THE DIRECT DETERMINATION OF ORGANIC SULFUR IN RAW COALS

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INTRODUCTION

The sulfur content among coals varies to some degree in total quantity and in the forms present. Generally, the forms of sulfur in coals are the inorganic (sulfide and sulfate) and the organic (a complex mixture of organo types). The sulfate content is usually present in low amounts except in some instances where weathering has converted some of the pyrite to sulfate. The sulfide form can occur as the minerals pyrite and marcasite in a rough size range from 0.25 to 200 micrometers.

The organic sulfur in coals is intimately bound to the coal molecule and is difficult to determine directly when other forms are present. The organic sulfur content in most american coals range from about 0.5 to 3%.

A total sulfur analysis will give the information on whether present SO_2 emission standards will be met upon combustion of the candidate coal. If the total sulfur is too high, and stack gas cleaning is not available, some form of desulfurization is required before this energy source can be used. Cleaning processes can remove varying amounts of the inorganic forms, and some organic sulfur may also be extracted, but for all intents, the content of this latter form may be regarded as the lower level at which coal can be beneficiated. Therefore, the baseline level of organic sulfur is important to know so that economic and time effective inorganic sulfur extractions can be applied which in turn can comply with combustion standards.

Current ASTM methods provides for the direct analyses of the total, sulfate, and sulfide sulfurs. The accepted techniques for determining the sulfur forms in coals are the ASTM[1] standard wet methods. The total sulfur is determined by the Eschka method (D3177-75) and the sulfate and sulfide by selective acid leaches (D2492-68). The organic sulfur is then obtained from the difference of the total and the two inorganic forms since no reliable direct method is available. The possible accumulation of errors and the time required (~1 1/2 days) to obtain the organic sulfur by difference has made this approach undesirable but necessary.

The precision of the organic sulfur value obtainable from this approach was calculated from numerous analyses at BMI in conjunction with precision estimates of the respective ASTM methods. At two standard deviations (95 confidence level) the precision was found to be ±25%.

Instrumental methods also can be used to determine the inorganic forms and total sulfur for an estimation of the organic sulfur content. The two methods use X-ray analyses on pressed pellets of pulverized coal. In one, Hurley & White[2], use X-ray fluorescence to characterize for all of the sulfur forms by wavelength shift of the SK_β peak caused by variation in the sulfur bonding. The second[3] is discussed in an unpublished report on sulfur determination in coals, and utilizes X-ray fluorescence for total and sulfate sulfurs and X-ray diffraction for sulfide sulfur. Organic sulfur is obtained by the difference in the latter technique.

Both of the X-ray methods agree with corresponding wet chemical data on the same samples. The precisions of these instrumental methods therefore, are at least as good as the ASTM procedure but the time of analyses is reduced to several hours. A direct method for determining organic sulfur in coals was reported by Sutherland[4] using the electron microprobe on pressed pellets of coal.

A BMI supported program, therefore, was initiated to develop a direct and specific method for determining the organic sulfur content in coals and in the presence of the other sulfur forms. The approach taken entailed the low temperature reaction of ionized oxygen species with raw coals to yield volatile SO_x components which are the reaction products with the organic sulfur content of the coals. The SO_x products can be collected in a suitable trap maintained at low temperatures and subsequently analyzed.

Equipment

For this purpose, the instrument used for the oxidation of coals during this program was the LFE LTA 600L low temperature asher. The generator operates at a crystal controlled frequency of 13.56 MH_2 and has an output capable of delivering 300 watts of continuously variable power distributed among five separate reaction chambers. Normal ashing is carried out under continuous rough (300 l/m capacity) so as to maintain a pressure of 1 torr at an oxygen input flow of about 50 cc/min. The low temperature oxidation technique has been used to study the mineral matter content of coals. As indicated previously, the technique utilizes the oxidative properties of the reactive ionic and atomic species of oxygen which are produced when molecular oxygen is passed through a high frequency field. The ionized oxygen species are directed to the surface of the raw coal where selective oxidation of the organic content leaves the mineral matter relatively unaltered for study. The reaction produces volatile oxides of the total organic content. These products are CO, CO_2, H_2O, SO_x, and NO_x, and they are normally allowed to be discharged through the vacuum pump. The temperature of the coal surface reaction under these conditions can vary from 50 to 300°C depending primarily upon the power applied to the RF coils. Frazer et al[5] and Mitchell et al[6] used low temperature ashing of coals to study mineral stability under a variety of conditions. Although better stability of minerals were observed than that shown by the air oxidation method at 400°C, however, it was noted that pure pyrite could be oxidized at the high temperatures, 200-300°C.

To provide for the collection facility of the desired vapor species, the exit of one of the reaction chambers was rerouted to accommodate a glass trapping system. This modification is shown schematically in Figure 1. The all glass assembly, with ball joint connectors includes a stop cock (D), a trap (C) to collect the oxidized species and a connector at (E) to either evacuate during a run or to attach a gas bubbling trap for collecting the SO_2 at the end of a run. The remaining chambers were left entact so as not to interfere with the operation of the instrument.

Figure 2 shows the sample holder used for loading the sample for the oxidation run. Sample plate (A) is placed into the holder as shown after loading with coal. The sample holder containing the sample is inserted in the modified sample chamber. This overall arrangement provides ease of handling of the sample.

Reaction and Collection Procedure

A weighed sample is loaded into the sample holder onto a glass plate. The sample holder is inserted into the reaction chamber (A) through part B. The system is carefully evacuated to about 0.2 torr. As the oxidation of the coals progress, the temperature (-196 C) and pressure (1 torr) conditions permit trapping of the SO_2 and SO_3 gases as solids.

The generator is turned off after, upon visual examination, the samples appear to be completely oxidized. The oxidation time can vary from 1 to 3 hours. Helium is slowly admitted through stop cock (D) until the system can be opened to the air. A glass impinger bottle containing about 50 cc of 3% H_2O_2 solution is attached to (E). With a slow purge of He through the trap and impinger, the Dewar is removed to permit the transfer of the condensed SO_2 into the peroxide scrubber. The trap is then rinsed with a peroxide soltuion to collect the SO_3 component of the product. The two solutions are combined for sulfate analyses using the Dionex Mod 10 Ion Chromatograph.

Samples

The coals which were selected for this program were used as received except that they were ground to pass -200 mesh sieve (74 μm). Wet chemical sulfur analyses were obtained on these coals. In addition to a reproducibility study on one coal, several other coals of varying sulfur and ash contents were run to establish the suitability of this method to coals possessing varying chemical contents. The candidate coals are listed in the Table 1. along with their pertinent makeup.

The amount of coal samples taken for these runs were in the 20-30 milligram range. The resulting sulfur collections were expected to be of sufficient quantity to be determined by the analytical method to be used. Small charges were used in efforts to reduce the oxidation time to several hours. After the initial surface of coal is removed, the penetration of the ionized oxygen to the coal underlying the ash is time dependent. The possible errors introduced in the overall determination of organic sulfur due to macroscopic inhomogenieties accentuated by the small sample charges could be evaluated in the precision series.

TABLE 1. SAMPLES USED IN LOW TEMPERATURE OXIDATION STUDIES

Sample Coal	Sulfur, %				Ash, %	Moisture
	Total	Pyritic	Sulfate	Organic		
719-2 (Ohio)	6.3	1.58	2.74	1.9	14.2	3.5
719-3 (Ohio)	5.2	3.6	0.07	1.4	17.1	1.2
Hazard #4 (Kentucky)	1.52	0.66	0.04	0.82	12.8	1.1
Colstrip #2 (Western)	0.68	0.18	0.14	0.36	9.0	16.0
Beach Bottom #1 (W.Va.)	1.97	1.35	0.03	0.59	25.1	1.7
Organic Compounds						
Dithiopropionic	17.7	0	0	17.7	0	-
2-Thiophene Carboxylic Acid	24.7	0	0	24.7	0	-

The pure organosulfur compounds shown were also run since the results would represent ideal recovery experiments in the absence of interfering mineral forms. The sample charges used for these runs were in the 5-10 milligram range.

A study was also made of the stability of FeS_2 under the ashing conditions for coal. Oxidation of this compound yields volatile SO_2 which would be indistinguishable from that derived from the organic sulfur in coal. In addition, the pure FeS_2 was also mixed with other components to assess their affect upon its conversion. These materials include pure SiO_2, graphite, ash, and coal.

EXPERIMENTAL RESULTS

Oxidation Study of FeS_2

It was first necessary to establish conditions which prevented or reduced considerably the oxidation of pyrite to yield SO_x. The experimental conditions which were varied for the FeS_2 study included applied power to the plasma, oxygen flow, position of samples in relation to the plasma, particle size of FeS_2, and mixtures of various materials with pure FeS_2. For the runs with only FeS_2, it appears that the conversion to Fe_2O_3 and volatile SO_2 occurs under any condition. However, the severity of conversion increases directly with the applied power and inversely with particle size. The position of the sample in the chamber and the rate of oxygen flow used has minimal, if any, affect upon the oxidation of FeS_2.

The runs made using mixtures of FeS_2 with the listed additives produced mixed results. It was found that by adding graphite, SiO_2, or an organic sulfur compound to pure FeS_2 did not prevent the FeS_2 reaction with oxygen. However, admixtures with coal or fly ash appears to prevent FeS_2 oxidation. The reason for the apparent inhibition of the reaction is not known but seems to be associated with characteristics of the ash other than SiO_2. The presence of the natural ash in coals accelerates the reaction of the organic phase with the plasma. In samples containing no ash, such as graphite or an organosulfur compound, the reaction with ionized oxygen is slower.

Coal Studies

Coals were oxidized using the optimum instrumental conditions as determined to be suitable for the pyrite studies. These were found to be (1) applied power of 150 watts overall (30 watts/chamber); (2) oxygen flow at 30 cc/min; (3) and a pressure of 1 torr. The sample charge of about 25 milligrams was used. The collected sulfates were determined on a Dionex Model No. 10 Ion Chromatograph.

Using the above conditions for a coal (719-2), a series of ten runs supplied a measure of the repeatability of this technique for the organic sulfur recovery in one coal. These recovery data and precision are shown in Table 2. The ratio of the obtained/expected values allow for the calculation of the relative standard deviation of 19% at the 95% confidence level. This is slightly better than that achievable by the indirect ASTM method.

The repeatability data shown in Table 2 includes a wide range of variables. These include (1) possible inhomogeneity of small coal charges, (2) ability to duplicate reaction and collection techniques, (3) analyses of sulfate solutions, and (4) runs extended over a period of several weeks.

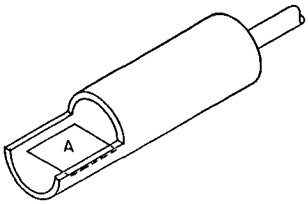

FIGURE 2. SAMPLE PLATE AND HOLDER INSERT

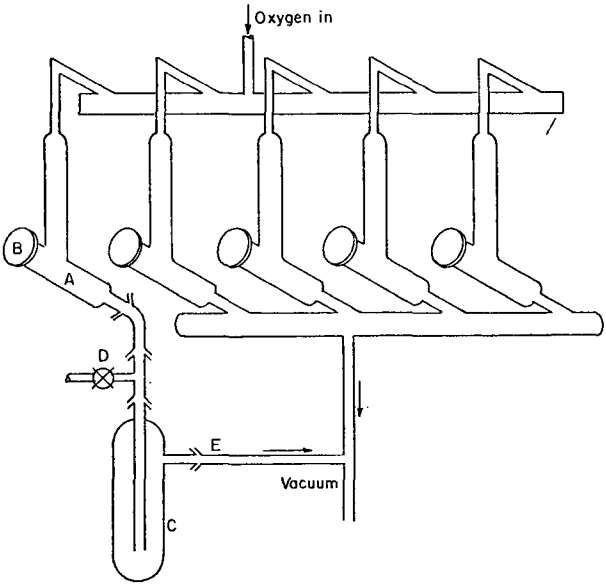

FIGURE 1. SCHEMATIC OF LOW-TEMPERATURE ASHER SHOWING MODIFIED REACTION CHAMER AND GAS FLOWS

TABLE 2. REPEATABILITY RUNS OF THE ANALYSES OF ORGANIC SULFUR FROM OXIDATION OF 719-2 COAL

Net Organic Sulfur, micrograms Expected	Obtained	Ratio Obtained/Expected
440	450	1.023
405	410	1.012
420	475	1.131
420	360	0.861
380	360	0.949
430	450	1.047
440	440	1.00
415	380	0.916
430	350	0.814
Mean		0.971
% SD (95%)		19.0

The second study involving coal 719-2 was to oxidize for SO_x recovery after spiking with quantities of FeS_2 in a particle size range of <37 μm. The sulfide was premixed with coal at about the 12% level so that the charge to be oxidized was about 25 milligrams of coal and 3 milligrams of pure pyrite. The mix runs were similar to the coal-only runs for the overall procedure. Results of the coal-FeS_2 runs are shown in Table 3. The relative standard deviation at the 95% confidence level is seen to be 17%.

TABLE 3. ANALYSES OF ORGANIC SULFUR FROM OXIDATION OF 719-2 COAL SPIKED WITH PURE FeS_2

Organic Sulfur, micrograms Expected	Obtained	Ratio Obtained/Expected
350	330	0.943
345	350	1.014
370	440	1.190
300	320	1.07
Mean		1.054
% SD (95%)		17.0

The third major experiment involved the repeatability of this technique when applied to a wide range of coals. The basis for selection included a variation in total, pyritic, and organic sulfurs as well as the ash content. The coals used for these runs are listed in Table 1.

The four coals were run in triplicate using similar procedure conditions as the two previous studies with coal 719-2. The results on the four coals are shown in Table 4. One run (colstrip) appears to be out of line, but the other ratio data seem to be well within the errors associated with either the ASTM or this direct method. The results show that this direct (oxidation)

method does provide a reasonable estimate of the organic sulfur content in a variety of coals.

Theoretical recoveries of S in pure organic compounds were the 90-95% range. The melting points of the two organo sulfur components are near the temperatures achieved during the oxidations. It is uncertain what, if any, affect this has on full recoveries.

TABLE 4. APPLICATION OF THE OXIDATION TECHNIQUE TO VARIOUS COALS

	Organic Sulfur, micrograms			General Constituent
	Expected	Obtained	Ratio	Range
Colstrip #2	77	123	1.6	Low pyrite, OS, Ash
	75	85	1.1	
	70	80	1.1	
Hazard #4	220	173	0.79	Medium pyrite, OS, Ash
	185	173	0.94	
	200	100	0.95	
Coshocton 719-3	330	300	0.91	High pyrite and OS, medium ash
	330	313	0.95	
	325	340	1.05	
Beach Bottom #1	180	195	1.1	High pyrite and ash, medium OS
	185	210	1.1	
	170	190	1.1	

Discussion of Problems

Other oxidized products of coals were condensed at the liquid nitrogen temperatures. Although no attempts were made to analyze the full contents of the condensed material, small amounts of ozone were present in most runs. Accidental leaks in the system during a run appears to deplete not only the ozone, but also the condensed SO_2. The resulting NO_x apparently reacts with SO_2 to form a NO-SO complex which makes it unavailable for the analytical method used.

The condensed SO_2 is reasonably stable at the trap temperature and pressure used to carry out the oxidation. The calculated loss through vaporization is about 40 nanograms per hour.

Other SO_x collection techniques were tried in efforts to simplify its recovery for analysis. One attempt included the possible catalytic conversion of SO_2 to SO_3 for its lower temperature collection. Poisoning of the platinum surface occurred about half way through the run to make this approach unsuccessful. The second attempt involved placing a NaOH-laden quartz wool plug in the rear of the holder insert. This appears to be very effective in capturing the SO_x vapor. However, to be effective the plug should be slightly moist, and this introduces some vacuum problems which have not been studied too thoroughly.

Predeposition of SO_3 (probably as H_2SO_3 or H_2SO_4) on the walls of glass system can occur at high SO_x concentrations. The deposition on the glass surfaces was very much in evidence in the investigations with pure FeS_2. Blank levels were found after coal runs.

CONCLUSIONS

Based upon the experimental work carried out on this program, a direct method for determining the organic sulfur content in coals has been developed. The procedure makes use of the relative ease of oxidation of the organically bound component of coals with ionized plasma of oxygen to yield volatile oxidic species peculiar to the total organic makeup. The desired products are condensed at a low temperature for subsequent analysis.

The work reported herein has demonstrated that this technique is specific for the organic sulfur content of coals within the error of the overall procedure. Repeatability runs on one coal (719-2) has produced relative standard deviations better than those obtained for organic sulfur using the different methods of ASTM. Similar precision was obtained from the same coal even when spiked with comparatively large quantities of pure FeS_2 in the particle size range of <37 μm. No sacrifice in the recovery amounts of the expected organic sulfur in the coal were indicated in these spiked runs. Successful application of this technique to other coals of varying constituents has provided some measure of the ruggedness and confidence of this approach. Also the repeatability runs indicate that the use of the 25 milligram sample charge is justified. Any error which may arise from the inhomogeneous distribution of organic sulfur in the use of small charges appears to be minimal or within the experimental precision of the method.

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OXYGEN DETERMINATION AND STOICHIOMETRY OF SOME COALS

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INTRODUCTION

Chemical coal analysis is divided into two categories -- the Proximate and the Ultimate. In the Proximate Analysis one determines and reports "Moisture", "Ash", "Volatile Matter", and "Fixed Carbon". In the Ultimate coal analysis one actually determines the concentration of hydrogen, carbon, nitrogen and sulfur, reports in weight percent and estimates a quantity called "Oxygen by Difference" by subtracting the sum of the above elements plus the "Ash" from hundred. (1,2, 3,4,5)

In addition, (1,2,3) the coal chemist distinguishes and attempts to determine three types of sulfur in coal (the sulfate sulfur, the pyrite sulfur, and the organic sulfur), and also tries to determine, or, at least, estimate, the Mineral Matter as originally present in coal. Chlorine, as well as several trace elements, especially those that can affect the environment (Hg, Cd, Pb, As, Se, Zn, etc.) are often also sought.

When we examine the nature of coal analysis reporting, we notice that in the Proximate category only the term "Moisture" may be equated with a chemically defined composition, namely, that of water. However, should this "Moisture" contain hydrocarbons or nitrogen volatilized at the drying temperature, then a simple weight loss method would not be sufficient to give chemically meaningful values. Thus we must describe and treat this "Moisture" (when so determined) as "weight loss" after drying in an oven at a given temperature for a certain time.

The quantity called "Ash" or "High Temperature Ash" (HTA) constitutes the total weight of incombustible residue derived from the inorganic mineral matter through dehydration, decomposition, oxidation and alteration caused by high temperature ($\sim 900^{o}C$) ignition of the coal in air. It is then a mixture of a heterogeneous character and is of an indeterminate and varying composition which is in some way related to the original bulk of minerals in coal. Subtracting the Total Ash in the Ultimate Coal Analysis in order to estimate the "Oxygen by Difference" introduces, therefore, indeterminate errors into otherwise stoichiometrically quite acceptable procedure of subtracting a sum of determined major elements from hundred in order to estimate the completeness of the analysis and assuming that the difference should be oxygen. One should also bear in mind that any method based on calculation by difference results in reflection of all errors in such a value.

From the standpoint of oxygen stoichiometry, the other two quantities of the Proximate Coal Analysis -- the "Volatile Matter" and the "Fixed Carbon" are of little importance because the first gives the bulk volatilized matter minus "Moisture"; the second is derived by subtracting the sum of the other three quantities ("Moisture" + "Ash" + "Volatile Matter") from hundred.

