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A DATA BASE FOR THE ANALYSIS OF COMPOSITIONAL CHARACTERISTICS OF COAL SEAMS AND MACERALS

Quarterly Technical Progress Report, August—October 1980

By
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February 1981
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The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

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1855

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ABSTRACT

The basic objectives of this program are, first, to understand the systematic relationships between the properties of coals, and, second, to determine the nature of the lateral and vertical variability in the properties of a single seam.

Six coal samples were collected during the quarter, all from Pennsylvania. One maceral concentrate was prepared.

One hundred and fifty two coal samples and 281 printouts of coal data were provided on request to the coal research community.

In order to measure the efficiency of the nitric-acid extraction of pyrite in the ASTM sulfur forms analysis, the residual iron was determined after extraction of six samples of the Lower Kittanning seam, all of high volatile bituminous rank ground to minus 100 mesh. In all cases, the amount of unextracted iron was small, so the error in organic sulfur (by difference) also was small.

A total of 69 samples have been obtained from the Lower Kittanning seam in western Pennsylvania and eastern Ohio. The samples were taken from 39 sample sites and consist of 39 channel samples and 30 hand-picked vitrinites. A complex statistical analysis of petrographic, physical and chemical properties of these samples was performed in order to study their relationship with thermoplastic and liquefaction behavior. The parameters of the thermoplastic properties were obtained using a Gieseler plastometer. The liquefaction conversion with tetralin was determined in tubing bomb reactors at 400°C for 1 hour. Factor analysis on the whole sample population indicated that both liquefaction conversion and some of the measured thermoplastic properties are significantly related with rank. Temperature of softening and degree of fluidity, however, did not load on the rank component.

^{13}C nmr spectra were obtained for six of our vitrinite concentrates by the University of Utah. The aromaticities determined for fairly wide rank range of these samples varied only from 0.66 to 0.72. However the series showed progression from highly functional aromatic structure at low rank to one with little functionality at high rank. The spectra show no indication of a consistent loss in aliphatic oxygen.

The surface areas and micropore volumes of two fractions, -20 and -100 mesh, of five vitrinite concentrates have been measured from CO_2 uptake at 25°C. An increase in these values is observed with decreasing particle size. Total open pore volumes were calculated from particle and helium densities.

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OBJECTIVES AND SCOPE OF WORK

The major objective of the program is to use the Penn State Coal Data Base to investigate the systematic relationships between the properties of U.S. coals.

To do this, we will build on the data base established for over 1000 coals during prior OCR, ERDA and DOE programs. A program to obtain a limited number of additional samples will be entailed so that specific investigations may be undertaken. The intent is to gain better understanding of the basic nature of coal interrelationships and the variability of its properties.

The following studies are included in the program:

a) A statistical study of the interrelationships between the properties of the organic fraction of coals. The extent to which natural groupings of U.S. coals might exist will be investigated by cluster analysis. Cause for the groupings will be sought in such factors as age of coal, source material and thermal/burial history.

b) A statistical study of the interrelationships between the properties of the inorganic fraction of coals. Correlations will be sought between the major, minor, trace element and mineralogical analyses of coals in the data base.

c) Studies of the lateral and vertical variability of properties within a single coal seam in response to changes in depositional environments and post-depositional metamorphic changes. The Lower Kittanning seam has been selected because of its broad extent and the range in environments by which it is thought to have been affected. Properties which will be studied include the petrographic characteristics, the minerals and the fluid characteristics.

An additional factor analysis will be performed on a range of compositional data together with fluid characteristics and conversion in tubing bomb reactions with tetralin; in this way the possibility that plasticity and liquefaction involve some common mechanisms will be investigated.

Oxidation can result in severe deterioration of the plastic behavior of coals. Because any parallel reduction in the liquefaction potential of coals could be critical to the economics of a process, we will study the relationship between the fluid and liquefaction properties of coals which have been exposed to varying degrees of natural and laboratory oxidation.

d) The basic physical and chemical properties of pure coal macerals. Detailed analyses of vitrinite concentrates will be made to determine what significant differences in functional group content, aromaticity, density, porosity, and optical properties arise from variation in the environmental conditions during peat deposition and in the thermal histories of coals. To the extent possible the same determinations will be made on concentrates of other macerals. One emphasis will be placed on comparisons between vitrinite macerals thought to be representative of different environments existing during deposition of the Lower Kittanning seam. Another particular subject for investigation will be the nature and extent of differences between vitrinite macerals from the Eastern Province and those of equivalent rank from the Interior Province. The significance of our findings to industrial processes will be reported.

e) Feed coals and the solid residues of liquefaction experiments conducted or co-ordinated by Pittsburgh Energy Technology Center will be subjected to mineralogic and petrographic analysis. The possible influence of the mineralogic and maceral compositions on the experimental results, will be sought.

1. SAMPLE COLLECTION

Three sampling trips in Pennsylvania during this quarter were made to collect six samples of the Lower Kittanning seam (PSOC-1330 to PSOC-1335). One maceral concentrate was prepared during the report period.

(C.P.D.)

2. BASIC COAL CHARACTERIZATION

Proximate Analysis by Means of Fisher Coal Analyser

A boost transformer* was installed in our 208 V ac line to give us 228 V ac. This has given us the correct operating voltage as specified by Fisher. We are now using the Fisher Coal Analyzer Model 490 for our proximate analyses on a routine basis. Table 1 is a comparison of our data with those from a commercial analytical laboratory for four bituminous coals, obtained after the installation of the boost transformer.

The ash contents are somewhat lower than those given by the commercial laboratory, but according to ASTM criterion of reproducibility, are not considered suspect. The moisture values are not comparable because the sample bottles were opened over a year ago and undoubtedly lost some water, at least in the two high moisture coals. Other moisture comparisons indicate identical results.

The volatile matter values are suspect in that they differ (3 out of 4) by more than 1.0%. It is a consistent bias of about 4% and could be attributed to the differences in instrumentation and method. The ASTM method calls for the placement of a 1.0 gram as-received sample (in a tightly covered platinum crucible) in a vertical tube furnace set at 950°C for exactly 7 minutes. The Fisher method uses a dried 1.0 g sample, which is put into a fused quartz crucible with tightly fitting lid. This is placed into a cold furnace and heated at an average rate of about 25°C/min to 950°C, and then kept at 950°C for 7 minutes. That is, it takes about 45 minutes for the Fisher instrument to go through the volatile matter temperature cycle for up to twenty samples.

In order to substantiate the bias in the volatile matter determination, more comparisons will be made. If there is a definite bias we will have to determine what kind of correction is required.

Carlo Erba Model 1106 Elemental Analyser

We have continued to refine the operating characteristics of the Carlo Erba Model 1106 Elemental Analyser for the determination of C, H, N, O and S. The "in delay" and "cycle" times that had caused continual problems by sticking have been replaced. The instrument now seems to be performing properly with minimum attention during the runs.

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*Westinghouse Cat. #6E217

Table 1. Comparison of Data - Proximate Analyses

Sample		Moisture	Volatile Matter	Ash Content	Fixed Carbon
TD 356	Found	0.95%	32.30%	10.23%	57.47%
	Std. Dev.	0.22	0.36	0.19	0.49
	n	7	7	7	7
Commercial Lab.		0.91	34.00	10.41	55.59
TD 357	Found	3.12	36.84	10.01	53.15
	S.D.	0.23	0.53	0.10	0.56
	n	8	8	8	8
Commercial Lab.		6.52	38.11	10.29	51.60
TD 359	Found	1.00	24.84	9.45	65.71
	S.D.	0.28	0.43	0.21	0.54
	n	6	6	6	6
Commercial Lab.		0.77	25.58	9.46	64.96
TD 361	Found	4.18	38.37	11.75	49.88
	S.D.	0.34	0.49	0.24	0.56
	n	9	9	9	9
Commercial Lab.		7.00	40.20	12.25	47.55

Note: Samples were supplied by a commercial analytical laboratory. Their values are considered "statistically correct."

Penn State values were obtained with the Fisher Coal Analyzer, Model 490 over a two-month period.

The stainless steel chromatographic column containing Poropak Q has been replaced with a glass column containing Poropak Q that has been treated with methanol, acetone and chloroform. This new column and packing significantly shortens the analysis times for C, H and N, as well as giving sharper resolution of the peaks. This column also should permit the determination of sulfur at the same time as C, H and N, but in our preliminary investigations we have not been able to recover all the sulfur. This could be due to a problem with the packing materials in the reaction column or the fact that we have been unable to attain the necessary temperature of 780°C in the reduction column.

Reliability of Determinations of Pyritic Iron in Coals Using Standard Procedure

Edwards *et al*., (1) were the first to report, from their microscopic examinations of acid-insoluble residues, that the procedure for dissolving iron in nitric acid in the standard analysis for forms of sulfur failed to extract all of the pyrite from some higher rank bituminous coals. Since this study, the reliability of the standard procedure (in the U.S.A., ASTM Standard Test Method D 2492-68) has been a matter of controversy, some authors apparently finding larger and more widespread errors than those found by Edwards *et al*. The controversy has been reviewed recently (2).

In the course of a study with wider objectives, we have recently obtained some data that bear on this matter, and in view of the controversy thought it worthwhile to report the data at this time.

We have carried out the procedure of ASTM Standard No. D 2492-68, for forms of sulfur in coals, with the exception of using -100 mesh material instead of the standard -60 mesh. The six coals studied were all subsections (lithotypes) selected from the Lower Kittanning seam, five from various locations within the state of Ohio and one from western Pennsylvania. In ASTM rank class, they were all close to the hvAb/hvBb boundary. The filtered residues from the nitric acid extraction were washed, dried and subjected to ashing at 750°C by ASTM Standard Method D 3174-73. The ash was decomposed and solubilized by treatment with an aqueous mixture of HF and $HClO_4$ solutions. Fe was determined in the solutions by atomic absorption spectroscopy. The results, expressed as the equivalent amount of sulfur in the original coal, are included in Table 2.

It will be seen that only small amounts of iron are left unextracted in any of the six samples we have studied. However, it will be noted that in the case of the sample of lowest organic sulfur content, the presence of unextracted iron is perhaps of significant magnitude; correction for this lowers the organic sulfur content from 0.55% to 0.44%. However, in no case is there a major error. When these findings are added to similar data, also arising from material balances, that have already been published (3,4), there results, we submit, a high degree of confidence in the standard procedures, except, perhaps, in the case of such high-rank coals as those with which Edwards *et al*., had troubles.

Acknowledgments

We are indebted to Mr. J.C. Devine for the experimental measurements reported.

Table 2. Distribution of Sulfur in Subsections (Lithotypes) from the Lower Kittanning Seam

PSOC No.	Pyritic S, %	Residual* Pyritic S, %	Sulfate S, %	Organic S, % (diff.)	Organic S(corr.), %[†]	Total S, %
1273	4.14	0.051	0.12	1.54	1.49	5.80
1276	2.36	0.055	0.15	2.12	2.07	4.63
1277	2.53	0.051	0.28	2.09	2.04	4.90
1279	4.13	0.108	0.25	0.55	0.44	4.93
1282	1.19	0.082	0.08	0.61	0.53	1.88
1299	3.39	0.086	0.07	1.28	1.19	4.74

[*] Calculated from iron determined in sample after nitric acid extraction.
[†] Corrected for unextracted pyritic iron.

