No. 6, IBCSP-1; toluene residue from sequential extraction. Left: reflectance of a large resinite particle. Right: fluorescence of a large resinite particle with 546 nm excitation.



Fig. 4. Sample no. 6603, Illinois Coal No. 6, IBCSP-5; THF residue from sequential extraction. Left: reflectance of a large resinite particle surrounded by vitrinite. Right: fluorescence of resinite with 546 nm excitation.



Fig. 5. Sample no. 3805, Illinois Coal No. 6, IBCSP-1; DMF residue from sequential extraction. Left: reflectance of resinite surrounded by vitrinite and other liptinites; with pyrite showing as bright areas. Right: fluorescence of resinite and other liptinites with 546 nm excitation.



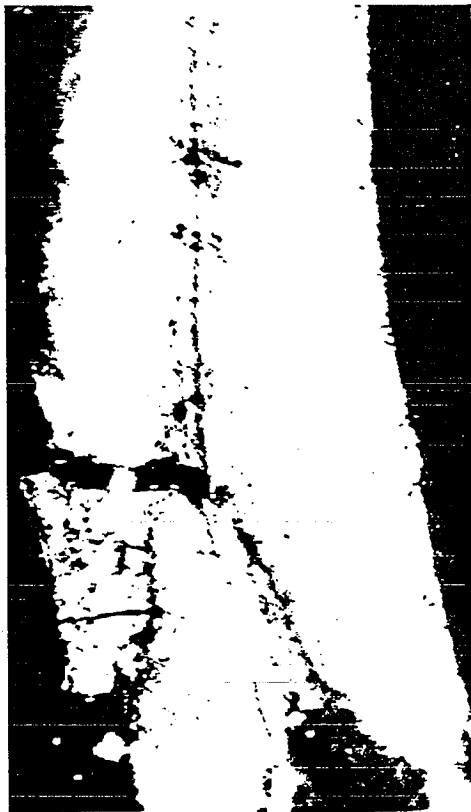


Fig. 6. Sample no. 9368, Illinois Coal No. 6, APCSP-6; pyridine residue from sequential extraction. Left: reflectance of resinite infilling of vitrified cell structures. Right: Fluorescence of resinite infilling with 546 nm excitation.



Fig. 7. Sample no. 3805, Illinois Coal No. 6, IBCSP-1; DMF residue from sequential extraction. Fractures caused by solvent swelling.



Fig. 8. Sample no. 4812, Illinois Coal No. 6, IBCSP-2; toluene residue from sequential extraction of weathered coal. Fluorescence of a resinite particle with 546 nm excitation.



Fig. 9. Sample no. 6622, Illinois Coal No. 6, IBCSP-5; toluene residue from sequential extraction of methylated coal. Left: reflectance of vitrinite, inertinite, and liptinite macerals. Right: fluorescence of vitrinite, inertinite, and liptinite macerals with 546 nm excitation.

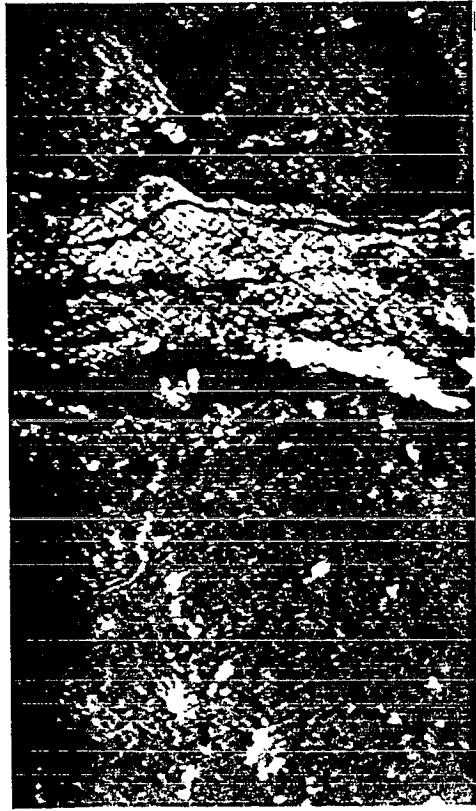


Fig. 10. Sample no. 6622, Illinois Coal No. 6, IBCSP-5; toluene residue from sequential extraction of methylated coal. Left: reflectance of vitrinite and liptinite macerals. Right: fluorescence of vitrinite and liptinite macerals showing marked decrease of fluorescence in the center of the large liptinite maceral with 546 nm excitation.