In order to attempt to quantitize the coal analysis further, we need thus a direct determination of oxygen, and once we have data for total oxygen, we must attempt to restructure the recalculation of coal analysis into a stoichiometrically more meaningful form. When this is done, the Material Balances of coal analyses should become more meaningful to the chemist and the engineer. The inadequacies of the chemical coal analysis recalculations and of the attempts to derive

from these stoichiometric data, as well as the need for a direct oxygen determination have been long recognized. We quote W. H. Ode of the U. S. Bureau of Mines (1963)(6): "The disadvantage of such an indirect method is that all of the errors of the other determinations are placed on the oxygen, and a Material Balance (emphasis ours) cannot be obtained to aid in checking the accuracy of the Ultimate Analysis".

Once a direct determination of oxygen is made, the coal analyst has to reconsider the standardized methods (3,4) of reporting and calculation of coal analysis. For example, the comparison of "oxygen determined" to "oxygen calculated by difference", using the standard methods, can be meaningless as Given (1975) has rightly pointed out (p. 9)(5) referring to the work of Hamrin, et al (1975) who have used a fast-neutron activation method similar, but not identical to ours to determine oxygen in Kentucky No. 9 coal (7). (See work by James, et al (1976)(16), Chyi, et al (18) and Block and Dams (17)).

We have suggested in 1974(8) the use of the ultra accurate fast-neutron activation method in coal analysis. Such method was first developed by Volborth and Banta in 1963 (9) for the analysis of rocks, lunar samples, and industrial materials (10,11,12). We have further perfected and adapted this method to the analysis of coal ash (13), coal (14), and the computerized recalculation of Material Balances (15) of six subbituminous Wyoming coals. This paper discusses specific problems we have encountered and presents new data on a wide variety of coals submitted by the Pennsylvania State University (Dr. Alan Davis) from the well characterized collection from an ERDA supported, computerized data bank (5) and some by the Illinois State Geological Survey (Dr. Harold J. Gluskoter and Dr. Rodney R. Ruch). We also utilize the data on the subbituminous coals from Wyoming (15) described earlier.

EXPERIMENTAL

The method used has been described in detail elsewhere (8,9,10,11,12,14). It consists of 20 seconds irradiation and 20 seconds counting of two samples, a standard and the unknown, simultaneously. A special feature of our system is the alternate switching of samples into opposite transfer channels to correct for electronic drift and bias. The nuclear reaction $^{16}O(n,p)^{16}N$ and counting of the resulting 6.1 and 7.1 MeV gammas with a half life of 7.3 seconds are used. The coal samples are packed into plastic containers (rabbits) and are sealed. Moisture at 105°C is determined on all samples, and the addition or loss of weight occurring while the samples are being packed is also determined by keeping a small sample exposed to ambient conditions for the duration of exposure. Some dried coal powders are very hygroscopic, gaining from 0.2 to .6% in weight during the 10 to 15 minutes of the packing procedure. Oxygen is determined on homogenized just opened "as received" samples on which moisture is determined in our laboratory at the time of packing. Oxygen is also determined on the dried samples (105°C). The precision of this method is ±0.2% (absolute) or better. A simple computer program computes the oxygen percentage in "as received" and in dried samples taking the determined moisture as H_2O into account. These data are input into a larger computer program which uses also data provided by the laboratory submitting the samples. These include the data of the Proximate and the Ultimate Coal Analysis. This program recalculates, using the ASTM Standard formulas (1,2,3), the coal analyses data based on our "Moisture", and gives the corresponding data on "Dry" and "Dry-Ash-Free" (DAF) basis. The result is four columns of analytical data on a coal sample, including the source data recalculated to our Moisture basis (See Table 1). The printout includes "Oxygen by Difference" calculated in each column and Oxygen Determined on "As Received" sample as well as on sample dried at 105°C. The determined oxygen is recalculated based on the total coal analysis data so that it can be compared in each column with the corresponding oxygen based on other methods of reporting of coal analyses.

The experiment is so designed as to permit the chemist to detect and estimate the minimum extent of oxidation of the coal in air during the Moisture determination at 105°C. This is done by comparison of determined versus back-calculated data on both samples in "As Received" and "Dry" columns.

Assuming that no other losses than water and no oxidation occur, the determined oxygen in the "Dry" column should closely correspond to the calculated based on oxygen determined in the "As Received" sample. If the oxygen in the mineral matter or, if unavailable, of the ash has been also determined or estimated properly and the analyses of C, H, S, N and Cl are accurate, a good sum should then be an indication of completeness of such a coal analysis. Higher oxygen determined in dry sample than that calculated based on "As Received" column should indicate oxidation or evolution of non-oxygen bearing gases (retention of more oxygen than was assumed). These processes could also balance out so that while no apparent weight loss occurs, oxidation and evolution of N_2, CO_2, CH_4, C_2H_6 etc. has taken place. The correctness of the assumption that all moisture is water can thus be checked only approximately for each coal as analyzed. It must be understood that oxidation of coal parallel with a water loss would tend to result in too low values for "Moisture" and depletion of the system of that quantity of hydrogen associated with H_2O. Low reporting of "Moisture" does also result in too high calculated values for C, H, S, and N, and, therefore, in too low "Oxygen by Difference" values causing too high summations if oxygen content is determined independently. All of these effects have a tendency to increase the oxygen content in the dried coal. Thus in most coals, one would expect an increase in determined oxygen in oven dried samples.

Decreases of oxygen content in dried coal (after the weight loss has been accounted for as water) could be due to removal of surface oxygen and replacement of it by nitrogen or coal-derived methane, for example. This effect should be mostly negligible, especially since most coal would tendto oxidize at least somewhat during heating in air, masking this phenomenon.

RESULTS AND CONCLUSIONS

Thirty-three coals ranging in rank from Lignite to Bituminous coals and including subbituminous, high volatile, medium volatile and low volatile bituminous coals were analyzed and their analyses recalculated in the manner described above.

To illustrate the behaviour of these coals upon drying, the deviations between oxygen in "Dried" versus "As Received" samples were plotted in Figure 1.

Compared on DAF basis, seventeen (17) of these coals show oxygen content higher when determined in the oven dried coal (105°C) than that recalculated to this basis from oxygen determined on "As Received" (by us) coal. In twelve (12) coals no change within the precision limits of ±0.3% absolute could be observed and in four (4) coals oxygen contents lower than the precision limit were detected. Thus only about 12% of all coals analyzed showed effects of some process that may be called reduction, whereas 52% of all coals analyzed showed detectable oxidation and about 36% showed insignificant changes undectable by our method. This confirms the predicted behaviour in the last paragraphs of the previous chapter. Oxygen loss in the dried coal at 105°C is unlikely because most of the processes that can occur concurrently would tend to oxidize or increase the oxygen content if the gases evolved do not contain or contain less oxygen than the water as assumed. Only molecular oxygen if driven off the surface would cause a decrease of overall oxygen in the dried coal. It is clear that there is a positive bias in this comparison as seen in Figure 1 and that it is not dependent on the rank of coal.

A typical recalculation of two coal analyses derived from computer printouts is given in Table 1. The first analysis is of a High Volatile A Bituminous Coal

TABLE 1

OXYGEN DETERMINATION BY FAST NEUTRON ACTIVATION ANALYSIS IN COALS
RECALCULATED ANALYSES

PROXIMATE ANALYSIS	HVA BITUMINOUS COAL, WEST VIRGINIA, PSOC-121			LIGNITE, TEXAS, PSOC-140		
	AS REC'D	DRY	DAF	AS REC'D	DRY	DAF
% MOISTURE	1.29 ±0.1*			33.96 ±0.1*		
% ASH	2.52	2.55		6.10	9.37	
% VOLATILE	37.89	38.38	39.39	29.59	44.81	49.45
% FIXED CARBON	58.31	59.07	60.61	30.26	45.82	50.55
SUMMATIONS	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS						
% HYDROGEN	5.65 *1	5.57	5.72	6.91*1	4.71	5.20
% CARBON	81.16	82.22	84.37	42.95	65.01	71.72
% NITROGEN	1.72	1.75	1.79	0.75	1.14	1.26
% ORGANIC SULFUR	0.93	0.94	0.97	0.43	0.65	0.71
% OTHER SULFUR	0.27	0.27	0.00	0.21	0.32	0.00
% OXYGEN (BY DIFF)	(7.75)	(6.69)	(7.15)	(42.58)	(18.80)	(21.10)
% O (BY FNAA) AS IS	9.18 ± .04*	8.14	7.15 *2	47.34 ± .15*	26.01	23.95 *2
% O (BY FNAA) DRIED	9.17 *4	8.13 ± .07*	7.14	48.03 *4	27.06 ± .13*	25.10
SUM INC. FNAAO (AS IS)	99.03	99.02	100.13	98.59	97.87	102.88
SUM INC. FNAAO (DRIED)	99.02	99.01	100.12	99.28	98.91	104.03
% CATIONS, ETC, AS ASH	1.36 *3	1.38	0.00	3.34 *3	5.06	0.00
SUMMATION (AS IS)	100.15	100.15		101.55	102.35	
SUMMATION (DRIED)	100.14	100.14		102.24	103.39	

* DETERMINED BY US. *1 INCLUDES H FROM MOISTURE *2 EXCLUDES ESTIMATED OXYGEN IN ASH

*3 ESTIMATED AS 54% OF ASH CONTENT *4 BASED ON MOISTURE CONTENT

TABLE 2

DIFFERENCES BETWEEN OXYGEN BY DIFFERENCE AS REPORTED IN CLASSICAL COAL ANALYSIS AND OXYGEN DETERMINED BY NA AND OXYGEN RECALCULATED, ASSUMING ASH CONTAINED 46% O

COAL NO.	%O DIFF AS REPORTED U.S.B.M. "AS RECEIVED"	O DETD NA	O DIFF CALC (ASH 46% O)	% ASH
K-46566	36.6	42.34	44.34	7.70
K-46218	32.3	35.90	37.82	5.50
K-46217	31.7	36.15	37.89	6.20
K-46216	33.2	36.85	38.13	4.90
K-46565	38.8	43.28	44.19	5.40

from the Tioga Seam, Tioga No. 1 Mine, Nicholas County, West Virginia (PSOC-121). In this analysis the moisture determined in our laboratory (1.29%) is within .2% of the moisture reported (1.52%) in the Source Data (Pennstate University), the Ash is low (2.52%) and most of the sulfur is organic. Both these factors assure that the errors due to the fact that ash is not mineral matter will be small. Indeed, this analysis balances well, the oxygen based on direct determination in coal "As Received" by us as well as oxygen determined on dried coal at 105°C corresponds closely. Thus we can say that this coal does not oxidize perceptibly during drying in air and that the moisture is probably all water (H_2O). Having not analyzed the ash, we estimate that it contained 46% oxygen, as shown by us (13) for U.S. coals and by Block and Dams (17) for some European coals. Thus it must contain 54% cations including sulfur and chlorine, and we add this amount to the summations which are first derived by adding the determined C, H, N, S, and total O% (determined by FNAA). The good second summation shows that in this coal our assumptions and approximations were justified.

The second compilation is of a Lignite from the Darco Mine, Harrison County, Texas, PSOC-140. Determined moisture (33.96%) compares closely with that reported by Pennstate (33.39%). The oxygen determined in the dried coal (105°C), however, is 1.05% (absolute) higher than would be expected based on recalculated oxygen based on oxygen determined in the "As Received" coal. This indicates considerable oxidation and possibly evolution of gases containing less oxygen than water. This coal contains relatively little pyrite sulfur (.21%) and only 6.2% ash, so that the estimated 54% cations plus sulfur plus chlorine may be used to approximately balance the analysis when the determined oxygen values are summed up in the DAF column. Since we know that this coal has oxidized by addition of approximately 1.05% O (absolute), we can assume that the "Moisture" loss should have been reported higher by at least that amount. Assuming that all other determinations were done correctly, the use of the too low Moisture value would result especially in proportionally too high calculated value for C, H, N, and S, and thus too low values for O by Difference, which seems to be the case. This can be seen by comparison with the determined oxygen in "as received" coal calculated to DAF basis. When this oxygen value is used in the summation, one may approximately estimate whether the state of the complete coal analysis as reported is satisfactory. In this case, a bulk error of roughly about 3% is indicated. It can be due to a combination of interrelated factors, which can be a cause for erroneous moisture determination, each to a different degree. These are: a) oxidation during moisture determination; b) evolution of gases other than H_2O containing none or less oxygen than water (N_2, CO, CO_2, CH_4, C_2H_6, etc.); c) calculation errors based on faulty moisture determination which may cause a dilution effect especially on the major components, such as the carbon value, for example; d) analytical errors and bias; e) the fact that ash is not mineral matter and that pyrite sulfur should be counted as pyrite, FeS_2, as Given has pointed out (5)(pp. 31-33).

The treatment of the coal analyses described above raises several critical questions, of which only the most important can be discussed here. A few assumptions have been made above which strictly speaking are not true, and once one attempts to quantitize the coal analysis, then why not proceed logically by removing all approximations and report on a stoichiometric basis?

It turns out that this cannot be done in one step without demolishing a century-old convention due to the complex nature of computations of the classical coal analysis. The basic reason for the way a coal analysis is computed today is the variable nature of the coal substance and the inability of the coal chemist to procure a rapid and inexpensive oxygen analysis within the Ultimate Analysis Family. This situation has resulted in efforts to somehow bypass this dearth of information and turn out computations which would approximate the true chemical stoichiometric balances in the composition of coal as closely as possible. In short, the coal chemist has accepted the value for "Ash" as representative of the

mineral matter in the "As Received", the "Dry" and the derivation of the "DAF" columns. Also, in the calculation of the "Oxygen by Difference", the whole Ash is customarily deducted from hundred. Obviously, by definition, one cannot equate this quantity with oxygen determined directly and a quick comparison in Table 2 shows that such correlation can lead to gross errors and misunderstanding. Nevertheless, inadvertently such comparisons are often made especially in industry. This is presently the rule, and worse, when "Oxygen by Difference" is used to plot such ratios as H/C versus O/C (19,20) where by implication and the use of the chemical symbol, a very misleading picture is given.

In Table 2 we have compiled "Oxygen by Difference" data as reported by the U.S. Bureau of Mines on "As Received" basis (first column) with oxygen determined by FNAA on samples as received by us and back-calculated based on our moisture data (second column) with oxygen by difference calculated in our computer program assuming that the ash contained 46% O (third column) and subtracting only the oxygen of the ash. While comparison of the conventional "Oxygen by Difference" with oxygen determined makes little sense, this column shows improvement in terms of comparison of oxygen by difference so calculated with the determined oxygen. We seem to be thus on the right path, and able to see whether the overall assumptions were correct.

The ash portion of coals varies from a few percent to about 20 percent and more. To correct for the inadequacy of reporting and subtracting as such, Parr in 1932 (21) has proposed to estimate the Mineral Matter by the formula: % Mineral Matter = 1.08 x % Ash in Coal + 0.55% Sulfur in coal, where the factor 1.08 is the empirically derived value for water of hydration of the minerals usually found in ash.

Based on similar consideration, King, et al in 1936 (22) have derived a more accurate Mineral Matter (MM) calculation formula: % MM = 1.09 x % Ash + 0.5 x % Pyritic S in Coal + 0.8 CO_2 in Coal - 1.1 x % SO_3 in Ash + % SO_3 in Coal + 0.5 x % Cl in Coal.

These formulas have been derived from accurate stoichiometric relations considering decomposition of hydrated minerals, oxidation and formation of Fe_2O_3 from FeS_2, etc. The stoichiometry and accuracy of Mineral Matter Evaluation can be further improved by reconstituting the main minerals based on the analysis of ash. These are kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and pyrite, FeS_2, as shown by Rees (2).

The fourth column of Table 2 compares the ash contents of the coals. In our stepwise approach to the stoichiometric interpretation of coal analysis, we have found improvement if we estimate the composition of the ash. Obviously this is only an approximation and, as pointed out by Given (5), one should better use the DAF column where the influence of the mineral matter content, sulfur, and ash is further minimized. One could assume according to Parr (21) that mineral matter contains about 8% H_2O, or 9% according to King, et al (22), in which case our calculated oxygen by difference should become somewhat lower because oxygen of the water of hydration in the mineral matter should also be subtracted. Indeed, in all our cases, we obtained a better agreement with determined oxygen if this is done. All of these coals have a relatively low ash content, but nevertheless, the overall effect is about .5% less Oxygen. Taking sulfur in ash into account should further improve the agreement. Thus in many coals one may need only a recalculation of ash according to the mineral matter formulas to check stoichiometry and balance the summations. Oxygen determination gives us thus important information in characterizing coals. It may help to point out rapidly any unusual mineral composition or oxidative behaviour. Coals, where oxygen by difference value calculated by subtracting not the whole ash but only the corresponding quantity of oxygen calculated by the Parr formula agrees closely with oxygen determined, where summations balance out, may be regarded as sufficiently characterized. In

pyrite-sulfur-rich coals and coals with carbonates or unusual components, the more complex formula by King, et al (22) may be used. Where neither of these formulas produce a good balance, more detailed chemical work is indicated. As pointed out by us before, oxygen analysis in coal ash characterizes also the mineral matter and gives useful information on the total of all other constituents including S, Cl, etc., in ash (13).

Considerable effort has thus been spent to interpret the ash and from it the mineral matter portion of coal. One may ask why spend so much effort to evaluate a relatively minor segment of coal analysis in order to achieve stoichiometry as long as a major constituent -- oxygen -- remains undetermined. Obviously the coal chemists have done everything in order to approach true stoichiometry and be able to interpret the chemistry of coal and report the analyses in as balanced a form as possible.

We propose, therefore, that adding direct oxygen determination to coal analysis as we have done, and furthermore, determining the oxygen content in ash should bring us closer to the true stoichiometric interpretation of coal analysis. From the computer printouts of the 33 coals we have analyzed for oxygen, we can see that a single oxygen determination in a coal "As Received" quite accurately characterizes the coal as to rank, and that once the normal carbon to oxygen ratios are established for a wide variety of coals, major deviations, due to high pyrite-sulfur content or unusual mineralogy can be easily spotted (see Figure 2). This plot was obtained from the 33 recalculated coal analyses.

We distinguish stages or steps of progressively more correct approach to stoichiometric quantitation and recalculation of coal analysis. The first step is to analyze the "As Received" and "Oven Dried" coal at 105°C for oxygen and to estimate the oxygen in Ash based on former work (13,17), which shows that in a great variety of normal coals, oxygen in ash varies between 44 and 48 weight percent. In 29 calculated analyses out of a total of 33 plotted, this assumption is indeed meaningful. Reasonably good summations and balances are so obtained (see Figure 1 and Table 3), except for coals with 2 to 8% S.

Secondly, When an actual oxygen analysis on ash corresponding to the coal analyzed is performed, the data should balance somewhat better. Any unusual deviations in the oxygen content of the high temperatue ash would then be a signal necessitating closer scrutiny and checks of the type of mineral matter. This approach provides a better approximation, giving us more information because actual accurate oxygen determination in coal ash furnishes us with an exact sum of the cations plus sulfur and chlorine in that ash. This means that better and more meaningful summations will result. This work is in progress.