Table 3. Analyses Requested and Completed since February 1, 1980

	Number Requested	Number Completed
Proximate Analyses	96	83
Ultimate Analyses	60	24
Forms of Sulfur	110	78
Low Temperature Ash	97	54
High Temperature Ash	93	59
Ash Analysis	89	36

Status of Other Analyses

Table 3 is a status report of chemical analyses requested and those performed since the start of the project, February 1, 1980.

Maceral analyses were completed for 28 coals and eight reflectance analyses were performed during the quarter. Also, the Free Swelling Index was determined for 52 coals samples and the Gray-King coke types for 38 samples.

(N.S., P.H.G., C.P.D.)

3. SERVICE TO OTHER AGENCIES

A total of 152 characterized coal samples were supplied to other agencies engaged in coal research and printouts of analytical data for 281 coals also were supplied.

These agencies included: United Technologies Research Center, The Chemical Engineering Department of Purdue University, Gulf Research and Development, Columbia Gas System, ARCO Oil and Gas, Engineering Research Institute, the Chemical Engineering Department of West Virginia, University Systems Consultants, E.I. DuPont DeNemours, the Chemical Engineering Department of Auburn University, The University of Tennessee, Pittsburgh Energy and Technology Center, Dow Chemical Company, Amoco Research Center, The Engineering Department of Colorado School of Mines, and Iowa State University.

(C.P.D.)

4. DATA BASE MANAGEMENT

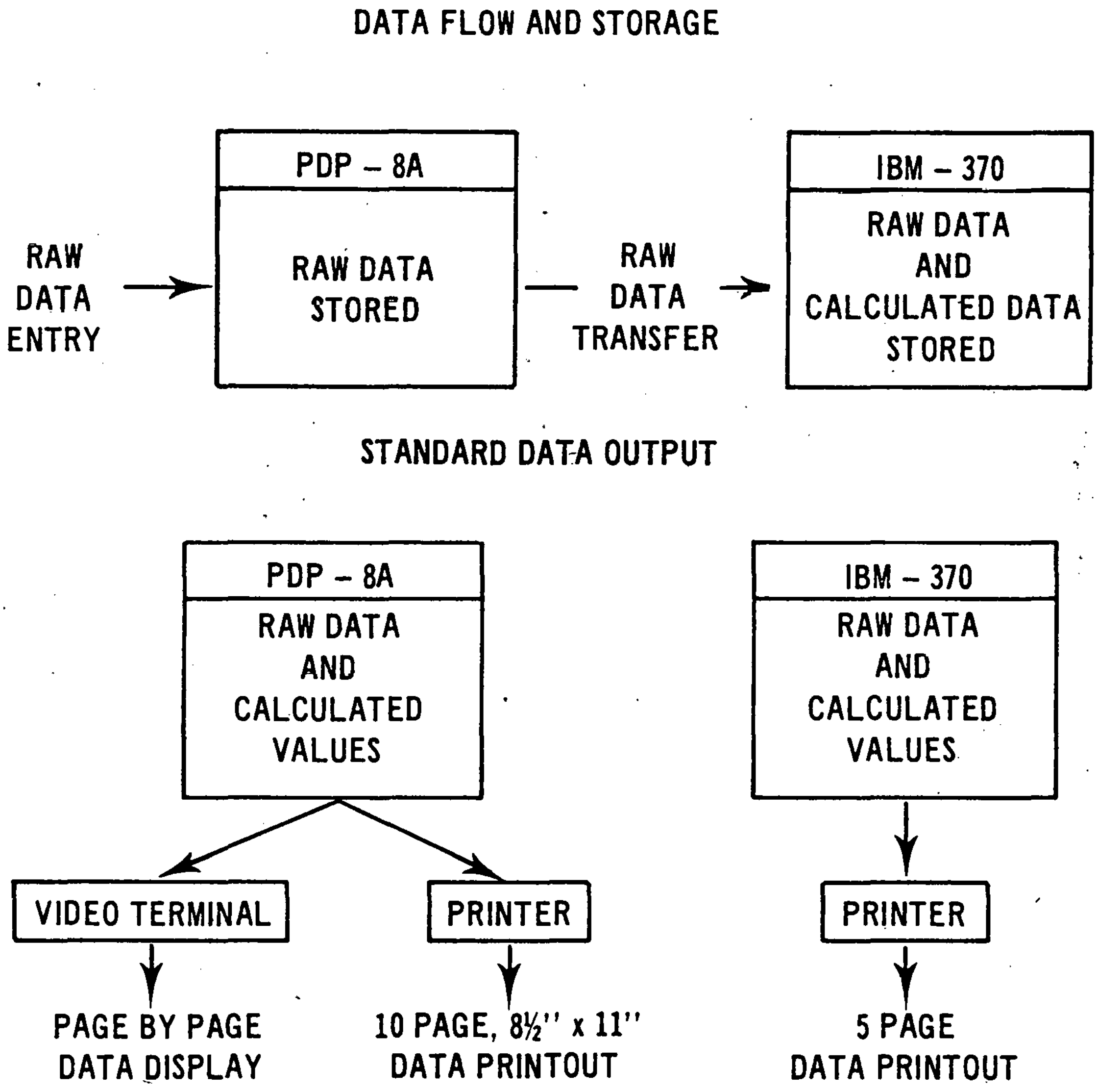
During the current report period, sampling data and sample information have been entered into the Penn State Coal Data Base for an additional 300 coal samples. Analytical data associated with 200 coal samples also have been entered.

As partially described in preceding reports, data flow and storage are as described in Figure 1. All raw data including sample and sampling information are entered into the Data Base via english language input into the minicomputer component of the system. A potential for entering as many as 375 separate informational items (including numerical data) exist for each coal sample. As shown in the figure, only raw data are stored in the minicomputer. New raw data are transmitted to the IBM 370/3033 by means of a MODEM telephone link, where an additional 226 calculated values (daf, dmmf, etc.) are determined and stored. Although only raw data are stored in the minicomputer, its ability to provide print-outs of both raw and calculated values is not limited. As shown in Figure 1, the "Standard data output" for the PDP-8A system includes both raw and calculated values in the form of a 10-page compendium for each coal sample, printed on a conventional 8 1/2 x 11" sheet. Also as shown, the same information can be examined in a video display. A 5-page "standard data output" from the IBM 370 is in the form of large 11 x 15" sheets. A comparison of the capabilities of the two components of the integrated data system is given in summary form in Table 4.

The minicomputer system has been developed as a cost-effective means of providing coal data to the coal research community; thus, it bears the burden of our data service function. It also now provides an efficient and cost-effective means of data entry and editing as corrections to the data are simply made and require no programming knowledge.

As of October 31, 1980, the Penn State Coal Data Base is complete through PSOC-999. All corrections have been made, and an extensive amount of seam profiles information has been added. Preliminary changes have been made in the data base source program to allow for the entry of coals with PSOC numbers beyond 999. Work will be started shortly on transferring the new data from the PDP-8A to the IBM 370/3033.

(W.S. and D.W.)


DATA FLOW AND STORAGE

STANDARD DATA OUTPUT

Figure 1. OPERATION OF THE PENN STATE DATA BASE

Table 4. Comparison of the Capabilities of the PDP-8A and IBM-370 Data Base Systems

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PDP-8A Capabilities

1. Printout of standard data formats (1 to 10 pages for each coal)
2. Search data base on any raw data parameter
3. Sort raw data generated by search
4. Display searched and sorted raw data, together with any associated calculated values
5. Print searched and sorted raw data together with any associated calculated values

IBM-370 Capabilities

1. Printout of standard data formats (in 1-, 3-, or 5-page versions)
2. Search data base on any raw data parameter or calculated value
3. Sort raw data or calculated values generated by search
4. Print searched and sorted raw data and/or calculated values
5. Statistical manipulation of data

The PDP-8A also provides an interactive computerized data system allowing the researcher to search, sort and interrogate the Data Base in many ways again without any need for a knowledge of computer languages. A new high-speed (500 characters per second), and high-quality printer is now on order and its installation will further enhance the abilities of the minicomputer system to serve the investigators at Penn State and the coal community at large.

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5. STATISTICAL STUDY OF INORGANIC DATA ON COALS IN THE DATA BASE

Inorganic constituents of coals can be divided into three groups according to their origin (5): those accumulated by the original plants, those formed or deposited at the same time as the coal (syngenetically); and those emplaced after burial and consolidation of the coal. Although it may not be possible to assign an element to one of these groups, its origin may influence its correlation with the other inorganic constituents.

The original plant material is generally believed to make only a minor contribution to the amount of mineral matter in the coal. Berkowitz (6) states that although grasses may contribute silica and lycopods contain a relatively large amount of alumina, larger amounts are generally due to sedimentary processes. Correlations of trace elements from plant material are also likely to be poor, according to Casagrande and Erchull's (7) comparison of different environments and sediment amounts in the Okefenokee Swamp. They concluded the plants affect the amount of trace metals formed in peat and subsequent coal but "the role of plants in metal distribution found in coal is minimal".

Minerals formed in place during peat deposition will be influenced by the existing environmental conditions at the time, while those deposited by transportation are governed by source area and the transportation process. Zubovic et al., (8) studied 10 seams in Illinois, Indiana, and Kentucky, concluding that minor element content is partially derived from rocks in the source area. Vertical variation of minor elements among seams may be due to a change in character of beds exposed in the source area. Sediment derived from a given level in an igneous body will reflect the trace element content at that level, as determined by differentiation of the magma. Erosion of the upper part of the body often will contribute the silicic trace elements Be, B, Ga, Ge, Mo, Y, and La. The lower part (formed from early magma differentiation) often will yield the mafic trace elements V, Cr, Co, Ni, and Cu. Since mafic minerals weather more rapidly than silicic minerals, recycling of igneous rock grains into sedimentary rocks decreases the mafic:silicic element ratio from the original value in the igneous rock. Zubovic et al. found that this ratio increases upward in certain vertical sequences of coal seams. Their conclusion was that the change in the ratio "reflects the progressive exposure and erosion of deeper seated rocks as Pennsylvanian sedimentation progressed."

Minerals formed after burial and consolidation of the coal will reflect the composition of mineral-bearing solutions and the geochemistry of the area, e.g. sphalerite in Illinois coals.

Distinct mineral species, major elements, and trace elements are determined in the analysis of the inorganic coal fraction. Correlations between components can then be assigned to one of the six combinations of these categories, or may be organically related.

Correlations between two minerals may be expected for minerals which form under similar conditions in the coal, or which are likely to have been associated in source rocks. Conversely, a high correlation between minerals of different genesis or source rock affinity would not be expected.

Mineral-major element correlations would be expected in the straightforward case of the element being a major constituent of the mineral. Otherwise, the correlation may be inherited from a high mineral-mineral correlation, in which a component of one mineral correlates with the other mineral.

Mineral-trace element correlation can be expected from substitution of the trace element for the normal constituent element, e.g., Mn correlating with calcite owing to Mn substituting for the Ca in calcite. The trace element may also occur in solid solution in the mineral, as Cd in sphalerite (9).

Correlation between major elements can be found when the elements occur in the same mineral, e.g. correlation of Fe and S from pyrite. Similarly Si, Ti, Al and K can be expected to correlate since they are found together in the aluminosilicate minerals.