Fig. 11. Sample no. 6626, Illinois Coal No. 6, IBCSP-5; DMF residue from sequential extraction of methylated coal. Left: reflectance of lower resinite particle and upper vitrinite. Right: fluorescence of lower resinite particle showing reduced fluorescence in right center with 546 nm excitation.

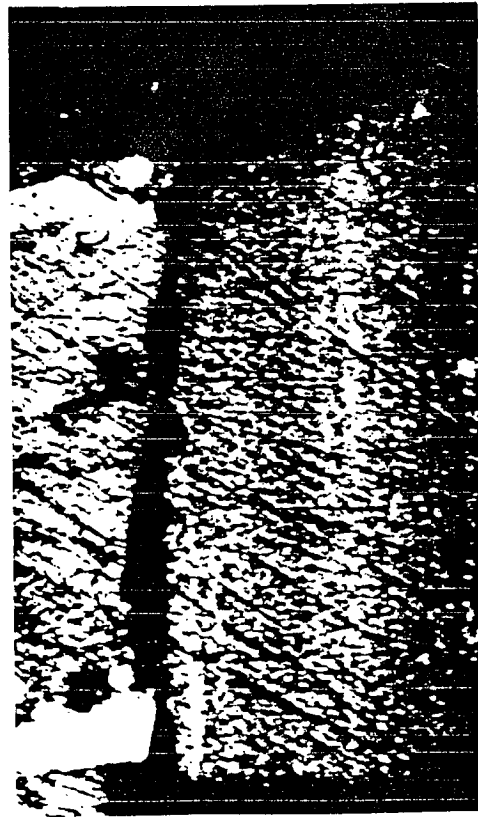


Fig. 12. Sample no. 6628, Illinois Coal No. 6, IBCSP-5; pyridine residue from sequential extraction of methylated coal. Left: reflectance of vitrinite, inertinite, and liptinite macerals. Right: fluorescence of large resinite particle showing marked reduction of fluorescence in the center with 546 nm excitation.

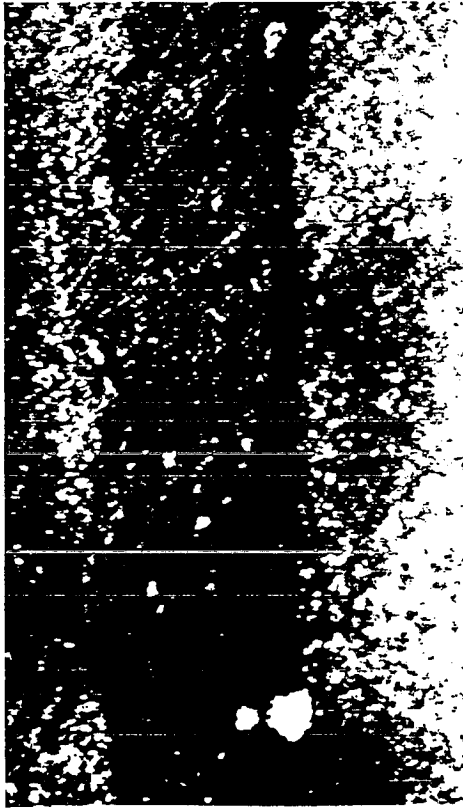


Fig. 13. Sample no. 6628, Illinois Coal No. 6, IBCSP-5; pyridine residue from sequential extraction of methylated coal. Reflectance of two resinite particles separated by a band of vitrinite.



Fig. 14. Sample no. 6628, Illinois Coal No. 6, IBCSP-5; pyridine residue from sequential extraction of methylated coal. Fluorescence of vitrinite and cutinite showing detailed cellular structure.