Thirdly, to proceed further toward yet better stoichiometric balance, one can either calculate the mineral matter by the Parr formula (21), or better, by the King (22) formula as stated above. For this, however, one needs to determine total sulfur in coal in the first case, and an analysis for pyrite sulfur, CO_2, Cl, and SO_3 in coal, and SO_3 in ash and, if the content of kaolinite, pyrite and SiO_2 is to be calculated, also an analysis of ash for Al_2O_3, SiO_2, and S.

Because such a chemical approach is time consuming, and not entirely satisfactory, one may for our purposes better determine the Mineral Matter by preparing the so-called Low Temperature Ash (LTA) from the coal as proposed by Gluskoter in 1965 (23) and used by O'Gorman and Walker in 1971 (24) and further refined by Fraser and Belcher in 1972 (25) and Kinson and Belcher in 1975 (26). This method consists of radio frequency ashing of coal at temperatures of 100° to 150°C and appears to give results which are perhaps the closest approximation to the true Mineral Matter in coal on "As Received" or "Dry" basis. Mineralogy of LTA ash has been recently (1976) studied by Mitchell and Gluskoter (27). An analysis of oxygen

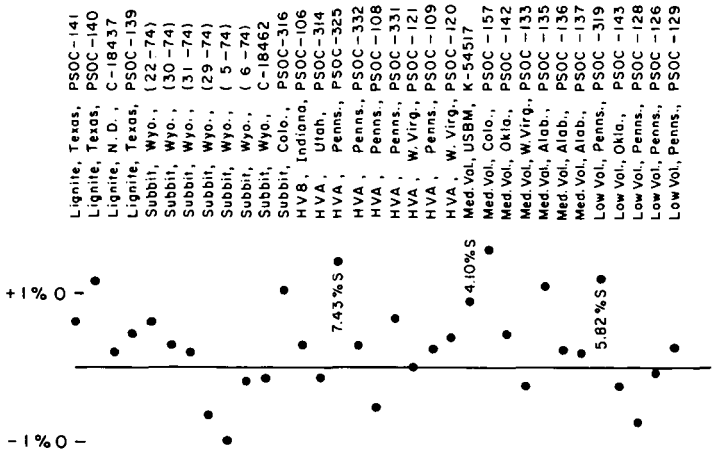

FIGURE 1. PLOT SHOWING INCREASES AND DECREASES OF OXYGEN IN 33 COALS WHEN DRYING AT 105°C. % O DRY COAL MINUS % O AS RECEIVED COAL. NOTE SULFUR-RICH SAMPLES.

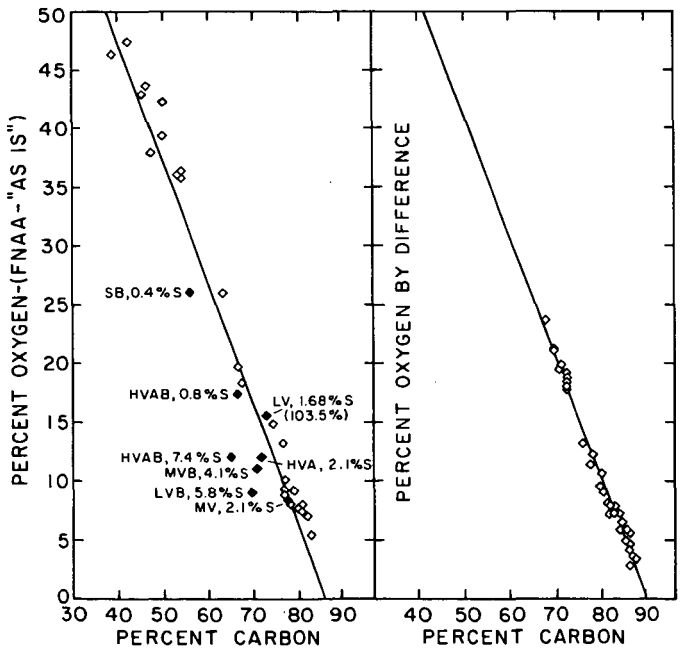

FIGURE 2. D/C PLOT OF 33 COALS ON "AS RECEIVED" BASIS USING OXYGEN VALUES DETERMINED BY FNAA, AND "BY DIFF".

in Low Temperature Ash has been performed by us on two samples (13), however, so far we have not been able to obtain the corresponding coals. In sulfide rich coals, since pyrite is not oxidized during LTA procedure, the large error caused in the Oxygen by Difference estimation in all columns for the coals PSOC-325, PSOC-319, K-54517, in Table 3, would be minimized, if oxygen were determined directly in LTA ash. A similar approach has been taken by Hamrin, et al in 1975 (7). Assuming that the minerals in coal are not destroyed by radio frequency heating, this approach if combined with oxygen analysis in coal on "As Received" and "Oven Dried" basis as done by us may be the best way of determining the true "Organic Oxygen" in coal. We are now installing the necessary equipment in order to be able to further investigate this question.

Given and Yarzab (pp. 31-33) (5) have in 1976 emphasized the inadequacy of the ASTM Standard D 3180 reporting in sulfur-and mineral-matter-rich coals and propose the use of the British Standard 1016 Part 16 corrected procedure which distinguishes organic sulfur and recalculates the percentage of pyrite in mineral matter based on the pyrite sulfur. This is a better approach stoichiometrically as can be seen from the comparison of data given by these authors (ibid p.32). We have used at this stage the ASTM Method (see Table 3) which reports the total sulfur subtracting it from hundred on the "Dry" basis. We find that the "Oxygen by Difference" value if calculated by the British Standard Method adopted by the Pennsylvania State University agrees indeed much better with our determined values for oxygen. Therefore, where data on the type of sulfur were available, we have distinguished organic sulfur and included it in the DAF column, but have excluded the sulfate and pyrite sulfur in coal. We realize that even this approach is not fully satisfactory and intend to introduce the exact procedure recommended by Given.

In Table 3 we have compiled our data based on Pennstate data on DAF basis. Twenty-five analyses of coals not reported by us elsewhere are given. The coals are plotted in sequence based on increasing Fixed Carbon content. To save space, information on Moisture as originally reported, and as determined by us, as well as the percent Ash as reported on "As Received" basis are given in parentheses under Proximate Analysis, but do not figure in summations. These data permit the reader familiar with coal analysis and classification to make meaningful comparisons. The varying ash content is also an important criterion of accuracy expected in comparison of "oxygen by difference" with actual "oxygen determined", especially in sulfur-rich coals. In the Ultimate Analysis columns "Other Sulfur" when available is given also in parentheses, but not summed, because, as one can see in coals PSOC-325, K-54517, PSOC-137 and PSOC-319, our method permits one to estimate the approximate sulfur content based on summations. Note the retention of sulfur in carbonate-rich coal's ash (13).

It can be seen that "oxygen by difference" on DAF basis agrees reasonably well with determined oxygen in all coals that do not contain sulfur. Coals with high ash content but low sulfur also tend to balance reasonably well (see PSOC-106). Low ash coals in general give better summations (as expected) than high ash coals. The presence of high sulfur masks the effect of high ash and causes low summations if oxygen is determined. Good agreement between "oxygen by difference" and determined oxygen for "As Received" and "Dried" coal seems to indicate a well balanced analysis and minimal oxidation effects upon drying. Differences in the two determined oxygen categories tend to be mostly due to oxidation and evolution of other gases than H_2O, and, therefore, also point toward an erroneous Moisture determination due to the canceling effect of oxidation when based on weight loss.

The data on sulfur-rich coals seem to indicate that much of the sulfur, even though reported as "other" or "sulfide" sulfur is in some way bound to the coal molecule with the sulfur replacing oxygen. A part of the "inorganic sulfur" appears to compete for oxygen sites in coal in some way because all sulfur-rich coals analyzed show relatively much lower determined oxygen concentration in the

TABLE 3

OXYGEN DETERMINATION BY FAST NEUTRON ACTIVATION ANALYSIS (FNAA) IN COALS

RECALCULATED ANALYSES

PROXIMATE ANALYSIS	C18457	PSOC-139	C18462	PSOC-141	PSOC-314	PSOC-325	PSOC-316	PSOC-108	PSOC-332
% MOISTURE(SOURCE)	(6.80)	(30.29)	(5.90)	(33.16)	(4.08)	(2.86)	(12.12)	(1.41)	(5.65)
% MOISTURE(DETD)	(7.98)	(21.06)	(5.48)	(22.14)	(4.07)	(1.30)	(12.88)	(1.62)	(3.81)
% ASH	(9.40)	(10.70)	(9.56)	(6.03)	(9.63)	(15.76)	(4.55)	(9.37)	(13.08)
% VOLATILE	51.07	50.89	50.39	49.15	47.91	44.68	40.97	41.31	41.45
% FIXED CARBON	48.93	49.11	49.56	50.85	52.09	55.32	59.03	58.69	58.55
SUMMATIONS	100.00	100.00	99.95	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS									
% HYDROGEN	5.11	5.59	5.42	5.25	6.11	5.64	5.52	5.57	5.86
% CARBON	69.56	72.29	72.66	71.70	80.25	80.72	78.56	82.90	82.37
% NITROGEN	0.93	1.30	1.50	1.35	1.63	1.41	2.30	1.22	1.61
% ORGANIC SULFUR	0.79	0.76	1.02	0.74	0.66	0.00	0.48	1.21	0.71
% OTHER SULFUR	(0.20)	(0.08)	(0.40)	(0.10)	(0.16)	(7.43)	(0.07)	(2.08)	(0.83)
% OXYGEN (BY DIFF)	(23.62)	(20.03)	(19.40)	(20.97)	(11.35)	(12.23)	(13.14)	(9.10)	(9.45)
% O (BY FNAA)AS IS	25.17	19.61	21.13	23.19	11.87	4.29	15.04	7.09	9.49
% O (BY FNAA)DRIED	25.04	22.09	20.97	23.83	11.73	5.82	16.08	6.55	9.78
SUM INCL FNAAO(AS IS)	101.55	99.58	101.73	102.24	100.53	92.07	101.90	98.05	100.04
SUM INCL FNAAO(DRIED)	101.32	102.06	101.57	102.88	100.39	93.59	102.94	97.52	100.33

PROXIMATE ANALYSIS	PSOC-106	PSOC-331	PSOC-109	PSOC-120	K-54517	PSOC-157	PSOC-137	PSOC-135
% MOISTURE(SOURCE)	(6.40)	(5.31)	(1.88)	(1.93)	(2.30)	(1.41)	(0.71)	(0.71)
% MOISTURE(DETD)	(3.60)	(4.31)	(1.72)	(1.46)	(1.53)	(5.01)	(1.74)	(0.81)
% ASH	(13.46)	(4.78)	(5.05)	(5.89)	(13.60)	(6.63)	(7.00)	(4.92)
% VOLATILE	39.91	39.87	37.85	34.01	28.66	26.63	26.43	24.85
% FIXED CARBON	60.09	60.13	62.15	65.99	71.34	73.37	73.57	75.15
SUMMATIONS	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS								
% HYDROGEN	5.52	5.62	5.50	5.12	5.04	5.18	4.82	4.93
% CARBON	82.76	83.97	84.62	85.44	85.73	89.11	86.97	88.39
% NITROGEN	0.55	1.62	1.39	1.54	1.43	2.36	1.53	0.75
% ORGANIC SULFUR	0.54	0.75	0.58	0.69	0.00	0.53	0.81	0.59
% OTHER SULFUR	(0.12)	(0.07)	(0.09)	(0.03)	(4.10)	(0.06)	(2.07)	(0.05)
% OXYGEN (BY DIFF)	(10.64)	(8.04)	(7.90)	(7.21)	(7.80)	(2.82)	(5.87)	(5.84)
% O (BY FNAA)AS IS	12.24	9.69	9.99	6.62	3.99	1.64	4.15	2.38
% O (BY FNAA) DRIED	12.55	10.34	10.24	7.04	4.88	3.23	4.35	6.47
SUM INCL FNAAO(AS IS)	101.60	101.64	102.15	99.50	96.20	98.82	98.30	99.60
SUM INCL FNAAO(DRIED)	101.91	102.30	102.40	99.92	97.08	100.42	98.50	100.70

PROXIMATE ANALYSIS	PSOC-136	PSOC-142	PSOC-133	PSOC-319	PSOC-143	PSOC-128	PSOC-126	PSOC-129
% MOISTURE(SOURCE)	(0.63)	(0.94)	(0.76)	(1.85)	(0.88)	(1.24)	(0.64)	(1.67)
% MOISTURE(DETD)	(0.75)	(1.28)	(0.69)	(1.36)	(0.94)	(0.80)	(0.99)	(1.33)
% ASH	(2.40)	(10.08)	(6.05)	(15.90)	(8.74)	(13.40)	(6.97)	(6.23)
% VOLATILE	24.75	23.22	22.90	22.01	21.73	21.06	20.02	19.82
% FIXED CARBON	75.25	76.78	77.10	77.99	78.27	78.94	79.98	80.18
SUMMATIONS	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS								
% HYDROGEN	4.65	4.46	4.38	4.57	4.74	4.72	4.79	5.01
% CARBON	88.06	89.04	90.51	86.49	88.95	87.23	89.15	89.86
% NITROGEN	1.74	0.20	1.06	1.62	1.49	1.09	0.92	1.01
% ORGANIC SULFUR	0.58	0.70	0.60	0.10	0.63	0.45	0.48	0.45
% OTHER SULFUR	(0.02)	(0.42)	(0.02)	(5.82)	(0.07)	(1.68)	(0.65)	(0.31)
% OXYGEN(BY DIFF)	(4.97)	(5.60)	(3.44)	(7.22)	(4.19)	(6.51)	(4.65)	(3.68)
% O(BY FNAA)AS IS	3.79	4.05	3.86	0.52	3.63	10.04	4.01	3.68
% O(BY FNAA)DRIED	4.02	4.51	3.50	1.70	3.37	9.29	3.84	3.95
SUM INCL FNAAO(AS IS)	98.82	98.47	100.43	93.30	99.46	103.54	99.40	100.02
SUM INCL FNAAO(DRIED)	99.05	98.92	100.07	94.48	99.20	102.79	99.23	100.29

DAF column than other normal coals. Thus, our method when further developed may help to evaluate the role of "Organic Oxygen" and "Organic Sulfur" in coal. We have started recalculations based on the Parr formula and the King formula to simulate the mineral matter closer in order to correct the DAF column for the effect of the additional oxygen associated with the hydrated portion of minerals. Such correction increases the proportion of C and N, and decreases somewhat the oxygen by difference values (as well as hydrogen). When this is done, more accurate "Sulfur by Difference" values can then be estimated from summations in Table 3. Thus, accurate oxygen determination permits us to estimate approximately the total sulfur when other components routinely determined in coal analysis are known. Oxygen determination in ash also aids in this case substantially, because if it is lower than the regular content (46 ± 2% O) considerable sulfur or heavy constituents in ash may be indicated.

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NEUTRON-GAMMA TECHNIQUES FOR ON-STREAM ANALYSIS OF COAL

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Rapid analysis of coal is required during buying and selling and for process control of coal preparation plants, coal-burning power stations and coal conversion plants. Modern process control is concerned not only with optimization of process parameters but also with minimization of environmental pollution. The components whose determination is most often needed are calorific value, total ash, moisture content and sulfur content. Other important components include ash fusibility, boiler fouling index, ash electrical conductivity, and nitrogen, chlorine and alkali metals contents.

Process control requires that the analytical result be available within the response time of the process being controlled. For the bulk solids considered here, such times are usually in the range 5 to 50 minutes. Thus, any analysis method, however rapid, is ruled out if it requires sampling and sample preparation times longer than this. Neutron-gamma techniques are non-destructive, non-contact, instrumental methods for elemental analysis of solids and liquids. They are unique in that the analyzed sample volume can be of the order of 30 cm cube. This is because the mean free paths of the incident neutrons and excited characteristic gamma rays in solids and liquids have that order of magnitude. Coal samples of these dimensions can have maximum particle sizes of up to 1 to 2 cm and still be "representative". Therefore sample preparation, if necessary at all, need only take a few minutes. In addition, the methods are amenable to continuous analysis of moving material. Thus even larger amounts of coal can be scanned during a given measurement time with consequent improvement of "sampling statistics".

Since these methods are specific to elements, satisfactory correlation must be assumed or proved between the desired components and the elements determined. Obviously there is no problem with elemental components such as sulfur, nitrogen and chlorine. Calorific value is well correlated with carbon and hydrogen content.[1] Ash content is correlated with the concentrations of the ash-forming elements, the major ones of which are Al and Si.[2] Ash fusibility is correlated with the basicity ratio which is a function of the basic and acidic oxides of the ash-forming elements (Al_2O_3, SiO_2, CaO, Na_2O, K_2O and to a lesser extent MgO and FeO_x). Moisture is correlated with hydrogen as long as the C/H ratio of the particular coal remains constant.

Early investigations of neutron-gamma methods concluded that, for most key analyses, a neutron generator had to be used as the source and this was not considered practical for plant conditions.[3,4] Consequently an on-stream coal-ash monitor based on X-ray backscattering, and using a small, sealed radioisotope X-ray source, was developed[3] and has been in commercial use for about 10 years. However, the X-ray method is limited to total ash monitoring and the coal must be sampled, dried and crushed to less than about 5 mm particle size before analysis. The availability in 1967 of Cf-252 sealed radioisotope neutron sources rekindled interest in neutron-gamma methods and an on-stream sulfur monitor[5] and moisture meter[6] have now been developed to plant prototype stage. Other feasibility studies for multielement coal analysis have been conducted[7-10] but, to our knowledge, they have each been restricted to consideration of a single neutron-gamma method and have not been able to demonstrate feasibility for analysis of more than a few of the vital elements necessary for proper on-stream analysis of coal.

The studies reported in this paper show that it is possible to determine essentially all of the major and minor elements in coal necessary for process control by not restricting oneself to a single neutron-gamma technique. Furthermore, the optimum nuclear reaction for each element can then be chosen, so reducing the demands

on the gamma-ray detector and electronics. This in turn makes possible the use of the simplest and most practicable instrumentation for reliable plant operation.

NEUTRON-GAMMA METHODS AND INSTRUMENTATION

Methods

In neutron-gamma methods of analysis neutrons from a suitable source bombard the sample, exciting nuclear transitions. Excited nuclear states decay at once with emission of "prompt" gamma rays whose energies are characteristic of the excited nucleus and whose intensities are proportional to source strength, element concentration and spectrometer efficiency, as in other methods of spectral analysis. If the sample and source are separated, the prompt gamma-ray emission stops but "delayed" or "activation" gamma emission is usually still present. The intensity of the activation gamma rays is, as before, proportional to element concentration but also falls off exponentially with time according to the half-life of the product nucleus. The incident neutrons can have any energy from several MeV ("fast" neutrons) to less than 0.1 eV ("thermal" neutrons). Fast neutrons excite several useful reactions and thermal neutrons excite several others. So in practice we can speak of four types of neutron-gamma analysis: (1) fast neutron-prompt gamma; (2) fast neutron activation; (3) thermal neutron-prompt gamma; and (4) thermal neutron activation.

Although the cross sections for producing prompt gamma rays are relatively high, yielding large signals, their detection must take place in the presence of a high background from the nearby neutron source. The design of a practical prompt gamma-ray analysis system is, therefore, a compromise between high detector background and geometrical losses due to the bulky neutron and gamma-ray shielding required. The main advantage of neutron activation is that the source and sample can be separated, enabling the signal to be measured at low background. Activation gamma spectra are also less complex. The cross sections for activation gamma emission are generally lower than those for prompt gamma emission but the much lower background outweighs this, resulting in activation often being the preferred reaction if a choice exists. Table I lists the main characteristics of the preferred methods for analysis of the important elements in coal.