Trace elements will be associated with major elements when the trace element substitutes for the major element in a common mineral (Mn for Ca in carbonates as discussed above). Such a correlation also will occur when a major and trace element together form a minor mineral, such as Na with Cl in NaCl (9), but where greater amounts of Na are present in other associations.

There are numerous causes for positive correlations between trace elements. Similar environmental conditions may cause deposition of certain groups of trace elements in minerals without those minerals being otherwise genetically associated. For example, Ba in barite correlates with Zn and Cd in sphalerite (9).

The chalcophile elements As, Co, Ni, Pb, and Sb are expected to correlate with each other owing to their chemical affinities. Gluskoter also found that although many rare earth elements are correlated this may be partially due to the analytical threshold value and the low levels of these elements rather than true chemical affinities. Ag also correlated with the rare earth elements.

(D.G. and A.D.)

6. STUDIES OF THE LATERAL AND VERTICAL VARIABILITY OF CHARACTERISTICS OF COAL SEAMS

A. Petrographic Characteristics of the Lower Kittanning Seam

The objective of this study is to determine vertical and lateral petrographic changes within the Lower Kittanning coal seam and to ascertain any relationships between these changes and the depositional setting of the Lower Kittanning peat swamp of Middle Pennsylvanian age in western Pennsylvania.

The environmental settings which existed during deposition of the Lower Kittanning seam has been mapped by E.G. Williams (10) based on faunal evidence in the shales (the Lower Kittanning shales) immediately overlying the Lower Kittanning coal (Figure 2). The facies changes depicted in the shale indicate a NE-SW trending shallow basin which underwent a marine incursion during deposition of the Lower Kittanning shales. It is reasonable to assume that the encroaching marine waters exerted a certain degree of influence on the subjacent peat deposits. Petrographic studies of the Lower Kittanning coal will be employed to ascertain the extent of this influence of changing environments on the resulting compositional nature of the coal.

Related studies on the Lower Kittanning coal have been conducted by D. Habib (11) and F. Ting (12). Habib studied the distribution of spore and pollen assemblages in the Lower Kittanning coal along an east-west transect from central Clearfield county west to the Pennsylvania-Ohio border (see Figure 2 for sample sites). He concluded that "the spatial arrangement of spore and pollen assemblages in the Lower Kittanning coal suggests a genetic relationship with the environmental conditions within which the overlying sediments were deposited.... The salinity factor resulting from proximity to the seam seems most plausible in explaining the distribution of the assemblage zones."

Like Habib, Ting (12) sampled an east-west transect across the strike of the basin ranging from Jefferson County in the east to Lawrence County along the western border of Pennsylvania. The majority of Ting's samples were from the "marine-influenced" central portion of the basin. He also included 3 sets within the north-western "brackish" and 1 in the north-western "fresh-water" influenced areas (sample sites shown in Figure 2). His finding led him to conclude that the Lower Kittanning seam in any locality would be composed of up to 5 different types of coal layers containing characteristic maceral assemblages (lithotypes). These "lithotypes" occur in a definite sequence although one or two of the lithotypes may be missing at any one locality. However the sequence of occurrence does not change in such cases." Also, "the sequence of occurrence of lithotypes relates rationally to the nature of the overburden... and to the paleogeography and tectonic history as interpreted by others."

The Lower Kittanning coal, as a result of its extensive occurrence over a large area, experienced not only differences in depositional settings but also in its geologic and tectonic history. Generally as one moves eastward from the center of the basin toward the Allegheny front the rank of the Lower Kittanning increases to the low volatile (R_o 1.7 - 1.9%)

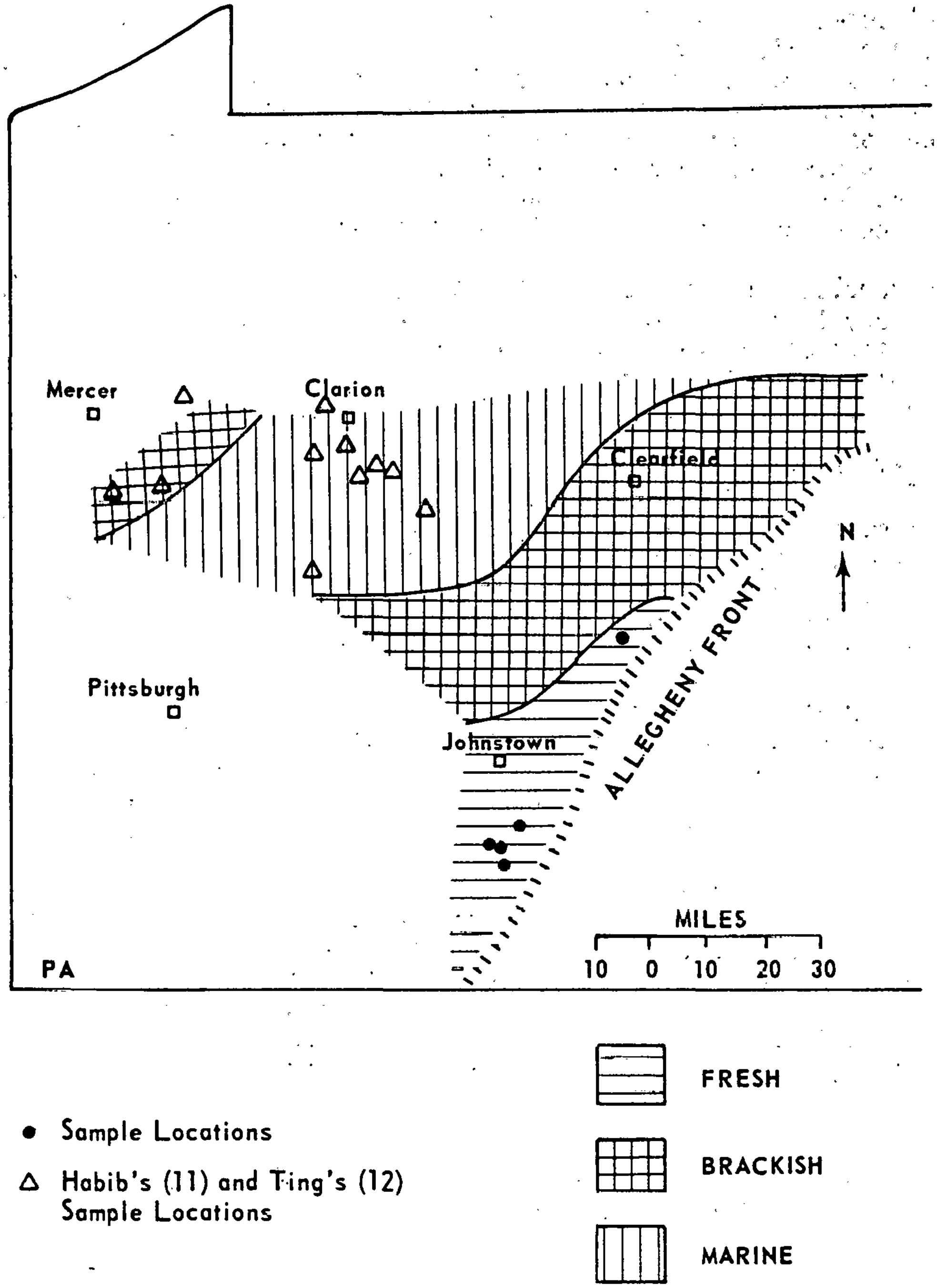

Figure 2. PALEOENVIRONMENTS OF THE LOWER KITTANNING SEAM
(based on faunal evidence from overlying shales)
after E.G. Williams, 1960 (10)

rank range of bituminous coals. As a result of this rank variation, the individual constituents of the coal become more homogeneous in appearance both megascopically and microscopically. The coal samples studied by Habib and Ting were all of the lower rank bituminous coal, and therefore the changes in maceral appearance and characteristic were not a factor under consideration in their studies. One of the questions the present study will investigate is, are the petrographic differences which reflect variation in coal swamp environment still discernable in the higher rank Lower Kittanning coals occurring in the eastern "freshwater" portion of the coal field? It is our hope that the use of special petrographic techniques will be effective for the seam in this area, since no thorough petrographic investigation of environmental variation has been done here.

Five samples from the eastern "freshwater" areas have been collected for this study to date. Their locations are indicated in Figure 2. Two additional samples are to be collected from within the "marine" environment. The vertical variability within each sample will be determined as well as the lateral variation as a function of environment.

Procedure of Analysis

The samples to be analyzed for this study were collected in complete intact columns. They were cut, in the laboratory, into a series of blocks approximately 6 x 8-10 x 1 cm and mounted in polyester resin for polishing. Faces of the blocks perpendicular to the bedding were then polished for analysis by reflected light microscopic techniques.

The analytical procedure commences with the megascopic description of the seam using a modified standard coal lithotype terminology. These data will be used for a gross comparison of the coal lithotype characteristics between samples collected in the course of this study. However, the microscopic composition of the coal is not necessarily reflected in its megascopic appearance. What to the naked eye may appear as two clarains, may show important and distinctive differences when viewed microscopically. It is these differences which are of major importance in deciphering the early geologic history of the coals. With this in mind the polished column samples will be analyzed microscopically using a point-counting technique adapted for the physically large specimens involved. The petrographic composition of the coal will be analysed using the existing nomenclature of the Stopes-Heerlen system, modified as necessary for this particular suite of samples.

(S.D.A. and A.D.)

B. Vertical and Lateral Variations of the Herrin (No. 6) Coal in Northwestern and West Central Illinois

Purpose

The purpose of this study is to examine the vertical and lateral variability with respect to petrography and mineral partings of the Illinois Herrin (No. 6) Coal for the areas of northwestern and west central Illinois. The depositional environments of the No. 6 coal in these two areas will be inferred from the maceral composition and the two areas will be compared.

The study should also contribute to an understanding of the development of the No. 6 Coal Swamp.

Preparation of Polished Blocks for Maceral Analysis

Maceral analysis will be performed on polished blocks of coal encompassing the entire length of the coal column samples, from roof rock to underclay, without gaps. Preparation of the polished blocks requires embedding them in a plastic medium to preserve the integrity of the sample. Upon arrival of the samples at The Penn State Coal Research Section coal preparation laboratory, each coal column segment was completely covered with a plastic, specifically Paraplex polyester resin, to preserve it from physical and chemical disintegration. The samples can safely be stored indefinitely in this manner while awaiting preparation.

When ready for preparation, column segments are cut with a rock saw into dimensions approximating 4 to 8 cm wide by 4 to 10 cm long by 2 cm deep, with care being taken not to lose material when sawing between segments. The vertical sides of the coal blocks are then ground on a belt sander until the surfaces of the slab are smooth and even. The ground blocks are then placed in specimen molds and embedded in polyester resin. When the resin has hardened the blocks are trimmed to a size manageable for polishing either with the rock saw or by belt grinding. The sides of the blocks are smoothed by belt grinding. The block surface to be examined is ground on 320 grit paper with tap water followed by 400 grit paper. The blocks are polished on a microcloth covered lap using tap water and 3.0 and 0.05 μm alumina slurry, in succession. Final polishing is not carried out until shortly before the blocks are to be analyzed.

(S.R. and A.D.)