Fig. 15. Sample no. 6633, Illinois Coal No. 6, IBCSP-5; toluene residue from sequential extraction of butylated coal. Left: reflectance of a coal particle showing incomplete penetration of alkylate. Right: fluorescence of a coal particle showing effects of alkylation on fluorescence properties with 546 nm excitation.

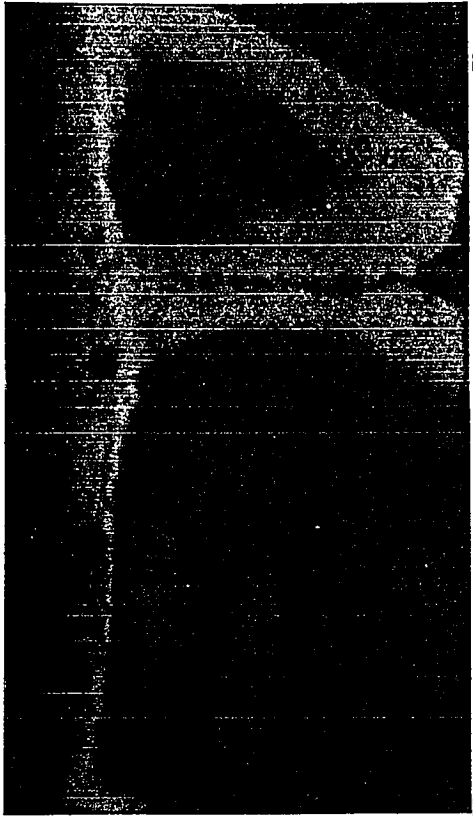
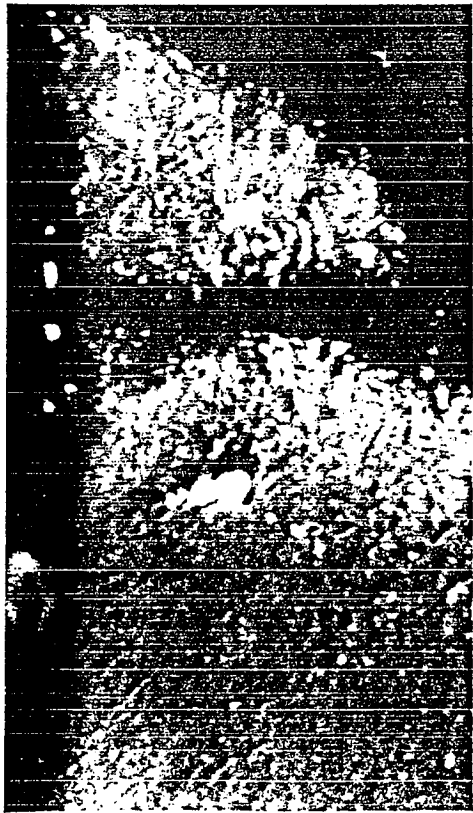


Fig. 16. Sample no. 6633, Illinois' Coal No. 6, IBCSP-5; toluene residue from sequential extraction of butylated coal. Left: reflectance of large resinite particles. Right: fluorescence of large resinite particles showing severe alteration of fluorescence in the interior of each particle with 546 nm excitation.



Fig. 17. Sample no. 6639, Illinois Coal No. 6, IBCSP-5; pyridine residue from sequential extraction of butylated coal. Left: reflectance of a large liptinitic mass. Right: fluorescence of a large liptinitic mass showing an extreme marginal effect of increased fluorescence caused by butylation, 546 nm excitation.

Table 6. Data from analyses of vitrinite percent reflectance (% R<sub>o</sub>), measured in oil.