Instrumentation

A neutron-gamma analyzer consists essentially of a neutron source, a gamma-ray spectrometer and a sample presentation system. Instrumentation suitable for in-plant operation must be ruggedly constructed and packaged, and must be capable of operating reliably over long periods, unattended. It should, therefore, be as simple as possible, use solid state circuitry in preference to vacuum tubes, have the minimum number of moving parts, avoid vacuum systems and ultra-high voltages, and operate without the need for special supplies such as liquid nitrogen, cooling water and compressed air.

Three types of neutron source exist, nuclear reactors, neutron generator tubes and radioisotope sources. Radioisotope sources have advantages of small size, rugged, solid state construction and stability of output. However, their steady decay has to be corrected for and forces renewal after about two half-lives. Also they cannot be "turned off" and they provide a potential radioactive contamination hazard in the event of an accident. Since Cf-252 sources have withstood being dropped 20,000 feet down a borehole and fished out without developing radioactivity leaks, we feel that the combined probability of an accident plus serious contamination is very low. Since it will be shown that the required analyses can be performed using relatively low neutron outputs ($< 10^9$/sec) the need to "turn off" the sources doesn't arise. Only 1 or 2 feet of biological shielding is required for neutron sources of this strength and they can be handled for short periods without any shielding, using the proper tools. As for the radioactivity induced in the sample

TABLE 1

PREFERRED NUCLEAR REACTIONS FOR IMPORTANT ELEMENTS IN COAL

Element	Nuclear Reaction	Threshold Neutron Energy	Main Gamma Energies (MeV)	Half Life
Hydrogen	(n,γ)	Thermal	2.23	Prompt
Carbon	$(n,n'\gamma)$	4.8 MeV	4.43	Prompt
Nitrogen	(n,γ)	Thermal	10.83,10.32	Prompt
Sodium	$^{23}Na(n,p)^{23}Ne$	3.75 MeV	0.44	38 sec
	$^{23}Na(n,\gamma)^{24}Na$	Thermal	1.37,2.75	15.0 hrs
Aluminum	$^{27}Al(n,p)^{27}Mg$	1.9 MeV	0.84,1.01	9.5 min
	$^{27}Al(n,\gamma)^{28}Al$	Thermal	1.78	2.31 min
Silicon	$^{28}Si(n,p)^{28}Al$	3.96 MeV	1.78	2.31 min
	$(n,n'\gamma)$	1.9 MeV	1.78	Prompt
Sulfur	(n,γ)	Thermal	5.42	Prompt
Chlorine	(n,γ)	Thermal	6.11	Prompt
	$^{37}Cl(n,\gamma)^{Cl38}$	Thermal	1.64 and 2.17	37.3 min
Potassium	^{40}K	Natural Radioactivity	1.46	1.3×10^9 yr
Calcium	$^{48}Ca(n,\gamma)^{49}Ca$	Thermal	3.1	8.9 min
Titanium	$^{50}Ti(n,\gamma)^{51}Ti$	Thermal	0.32,0.93	5.8 min
Manganese	$^{55}Mn(n,\gamma)^{56}Mn$	Thermal	0.85,1.81,2.1	2.58 hrs
Iron	(n,γ)	Thermal	7.63	Prompt
	$(n,n'\gamma)$	0.86 MeV	0.84	Prompt

by neutron irradiation, it is both short-lived and completely negligible, being a few orders of magnitude lower than can be detected by a dose rate meter and of the same magnitude as natural K^{40} radioactivity. Two sources were used in the present study, a 38 Ci Pu^{238}-Be fast neutron source (half-life 86 yrs) and a moderated, 100 μg Cf^{252} thermal neutron source (half life 2.6 yrs).

The second major component of an analysis system is the gamma-ray spectrometer which consists essentially of an energy-dispersive gamma-ray detector, HV supply, pulse amplifiers, an analog-to-digital converter, and a multichannel analyzer with microcomputer for spectrum acquisition and data analysis. High resolution, liquid nitrogen cooled Ge(Li) gamma-ray detectors have been proposed for coal analysis and can resolve even the most crowded gamma spectra. However, these detectors are relatively easily and permanently damaged by neutron absorption or loss of cryogenic cooling. Also their gamma-ray detection efficiency is an order of magnitude lower than that of the more rugged NaI(Tl) detector and they cannot operate at count rates above about 10^4/sec without severe resolution degredation or signal losses due to dead time. Scintillation counters using NaI(Tl) crystals (or CsI(Na), CsI(Tl), CaF_2(Eu), etc.) do not require cooling or vacuum and are available in large sizes suitable for efficient gamma-ray detection. They can operate at count rates up to about 10^5/sec without special electronics (10^6/sec with special electronics). They are little affected by neutrons and the effects (induced radioactivity) are reversible and do not seriously hinder operation. The crystal-photomultiplier assembly must be temperature controlled to about $\pm$ 1°C and not subjected to thermal shock. The gamma-ray energy resolution (in the range 5 to 8%) is adequate to resolve most gamma energies of interest. All the experiments reported here were conducted with a NaI(Tl) detector and standard electronics, a schematic of which is shown in Figure 1. Figure 2 shows a schematic of one measuring head indicating the relative position of source, sample, detector and shielding. Figure 3 shows a photograph of a typical measuring head and the electronic system suitable for operating three such heads. A minimum of three heads would be required if all four neutron-gamma techniques were needed for a particular multielement analysis.

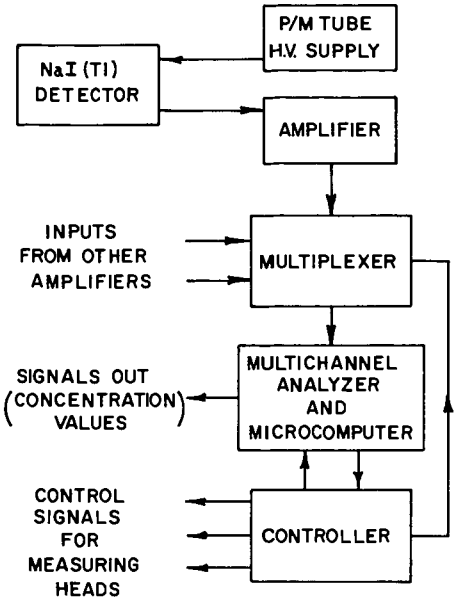

FIGURE 1 SIMPLIFIED ELECTRONIC SCHEMATIC

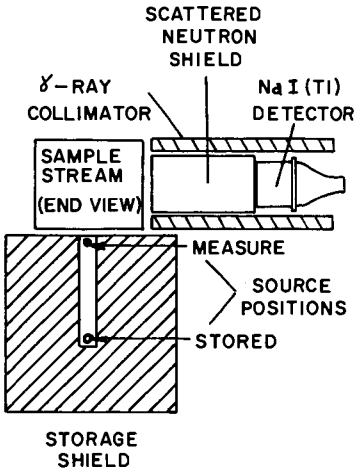

FIGURE 2 SCHEMATIC OF MEASURING HEAD

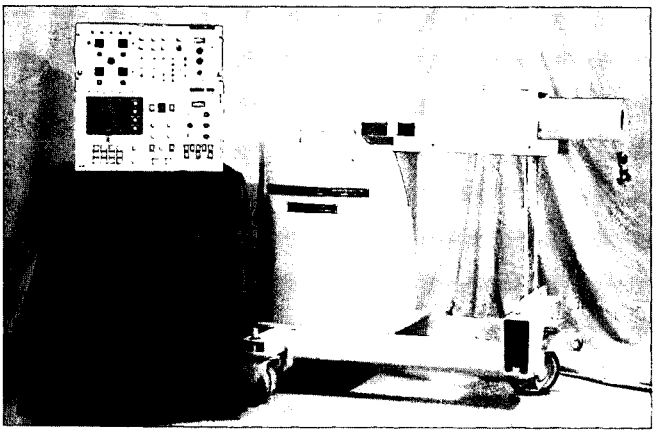

FIGURE 3 PHOTOGRAPH OF MEASURING HEAD AND ELECTRONIC SYSTEM

The sample presentation used in this study consisted of the manual placement of 20 Kg samples (in 28 in. dia. cylindrical holders). A continuous presentation system would consist of a means of transporting a stream of coal having well-defined dimensions (∿ 30 cm x ∿ 30 cm cross section) past the measuring heads at approximately 5 to 50 cm/sec. The coal stream could be enclosed suitably (e.g., in a sheet metal tunnel) since the incident neutrons and emitted gamma rays easily penetrate thin engineering materials. Representative sampling and splitting the primary plant streams to yield such an analytical stream is routine in coal engineering.[11]

EXPERIMENTAL RESULTS AND DISCUSSION

Sensitivity studies were made using simulated coal samples consisting of sugar spiked with (1) $MgO + SiO_2$, (2) $Fe_2O_3 + S$, (3) $Na_2SO_4 + Al_2O_3$, (4) $CaCO_3 + NH_4NO_3$. In addition unspiked sugar and a sample of -1/2 in. bituminous coal were examined. All the samples were measured using each of the four neutron-gamma methods. All the gamma-ray spectra obtained were relatively simple and comprised a few prominent, well-resolved peaks. Thus data analysis consisted simply of integrating each peak and subtracting background measured in a group of adjacent channels. Table II summarizes the results. The neutron-gamma method used in each case is listed along with the sensitivity obtained. Also, typical concentration ranges for these elements in U.S. coals are given. It is seen that the sensitivities obtained are adequate for all the elements tested.

TABLE II

PRELIMINARY RESULTS OF SIMULATED COAL ANALYSIS

Element	Concentration Range in U.S. Coals	Method Used	Gamma-Ray Energy (MeV)	Source	Measurement Time (sec)	Sensitivity (1 Std. Dev.)
H	∿ 5%	Thermal n. Prompt γ	2.23	Cf-252	500	0.01% H
C	65-75%	Fast n. Prompt γ	4.43	Pu-Be	500	0.2% C
N	∿ 2%	Thermal n. Prompt γ	10.32, 10.83	Cf-252	500	0.1% N
Na	0.01-0.2%	$Na^{23}(n,\gamma)Na^{24}$ Thermal n. act^n	2.75	Cf-252	300 + 300*	0.01% Na
Al	0.6-2.5%	$Al^{27}(n,\gamma)Al^{28}$ Thermal n. act^n	1.78	Cf-252	300 + 300*	0.003% Al
Si	1-6%	$Si^{28}(n,p)Al^{28}$ Fast n. act^n	1.78	Pu-Be	300 + 300*	0.05% Si
S	0.2-7%	Thermal n. Prompt γ	5.42	Cf-252	500	0.03% S
Ca	0.1-1.8%	$Ca^{48}(n,\gamma)Ca^{49}$ Thermal n. act^n	3.09	Cf-252	300 + 300*	0.1% Ca
Fe	0.4-3%	Thermal n. Prompt γ	7.63	Cf-252	500	0.1% Fe

Neutron-gamma techniques yield linear calibrations of gamma peak area vs element concentration from the detection limit to 100%. This and other work with the same equipment[12] showed that heterogeneity and matrix absorption effects, common in other instrumental analysis techniques, were negligible. One exception to this is thermal neutron absorption caused by increasing hydrogen content of the sample. The effect is proportional to the 2.23 MeV H peak area, and monitoring that peak can yield a satisfactory correction. Alternatively, it is possible to monitor the thermal neutron flux in the sample.

*Activation time plus counting time.

The only other interferences found were peak overlaps in the gamma-ray spectra. These are all readily resolved and present work is concentrated on finding the simplest methods to do this. We have shown that one such interference, between Al and Si, is resolved by using two neutron-gamma techniques. Al and Si activate to the same isotope, Al^{28}, so that neither gamma energy nor time resolution can be used to discriminate between the signals. The dual source technique(13) uses two separate irradiations, by different sources, of similar samples. In one case fast neutrons preferentially excite Si and in the second, thermal neutrons preferentially excite Al. Solution of a pair of simultaneous, linear equations provides accurate Al and Si concentrations. In other interferences, for example, Mn on Al, Si and Cl, Ca on Na, the interfering species emits other gamma rays with a fixed intensity ratio to the interfering one. Measurement of the intensity ratio, which is an instrumental constant, and the intensity of the resolved lines is a straightforward way to correct for this type of interference. A microprocessor-based calculator interfaced to the multichannel analyzer then provides a ready method for solving the linear equations and yielding concentration data suitable for direct digital readout and plant control.

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An ASTM Approach to the Standardization of New Techniques for Coal Analysis

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ASTM Committee D-5 on Coal and Coke is responsible for development of specifications for coal and for coke produced from coal; the development of methods of sampling, analysis, and testing; the development of specifications for classification of coals on the basis of chemical and physical characteristics; the standardization of terminology; and the promotion of research and dissemination of knowledge in these fields. The work of the committee is co-ordinated with other ASTM committees and other organizations having common interests.

The committee is made up of producers, users and those whose general interests are in coal as a resource and its utilization. The standards produced by the committee reflect this balance of membership. To ensure that standards are kept up-to-date in the opinion of those who use them, the Society dictates that all standards must be reviewed every five years and, if they are neither reapproved nor revised, they must be withdrawn as standards. To further ensure that modern standards are available when required, an ad hoc task group is appointed by the committee at regular intervals to study existing standards, to critically evaluate them in the light of current usage and to recommend the needed changes. The task group may also suggest the standardization of tests necessary to coal-conversion processes such as gasification and liquefaction.

ASTM Standards for coal and coke have never been static, nor are they considered to be the last word; they are, however, the best available at the time. Revisions to existing methods are made frequently within the five-year review period. All revisions other than those of an editorial nature must be approved by letter ballot of the committee before they are accepted.

Analytical procedures for coal and coke may be divided into two groups: those based on empirical methods developed in the early years of this century, and those based on stoichiometric chemical reactions. Empirical test methods, such as moisture, ash and volatile matter, were developed in the industry to fulfil a commercial need and finally they became standards. These tests remain much the same today as when they were adopted 60 or 70 years ago. Using these tests, a considerable bank of data has been accumulated, which can be compared with current analyses carried out by essentially the same methods.

On the other hand Standard methods based on stoichiometric reactions have progressed rapidly in the past 10 to 15 years. Ash analysis, i.e. mineral analysis of coal and coke ash for the ten major constituents, has progressed from the time-consuming wet chemical procedures, through a combination of wet chemical, flame-photometric, and spectrophotometric methods which resulted in the adoption of D 2795 in 1969. The latest editorial revision was in 1975. In the intervening time it was realized that better and less time-consuming methods were available and work is well advanced in developing an atomic-absorption procedure using a lithium tetra-borate fusion technique. The new method has good precision and can be carried out with relative speed. One of the major difficulties in this program has been the lack of standard reference samples for the major elements present in coal ash. Standard

Reference Materials for total sulfur in coal, mercury in coal and fly-ash and several other trace elements in coal and coal ash have been available for some time from the National Bureau of Standards. Steps are being taken to request NBS to prepare Standard Reference Materials for the major elements in coal and coal ash.

Concern with the environment and laws governing the levels of allowable pollution from the use of coal have prompted the standardization of analytical methods for the determination of these pollutants. Many analytical methods have been developed by governmental agencies and universities, using a wide range of techniques. The task of filtering out the best and most practical methods with reference to coal has fallen on Committee D-5. Many of the proposed methods require expensive and highly sophisticated instrumentation. We in ASTM feel that an acceptable standard method must be within the financial reach of those expected to use it. Very few laboratories have the capabilities of carrying out certain test methods because of the high cost of instrumentation. Atomic absorption spectrometry is now considered quite common on this continent, and is no longer considered exotic. The principles are well established and most laboratories have operating experience. On this assumption we feel justified in standardizing methods using this approach. We still have reservations when it comes to the standardization of methods based on X-ray fluorescence (XRF), neutron activation etc. There is no doubt that these methods will be acceptable in the near future as techniques improve and the costs come within the reach of commercial laboratories.

Many new techniques have been suggested for coal analysis; one is the micro-determination of carbon and hydrogen which has proven to be a valuable tool in research where the amount of sample may be limited to a few milligrams. The micro method requires that the sample weight be in the order of 10 milligrams. To extract a representative sample of that size from a laboratory sample of coal (-0.250mm, #60 U.S. Standard Sieve or even -0.074mm, #200 U.S. Standard Sieve) is difficult if not impossible. A semi-micro technique can probably be developed. However the Liebig method as described in D 3178 will suffice until a new method is developed.

A semi-micro method for the determination of nitrogen in coal is being studied at present. As this procedure is faster than the Kjeldahl method, requires less space and is less costly, it is likely to receive early acceptance as an alternative to D 3179.

Many methods have been proposed for the determination of sulfur in coal and coke, and to-date only a few have been found suitable for standardization. The basic method with which all methods are ultimately compared is the Eschka Method. The Bomb-washing and the High-temperature-combustion methods are acceptable alternatives. Combustion methods, using induction or glow-bar-heated furnaces to convert the sulfur compounds to SO_2 have been examined and found to be unsuitable as standard methods. It is reported that newer designs of this type of equipment are much more reliable. Experience indicates that frequent standardization against analysed standards is advisable.

Also with reference to sulfur determinations, improvements have been incorporated in the method of determining pyritic sulfur in coal. In the present method, D 2492 Forms of Sulfur, pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid followed by a titrametric determination of iron as a measure of pyritic sulfur. Appropriate corrections are made for non-pyritic iron.

As an alternative procedure the pyritic iron may be determined by atomic absorption.

Over the years D-5 has been presented with the problem of developing a standard to cover coal stockpile inventory which is of concern to utilities and other large users of coal. This task has been carried out for years by time-consuming

measurement of the pile to determine its volume as accurately as possible followed by an also-time-consuming sampling program to determine the average density of the coal at varying depths in the pile. From these measurements, which were rough at best, the tonnage was calculated. We have now been asked by CAPCO (Central Area Power Coordinating) Group, to co-operate in their program to develop a standard. This group, some of whose members are from D-5, are studying the feasibility of the use of a nuclear probe and scaler which would operate on the basis of gamma radiation and reflection to accomplish the required measurements. A second approach under consideration is the use of a radio-echo device. D-5 cannot participate directly in the development stages but will be interested in standardization when the necessary instrumentation is developed.

D-5 has an ash analysis standard, and a standard method for the preparation of ash. We have now been requested to develop a method for the preparation of an ash (fly-ash) which is non-standard, to simulate ash produced under pulverized fuel burning conditions. Ash produced under such conditions would be vastly different from that prepared under the standard conditions specified in D 2795, i.e. from room temperature to 500°C in one hour and 750°C in two hours, and finally ignited to constant weight at 750°C in a well-ventilated muffle furnace. Ash produced under the conditions prevailing in a pulverized fuel burning system would be subjected to much higher temperatures, thus causing the volatilization of elements such as sodium. It is also true that some of these volatile constituents may recombine to varying degrees, producing compounds not normally found in the standard ash. A group on the west coast has asked for our co-operation in this project, which will involve the ashing of a relatively large sample of coal under specific conditions. The specific conditions necessitate the use of a specially designed mini-furnace to burn the coal in a pulverized form to produce the simulated ash. The design and construction of the furnace will be undertaken by this group.

The group representing utilities and manufacturers of electrostatic precipitators require an ash prepared in this manner so that, when a chemical analysis, resistivity measurements and other tests are made, the data so obtained can be correlated with the ash (fly-ash) present in the stack from which they are attempting to remove the particulate emissions. An ash prepared by conventional standard methods does not meet these requirements.