C. Analysis of the Factors Controlling the Fluid Behavior of Lower Kittanning Seam Samples, Their Response to Oxidation, and Relationship to Liquefaction Behavior

Introduction

A major goal of coal research is to develop the capability of predicting the behavior of coals in utilization processes from their physical, chemical and petrographic characteristics. Such undertaking must take into account the depositional and geologic history of the coal, and the heterogeneous nature of coal which results from the interplay of the various coal-forming processes.

In work done by Yarzab et al. (13), statistical correlations between liquefaction behavior and various properties of 104 coals were presented. These coals came from different geological provinces and exhibited a wide range of properties. Such a study has been quite beneficial in showing the extent to which coals from different geological provinces vary in their intrinsic properties. In the present research a systemmatic and quantitative chemical, physical and petrographic study of samples from a single seam within one depositional basin enabled us to investigate the influence of depositional and geological factors on the intrinsic properties of the coal.

Thus, we were able to ignore factors which may relate to geologic province or stratigraphic position. It also enabled us to consider some of the influences within the depositional basin.

As outlined in the previous quarterly report (DOE-30013-2), the Lower Kittanning seam underwent a major variation in metamorphic grade as well as having been deposited in a range of different environments. This variability in physical, chemical and petrographic properties has enabled us to statistically study the effect of these variables upon the fluid and liquefaction behaviors of the samples.

Experimental

A total of 69 samples from 39 sample sites were selected for this study. All were taken from the Lower Kittanning seam in western Pennsylvania and eastern Ohio. The samples ranged in rank from hvCb to lvb. The sample set consisted of 39 channel samples and 30 hand-picked vitrinite concentrates. Combining these two sample types gave us a wide variation in total vitrinite, sulfur forms and ash content for a greater range of rank than that examined by Yarzab et al. (13).

A series of seven analyses and tests were performed on the sample set, namely; proximate and ultimate analyses, sulfur forms analysis, maceral analysis, mean maximum reflectance of vitrinite, the Gieseler fluidity test and the bench-scale liquefaction test.

A standard analysis was used to determine the content of total reactive macerals (TRM) in each sample. This TRM content was calculated as the sum of the percentages of vitrinite, liptinite, and micrinite on a mineral-matter free basis.

Numerous approaches have been used to study the thermoplastic behavior of coals. In this study, an automated Gieseler plastometer was used following the procedures outlined by the ASTM with the exception of the use of a 20 gm-in. torque. The lower torque was needed owing to the extreme fluidity of many of the samples.

Liquefaction runs were performed in duplicate within stainless steel microreactors (14). In each run, samples were mixed with tetralin and rapidly heated and agitated in a fluidized sand bath at 400°C for 1 hour. The degree of conversion was determined as the amount of material converted to ethyl acetate soluble material after a 24-hour Soxhlet extraction.

Preliminary Results and Discussion

Normalization of Data

Seventeen coal properties were considered in the statistical analyses (Table 5). The frequency distribution for these variables were analyzed for normality using tests for skewness and kurtosis along with the Chi-square "goodness of fit" test. Mathematical transformations were performed on variables which deviated from a normal distribution in order to obtain the distribution closest to normal.

Table 5. Variables Used in Statistical Study

Dial Divisions/Minute (ddpm)

Softening Temperature, °C

Temperature of Maximum Fluidity, °C

Resolidification Temperature, °C

Temperature Range of Fluidity, °C

Liquefaction Conversion, %

Mean Maximum Reflectance, %

Total Reactive Macerals (TRM), %

Carbon, % dmmf

Hydrogen, % dmmf

Oxygen, % dmmf

Nitrogen, % dmmf

Chlorine, % dmmf

Pyritic Sulfur, % dry

Organic Sulfur, % dry

Volatile Matter, % dmmf

Ash, % dry

Classification of Sample

One concern in such a statistical study is whether the samples are from a single population. For example, a skewed distribution of many variables may be the result of sampling from several populations. Our data, however, were not abnormally skewed, possibly because they were obtained from a single depositional basin.

Classification of our samples to test if one or more populations existed was not highly justified statistically. However, we were concerned that the use of two sample types (coal channel and maceral concentrate) might create nature sample type groupings. Therefore a cluster analysis of the data was performed.

When two cluster groups were called the first group contained 53 members and the second 16 members. Figure 3 demonstrates these two groups in a plot of reflectance (log x) vs. ddpm. Note that Group 2 represents the samples with high fluid properties; when further groups were called, only the second cluster class was further subdivided in such a manner as to indicate that a single population of data was present. Subdivision into such separate cluster groups would not benefit the statistical study and therefore was not done.

Principal Component Analysis

Some of the characteristics investigated in this study were introduced very early in the history of a coal (for example, the proportion of the inertinite group macerals), and have not been altered significantly through most of the subsequent changes. Other variables (for example, reflectance and volatile matter) of course, are altered during coalification, although the processes of coalification affect the variables of rank at different rates. Because of this, the selected variables must be compared simultaneously in order to detect any discernable patterns. This was done with the aid of a factor analysis.

The first step in a factor analysis is the determination of interdependence among variables. This degree of linear correlation is measured by the correlation coefficient which is expressed within the factor analysis in a correlation matrix. Inspection of the correlation matrix indicated that a linear relation existed between liquefaction conversion and parameters of rank. This is also illustrated in Figures 4, 5 and 6. Figure 4 is a comparison of conversion data against volatile matter content, in which a positive linear relation exists (correlation coefficient of .90). A plot of vitrinite reflectance versus liquefaction conversion is seen in Figure 5. Here an inverse relationship exists with a correlation coefficient of -.94.

Relationships among some of the parameters of thermoplastic behavior and conversion data showed linear relationships. Figure 6 shows a plot of the temperature of maximum fluidity versus liquefaction conversion. This relationship is an inverse one with a correlation coefficient of -.87. The plot of temperature of resolidification versus conversion (Figure 7) shows that these variables are inversely related (correlation coefficient of -.82).