Sample no.	Coal	Source	Extraction Residue	Percent Reflectance		
				Min.	Max.	Mean
0386	I11#6	IBCSP-1 <sup>a</sup>	FRESH	0.39	0.66	0.52
3801	I11#6	IBCSP-1	TOLUENE	0.35	0.61	0.49
3803	I11#6	IBCSP-1	THF	0.27	0.64	0.52
3805	I11#6	IBCSP-1	DMF	0.34	0.57	0.44
3809	I11#6	IBCSP-1	PYRIDINE	0.27	0.55	0.41
0381	I11#6	IBCSP-1	OXIDIZED	0.32	0.53	0.42
3812	I11#6	IBCSP-1	TOLUENE	0.31	0.53	0.40
3814	I11#6	IBCSP-1	THF	0.33	0.50	0.40
3817	I11#6	IBCSP-1	DMF	0.31	0.48	0.40
3820	I11#6	IBCSP-1	PYRIDINE	0.28	0.49	0.39
0486	I11#6	IBCSP-2 <sup>b</sup>	FRESH	0.42	0.64	0.53
4801	I11#6	IBCSP-2	TOLUENE	0.42	0.64	0.52
4803	I11#6	IBCSP-2	THF	0.38	0.55	0.43
4805	I11#6	IBCSP-2	DMF	0.38	0.53	0.44
4808	I11#6	IBCSP-2	PYRIDINE	0.34	0.55	0.45
0481	I11#6	IBCSP-2	OXIDIZED	0.40	0.57	0.47
4812	I11#6	IBCSP-2	TOLUENE	0.26	0.49	0.38
4815	I11#6	IBCSP-2	THF	0.31	0.54	0.43
4818	I11#6	IBCSP-2	DMF	0.25	0.42	0.31
4821	I11#6	IBCSP-2	PYRIDINE	0.22	0.41	0.29
0660	I11#6	IBCSP-5 <sup>c</sup>	FRESH	0.43	0.68	0.57
6601	I11#6	IBCSP-5	TOLUENE	0.42	0.66	0.58
6603	I11#6	IBCSP-5	THF	0.41	0.59	0.49
6605	I11#6	IBCSP-5	DMF	0.39	0.57	0.48
6608	I11#6	IBCSP-5	PYRIDINE	0.35	0.57	0.44
0936	I11#6	APCSP-3 <sup>d</sup>	FRESH	0.48	0.75	0.56
9361	I11#6	APCSP-3	TOLUENE	0.41	0.66	0.52
9363	I11#6	APCSP-3	THF	0.32	0.54	0.45
9365	I11#6	APCSP-3	DMF	0.34	0.55	0.45
9368	I11#6	APCSP-3	PYRIDINE	0.38	0.51	0.43