Fuel calorimeters manufactured today are highly sophisticated as compared to those in use in the thirties. While thermometers may still be used to measure temperature-rise they have in many instances been made superfluous by the introduction of thermisters. Most modern adiabatic calorimeters have both, thermometers manufactured to ASTM standards and thermisters with digital read-out, and in some instances a print-out attachment is added. The use of this modern instrumentation, while not sanctioned by ASTM, is found to be very satisfactory in helping to eliminate the human element.

The manual operation of the cold - and hot-water valves in an adiabatic calorimeter has been superseded by automatic operation. This new instrumentation is good and exceedingly reliable.

The determination of volatile matter in coal and coke can now be carried out in duplicate, using equipment programmed to lower the crucibles into the furnaces at the required rate, to hold them there for a given time and then to withdraw them.

While many of the methods have remained basically the same for many years, automation has assisted the analyst to turn out more work with precision equal to or greater than that with the manual methods.

In conclusion it should be pointed out that D-5 is not against the use of new technology in the preparation of standards but, by the time the technology has been advanced and proven reliable, it is no longer new. To be considered worthy of standardization a new approach must be faster than the one it is to replace, must have equal or greater precision, and the equipment required must be within the reach of the laboratories who will be expected to use it.

Characterization of Liquids and Gases Obtained by Hydrogenating Lumps of Texas Lignite

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INTRODUCTION

The increased cost of natural gas and the high cost of fuel oil have increased the importance of Texas lignite as a potential source of chemicals and as a fuel for generating electricity. The lignite resource in Texas has been estimated (1) as 10 billion tons at depths less than 200 feet and 100 billion tons at depths of 200 to 5000 feet. The shallow basin lignite can be recovered by strip mining but the deep basin lignite will probably have to be recovered by *in situ* mining methods. *In situ* liquefaction and comminution have considerable potential for recovering deep basin lignite (2,3,4).

In order to evaluate the potential of underground liquefaction, autoclave experiments have been conducted at pressures of 500 to 5000 psi and temperatures of 650 to 800°F. The charge to the autoclave has been cylinderical cores, 1 1/2 inch in diameter and 3 to 5 inches long, hydrogen, helium and hydrogen donor solvents. In order to gain insight into the reaction mechanisms underlying the conversion process, the liquid and gas products have been analyzed by use of several methods. Generally, coal-derived liquids have been characterized after separating different species by use of solvents with different chemical affinities (5,6). Since the composition of the lignite derived fluids are less complex compared to other coal-derived liquids, an analytical procedure based on boiling points of the components is used.

EXPERIMENTAL

Three Gow-Mac gas chromatographs, Model 69-550, with thermal conductivity detectors were used for simultaneous analysis of gases and liquids. The oven temperatures were manually programmed. Commercially available helium is used as carrier gas. Helium is purified by passing it through molecular seive 5A (3 ft. X 1 1/2" O.D. stainless steel column) and through a high capacity purifier (Supelco Carrier Gas Purifier) to remove the traces of oxygen and water. The gas chromatographs accept only 1/4" columns with a maximum length of 10 ft. Samples were injected directly into the column to avoid the recovery loss in the injection port. The products from lignite liquefaction experiments, which were analysed by gas chromatography can be classified as follows: (a.) gases; (b.) low boiling point liquids (boils below 100°C); (c.) high boiling point liquids (boils above 100°C).

Porapak N was used for identifying methane, carbon dioxide, ethylene, ethane, hydrogen sulfide, propane, water, isobutane and *n*-butane. After an initial 1 min. hold at 25°C, a shotgun temperature program - 25°C to 140°C at a rate of 15 to 20°C per min. - was used to get excellent separations. Molecular Sieve 5A could separate hydrogen, carbon monoxide, oxygen and nitrogen from the gas samples at room temperature. Porapak S also gave a separation similar to Porapak N but did not separate propane and water under identical conditions. The thermal stability of Porapak S (max. temp. 250°C vs. 190°C for Porapak N) favored it as a choice for a few samples.

The low boiling liquids were separated on two Durapak columns. Durapak *n*-octane on poracil C is good for separating aliphatic components while Durapak OPN on poracil C separates the aromatic compounds. The sample is run on both columns simultaneously under identical conditions. A shotgun temperature program from 25 to 150°C gave

fairly good separation of the components.

The high boiling point liquids contain nonvilatile components as well as lignite fragments which may deposit on the columns. The samples were cleaned to get the desired boiling point range by using a fractional sublimator. The sublimator consists of two concentric glass tubes. The outer tube holds the sample and the inner tube contains a coolant, like liquid nitrogen or dry ice-acetone mixture. The space between the tubes is evacuated while the outer tube is heated by a jacket type furnace. The temperature of the furnace is controlled by a Thermolyne proportional temperature controller. The sample temperature is recorded on a strip chart recorder. The sample evaporates and deposits on the outside of the inner tube (liquid nitrogen cold finger). The sample temperature and the degree of vacuum controls the volatility of the fractions deposited.

The clean samples from the sublimator were analysed using five different 8 ft. columns with packings that can withstand column temperatures well above 300°C without appreciable bleeding. The column temperature was programmed from 80°C to 280°C at a rate of 1.5 to 2°C per minute. The same sample was analysed with different columns under identical conditions. A hydrocarbon standard of *n*-alkanes ranging from C_{10} to C_{36} along with pristane and phytane was used to qualitatively identify the boiling point range of the components separated on different columns.

Detailed analysis of the lignite derived products were done on GC-MS. The apparatus mainly consists of a Hewlett-Packard 5710A Gas Chromatograph. A 5980A Mass Spectrometer, a 5947A Multi Ion Detector and a 5933A Data System. The gas chromatograph is able to accept packed columns as well as glass capillary columns. A 30 ft. X 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP and a 30 M glass capillary coated with OV 101 were used for most of the GC-MS studies. OV 101 is a methylsilicone polymer similar to the SP 2100 used in the Gow-Mac gas chromatographs. The hydrocarbon standard was used to determine the boiling point range of the components as well as the fragmentation pattern of the *n*-alkane series.

The proton nmr spectra of the samples dissolved in $CDCl_3$ were taken on a Varian T-60 nmr spectrometer. JEOL PS-100-PFT was used for scanning C^{13} nmr spectra of samples in $CDCl_3$. Samples used for these studies were not sublimated. The samples, therefore, contained high molecular weight species as well as minute suspended particles.

RESULTS AND DISCUSSION

The gaseous products from different lignite liquefaction experiments were composed of the same components but the composition varied depending on the experimental conditions and the lignite sample cores used. The gaseous components were identified using known standards and simple chemical tests. Figure 1 is a typical gas chromatogram for the gas sample obtained during the hydrogenation of wet Texas lignite. Carbon dioxide is the major component. Hydrogen sulfide is present in an appreciable concentration. Once both carbon dioxide and hydrogen sulfide were removed from the gaseous mixture, the product has a composition comparable to commercial natural gas containing a series of low molecular weight hydrocarbons with methane in large proportion.

Texas lignite is a low grade coal (8000 BTU per pound) with a high oxygen content (up to 30% of dry weight) and about a medium level of sulfur residues (nearly 2% of dry weight). Most of the carbon dioxide represents a major portion of the chemically bound oxygen in lignite which may exist as carboxylic groups. Hydrogen sulfide could be liberated from the sulfhydryl groups (thiols, sulfides, disulfides and chelated sulfur residues) and elemental sulfur (at least a small fraction) in the lignite.

The lignite-derived liquid obtained in this work is less complex than the bituminous coal-derived liquid. The lignite-derived liquid was divided into low boiling liquid and high boiling liquid in order to use two Durapak columns which have an upper temperature limit of about 150°C for the separation of aromatic and aliphatic compounds. As a matter of fact both the low and high boiling point liquids could be separated on any of the five columns used for high boiling liquid but the Durapak columns gave a much better resolution for the low boiling point liquid.

The low-boiling liquid is a clear colorless liquid which turns dark and cloudy on exposure to air at room temperature for a few hours. Figure 2 shows the total ion monitor chromatogram of the liquid using a 30 ft. 1/8" column packed with 3% OV 101 on Chromosorb W-AP. Table 1 summarizes the identification of major components and gives an overview of the general nature of the most common chemical species present in the low-boiling liquid. Aliphatic hydrocarbons, alkylated aromatics, furans and small amounts of thiophenes constitute the bulk of the sample. The mass spectra of these components clearly indicate the substance type, however, in cases where two or more hydrogen atoms have been substituted by alkyl groups, a large number of different patterns is possible. The mass spectra of some of these isomers are quite similar and so the identification has been done by using known standards or using individual boiling point range. All the possible isomers of some alkylated species are identified.

Table 1. Identification of Major Components in the Low Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Acetone	19	Ethylbenzene
2	1,1-Dimethylcyclopropane	20	Xylenes
3	C_6H_{12}	21	2,3-Dimethylthiophene
4	Ethylmethylketone	22	C_9H_{20}
5	Hexane	23	2-Methyl 5-propylfuran
6	Methylcyclopentane	24	Cumene
7	1-Methylcyclopentene	25	$C_{10}H_{22}$
8	Pentane-2-one	26	*t*-Butylcyclohexanone
9	Heptene	27	*p*-Ethyltoluene +
10	2,4-Dimethylpentadiene		trimethylthiophene
11	Dimethylcyclopentene	28	Trimethylthiophene
12	Heptene	29	Trimethylthiophene (iso.)
13	C_7H_{12}	30	C_3-Alkylbenzene
14	Toluene	31	*n*-decane
15	2-Isopropylfuran	32	Tetramethylbenzene
16	C_8H_{12}	33	Cyclopropylbenzene
17	Isopropylfuran	34	Tetramethylthiophene
18	1-Ethylcyclohexene	35	C_4-Alkylthiophene
		36	$C_{11}H_{24}$

High boiling-point liquid was cleaned using a fractional sublimator prior to gas chromatographic analysis. The residue from sublimation was about 20 to 40% of the charge to the sublimator. The sample was sublimated to limit the boiling-point range of the sample so that the column temperature could be set for an upper limit of 280°C. Column bleeding was the major problem in GC-MS studies. Figure 3 shows the chromatogram of a sublimated sample and Table 2 list all the components identified. The same sample was separated on a Dexsil 300 GC column (Figure 4). Comparing the chromatogram of the same sample on five different column helps to resolve some components which may not separate on a particular column under identical conditions. For the GC-MS analysis a 30 ft. x 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP gave a better analysis than a 30M glass capillary column coated with OV 101 under similar conditions.

The Dexsil 300 GC column separated components into sharper symmetrical peaks in a shorter time compared to other columns. SP 2250 is the slowest of all. When a sample containing naphthalene and tetrahydronaphthalene is used on five different

columns, SP 2250 gave the best separation while SP 2100 gave no separation. The efficiency of separation in decreasing order can be listed as follows: SP 2250, Dexsil 410 GC, Dexsil 400 GC, Dexsil 300 GC and SP 2100. The bulk of the high-boiling-point liquid sample consists of saturated hydrocarbons mostly *n*-alkanes ranging from C_{10} to C_{36} distributed over the entire boiling point range. The aromatic species were predominantly alkylated phenols, benzenes, indenes, hydrogenated indenes and naphthalenes. Aromatic hydrocarbons containing three or more rings were not detected in the sublimated sample. The *n*-alkanes are not distributed proportionately throughout the series, though not a single member is missing. Unusually large enrichment occures at C_{10}, C_{17} and C_{27}. Mass spectral data of these higher members is not good enough to distinguish between a *n*-alkane and a slightly branched alkane of a higher molecular weight. The peak assigned to *n*-C_{17} alkane may also be assigned to branched alkanes with more than 17 carbon atoms, namely pristane, a branched C_{19} alkane. Pristane is derived from the phytol residues of chlorophyll (7). The hydrogenation products of other diterpene residues in lignite may also contribute to peaks in the range of C_{17} through C_{19}. The branched C_{30} alkanes obtained by the hydrogenation of triterpene type residues may be responsible for the *n*-C_{27} alkane peak enhancement.

Table 2. Identification of Major Components in the High Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Phenol	24	Pentamethylindan
2	1-Ethyl-3-methylbenzene plus Decane	25	C_6-Alkylindan
3	*o*-Cresol	26	Trimethylnaphthalene (iso.)
4	*p*-Cresol	27	$C_{16}H_{34}$ plus Trimethylnahthalene (iso.)
5	*n*-Undecane plus methylcresol	28	*n*-Hexadecane
6	*o*-Ethylphenol	29	Diethyl methylnaphthalene
7	2,6-Dimethylphenol	30	$C_{17}H_{36}$ plus Tetramethylnaphthalene
8	*p*-Ethylphenol	31	*n*-Heptadecane
9	*p*-Cymene	32	Alkylated naphthalene
10	$C_{12}H_{26}$ plus 1,3-Dimethylindan	33	$C_{18}H_{38}$
11	*n*-Dodecane plus 2-Methyl-6-ethylphenol	34	*n*-Octadecane
12	3-Methyl-6-ethylphenol	35	$C_{19}H_{40}$
13	$C_{12}H_{16}$	36	$C_{19}H_{40}$
14	3-Methyl-6-ethylphenol	37	$C_{19}H_{40}$
15	$C_{13}H_{28}$ plus 1,6-Dimethylindan	38	*n*-Nonadecane
16	1,2-Dimethylindan	39	*n*-Eicosane
17	*n*-Tridecane	40	*n*-Heneicosane
18	$C_{11}H_{16}$(Methylated benzene)plus $C_{14}H_{30}$	41	*n*-Docosane
19	*n*-Tetradecane	42	*n*-Tricosane
20	Dimethylnaphthalene	43	*n*- Tetracosane
21	2,3-Dimethylnaphthalene	44	*n*-Pentacosane
22	$C_{15}H_{32}$	45	*n*-Hexacosane
23	*n*-Pentadecane	46	*n*-Hepacosane
		47	*n*-Octacosane

The high boiling liquid is composed of species with a very wide range of boiling points. Starting with phenol (181°C) at the low end and *n*-$C_{36}H_{74}$ (497°C) at the upper end. A careful examination of Table 2 reveals that fractional distillation or sublimation can be effectively used to separate the high boiling liquid into separate fractions enriched with phenols (180-230°C), aromatic hydrocarbons (230-300°C) and alkanes (300-500°C). Similarly the low boiling liquids can also be fractionated into

enriched samples. The minor components of the high and low boiling liquids are concentrated in these fractions and can be identified by use of GC and GC-MS.

The proton nmr spectra show the distribution of chemically bound hydrogen among the aromatic rings, aliphatic chains and other carbon atoms with varying chemical shifts due to different functional groups. The spectra give only a very qualitative picture about the chemical nature of the numerous components present in the lignite derived products. An approximate estimation of the aromatic and the aliphatic moieties in the sample could be attempted with reasonable success.

Due to the high resolution power of the C^{13} nmr spectroscopy a cumulative estimation of a sample containing many components may result in the disappearance of a large number of C^{13} absorptions in the noise. The sample spectra will show few nmr absorption peaks representing carbon centers with nearly identical chemical shifts. Each narrow peak is formed by summing up the nmr absorptions of C^{13} carbons from similar but different compounds. The C^{13} nmr spectra of a non sublimated high-boiling liquid derived from hydrogenated lignite has about ten major absorption peaks. These peaks are listed in Table 3. Three peaks are in the aromatic region (110-130 ppm) and seven in the aliphatic region (10-40 ppm). The peak at 14.19 ppm could be due to terminal methyl groups of saturated long chain hydrocarbons. The intense absorption at 29.91 ppm is due to methylene groups in the middle regions of one or more long chain saturated dydrocarbon compounds. Relatively very large area of the peak at 14.19 ppm suggests that n-alkanes are the bulk species in the lignite derived fluids. The C^{13} nmr studies also show that most of the GC peaks of alkanes are due to straight chain rather than branched hydrocarbons.

ACKNOWLEDGEMENTS

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Table 3. C^{13} NMR Data of Products from Hydrogenated Lignite

Peak No.	Chemical Shift ppm	Peak Height(rel)	Peak Area(rel)
1	14.19	7.16	22.17
2	19.77	6.62	27.30
3	22.84	11.07	38.04
4	29.53	20.94	65.52
5	29.91	122.68	603.50
6	32.10	11.77	42.25
7	37.64	5.72	25.24
8	115.54	6.22	10.52
9	128.37	8.95	57.72
10	129.57	7.67	22.30

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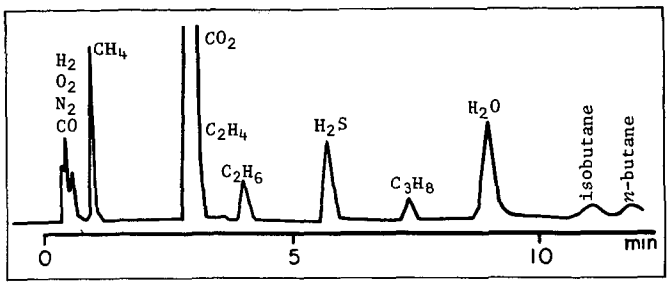

Fig. 1. Gas chromatogram of Texas lignite derived gas. Conditions: stainless steel column, 5ft x 1/4" O.D. packed with 80/100 Porapak N; carrier gas (helium) flow rate: 60 ml/min; temperature program: 25C (1 min.), 25-140°C at 15-20°/min.

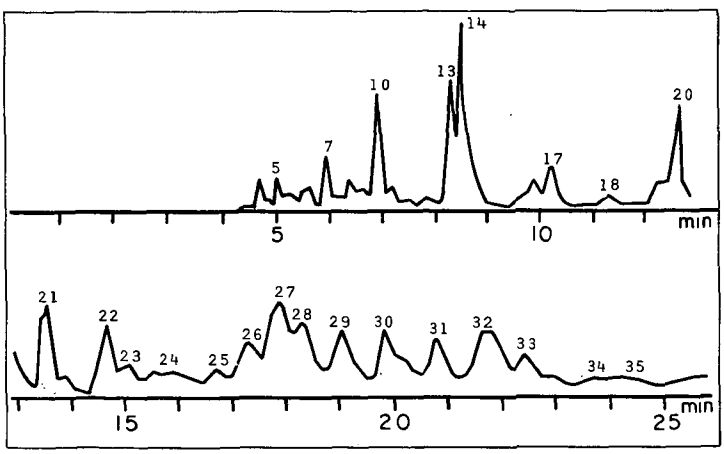

Fig. 2. Total ion current monitor chromatogram of low boiling liquid. Conditions: stainless steel column, 30ft x 1/8" O.D. packed with 3% OV 101 on 80/100 Chromosorb W-HP; carrier gas (helium flow rate: 20 ml/min; temperature program: 75-200°C at 2°/min. For identification of peaks see Table 1.