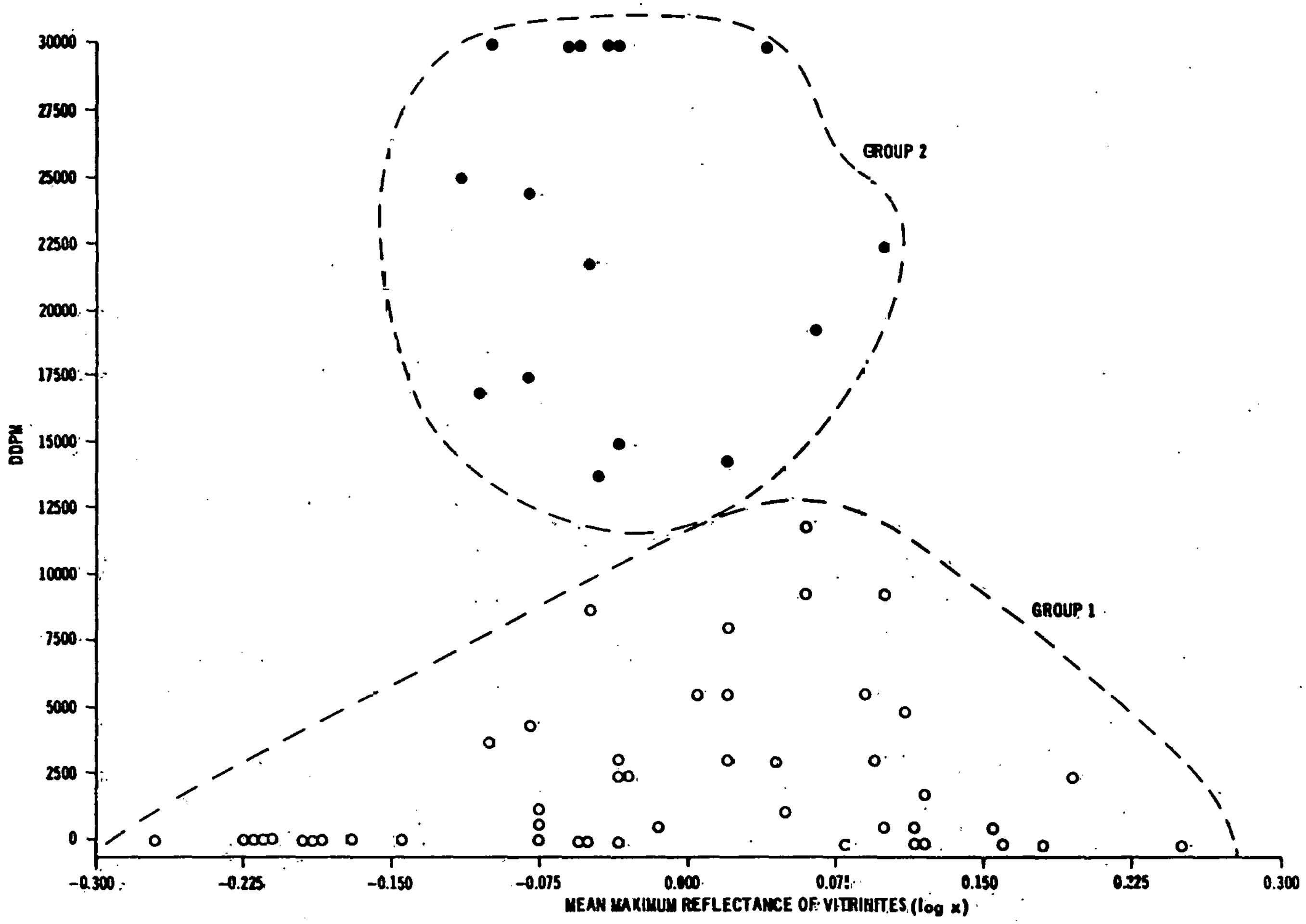

Figure 3. CLUSTERING OF COALS USING DDPM AND REFLECTANCE VALUES

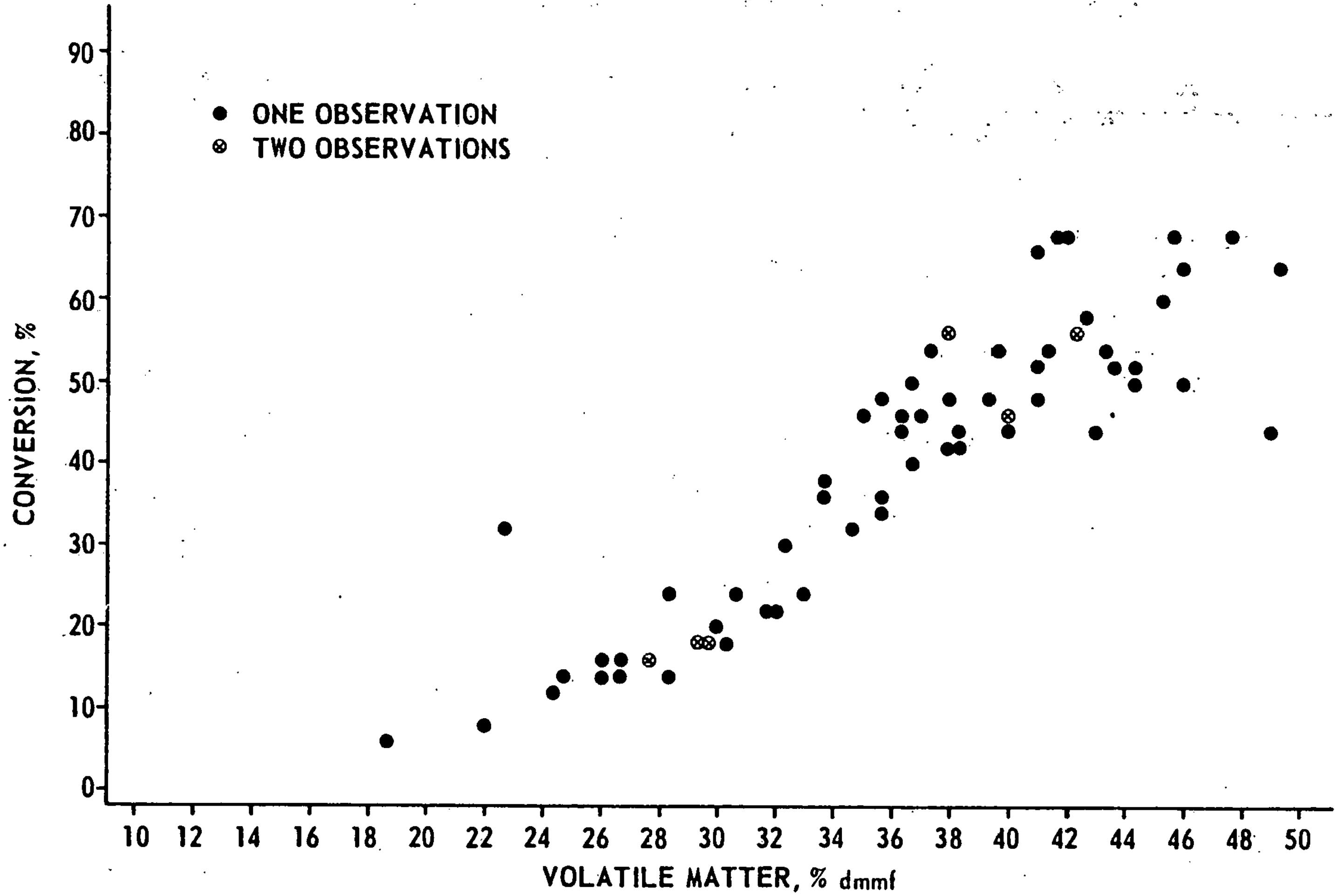

Figure 4. PLOT OF CONVERSION VERSUS VOLATILE MATTER

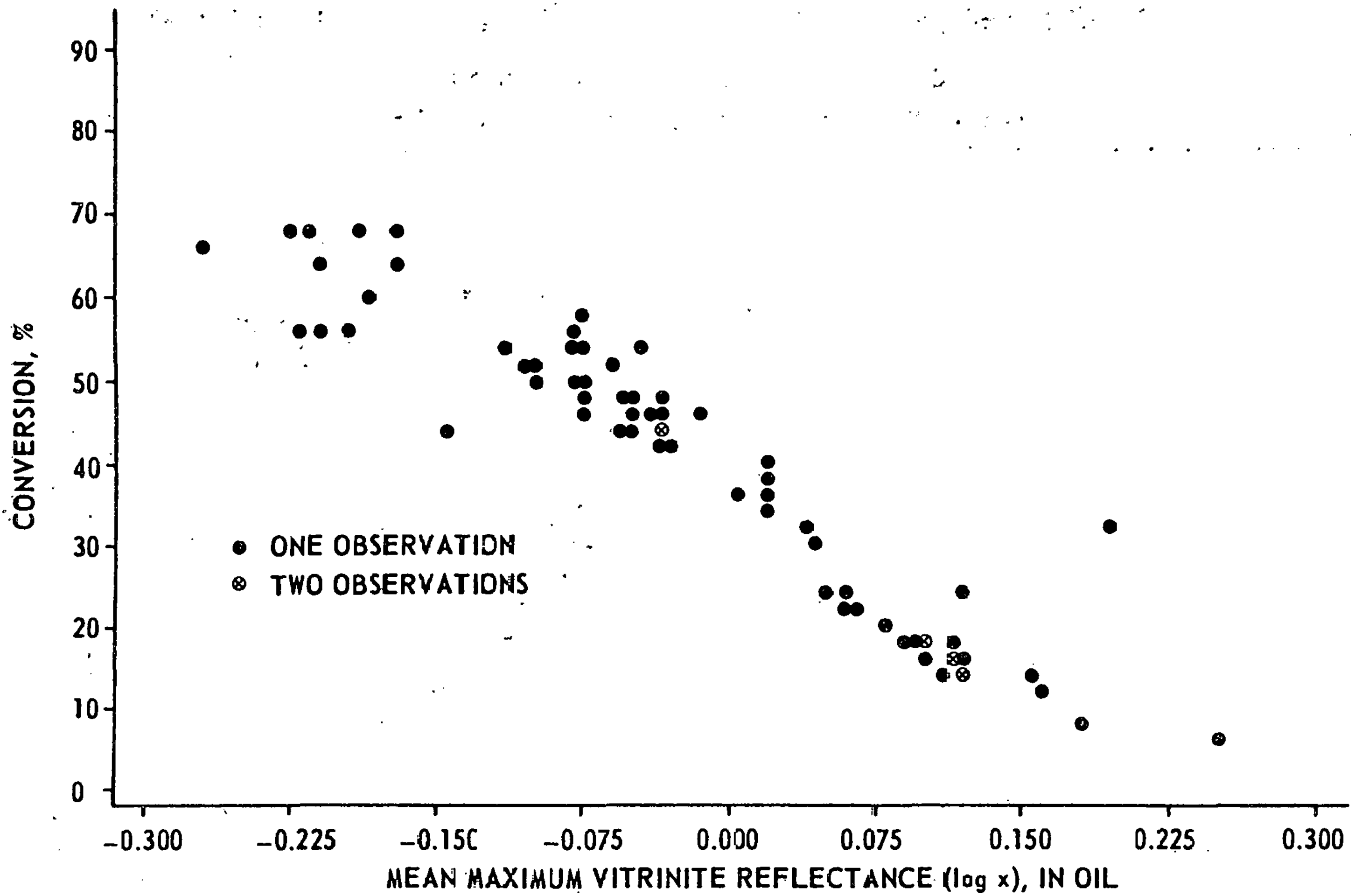

Figure 5. PLOT OF CONVERSION VERSUS REFLECTANCE

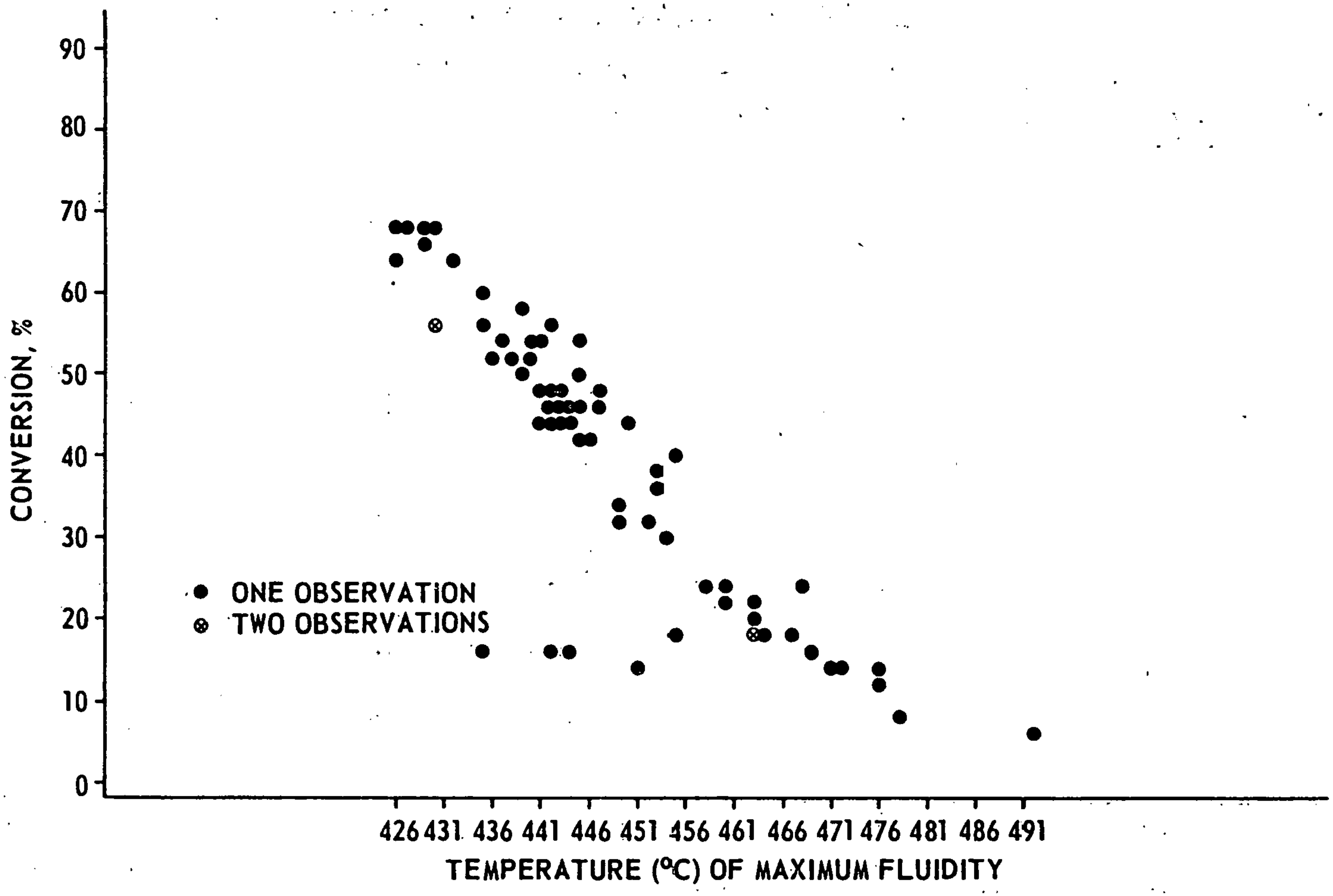

Figure 6. PLOT OF CONVERSION VERSUS TEMPERATURE OF MAXIMUM FLUIDITY

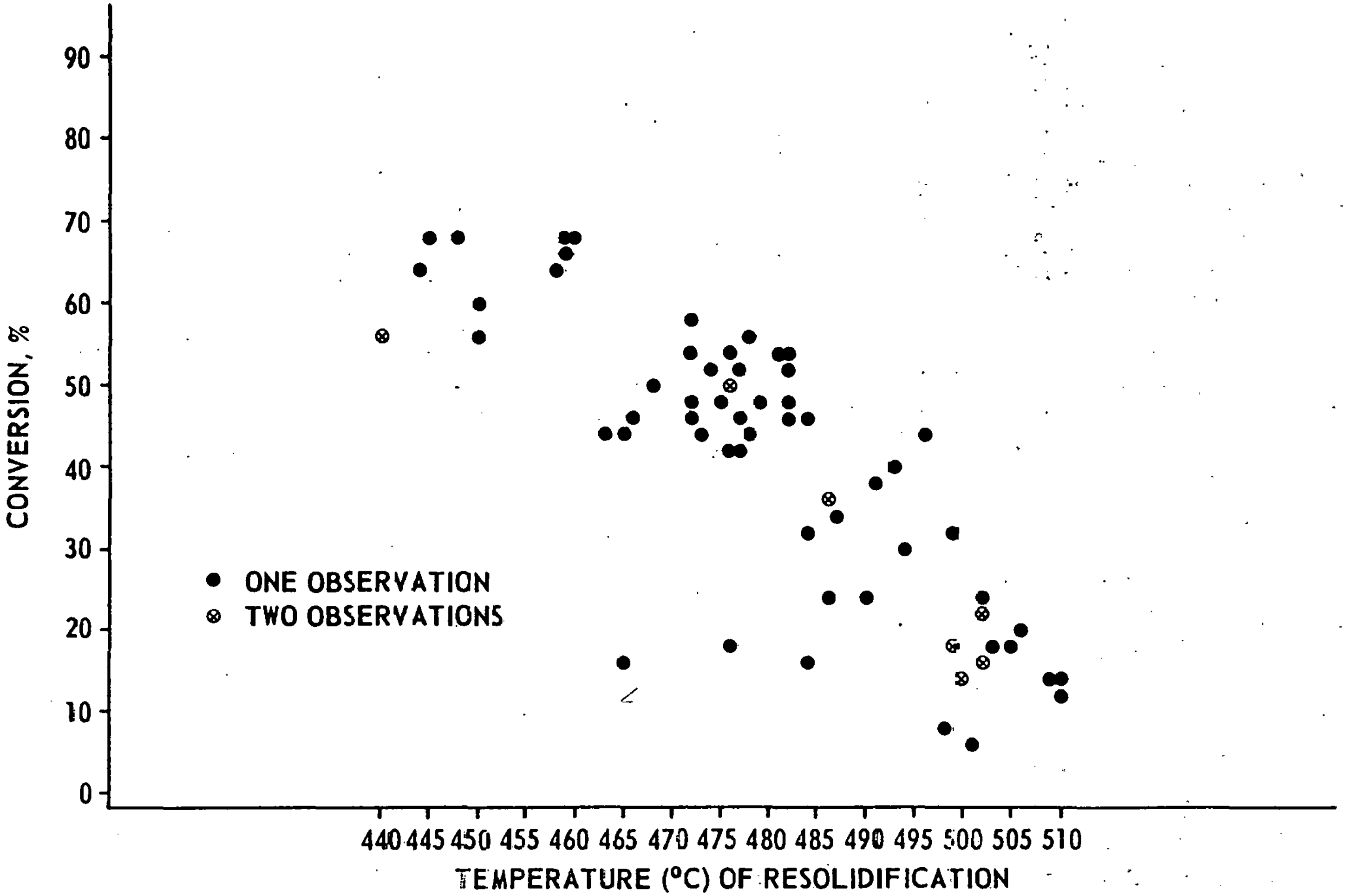

Figure 7. PLOT OF CONVERSION VERSUS TEMPERATURE OF RESOLIDIFICATION

The factor analysis further reduces the original number of variables to a fewer number of mutually uncorrelated underlying components (Davis, 1973). It is these components which are the sources of variance within the variables of the data set. Table 6 shows the four principal components or factors for the 17 variables of the samples considered in this study. Together they explain approximately 82 percent of the total data variance.

Analysis of Factor Components

The first factor contains nine of the seventeen variables. It accounts for approximately 40 percent of the total variance in the data set. The parameters loading on this component are mostly those whose values are altered by the process of coalification, namely; reflectance, volatile matter, carbon content, oxygen content and hydrogen content. In addition, liquefaction conversion along with temperature of maximum fluidity and temperature of resolidifaction were grouped into this factor, suggesting a rank dependence. Organic sulfur, which is not directly dependent on rank also was grouped into this factor.

The second factor accounts for approximately 19 percent of the total variance. The factors loading to this component are hydrogen, pyritic sulfur and three parameters of thermoplasticity, namely; maximum fluidity (ddpm), temperature of softening and temperature range of softening. The grouping of these variables cannot be explained readily; it suggests the possibility of a chemical-physical relationship in which there is some control of initial melting or the development of fluidity by the hydrogen content. Regardless of the relationship, these variables may contribute an independent source of information to the data set. One reason for the failure of the maximum fluidity to load in the first factor is that it does not have a linear relationship with rank, although it is known to be quite strongly rank related. Clearly this complicates the extent to which the maximum fluidity appears in other factors.

The third factor accounts for approximately 15 percent of the total variance. It includes ash, total reactive maceral and chlorine contents and one parameter of thermoplastic behavior, temperature of softening. Ash and total reactive maceral content are variables which are essentially unrelated to coalification processes but rather to the depositional history of the samples. The association of the temperature of softening with these variables suggests that this temperature is at least partially related to the petrographic composition of coals rather than to changes due to coalification.

The fourth component accounts for approximately 8 percent of the total variance. Its loadings are on nitrogen and chlorine.

Conclusions

Seventeen variables used to characterize the Lower Kittanning seam samples, through factor analysis, were reduced to four principal components. Together the components explained approximately 82 percent of the total variance.

Table 6. Principal Components Analysis for Full Set of Coals and Maceral Concentrates

	Loadings on			
	Factor 1	Factor 2	Factor 3	Factor 4
Reflectance, %	-.96			
Volatile Matter, % dmmf	.95			
Conversion, % dmmf	.95			
Carbon, % dmmf	-.92			
Temperature of Maximum Fluidity, °C	-.90			
Resolidification Temperature, °C	-.87			
Oxygen, % dmmf	.79			
Organic Sulfur, % dry	.61			
Hydrogen, % dmmf	.59	.57		
Temperature Range of Fluidity, °C		.74		
Dial Divisions/Minute (DDPM)		.68		
Softening Temperature, °C		-.66	.58	
Pyritic Sulfur, % dry		.60		
Total Reactive Macerals, %			-.77	
Ash, % dry			.74	
Chlorine, % dmmf			-.60	.55
Nitrogen, % dmmf				.78
Cumulative % Variation	40	59	74	82

The following conclusions can be drawn from identification of the four principal components.

1) Conversion is highly rank related.
2) Temperatures of maximum fluidity and resolidification bear a strong relationship to rank and liquefaction conversion.
3) Temperature of softening and the degree of fluidity do not load with rank in the factor analysis.
4) Temperature of softening loads with indices of petrographic composition (total maceral and ash values).

Plans for Future Work

Sampling of the Lower Kittanning seam is continuing in western Pennsylvania. On completion of chemical and physical analyses, the data from these samples will be added to the data matrix enabling a stronger multivariate statistical analysis to be performed. A total of 45 sample sites will be used in the final statistical analysis.

A study of the influence of oxidation and recrushing of coal on the thermoplastic properties of coals is planned. In this research, a coal will be subjected to oxidizing conditions and the reduction of fluid properties will be monitored. Subsequent splits of these samples will be recrushed and the influence of this secondary crushing on the fluid properties will be studied.