a Coal #1 Illinois Basin Uniform Sample Program

b Coal #2 Illinois Basin Uniform Sample Program

c Coal #5 Illinois Basin Uniform Sample Program

d Coal #3 Argonne Premium Coal Sample Program



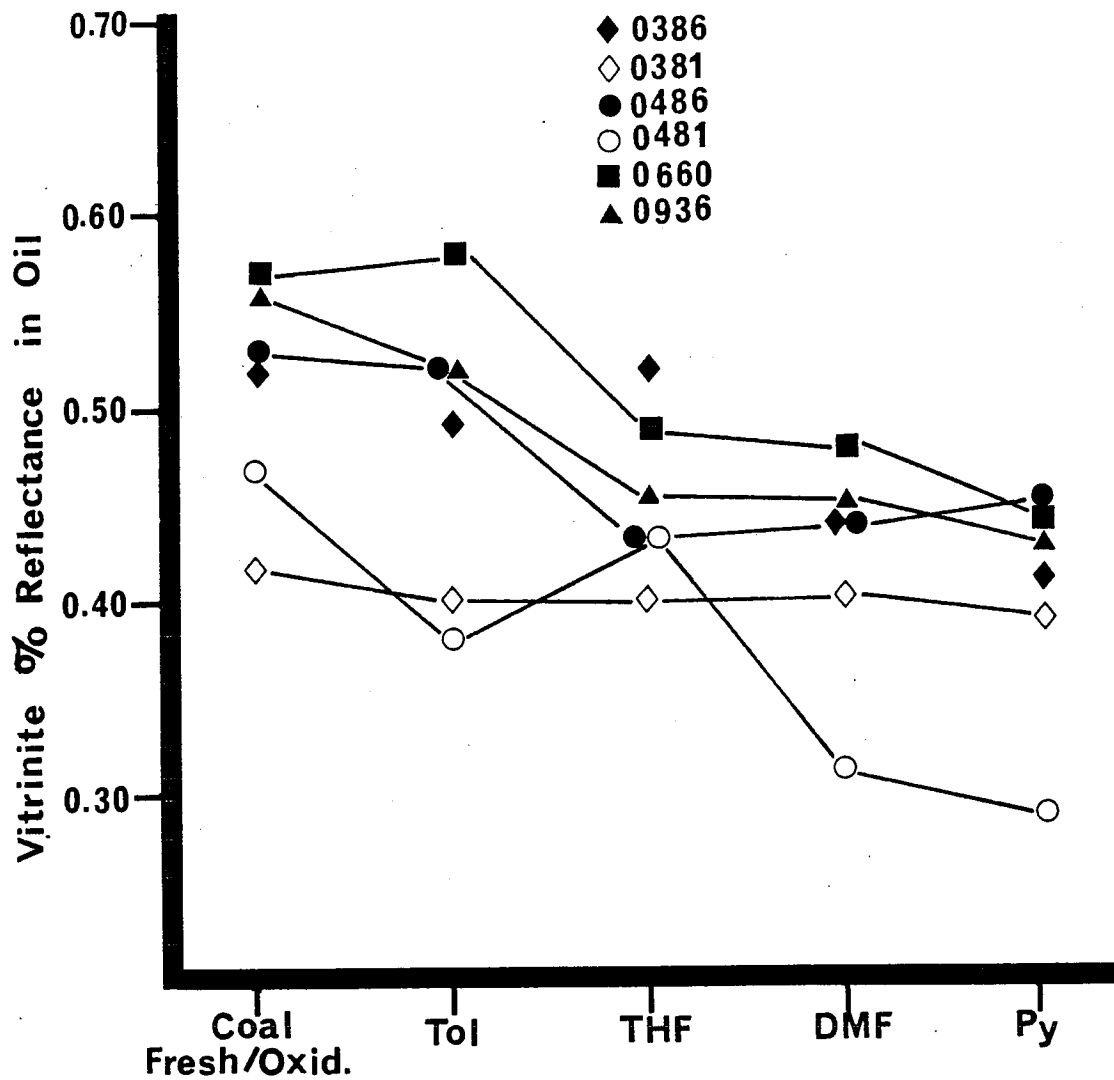


Fig. 18. Change in vitrinite reflectance percent with respect to fresh and weathered coals, and extraction solvents.

## CONCLUSIONS AND RECOMMENDATIONS

It was shown that chemical modifications of coals such as solvent extraction or alkylation can be correlated with changes in visual physical characteristics in specific maceral groups or subgroups in un-separated coal samples. Such techniques, if developed further, will enable maceral specific chemical behavior of coals to be investigated without expensive and difficult maceral separation and concentration techniques.

It was shown that sequential solvent extraction in the order toluene, THF, DMF, pyridine removes progressively larger and more polar material from Illinois coals. Both the yield and molecular size of extracts are decreased by artificial weathering at ambient temperature for several months. Removal of toluene and THF extracts from the coals causes little visual change to any macerals but DMF and pyridine cause extensive modification of resinite surfaces and reflectance properties. Vitrinite reflectance also decreases after extraction with these two solvents. Sulfur contents are higher in the more polar extracts, except for Colchester No. 2 coal, and decrease by 10-20% in extracts of weathered coals. Since yields are also decreasing, the amount of easily removed organic sulfur (as measured by solvent extraction) is seen to be significantly reduced by weathering.

Extending the petrographic examination of coals before and after sequential solvent extraction and alkylation to coals of different rank and geologic history, such as those in the Argonne Premium Coal Sample Program, would refine and validate these methods and provide additional valuable insight into both physical and chemical coal characterization.

If the decrease in organic sulfur mobility measured by solvent extraction extends to potentially commercial pre-combustion sulfur removal schemes, it will be important to assess coal storage conditions on the efficiency of these processes.