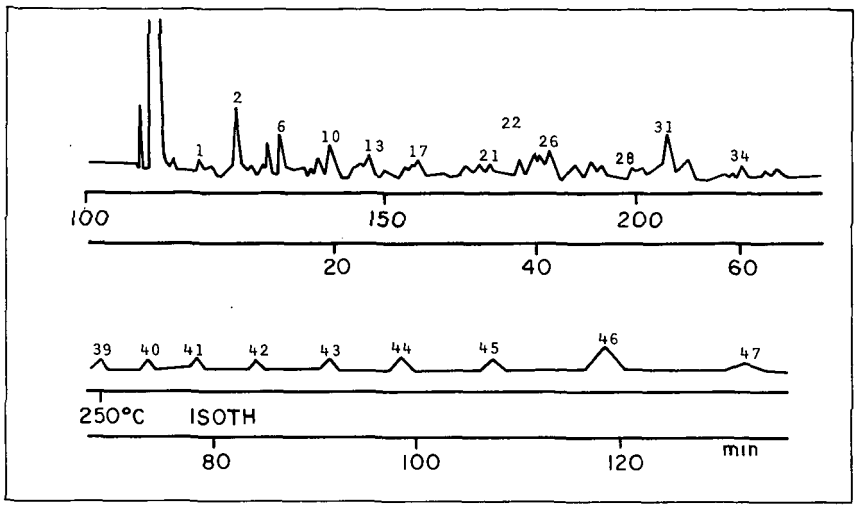

Fig. 3. Gas chromatogram of high boiling liquid. Conditions: stainless steel, 8ft x 1/4" O.D. packed with 10% SP 2100 on 100/120 supelcoport; carrier gas (helium) flow rate: 60 ml/min; temperature program: 100-250°C at 2/min. For identification of peaks see Table 2.

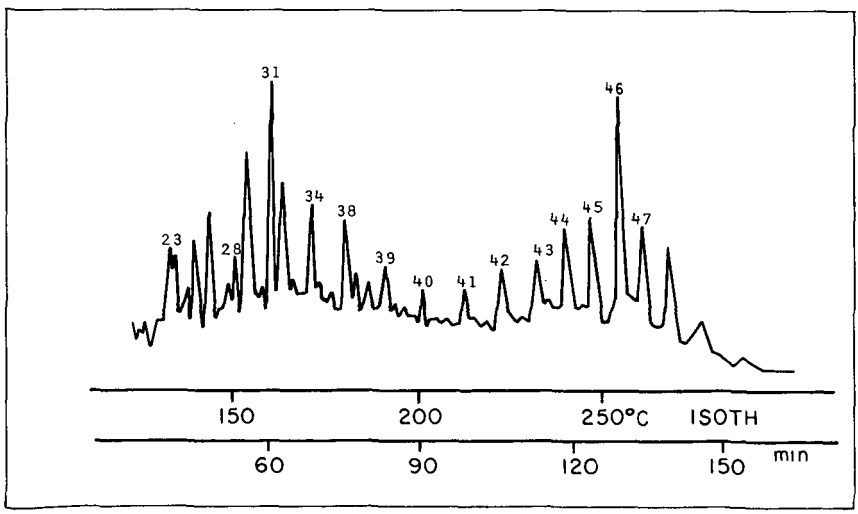

Fig. 4. High boiling liquid separated on a 3% Dexsil column. Column size and conditions are similar to those of Figure 3. For identification of peaks see Table 2.

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF MODEL HYDROAROMATIC HYDROCARBONS AND SOLVENTS

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INTRODUCTION

In recent years, a great deal of attention has been directed towards coal as an alternate source of gaseous and liquid fuels and chemicals which are currently derived from petroleum. Liquefaction of coal by catalytic hydrogenation was demonstrated by Bergius as early as 1912.[1] Subsequently other methods for coal liquefaction have been attempted and the kinetics of hydrogenation studied.[2] Coal can also be liquefied by hydrogen donor molecules, such as tetralin[3] and octahydrophenanthrene.[4] The initial reactions are thermal cleavage of carbon-carbon or carbon-oxygen bonds, resulting in free radicals. In the absence of hydrogen, free radicals polymerize producing high molecular weight solids. But if hydrogen donor molecules are present, the free radicals are stabilized resulting in low molecular weight liquids or gases. Tetralin is an efficient hydrogen donor molecule but many other structures can function in a similar manner.

Many coal liquefaction processes are currently in developmental stages - both catalytic and noncatalytic. These processes use coal-derived (anthracene oil) or petroleum-derived (decant oil) solvents. To enhance coal dissolution, they may be prehydrogenated or hydrogenated in-situ and the hydroaromatic hydrocarbons thereby formed partake in the formation of low molecular weight compounds from coal. An important aspect of coal liquefaction processes is therefore a basic understanding of the structure of the hydroaromatic molecules. Information is needed on the types that are present in aromatic solvents, the structures that are produced upon hydrogenation, their reactivity and the amount of "transferrable" hydrogen they may contain. The modus operandi that has succeeded in petroleum chemistry is separation of a complex mixture into simpler fractions, followed by their compositional analysis by spectroscopic techniques. The same method has been adopted here with promising results. The best spectroscopic technique capable of solving the problems posed above is carbon-13 NMR spectroscopy. However, because of the relative novelty of this technique, very little spectral information is available on hydroaromatic hydrocarbons and therefore a necessity arose to develop our own. This paper is a discussion of spectra and spectra-structure correlation of model hydroaromatic hydrocarbons, related compounds and fractions from partially hydrogenated condensed aromatic hydrocarbons.

RESULTS AND DISCUSSION

I Spectral Assignments in Model Compounds

The numbering scheme and structures for the sixteen compounds studied are presented in Figure 1. Assignments of resonance positions were accomplished by several techniques. As a starting point for making the assignments, resonances of quaternary aromatic centers[5] were separated from those due to carbons directly bonded to hydrogens, by examining the off-resonance spectrum in which the former retain their singlet structure. Furthermore, there are differences in the relative

sensitivity and the shieldings between these two types of carbon atoms. Quaternary carbons, under normal instrumental conditions, do not attain the full nuclear Overhauser enhancement and therefore their resonances appear with reduced intensity and they are deshielded more than the protonated carbons. Also, empirical chemical shift additivity correlation and known information on model compounds were used in assigning values to a given carbon atom.

The results for tetralin (I) in $CDCl_3$ are in good agreement with those reported for neat tetralin,[6] but our values are about 1 ppm upfield from those in neat tetralin, probably due to solvent effect. The contribution of the phenyl group along an alkyl chain is to shift the shielding of the α-carbon by +23.0 ppm, the β-carbon by +9.5 ppm and the γ-carbon by ca. -2 ppm.[7] This information along with the results for tetralin is utilized in assigning values to carbon atoms in 2(ar)-butyltetralin (II). The contribution of the aromatic ring of this molecule along the butyl chain is almost identical to that observed in n-butylbenzene. The effect of the chain on the saturated ring is marginal. The shieldings of C-6 and C-7 are unchanged, but a doublet, differing by 0.4 ppm in chemical shift, is observed around 29 ppm. An upfield shift of 0.4 ppm is similar in magnitude to the δ-effect observed in substituted cyclohexanes.[8] Therefore the line at 29.1 ppm is assigned to C-8 and the line at 29.5 ppm to C-5. Naturally, more pronounced effects have to be expected on the shieldings of aromatic carbon atoms. It is evident from the reduced NOE that resonances at 139.8, 136.6 and 134.1 ppm are due to three quaternary centers in the molecule. Butyl substitution decreases the C-2 shielding by +14.0 ppm and increases the C-4a shielding by -3.0 ppm. The latter is the familiar "para" effect. So C-2 is given the value 139.8 ppm and C-4a 134.1 ppm. The rest of the assignments are in Table I.

Assignment of values to carbons in 2(ar)-n-butyl-8-n-hexyl tetralin (III) is attempted, considering (I) and (II) as models. The contribution of a cyclohexyl ring along an alkyl chain can be derived from the results published by Adams and Lindeman[9] and are similar but not identical to those of a phenyl ring; α-carbon is deshielded by ca. +24 ppm, β-carbon by ca. +4 ppm, and the γ-carbon is shielded by -2 ppm, compared to the parent alkane. The contribution of the hexyl-chain to the ring carbons can be ascertained from the results on saturate hydrocarbons[9] and alkyl benzenes.[7] C-8a, due to the hexyl group on C-8, experiences a deshielding β-effect and a shielding γ-effect. These combined effects would place its chemical shift 4 ppm downfield from the corresponding value in tetralin or butyltetralin and so the value 141.2 ppm is assigned to C-8a. There appears to be γ-effect on C-1, similar in magnitude to that observed, for example, in n-butylbenzene: an upfield shift of 0.5 ppm. C-2, C-3, C-4 and C-4a are unperturbed. A normal alkyl chain, longer than C_4, decreases the shielding of substituted carbon by ca. +9 ppm and so one of the lines around 37 ppm is due to C-8. β-effect of lesser magnitude would place the resonance of C-7 around 27 ppm. C-5 is least perturbed and so its chemical shift value would be 29.5 ppm. Recalling the α, β, and γ effects of a cyclohexyl ring along the alkyl chain and remembering that the chain is n-hexyl, the chemical shift values to be expected for α, β, and γ carbons to the ring in the hexyl chain are respectively about 37, 27, and 29 ppm. This mutual interaction has resulted in three pairs of closely spaced lines and sorting them out is indeed a problem. The chemical shift value of C-5 in (II) and (III) can be expected to be identical. So the value 29.5 ppm is assigned to C-5 and 29.7 to C-8γ. In the off-resonance experiment the line at 37.2 is split into doublet, while the line at 37.7 into a triplet. So the former is assigned to C-8 and the latter to C-8α. The distinction that has been made between C-7 and C-8β is arbitrary. We have so far accounted for all the lines except the one at 20.1 ppm, which has to be associated with C-6. The upfield dis-

placement of C-6 (3.5 ppm) relative to that observed in (II) indicates a γ relationship between the hexyl chain and C-6. All the four carbon atoms in the saturated ring of tetralin are not coplanar with the aromatic ring. A 'half-chair' and 'half-boat' conformations are possible.[10] We think that the carbon atoms 6 and 7 are above the plane of the aromatic ring and consequently C-6 experiences an upfield γ steric shift.[8]

Chemical shift values for carbons in three gem substituted tetralins are given in Table I. The assignment of chemical shift values in 8,8-dimethyltetralin is facilitated by careful intensity measurement and the decoupling characteristics of signals. There are two interesting changes relative to tetralin; 16.2 and 4.3 ppm downfield shifts of C-7 and C-8, respectively, which is analogous to the shifts observed in 1,1-dimethylcyclohexane.[11] In 8,8-diethyltetralin (V), C-8 is further deshielded while the effect of ethyl substitution is the upfield displacement of C-7. Downfield displacement of C-8 is due to β-effect while the upfield displacement of C-7 is due to 'γ' relationship between the methyl carbon of ethyl group and the C-7 position. This trend is noticed in the transition from methylcyclohexane to ethylcyclohexane.[9] In 8,8-dibutyltetralin (VI), the shielding of C-8 is slightly increased, while curiously enough, the shielding of C-7 is decreased by +1.3 ppm. We have not understood these effects. The other changes are qualitatively similar to those observed in substituted cyclohexanes.[8,11]

Results for 9,10-dihydrophenanthrene (VII) and sym-octahydrophenanthrene (VIII) in $CDCl_3$ are similar to those reported by Retcofsky and Friedel[6] in neat liquid. But C-1, C-2 and C-3 in (VII) and C-4a and C-10a in (VIII) are not identical as suggested by their results. The carbon chemical shifts in (I) and (VIII) have been calculated by them by considering these structures as being benzene ring in which pairs of adjacent hydrogens are progressively replaced with six-membered hydroaromatic rings and equating them to appropriate multi-methyl substituted benzene. This scheme has provided values for the chemical shifts of aromatic carbons, agreeing well with the observed results. It remains to be seen whether this method is applicable to other molecules considered here. For example, is it possible to predict the shielding of aromatic carbons in 1,2,3,4-tetrahydrophenanthrene knowing the values for carbons in 1,2-dimethylnaphthalene? Several dimethylnaphthalenes have been studied by carbon NMR,[12] but no detailed information is yet available on 1,2-dimethylnaphthalene. Spectral information on a variety of multi-methyl substituted naphthalenes may facilitate assignment of values to carbons in partially hydrogenated pyrenes also. In the absence of such information, assignment of chemical shifts to appropriate carbon atoms in structures (VII) to (XVI) is accomplished by comparing the results with those of parent aromatic compound, among themselves and by other considerations.

In (X), the shieldings of carbons in positions 4b, 5, 6, 7 and 8 should be comparable to those in the corresponding positions of phenanthrene. So the lines at 122.7, 125.5, 125.6, 128.1 and 131.2 are associated respectively with C-5, C-6, C-7, C-8 and C-4b. To select values for other carbons, the molecule is considered as perturbed phenanthrene. The effect of saturated carbons is most pronounced at positions 10, 4a and 10a. A deshielding of +1.5 ppm is reasonable for C-10 and so the line at 128.3 ppm is assigned to it. The shieldings of C-4a and C-10a are expected to decrease by about +2 ppm and they are assigned the values 132.7 and 133.9 ppm, respectively. These assignments leave us with two lines, one at 132.2 ppm and the other at 124.5 ppm. For obvious reasons, the former has to associate with C-8a and by the process of elimination, the latter with C-9. C-9 is shielded due to the para effect, which raises the question why C-8a is not experiencing a similar para

effect. An examination of chemical shift of carbons in 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN), relative to naphthalene[12] provides a satisfactory answer, although qualitative. C-4 experiences a shielding para effect in 1-MN, while it is deshielded in 2-MN. C-4a experiences similar effects, but the magnitudes of these effects are not identical at these two centers. The combined effect of methyl substitutions at positions 1 and 2 is an upfield shift at C-4 and no change at C-4a. C-4 and C-4a in 12-DMN corresponds to C-9 and C-8a respectively in (X). The calculation of chemical shift values for carbons in 12-DMN, starting from 1-MN and 2-MN, although unorthodox without the knowledge of steric effect due to substitutions ortho to each other, has provided some information on the shieldings of C-9 and C-8a due to hydrogenation of one of the terminal rings in phenanthrene. Our assignments are further substantiated by the spectrum of octahydrophenanthrene (VIII) relative to 1,2,3,4-tetrahydrophenanthrene. The spectrum of VIII has three lines of equal intensity in the region where aromatic carbons absorb. The line at the lowest field is assigned to C-8a and C-10a and the line at 134.0 ppm to C-4a and C-4b. The combined effect of two saturate rings on the quaternary carbons results in the merging of lines due to C-4a and C-4b to a singlet, with a similar effect on C-10a and C-8a. The effect of a saturated ring on C-10 in (X) is a decrease in shielding by +1.4 ppm and on C-9, an increase in shielding by -2.4 ppm, compared to phenanthrene. C-9 and C-10 are subjected to similar changes by the other saturated ring in (VIII). C-10 is shielded by about the same magnitude and the shielding of C-9 is decreased by +2.0 ppm. The combined effect of increase and decrease in shielding, due to the successive hydrogenation of the outer two rings in phenanthrene, results in the same resonance frequency for C-9 and C-10.

The next interesting pair of compounds in the phenanthrene class are 9,10-dihydrophenanthrene (VII) and its dimethyl derivative (IX). As observed in other molecules in this class, para shielding effect is evident in (IX). But more interesting, this molecule constitutes another example of the recently reported deshielding 'δ' effect, where substantial downfield shifts are found in compounds containing spatially interacting δ function.[13] In the two partially hydrogenated phenanthrene molecules that we have so far examined, assignment of values to quaternary centers was accomplished by the procedure mentioned earlier and by using the results on phenanthrene published by Ozubko and co-workers.[14] In (IX), methyl substitution in strategic positions provided an additional handle in selecting values to quaternary carbons. The spectrum of (IX) has three lines with reduced intensity at 141.3, 135.1 and 134.7 ppm, of which the last one is the least intense. Quaternary carbons in position 5 (4) and 8a (10a) have protons in ortho positions, while that in position 4a (4b) is devoid of protons in its immediate vicinity. It is reasonable to expect that relaxation is determined by the $^{13}C-^{1}H$ dipole-dipole mechanism and consequently, C-4a should have the longest relaxation time (T_1). Based on this consideration, the line at 134.7 ppm is assigned to C-4a (C-4b). Substantial downfield shift (6.6 ppm) due to 'δ' shielding effect is observed for C-1 in 7,12-dimethylbenz[a]anthracene compared to 7-methylbenz[a]anthracene.[14] A larger downfield shift for C-5 (4) is possible due to mutual 'δ' effect added to the downfield shift due to methyl substitution, compared to C-5 in (VII). So the line at 141.3 ppm is assigned to C-5 (4) and the remaining line at 135.1 ppm to C-8a (10a). The difference in the relaxation times (T_1) between C-4a (4b) and C-8a (10a) surfaced in this molecule due to $-CH_3$ substitution at C-4 (5), and permitted an unambiguous assignment to quaernary centers, and has also helped us to understand the spectrum of (VII) and other lines in the spectrum of (IX). Carbon chemical shifts in tetralin follow the trend in o-xylene.[6] So it is reasonable to expect the trend in 9,10-dihydrophenanthrene to be similar to that in 2,2'-dimethylbiphenyl. But no spectral information is available on the latter. Nevertheless, approximate values for the chemical shifts of quarternary

carbons can be calculated from the chemical shift values of carbons in biphenyl.[15] This calculation indicates that the resonance of C-4a (4b) in (VII) should be at a lower field than that of C-8a (10a). Upon $-CH_3$ substitution in positions 4 and 5, the changes that can be expected are the shieldings of C-8a and C-10a to be practically the same, while those of C-4a and C-4b to be increased by about -2.5 ppm. The latter is a manifestation of γ steric effect. These changes are indeed observed, substantiating the assignment of values to C-8a (10a) and C-4a (4b) in (IX). There are four lines, three of which are closely spaced, in the spectrum of VII corresponding to four protonated aromatic carbons. Methyl substitution separates the three closely spaced lines and the separations have been useful in arriving at further assignments. Methyl substitution decreases the shielding of C-6 and increases that of C-8, leaving the value of C-7 unchanged. The para shielding effect -2.4 ppm is similar in magnitude to that observed in other aromatic structures. The complete assignments are in Table II, along with those for the saturated carbons.

The next class of compounds which have been investigated are pyrenes and partially hydrogenated pyrenes. The spectrum of 3-n-decylpyrene (XI) is included, although it is not a hydroaromatic, to understand the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene, and also to assess the contribution of a multi-nuclear aromatic structure along an alkyl chain. Shieldings at carbons 1,5,6,7,8,9,10,13 and 14 are similar to those for the corresponding carbons of pyrene (XVI). Amidst the group of lines corresponding to aromatic carbons directly bonded to protons, there is a line at 125.0 ppm with reduced intensity, which has to be associated with quaternary centers and we think that it corresponds to the line at 124.5 ppm in the spectrum of pyrene, which is assigned to C-15 and C-16.[16] The theory predicts that C-15 and C-16 should have similar chemical shift to other bridgehead positions. It is reasonable to explain both of these upfield shifts with an anisotropic ring current in the peripheral ring carbons. The line at the lowest field, 137.1 ppm, is assigned to C-3. The shielding of C-2 is likely to be slightly decreased and so the line at 126.3 ppm is assigned to it. The upfield shift of 3.9 ppm at C-4, relative to pyrene is again attributed to a γ steric shift. The remaining two lines are at 128.5 and 129.6 ppm. The shielding of C-11 is expected to increase by about -2.5 ppm due to para effect, and so the line at 128.5 ppm is assigned to it. By default the line at 129.6 ppm is assigned to C-12.