(J.T.S. and A.D.)

7. FTIR SPECTROSCOPY AND OPTICAL STUDIES

A. The Reflectance of Coal

The reflectance of vitrinite macerals in coal has been found to increase with rank. Vitrinite reflectance is particularly useful as a coal rank indicator because it is easily measured, requires only small samples of coal and does not necessitate separation of any single component from the coal. Most importantly, because it is measured on a single maceral type, reflectance is independent of petrographic variation of the sample.

This relationship between rank and reflectance indicates that vitrinite must undergo fundamental changes of structure and/or chemistry during the process of coalification. It is found that both the refractive and absorption indices change during coalification (15). The following brief investigation of the physical laws and relationships governing reflectance will show the ways in which the refractive and absorption indices affect reflectance.

Reflectance is the percentage of vertically incident light that is reflected from a plane polished surface. Reflection occurs at the boundary of two media with non-identical refractive indices. Reflectance is a function not only of the refractive indices of the two media, but also of their absorption indices, the angle of incidence of the light and the wavelength of the incident light.

The reflectance of light at the boundary of two non-absorbing media is determined by Fresnel's equation:

$$R = \tfrac{1}{2}\left(\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right) \quad \ldots \ldots \ldots \ldots \quad (1)$$

where i = the angle of incidence of the light
r = the angle of refraction

When the incident light is normal to the boundary this relationship can be simplified to:

$$R = \frac{(\mu_2 - \mu_1)^2}{(\mu_2 + \mu_1)^2} \quad \ldots \ldots \ldots \ldots \quad (2)$$

where μ_1 = refractive index of the first medium
μ_2 = refractive index of the second medium

When the first medium is air, Equation (2) can be further simplified to:

$$R = \left(\frac{\mu_1 - 1}{\mu_2 + 1}\right)^2 \quad \ldots \ldots \ldots \ldots \quad (3)$$

The refractive index (μ) of a substance is the ratio of the velocity of light in a vacuum to the velocity of light in that substance (Equation 4)

$$\mu = c/v \tag{4}$$

where c = velocity of light in a vacuum
v = velocity of light in the medium

Absorption of a medium is described by Lambert's Law which states that a beam of incident light, I_o, will be reduced in intensity to I as it passes through the absorbing medium of thickness x with absorption coefficient k (Equation 5)

$$I = I_o e^{-kx} \tag{5}$$

the absorption coefficient is further defined in terms of the index of absorption (K), the wavelength of the incident light in a vacuum and the refractive index of the absorbing medium (Equation 6)

$$k = (4\pi K\mu)/\lambda \tag{6}$$

Because coal is an absorbing material, Equation (2) must be modified to include the effect of absorption by the coal. Beer's equation (4) expresses this modified relationship by including a term for absorption in the second medium.

$$R = \frac{(\mu_2 - \mu_1)^2 + \mu_2{}^2 K_2{}^2}{(\mu_2 + \mu_1)^2 + \mu_2{}^2 K_2{}^2} \tag{7}$$

The percentage reflectance of coal measured in air (R_a) and oil (R_o) can be inserted in equations (8) and (9), which are derived from Equation (6), to obtain values for the refractive and absorption indices of the coal.

$$\mu_2 = \frac{\frac{1}{2}(\mu_o{}^2 - 1)}{\mu_o \frac{(1 + R_o)}{(1 - R_o)} - \frac{(1 + R_a)}{(1 - R_a)}} \tag{8}$$

$$K^2 = \frac{R_a\ (\mu_2 + 1)^2 - (\mu_2 - 1)^2}{\mu_2{}^2\ (1 - R_a)} \tag{9}$$

where μ_2 = the refractive index of the coal
μ_1 = the refractive index of the immersion oil

The study of reflectance characteristics of vitrinite concentrates from the Lower Kittanning coal will make use of the above equations to calculate the refractive and absorption indices of samples in the reflectance range (R_o) of .5% to 1.8%.

B. A Study of Some Optical Properties of Vitrinite Concentrates at Different Wavelengths of Light

Introduction

Fifteen to twenty-five vitrinite concentrates will be examined under the microscope in reflected light at different wavelengths over the visible region. These concentrates were collected from the Lower Kittanning seam from central Pennsylvania west into Ohio. Mean maximum and apparent reflectances will be taken on the samples in both air and oil media at each wavelength. Refractive index and anisotropy will also be determined.

The objectives of this research are as follows: 1) to investigate the lateral variability in the vitrinites from east to west across the Allegheny Plateau by examining the spectra of reflectance and refractive index; 2) to elucidate the chemistry and structure of vitrinite and possibly other macerals by comparison with FTIR spectra; 3) to determine the method's usefulness as a tool in rank determination; 4) to examine the applicability of the technique as a routine analysis of coal.