We have sufficient evidence, considered later, to believe that the di-plus triaromatic fraction of hydrogenated pyrene contains symmetric hexahydro and tetrahydropyrenes. Symmetric tetrahydropyrene in pure form has been studied by us and by subtraction, the chemical shift values for carbons in symmetric hexahydropyrene have been obtained. This information is utilized in understanding the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene (XII). In (XV) the chemical shift value for the carbons at positions 4,5,9,10 is 123.4 ppm. Alkyl substitution at C-4 has least effect on C-9 and C-10, and so they are assigned the values 123.5 and 122.5 ppm, respectively. The other line which we believe is due to a protonated aromatic carbon is at 126.1 and is associated with C-5. The shielding is decreased more than expected. Again, the line at the lowest field is assigned to C-4. The anisotropic ring current effect should be less pronounced in this compound compared to pyrene; consequently, the shielding of C-15 and C-16 is expected to be comparable to other bridgehead carbons. However, the NOE is less at these two centers compared to positions 11, 12, 13 and 14. The assignments are given in Table III.

The assignment of values to saturate side-chain and ring carbons is less complicated. The values for the side-chain carbons are given in Table IV, while those for ring carbons are included in Table III. Shifts for side-chain carbons in

(XI) and (XII) should be close and by comparing the spectrum of these two compounds upfield from 35 ppm, the lines due to hydroaromatic carbons are selected and their shielding should be comparable to corresponding carbons in symmetric hexahydropyrene, except for C-3. γ steric shift, observed in other structures, increases its shielding. The chemical shift values for carbons in symmetric tetrahydropyrene are given in Table III. The other compound that we have studied in this class is 1,2,3,9,10,11-hexahydropyrene and its values are also given in Table III.

II Compositional Analysis of Fractions From Hydrogenated Condensed Aromatics

In our studies on induced dissolution of coal by hydrogen donor solvents, several solvents in bulk quantities were prepared. They can be divided into two classes. One, resulting from the hydrogenation of fairly pure aromatic compounds and the second, from the hydrogenation of coal and petroleum-derived oils. The major effort in this study was the separation of the solvent and the reaction products into mono- and di-plus triaromatic fractions[17] and the examination of the fractions by different spectroscopic techniques to understand the reaction mechanism. Carbon-13 spectra of some of the fractions from the hydrogenated phenanthrene and pyrene model solvents are considered here. The composition of the fractions, even after separation, is extremely complex due to unconverted parent aromatic compound or compounds and numerous products resulting from cracking. However, the major contributions to the intensities in the saturate region are from hydroaromatic hydrocarbons, facilitating their recognition in the mixture. The analysis of real solvents is underway and will be discussed in a future publication.

The simplest system is di-plus triaromatic fraction of hydrogenated pyrene. In the region where saturated carbons absorb, three lines are observed at 31.4, 28.3, and 23.3 ppm. Resonance line positions of aromatic carbons are at 135.3, 134.0, 130.6, 130.1, 127.0, 125.9, and 123.4 ppm. From our previous experience, it is obvious that the line at 28.3 ppm is due to the four equivalent saturated carbons of tetrahydropyrene and the other lines associated with this structure are in the spectrum. The line at 31.4 ppm is twice as intense as the line at 23.3 and the one at 123.4 ppm, which does not belong to symmetric tetrahydropyrene, splits into a doublet in the off-resonance experiment. These observations suggest that these three lines in the spectrum are due to symmetric hexahydropyrene and the resonance lines due to quaternary centers are at 134.0 and 130.1 ppm. The structure of this compound is included in Figure 1 and complete assignments in Table III. There is no evidence for the presence of unsymmetric hexahydropyrene, which can be recognized because of bridgehead saturated carbons in the structure. The spectrum of di-plus triaromatic fraction of hydrogenated phenanthrene is also complex. However, if weak lines are ignored and only intense lines are considered, they account for two structures: 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene. The spectrum of the mono-aromatic fraction also has several lines, but intense lines are due to symmetric octahydrophenanthrene. The major hydroaromatic hydrocarbons that are formed on hydrogenation of phenanthrene are 9,10-dihydro-, 1,2,3,4-tetrahydro- and symmetric octahydro-derivatives. But unlike in the case of pyrene, a large number of other products are formed, some of which are due to ring openings.

It is accepted that the induced dissolution of coal is by hydrogen transfer from hydroaromatic hydrocarbons and so an effort was made to understand the carbon-13 spectra of model compounds and solvents. In a large scale process, it would be prohibitively expensive to use pure compounds or model solvents as a source of hydrogen. Hydrogenated coal and/or petroleum-derived solvents are attractive

substitutes. We are examining by carbon-13 NMR hydrogenated anthracene and decant oils and have identified several hydroaromatic structures in them. However, to understand the kinetics of hydrogen transfer reaction and thereby further improve the coal solvation process, the results have to be quantified. The cliche that carbon-13 NMR spectroscopy is analytically difficult is no longer true. Work is in progress in our laboratory to overcome some of the problems inherent to quantitative carbon NMR and initial results are gratifying. The composition of hydrogenated and unhydrogenated real solvents, quantification of results will be the subject of future reports.

EXPERIMENTAL

Materials

Compounds I and VII were obtained from Aldrich Chemical Company, Inc. and compound XIII from K and K Laboratories, Inc. Compound X is an API reference material. Compounds IV, V and VIII were specially prepared for us by Oklahoma State University. The rest were drawn from the hydrocarbon bank of Pennsylvania State University. All compounds and solvents were used without purification.

Spectra

Nuclear magnetic resonance spectra of ^{13}C in natural abundance were obtained by the pulsed FT technique at 20 MHz on a Varian CFT-20 spectrometer, which is equipped with 620/L computer with 16K memory. The free induction decays, after a sufficient number of transients have been accumulated, were smoothed with an exponential function and Fourier transformed. Samples were studied in 8 mm OD tubes at a concentration corresponding to about 200 mg in a total volume of 1.4 ml and at a probe temperature of 36°C. The solvent was invariably $CDCl_3$. The deuterated solvent was used as a field-frequency lock and chemical shifts are in ppm downfield from internal TMS. The initial spectrum in each case was obtained with proton noise decoupling; later as the situation demanded, off-resonance decoupling and suppressed NOE spectra were obtained to facilitate spectral assignment.

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Table I

^{13}C SHIELDINGS FOR RING AND SIDE CHAIN CARBONS IN I-VI (δ^C FROM TMS)

Position	Compound I	II	III	IV	V	VI
C-1	129.0	129.0	128.5	126.5	127.0	126.8
C-2	125.4	139.8	139.7	126.0	125.5	125.6
C-3	125.4	125.7	125.6	125.3	125.0	125.0
C-4	129.1	129.0	128.8	129.1	129.0	129.0
C-4a	136.9	134.1	134.0	135.6	137.8	137.4
C-5	29.4	29.5	29.5	30.9	30.8	30.9
C-6	23.4	23.6	20.1	20.0	19.8	20.0
C-7	23.4	23.6	27.6	39.6	30.8	32.1
C-8	29.4	29.1	37.2	33.7	40.1	39.8
C-8a	136.9	136.6	141.2	145.3	143.3	143.9
C-2α		35.4	35.5			
C-2β		34.0	34.0			
C-2γ		22.6	22.5			
C-2δ		14.0	14.0			
C-8α			37.7	31.9	34.4	42.7
C-8β			27.7		8.7	26.6
C-8γ			29.7			23.7
C-8δ			32.1			14.1
C-8ε			22.8			
C-8ζ			14.1			

Table II

^{13}C SHIELDINGS FOR RING AND $-CH_3$ CARBONS IN VII-X (δ^C FROM TMS)

Position	Compound VII	VIII	IX	X
C-1	127.2	30.2	124.3	30.3
C-2	126.8	23.8	126.4	23.2
C-3	128.0	23.2	129.0	22.9
C-4	123.6	26.3	141.3	25.5
C-4a	137.1	134.0	134.7	132.7
C-4b	137.1	134.0	134.7	131.2
C-5	123.6	26.3	141.3	122.7
C-6	128.0	23.2	129.0	125.5
C-7	126.8	23.8	126.4	125.6
C-8	127.2	30.2	124.3	128.1
C-8a	134.4	134.8	135.1	132.2
C-9	28.9	126.5	31.5	124.4
C-10	28.9	126.5	31.5	128.3
C-10a	134.4	134.8	135.1	133.9
C-4α			20.6	
C-5α			20.6	

Table III

^{13}C SHIELDINGS FOR RING CARBONS IN XI-XVI (δ^{C} FROM TMS)

Position	Compound XI	XII	XIII	XIV	XV	XVI
C-1	124.5	30.9	125.8	30.9	31.4	124.8
C-2	126.3	23.2	126.9	22.8	23.3	125.7
C-3	137.1	27.4	125.8	31.1	31.4	124.8
C-4	123.3	135.6	28.2	127.5	123.4	127.2
C-5	127.4	126.1	28.2	124.2	123.4	127.2
C-6	124.6	31.5	125.8	124.3	31.4	124.8
C-7	125.5	23.3	126.9	125.6	23.3	125.7
C-8	124.6	31.5	125.8	125.5	31.4	124.8
C-9	127.0	123.5	28.2	29.9	123.4	127.2
C-10	127.0	122.5	28.2	30.6	123.4	127.2
C-11	128.5	133.5	135.2	37.6	134.0	131.0
C-12	129.6	130.3	135.2	136.0	134.0	131.0
C-13	131.4	133.9	135.2	134.3	134.0	131.0
C-14	130.9	133.8	135.2	131.3	134.0	131.0
C-15	125.0	130.5	130.4	132.2	130.1	124.5
C-16	125.0	129.0	130.4	129.6	130.1	124.5

Table IV

^{13}C SHIELDINGS FOR SIDE CHAIN CARBONS IN XI AND XII
(^{C} FROM TMS)

Position	Compound XI	XII
CC-1*	33.5	33.4
CC-2	31.8	31.5
CC-3	29.8	29.9
CC-4	29.6	29.7
CC-5	29.6	29.7
CC-6	29.6	29.7
CC-7	29.3	29.4
CC-8	31.9	31.9
CC-9	22.7	22.7
CC-10	14.1	14.1

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*CC-1 is the first carbon α to the ring.

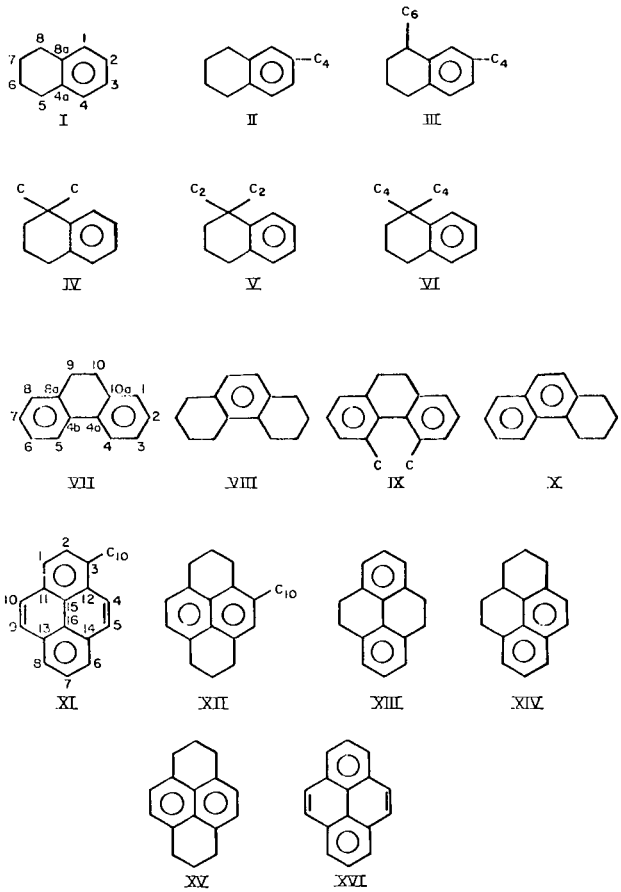

FIGURE I: NUMBERING SCHEME FOR HYDROAROMATIC HYDROCARBONS

Multielemental Analysis Using Proton Induced Photon Emission

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Energetic protons from a nuclear accelerator can be used to provide quantitative analysis for most elements from Li to Pu. The sample is prepared as a thin film and bombarded with protons to produce monoenergetic x rays and γ rays from all elements in the sample. Energy sensitive Si-Li and Ge-Li semiconductor devices are used to detect x rays and γ rays, respectively. The energy of the radiation identifies the element and the intensity determines the concentration of the element in the sample. A PDP 15/45 on-line computer is used to process data from one sample while data is being accumulated from the next sample. The analysis results are available from the computer at approximately the same time that new data accumulation is finished.

Proton excitation provides better sensitivity than electron excitation because the yield of characteristic x rays compared to background radiation is higher. Protons have an advantage over x-ray excitation because good sensitivity can be obtained for a much larger group of elements in a single measurement. In addition, the light elements Li, B, F, Na, Mg, Al, and Si can be detected by γ-ray emission following nuclear excitation.

The broad elemental range of Proton Induced X-ray Emission (PIXE) occurs because the production of characteristic x rays is very large in the energy region where the background radiation is maximum. The primary source of background radiation comes from showers of electrons which are released when a proton strikes the target. These electrons stop in the target and produce a continuous x-ray spectrum called Bremmstrahlung or braking radiation. The Bremsstrahlung intensity decreases rapidly as a function of energy and is essentially negligible above 10 keV for 4 MeV incident protons. The background at higher energy is primarily due to nuclear γ rays which occasionally interact with the x-ray detector. The probability for K x-ray emission also decreases with the atomic number of the element, but the x ray yield is still satisfactory up to the rare-earth elements because the background is so small. Elements heavier than La are detected by L x rays. The L x-ray yields for the rare-earths are good but their energy falls in the region of relatively high Bremsstrahlung so the sensitivity is poorer than for other regions. For heavier elements the L x rays occur above the Bremsstrahlung so the sensitivity is again excellent. The background in the γ-ray detector depends on the major components in the sample. For example, large quantities of Na or Cu in the sample can produce relatively intense γ-ray background.

Sample preparation. Solid samples are usually ground to a fine powder using Agate components in a vibrating mill or a mortar and pestle. A few milligrams of the fine powder is placed on a thin plastic film (2.5×10^{-3} mm thick) and weighed with a micro-balance. A few drops of liquid plastic are added and the sample is stirred with a plastic rod to make a uniform suspension of the fine powder. When the plastic solvent evaporates, the sample is firmly attached to the backing in a light weight matrix. The sample uniformly covers a 16 mm diameter circle. The plastic film with sample is mounted in a 35 mm photography slide frame. The sample is not damaged in the bombardment so it can also be studied with other techniques. Thin samples are preferable to minimize x-ray absorption and to avoid corrections due to slowing down of the protons in the sample. However, thick solid samples can be analyzed with slightly poorer sensitivity and accuracy. Materials desolved in an aqueous sample can also be deposited on thin films for analysis.

Target bombardment chamber. The proton beam passes through a 2.5×10^{-3} mm Al foil located 3 meters in front of the target to diffuse the beam and ensure that

the proton bombardment is uniform over the target area. The beam is restricted with a series of collimators to ensure that the protons can only strike the sample and the thin support film. Carbon or plastic films are used to cover all metal parts of the chamber that might be struck by protons scattered from or passing through the target. Bombardments are performed in vacuum. Eighty targets are held in the circular slide tray of a modified 35 mm slide projector. The target to be bombarded is dropped into the proton beam by the automatic mechanism of the projector. A variety of filters can be inserted between the target and the detector by remote control to reduce the intensity of abundant x rays which would interfere with the analysis of trace elements. The x rays pass through a 0.025 mm plastic window on the target chamber and a 0.025 mm Be window on the detector cryostat.

Detector and electronics. A Si-Li detector (1 cm diameter and 3 mm thick) provides 170 eV energy resolution for 5.9 keV x rays. A 40 cm^3 Ge-Li detector provides 2.0 keV resolution for 1.33 MeV γ rays. Normally when an x ray is absorbed in the detector, all of the x-ray energy is converted into an electrical pulse. However it is also possible for a Si x ray, created in the detection process, to escape from the detector. These "silicon escape" events create false peaks in the x-ray spectrum. It is also possible for electrons released in the detector process to leave the surface of the detector. These events produce a small tail on the low energy side of peaks in the x-ray spectrum. The computer must be able to correct for these two imperfections in the detector response in order to get accurate analytical results.

The electrical signal from the detector is amplified and passed through a noise filter which is essential for good energy resolution. Fifty microseconds are required for the noise filter to process each x ray pulse. If a second x ray is detected while the filter still contains a preceding x ray, the energy of both x rays is distorted. This problem is greatly reduced in our system by switching the proton beam off of the target shortly after the first x ray is detected. As soon as the noise filter has processed the x ray pulse, the beam is automatically returned to the target to produce a new x ray.

Even though the beam switching time is less than 0.5 μsec, there is still a small probability that a second x ray will be produced before the beam is removed from the target. When two x ray pulses pile up in the filter a single pulse is produced which corresponds to the sum of the energy of the two x rays. We have developed a circuit which recognizes pile-up events and rejects them unless the second x ray is emitted within 0.05 μsec of the first x ray. These remaining "simultaneous" pile-up events are rare, so they usually do not present a significant limit on the analysis.

The task of separating events which come from two x rays of similar energy is greatly simplified if the energy calibration of the electronic system is very stable. The energy calibration is always a function of the counting rate in the detector. Our system has correction circuits (Kevex Model 4532P Pulse Processor) which limit the calibration variation to less than 0.01% for counting rates up to 10^4 x rays per second.

The proton beam is collimated so that all protons which enter the target chamber must pass through the target. The total charge which is accumulated in the chamber during a measurement is recorded by a digital current integrator (Ortec Model 439) and stored in the computer. The quantity of charge on each proton is well known, so the computer converts the total charge into number of protons passing through the sample. The computer also corrects for the number of events lost due to pile-up (typically less than 3%).

Computer processing. The analysis process is monitored and the computer is controlled with an interactive video display. The first step in the analysis process is to subtract background radiation. Many experimental background spectrum are stored on a magnetic disk. The operator selects a background spectrum which represents the host material of the target being analyzed. The computer adjusts the background to match the target including the effect of the peak-tails described above. The background is then displayed on the video monitor as an overlay on the experimental data. Usually, the computer generated background accurately describes the actual background from the sample, but the operator can instruct the computer to refine the background by contacting the display with a "light pen".