Previous Research

Very few studies have investigated the optical properties of coal at different wavelengths over the visible region. Those that will be discussed here have examined the dispersion curves of reflectance, refractive index, extinction coefficient, and absorptive index of coals of varying rank. Some related their results to the structural properties of coal.

Cannon and George (16) were the first to investigate the optical properties of coals at different wavelengths. They used a series of light filters whose wavelengths ranged from 5000-7000Å. They found that the dispersion curves for measurements taken parallel to the bedding were parallel for all the coals studied. For anisotropic coals, measurements taken perpendicular to the bedding also gave parallel dispersion curves but with a different slope. Specific refractivity, a ratio of refractive index and density was found to be constant for all coals.

Friedel (17) looked at the reflectance of a single coal vitrain (84% C) in the ultraviolet and visible region and found no discontinuities in the dispersion curve. Since there was no increase in refractive and absorptive indices typical of polynuclear condensed aromatics, he felt that aliphatic and amorphous carbons may predominate the structure of coal.

Four coals ranging in rank from high volatile bituminous to anthracite were studied by McCartney and Ergun (18,19) over the region 4400-6710Å. They found that spectra of reflectance and refractive index of the anthracite showed opposite trends to those of lower rank bituminous coals.

Gilbert (20,21) studied the reflectance of seven vitrains in the wavelength range 2350-6000Å. He found that the dispersion curves were directly related to the carbon contents of the vitrains with no exceptions. He also examined the refractive index and absorption coefficient of these vitrains (22).

These were determined by measuring reflectance with the polarizer both parallel and perpendicular to the plane of incidence at two known angles of incidence. They were then read off prepared tables. The method was direct (i.e. no comparison standards were required for calibration), and no immersion medium was needed; however, this method assumed that the coals were isotropic.

McCartney and others (23) examined some coals ranging from lignite to anthracite in the u.v. and visible region. Readings were taken in air and water media. Contrary to the finding of Friedel (17), they reported a maximum in the spectrum of the extinction coefficient in the u.v. region which suggested significant amounts of aromatics.

Marshall and Murchison (24) studied the optical properties of vitrinites carbonized at up to 750°C in the wavelength region 4030-7090Å. Thirty maximum and apparent minimum readings were taken on particulate coal samples. The six lowest minimum readings were averaged and used to determine bireflectance. Refractive and absorptive indices were also calculated.

Exinites and inertinites as well as vitrinite were examined by Hevia (25). Reflectance readings were taken at five different wavelengths by changing filters. When he plotted the log of reflectance against wavelength, he found the slope of the spectra to be constant for collinites of low to medium rank. This slope decreased as rank increased and was reversed for meta-anthracites. For inertinites the slope was shallower than that of collinite of the same rank. There was more variation in the spectra of individual inertinite macerals than for vitrinites.

Jakeman and Cook (26) examined coals ranging from 0.48-1.95% reflectance over the wavelength region 4050-6560Å. They reported that the form of the dispersion curves for reflectance, refractive index, and absorptive index did not change with rank. No relationship existed between irregular spectra and vitrinite type.

Most of the studies discussed here found similar trends in the spectra of reflectance, refractive index, and absorptive index. All the spectra tended to increase with decreasing wavelength over the visible region 4000-6700Å. Jakeman and Cook (26) also reported an increase in the absolute amount of dispersion of reflectance with decreasing wavelength, but Hevia (26) found a decrease. Several workers (19,20,22,25,27) noted a reversal of the trend in the spectra for anthracites. Marshall and Murchison (24) reported a decrease then an increase in the absorptive index of uncarbonized vitrains with decreasing wavelength with a minimum at 5460Å. For vitrains carbonized above 600°C the trend of the dispersion curves for reflectance and refractive index was similar to anthracites.

McCartney and others (23) reported very little dispersion in refractive index for coals ranging from lignite to low volatile bituminous. For four coals it increased slightly with decreasing wavelengths. The reverse was true for three others.

Plan of Work

Future work will investigate the dispersion of reflectance absorption index in coals from Pennsylvania and Illinois.

(J.A.T. & A.D.)

8. PHYSICAL CONSTITUTION ANALYSIS OF COAL MACERALS

In our previous quarterly technical progress report (DOE-30013-2) we observed that we will be determining structural parameters of macerals by physical constitution analysis. This approach has the disadvantage of requiring major assumptions, some of which are disputed. Consequently we intend to compare our results with those done by ^{13}C nmr. Dr. Ronald Pugmire of the University of Utah has examined six of our vitrinite concentrates; his report is incorporated in the following section.

NMR Analysis of Coal Macerals

We have used cross-polarization (CP) and magic-angle spinning techniques (MAS) to examine a set of six vitrinite samples hand picked from the Lower Kittanning seam. The rank of the samples ranged from lvb to hvBb. The ultimate and proximate analyses and vitrinite reflectance are given in Table 7. This set of samples was selected in order to assess the nature of structural changes observed when carefully selected coal samples from a given seam are examined using CP/MAS techniques. In each case, the samples contained greater than 95% vitrinite.

For purposes of clarity, the CP/MAS spectrum of PSMC-67 is given in Figure 8 as a composite of ^{13}C chemical shifts of structural units containing H, C, and O. The vitrinite spectra thus display the range of chemical structural types that give rise to resonance lines in different spectral regions. No effort was made to eliminate from the presentation chemical species (e.g. acetylenes, allenes, etc.) which are not expected to be present to any significant extent in the coal. Nitrogen and sulfur were not included in the display for simplicity of presentation and also due to the low concentration of these elements relative to oxygen. The banded structure observed in Figure 8, however, does provide enough detail to discuss major structural types present. A casual observation demonstrates that a significant amount of aliphatic oxygen is present (50-95 ppm region). Assuming allene and acetylene groups are not present, the 75-95 ppm region suggests the presence of oxygen-containing structural types such as glucoside or pyranoside moieties which would be associated with cellulose; lignin; etc. containing materials. The 50-75 ppm range would contain aliphatic carbons associated with ether (either aliphatic or aromatic) and ester structural units.

Figure 9 displays the spectral changes that occur with rank progression. The spectra of PSMC-67, -53, and -43 represent the extremes and mid-point, respectively, of the rank of the samples. It is clear from an examination of the spectra that significant structural changes occur in the aromatic region with rank increase. These observations are as follows: 1) significant decrease in the intensity in the region beyond 150 ppm; 2) significant decrease in the 135-145 ppm region; 3) a decrease in the line intensity in the 110-120 ppm region. Observations 1 and 2 are most likely due to loss of aromatic oxygen (phenols, aryl-aryl and aryl-aliphatic ethers) and aromatic cyclic ethers (e.g. furans) and/or ring dealkylation. The 110-120 ppm region would represent alkene structures, β-carbons in aromatic

Table 7. Analyses and Aromaticities (f_a) of Maceral Concentrates

	C	H	S	O	N	H/C	Volatile Matter	Fixed Carbon		
PSMC-		(% daf)					(% daf)	(% daf)	R_o,%	f_a*
67	79.9	5.3	1.6	9.2	1.4	0.80	41.6	58.4	0.60	.67
19	77.1	5.5	2.5	6.2	1.4	0.86	41.0	59.0	0.83	.69
34	82.0	5.1	0.9	8.3	1.6	0.75	35.2	64.8	0.96	.72
43	81.9	5.3	1.7	4.6	1.5	0.78	34.4	65.6	1.09	.71
47	84.4	5.1	0.8	4.4	1.5	0.73	26.5	73.5	1.31	.72
53	84.2	4.4	1.3	3.7	1.4	0.63	18.6	81.4	1.71	.66

*error limit ± 0.05

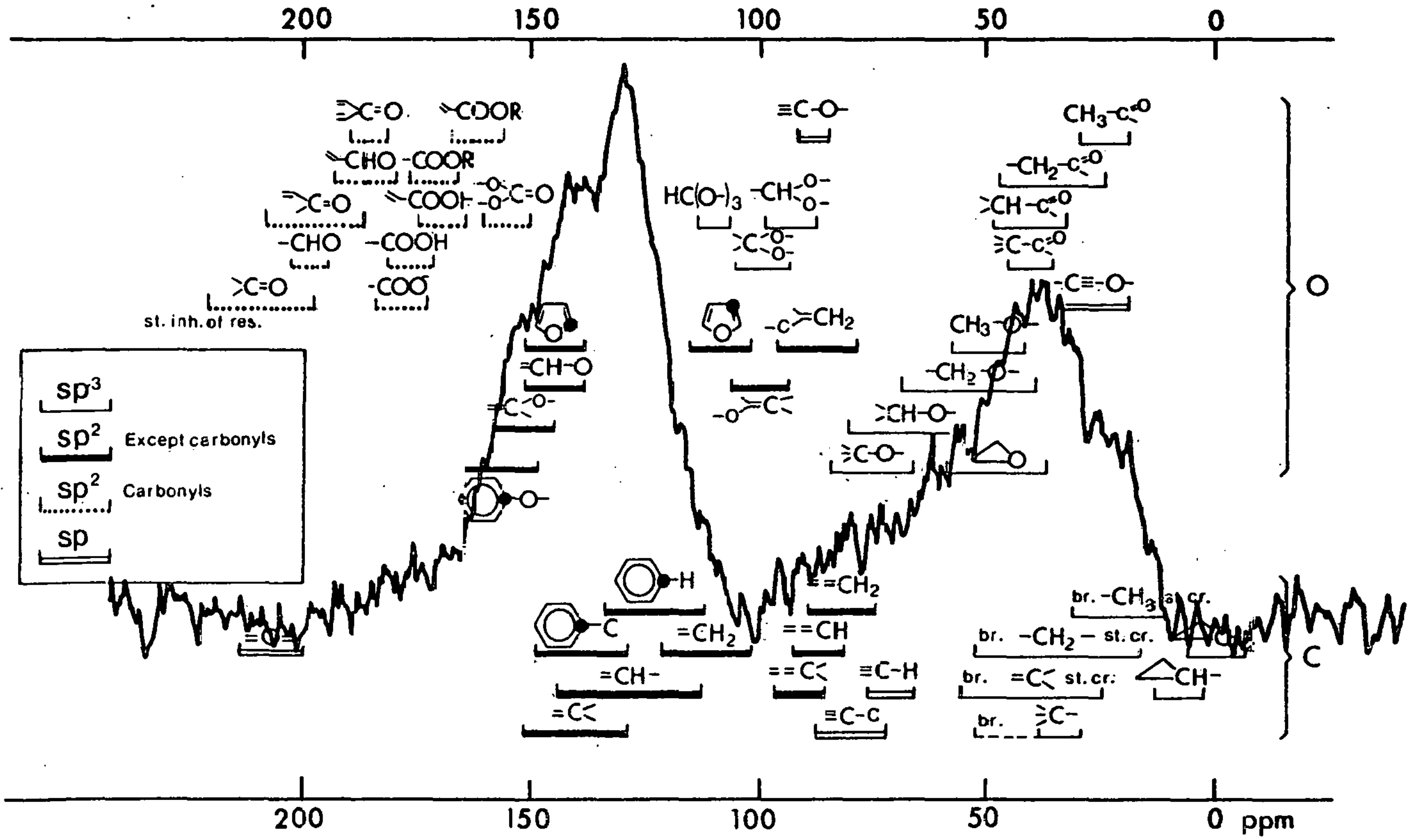

Figure 8. COMPOSITE OF ^{13}C NMR CORRELATION CHART AND SPECTRUM OF PSMC–67

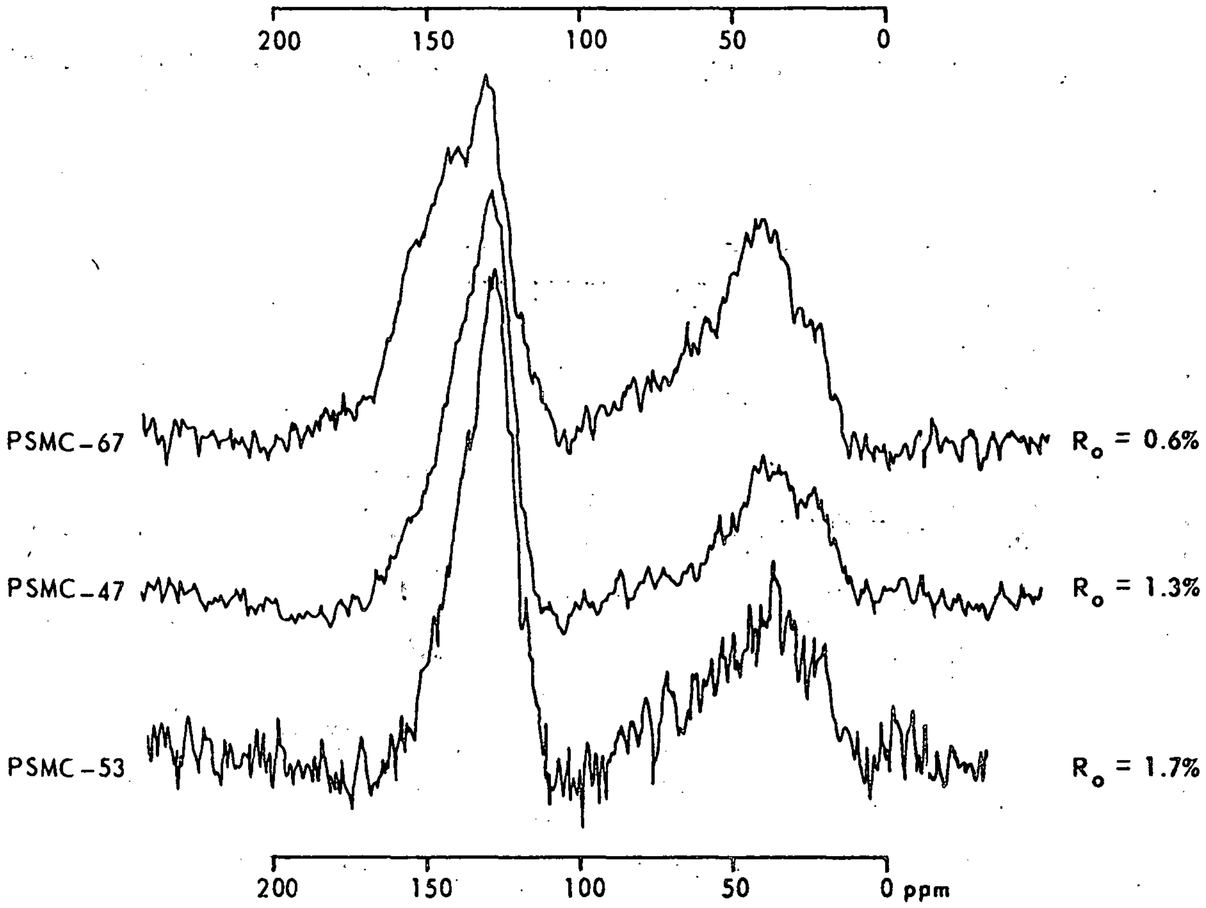

Figure 9. CP/MAS SPECTRA OF VITRINITES
The spectra represent the changes that occur with rank progression.

cyclic ethers (furans), and α-carbons in phenols and phenolic ethers. Hence, decreasing relative intensity in these spectral regions suggests loss of aromatic oxygen structural units and possible ring dealkylation.

The six sample series studied exhibited progression from a highly functional aromatic structure to one that displays little functionality. The aromatic band in PSMC-53 spans a chemical shift range characterized primarily by simple aromatic and condensed aromatic ring systems with significantly less functionality than observed in lower rank samples in this series.

In the aliphatic region, subtle differences are observed in the 15-40 ppm range. However, the aliphatic oxygen region of the spectrum (50-95 ppm) exhibits little perceptible difference, being characterized by a broad featureless band in each case. A careful examination of the spectra of all six samples gives no indication of loss in oxygen functionality that is observed in the aromatic region. The rationale is not clear for the loss of aromatic oxygen with rank progression with no concomitant loss in aliphatic oxygen in this sample set. Similar data from sample sets from additional coals of different rank, geological age and coal province, are needed to help interpret these observations.

Another highly interesting observation was made in this sample set. The f_a values (percent of observed aromatic carbon to total observed carbon) did not cover the range expected. In fact, little variation in f_a values was observed (0.67 - 0.72). While most workers in the field agree that paramagnetic centers (stable free radicals and paramagnetic materials in the mineral matter) will cause sufficient line broadening to prevent observation of carbons in the vicinity of such centers, it is generally assumed that such centers are randomly distributed through the coal structure and, hence, a representative structural framework is observed. Another possible source of error is lack of linear response by all carbons present. In the case of bridgehead carbons that are far removed from protons, spectral distortions could occur which would lead to low values of f_a. If one were to progress from a highly protonated aromatic ring structure to a highly condensed ring structure, a bias in the line intensities in the aromatic region may occur. If such were the case, the measured f_a values may not increase as rapidly as one might expect. This matter is the subject of investigation at the University of Utah.

(R.J.P., A.D. and J.T.S.)

9. SURFACE AREA AND DENSITY DETERMINATIONS ON COALS AND MACERALS

The work on measurement of surface areas from CO_2 uptake at 25°C, particle (mercury) and helium densities of various maceral and coal samples has been carried out as outlined in the previous quarterly technical progress report (DOE-30013-2).

Two fractions, -20 and -100 mesh, of five vitrinite concentrates were selected for measuring CO_2 uptake at 25°C. The surface areas and micropore volumes were calculated and the results are presented in Table 8. As was seen in case of coal samples (see DOE-30013-2), micropore volumes and surface area increase with decreasing particle size in case of all the vitrinites. It seems that on grinding to smaller size the closed porosity is opened up for increasing CO_2 uptake. Also the smaller particle size offers a shorter diffusion distance and equilibrium is established more rapidly (28).

The particle and helium densities of five vitrinite concentrates and one coal were determined following the procedure described in previous reports. The results for -20 mesh fractions are given in Table 9. Helium, being the smallest possible sorbate, should penetrate a porous solid to the greatest extent. That is, it exhibits the largest accessible pore volume. The total open pore volume accessible to helium was calculated from the following relationship,

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (10)$$

To obtain meaningful mercury densities of coals and macerals, it is important to determine the pressure at which the interparticle voids are filled and the mercury penetration plots show a sharp break. Gan <u>et al</u>. (29) have shown that the interparticle voids are filled at 60 psi <u>in</u> case of a 40 x 70 mesh fraction of coal. The size of the voids between the particles also vary with coal particle size. In smaller particle sizes, smaller voids exist, and, therefore, higher pressures are needed to fill the interparticle void volume. The size fraction studied by Gan <u>et al</u>., however, did not represent the whole sample. In the present study, the particle densities were estimated at 50 psi pressure. These densities obtained for samples PSMC-73, -77, and -78 appear low. It may be necessary, in these cases, to determine particle density at higher pressures. Such factors are being looked into and measurements on smaller fractions of coals and other maceral samples are currently under way.

The pycnometric densities are being measured with small pycnometer bottles (2 ml and 5 ml) for improving precision while using small weights of coals and macerals. The procedure adopted was described in the last quarterly technical report. Density of SP1-graphite in methanol was determined using different weights of graphite and a methanol density of 0.7914 g/cc (30). The results for an equilibrium time of 2 hr are given in Table 10. It is seen that the effect of weight of graphite on the density determined is insignificant. The measured values lie very close to 2.268 g/cc, the true density of graphite. The effect of extended equilibrium time on the densities of graphite, coals and vitrinite concentrates also is being studied.

The gravimetric estimations on the uptake of methanol on coals and macerals is also under way. The results of this investigation will be presented in the next quarterly report.

Conclusions

1. The micropore surface areas and pore volumes, determined from CO_2 uptake at 25°C, for vitrinite concentrates increase with decreasing particle size.

2. On using smaller pycnometer bottles, it is observed that density of graphite is independent of the weight taken for the estimation.

Table 8. Micropore Surface Areas and Pore Volumes of Macerals from CO_2 Uptake

Sample Description	Rank	Surface Area, m^2/g -20 Mesh	Surface Area, m^2/g -100 Mesh	Pore Volume, cc/g -20 Mesh	Pore Volume, cc/g -100 Mesh
PSMC-64	hvBb	183	203	0.052	0.058
PSMC-71	mvb	165	203	0.047	0.058
PSMC-73	?hvCb	190	211	0.054	0.060
PSMC-77	?hvCb	163	184	0.046	0.052
PSMC-78	?hvCb	167	224	0.048	0.064

Table 9. Total Open Pore Volume of Macerals and a Coal from Mercury and Helium Densities (-20 Mesh)

Sample Description	Rank	Particle Density (ρ_{Hg}) g/cc	Helium Density (ρ_{He}) g/cc	Total Open Pore Volume (V_T) cc/g
PSMC-21	mvb	1.306	1.442	0.072
PSMC-44	mvb	1.252	1.329	0.046
PSMC-73	?hvCb	1.037	1.220	0.145
PSMC-77	?hvCb	1.043	1.266	0.169
PSMC-78	?hvCb	1.087	1.252	0.121
PSOC-1141	hvAb	1.313	1.442	0.068

Table 10. Density of Graphite in Methanol

Weight of Graphite (g)	Density (g/cc)
0.2067	2.265
0.5175	2.265
0.8341	2.269
1.3195	2.262

CONCLUSIONS

1. Nitric acid extraction of pyrite in the determination of pyritic sulfur leaves only small amounts of unextracted iron in high volatile bituminous coals ground to 100 mesh. Consequently there should be a high degree of confidence in the ASTM standard procedure for pyritic sulfur (and hence organic sulfur by difference) for such coals.

2. The liquefaction conversions of 69 samples of the Lower Kittanning seam are highly rank related.

3. The temperatures of maximum fluidity and resolidification as measured by the Gieseler plastometer bear a strong statistical relationship to both rank and liquefaction conversion.

4. ^{13}C nmr aromaticities vary only slightly (f_a: .66-.72) for six vitrinite concentrates representing a fairly wide rank range (R_o: 0.6-1.7%).

5. This suite of vitrinite concentrate shows a progression from highly functional aromatic structures at low rank to one with little functionability at high rank. There is no concomitant loss in aliphatic oxygen.

6. The micropore surface areas and pore volumes of five vitrinite concentrates, determined from CO_2 uptake at 25°C, increase with decreasing particle size.

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