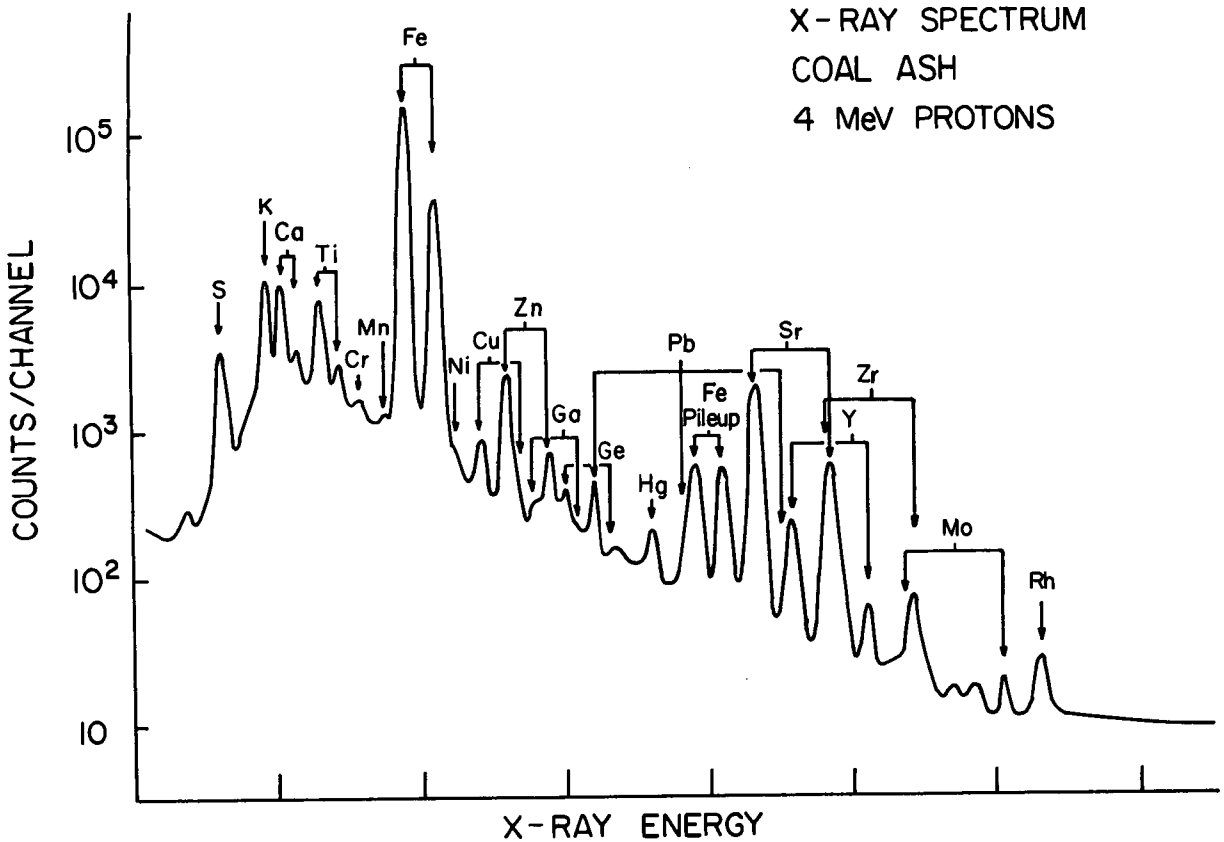
The computer also has stored experimental data which describe the shape and the position of the characteristic x-ray peaks in the spectrum. Even though the imperfections in the detector response are small, they can be important for large peaks. The computer locates large peaks and identifies their tails and the false peaks that are produced by Si-escape x rays. Very large peaks can also produce false peaks due to simultaneous pile-up. The computer includes these refinements and performs a least square fit to the data to determine the number of x rays at each energy of interest. The stability of the energy calibration, the advanced knowledge of the shape of the characteristic x-ray peaks, and the careful treatment of imperfections and false peaks are all essential factors for accurate analytical results.

A typical spectrum for the lower energy portion of a coal ash sample is shown in Figure 1. The results of the computer fit is displayed on the video monitor as an overlay on the data. The operator can easily recognize any element which has been missed or incorrectly inserted and instruct the computer with the light pen to refine the fit to the data.

Most elements emit two or more x rays (for example, notice the two peaks from Sr identified in Figure 1). The relative heights of these peaks have all been measured experimentally for single element calibration targets. The computer checks that the fit to the sample data agrees with these standards. The computer also looks for possible sources of error due to two x rays which have approximately the same energy. All of this information is printed out for the operator to evaluate the reliability of the analysis.

After the operator has approved the analysis of a sample, the computer uses the number of protons passed through the target and stored calibration tables for the proton energy and filter conditions to determine the weight of each element in the sample. These weights are divided by the total sample weight to calculate the fractional weight of each element.

System calibration. The basic relation which must be known to obtain analytic results is the number of x rays detected, per unit of protons, per unit of weight of the element. This x-ray yield has been measured for a fixed detector position, for each proton energy, and each filter condition. Thin film calibrators (typically 100 μgrams/cm^2) are used so that it is not necessary to correct for slowing down of the protons or x-ray absorption in the calibrators. Thirty metal films of known weight deposited on Mylar were obtained from Micromater Inc. Thirty five calibrators were made in our laboratory from commercial atomic absorption liquid standards. The x-ray yield is a slowly varying function of atomic number. The results of yield measurements for each proton energy and filter condition were least square fit to an algebraic function to obtain yield curves for all elements from Al to Pu. The RMS deviation of the individual measurements around the best-fit function was typically 3%. Gamma-ray yields were measured for each light element that is detected by γ rays.


X-RAY SPECTRUM
COAL ASH
4 MeV PROTONS
COUNTS/CHANNEL
10^5
10^4
10^3
10^2
10
X-RAY ENERGY
S
K
Ca
Ti
Cr
Mn
Fe
Ni
Cu
Zn
Ga
Ge
Hg
Pb
Fe
Pileup
Sr
Y
Zr
Mo
Rh

Limitations to analysis. As noted above the x-ray counting rate is limited by the noise filter which is essential for good energy resolution. Thus the number of x rays that can be observed from trace elements in a fixed time period will be limited by intense radiation from an abundant element. Analysis cost are directly effected by bombardment time, so the most practical solution is to reduce the intensity of the dominant radiation with an absorber. Energy selective filters can be useful for special problems, but the best general technique is to select a material where the probability of absorption decreases rapidly with increasing energy. The unwanted x ray can be controlled, but all lower energy x rays will be lost. However, higher energy x rays will be retained with minimum loss. Carbon is a good filter material and it is conveniently available in thin plastic films.

For coal samples we detect all elements heavier than Fe with 4 MeV protons and a 5 mm thick plastic filter to absorb Fe x rays. Elements from Al to Fe are observed in a separate measurement with 2.5 MeV protons. There is some x-ray absorption due to the windows which separate the target and detector. It would not be desirable to eliminate these windows because they prevent scattered protons from reaching the x-ray detector. The high intensity x rays from Fe and S in coal limit the data rate that can be obtained for light elements. However, light elements are frequently relatively abundant and their x-ray yields are large so good results can be obtained for most elements.

In some cases an intense x ray from and abundant element or a false peak due to simultaneous pile-up will have approximately the same energy as a low intensity x ray from a trace element. Then the sensitivity for that trace element will be limited to a fraction of the abundant element. These limitations are predictable so they can be included in the specifications for PIXE analysis.

Detection limits. The sensitivity is determined primarily by the time that the target is exposed to the proton beam. Other significant factors are background radiation, the presence of elements in high concentration, and energy interference for a few elements. The detection limit is relatively poor for P (approximately 250 ppm) but it rapidly improves to approximately 2 ppm for Cr, Mn, and Fe. The detection limit is approximately 1 ppm for most elements from Co to I, approximately 10 ppm for the rare-earth elements, and typically 3 ppm for the heavy metals up to Pu. The detection limit using γ rays for the light elements Li, B, F, Na, Mg, Al, and Si is usually a few ppm.

Results obtained for the analysis of NBS standard reference material 1632 (coal) are given in Table 1. The cost for this type of analysis would be $30 to $80 per sample depending on the number of samples that were analyzed.

In summary, PIXE is a powerful technique for multielemental analysis of a wide variety of samples. Very light elements can be observed by detecting γ rays and x rays in the same experiment. Although the original cost of the equipment is very large, there are many laboratories which already have the required facilities. After the system is developed the cost of analysis is low compared to other multielemental techniques of comparable sensitivity.

Table 1

Analysis of NBS Standard Reference Material 1632 (Coal) by PIXE

Results given in parts per million by weight

Element	Purdue PIXE N Result	Purdue PIXE ΔN Uncertainty	NBS Value N	NBS Value ΔN
Al	17600	1500		
Si	34000	4000	32000	
S	11300	1000		
Cl	850	80		
K	2540	250		
Ca	3500	300		
Ti	890	90	800	
V	35	3	35	3
Cr	17	3	20.2	.5
Mn	36	3	40	3
Fe	7900	800	8700	300
Co	10	6	6	
Ni	15.6	1.5	15	1
Cu	16	1.5	18	2
Zn	33	3	37	4
Ga	5.3	0.5		
Ge	2.4	0.3		
As	5.0	1	5.9	.6
Se	3.0	.3	2.9	.3
Br	20.5	1		
Rb	18.9	1		
Sr	140	10		
Y	7.5	.5		
Zr	35.5	1.5		
Nb	2.2	0.5		
Mo	2.2	0.5		
Ag		≤ .3		≤ 0.1
Cd	0.5	0.3	.19	.03
Sb	3.0	1		
Ba	310	30		
La	15	5		
Hg		< 1	.12	.02
Pb	23	4	30	9
Th	3.7	1	3.0	
U	2.1	1	1.4	.1

SIMULTANEOUS DETERMINATION OF MAJOR, MINOR AND TRACE CONSTITUENTS IN COAL ASH BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY. V. A. Fassel, E. M. Layton, and E. L. DeKalb, Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The present status of the simultaneous determination of major, minor, and trace elemental constituents in coal ash by the inductively coupled plasma-atomic emission spectroscopy technique will be reviewed. The coal ash samples are brought into solution either by lithium metaborate fusion or by a perchloric-nitric-hydrofluoric acid dissolution procedure. The relative merits of these two procedures will be discussed. Linear analytical calibration curves covering concentration ranges of three or more decades are obtained. Corrections for stray light effects may be required unless these background contributions are reduced to negligible proportions through the selection of appropriate gratings and for the use of interference filters. Analytical data in reference coal samples will be discussed.

Comparison of Atomic Absorption and D.C. Plasma-Arc Spectrometry in Multi-Element Analysis of Coal

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As part of a project at The Pennsylvania State University to characterize the inorganic constituents of American coals, an analytical scheme was developed whereby most of the major and minor elements (Si, Al, Fe, Ca, Mg, Ti, Mn, Na, K) in high temperature (750°C) coal ashes were determined by atomic absorption spectrophotometry (A.A.S.) and most of the trace elements (Ba, Be, Co, Cr, Ga, Ge, La, Mo, Ni, Pb, Sc, Sn, Sr, V, Y, Yb and Zr) determined by d.c. arc emission spectrography. However, after the acquisition of a d.c. argon plasma spectrometer, a study was conducted to determine whether this instrument was capable of assuming some of the functions of the atomic absorption unit or emission spectrograph. This was done because emission spectrometry offers many advantages over A.A.S. and conventional emission spectroscopy, primarily in the area of rapid analysis of sample. Whereas in A.A.S., only one element can be determined at a time, emission spectrometry has the capability of performing simultaneous multi-element determinations (up to 18 at one time for the instrument in this study). In addition, the emission spectrometer, unlike the emission spectrograph, has a direct numerical readout which is much more amenable to efficient data handling and manipulation than the conventional photographic plates. This, in turn, coupled with a more stable excitation source, leads to greater precision among different sets of data. Additionally, the superior dispersion (between 0.61 and 2.44 A/mm in the 2000-8000 a range) of the echelle grating eliminates many of the spectral interferences common to other spectrographs. Emission spectrometry is also, unlike A.A.S., not limited by hollow cathode lamps, does not employ explosive gases, and because of the higher source temperature, has fewer chemical interferences.

Because the plasma emission spectrometer accepts only liquid samples, it was decided to initially compare the instrument with A.A.S. The emission spectrometer employed here is the Spectrametrics Incorporated (SMI) Spectraspan III in which the excitation source consists of a high temperature (up to 10,000 K, typically 6000°K in the analytical region) d.c. argon plasma. The instrument nebulizes liquid samples with argon and introduces the aerosol into the plasma at a constant rate by means of a peristaltic pump. The emitted radiation is dispersed in the spectrometer by an echelle grating, the orders separated by a quartz prism and channeled into a series of photomultiplier tubes each of which are set so as to receive the radiation at one particular wavelength characteristic of each of the various elements of interest (e.g. Cu is determined by monitoring the Cu 3274 line in the 69th order, Mn by monitoring the Mn 2576 line in the 88th order, etc.)* The capability also exists for adjusting the system so that elements other than the 18 pre-set elements can be determined. The photomultiplier tube outputs for the various elements are connected with a micro-computer which manipulates the received data according to various programs (e.g. integration over a period of time, use of an internal standard, etc.) and prints out the results on an auxiliary printer. The raw data (arbitrary units in the range 0-9999) may also be printed out if so desired.

The sample preparation for the plasma spectrometer is essentially the same as that used for A.A.S. (1). The high temperature ash (750°C) of the test coal was ground to -200 mesh (<74 μ) to ensure sample homogeneity and a 200 mg sample was mixed with 800 mg of $LiBO_2$ and fused at 1050°C for 10 minutes; the resultant molten bead is then poured directly into 80 ml of a 4% HNO_3 solution. For plasma spectrometry, 6 replica solutions were prepared from this initial solution by taking six 5.00 ml aliquots and diluting each with 35.0 ml of a solution consisting of 0.5% Li

*Analytical lines are listed in Table 1.

Table 1. Analytical Lines Used for the Emission Spectrometric Analysis of Coal Ashes

Element	Wavelength (A)	Order
Al	3961	57
Ba	4554	50
Ca	3179	71
Cu	3247	69
Fe	2382	95
Ge*	2651	85
K	7698	29
Mg	2795	80
Mn	2576	88
Na	5895	38
Si	2516	90
Sr	4077	55
Ti	3349	67
Zn	2138	106
Zr	3601	62

*Used as internal standard.

in 2% nitric acid and containing 10 ppm Ge. The Li content of the final solution is about 4500 ppm and serves as an effective spectroscopic buffer while the Ge acts as an internal standard. Six replica solutions were also prepared for A.A.S. by diluting 5.00 ml aliquots of the initial solution with 30.0 ml of a 10,800 ppm La solution, the La acting as a releasing agent in the flame process. The appropriate sets of solutions were then ready to run on the plasma spectrometer and A.A. spectrophotometer along with sets of standards prepared in the same manner as the samples. However, the nature of the electronics on the plasma spectrometer is such that prior to the running of the solutions, it was necessary to calibrate the instrument with standards containing approximately the highest concentrations of the elements that one would expect in the solutions. Once so calibrated the instrument automatically extrapolates linearly between the calibrated maximum point and a blank to give a reading for each solution run. If, however, this calibrated upper limit should be exceeded by more than about 25% by a solution, no reading will be produced and the solution must be diluted before it can be analyzed. Although, in theory, only one standard need be run for the emission spectrometer, at least three or four were run as a check against both possible line curvature (e.g. distortion due to self-absorption) and errors in the preparation of any one standard. All of the standards used are shown in Table 2.

During the actual running of solutions in both plasma emission spectrometry and A.A.S., the standards were run first, then the six samples, then the entire set of solutions in reverse order so that two runs were performed on each solution. This was done to cancel out any instrumental drift which might occur from the first to the last sample. The results of three sets of runs; one set on the plasma spectrometer with the internal standard function off, one set with the internal standard on, and one set on the atomic absorption unit, are presented in Table 3.

Each number in Table 3 represents the mean of 6 replicas and is given ± 2 standard deviations. While the plasma spectrometer is theoretically capable of simultaneously determining all of the elements listed, in practice it was found that usually no more than 5 or 6 elements could be comfortably handled at any one time due to variations in the instrumental calibrations for each element over a long period of time (one-half hour or so). Consequently, the elements Fe, Mg, Ca, and Mn were run as a group while Si, Al, K and Na formed a second group. By A.A.S. of course, each element was determined separately. The results show that with the exception of Fe, all of the elements determined overlap each other within the 2σ significance range. Although no explanation can be given for the difference in iron values by A.A.S. and emission spectrometry, a titrimetric determination on another sample split gave a value of 4.37% Fe_2O_3 which is more in agreement with the emission spectrometric results. Table 3 also shows that the magnitude of the standard deviation tends to be significantly greater for the atomic absorption determinations than it is for either of the sets of data obtained from plasma emission spectrometry.

This is especially true for silica. Although part of the scatter may be explained by the observation that the silicon hollow cathode lamp was beginning to fail, the standard deviations obtained for silica in rocks and coal ashes by plasma emission spectrometry are nevertheless better than those obtained by A.A.S., even under optimum conditions. No attempt was made to rigidly define and compare detection limits for the various elements by emission spectrometry and atomic absorption because such limits tend to be affected by many factors which are easily altered (e.g. sample composition, gas flow and pressure, optical alignment, electronic stability, etc.). However, on the basis of observations made during this study, and ignoring the major constituents, it can generally be said that those elements that have strong emission lines or form refractory oxides are determined better at low concentrations by plasma emission spectrometry than by A.A.S.

The results in Table 3 also indicate that the standard deviations for the plasma spectrometric determinations in which an internal standard was employed tend to be somewhat better than those in which no internal standard was used, although the differences do not appear to be statistically significant.

Some studies here as to whether or not the plasma spectrometer is capable of adequately determining some trace elements currently done by conventional d.c. arc spectrography indicate that the elements Ba, Cr, Cu, Sr, V and Zr may be done on the spectrometer. In addition to the previously mentioned advantages of using the spectrometer, the initial results indicate that an improvement in precision also results. This is probably because of two factors, the first of which is the use of a more stable excitation source and second, the use of a larger sample size. A 200 mg sample is taken for the fusion technique while only 6 mg of sample is used per electrode for spectrographic analysis. The use of a greater sample size assumes added significance where trace elements tend to be concentrated in inhomogeneously distributed accessory minerals (e.g. Zr in zircon) (2).

Despite the use of a greater initial sample size, however, the dilution of the sample during sample preparation is considerably greater for the spectrometer than it is for the spectrograph. Consequently, the absolute quantities of the sample excited in the spectrometer are much less than that in the spectrograph. Because of this, the conventional spectrograph is still to be preferred for trace elements which are present in minute quantities such that when diluted, would fall below the detection limits of the spectrometer. However, since detection limits, as stated above, tend to be variable in nature, it is not possible to specify the concentrations of each element below which the spectrograph is to be preferred. This must be left to the judgement of the individual operator and laboratory.

Acknowledgment

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Table 2. Standards Used in Plasma Spectrometric and Atomic Absorption Analyses of High Temperature (750°C) Coal Ashes

Species / STD	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	TiO_2	Cu	Ba	Sr	V	Zn	Zr
G-2	69.2*%	15.1%	2.75%	2.00%	0.76%	0.034%	4.50*%	4.05*%	0.50%	-	1860ppm	477ppm	34ppm	-	300ppm
PCC-1	-	-	-	-	-	-	-	-	-	-	-	-	-	36ppm	-
W-1	52.6	15.0	11.06	10.96	6.52	0.175	0.63	2.15	1.08	110ppm	169	198	260	86	105
T-1	62.6	16.2	5.88	5.12	1.82	0.100	1.23	4.32	0.56	-	579	-	-	160*	170
BR	38.3	10.25	12.9*	13.9*	13.34*	0.205*	-	-	2.62*	72	1080	1350	240	160	-
NBS98	59.1	25.54	2.05	0.21	0.72	0.005	3.17	0.26	1.43	-	-	-	-	-	-
BR:NBS98 1:1	48.7	17.9	7.48	7.06	7.04	0.105	2.29	1.67	2.03	-	-	-	-	-	-
NBS98A	48.9	33.2*	-	-	-	-	1.04	0.082	-	-	-	-	-	-	-
NBS97	-	-	-	-	-	-	-	-	-	-	-	-	224	-	1850*
PSOC364	-	-	-	-	-	-	-	-	-	317*	2320*	5000*	400*	-	-
PSOC364:Blank 1:1	-	-	-	-	-	-	-	-	-	158	1160	2500	200	-	-
Blank+	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Used for high standard calibration of plasma spectrometer

+Blank is spec-pure silica

G-2 (granite), PCC-1 (peridotite), W-1 (basalt) are U.S. Geological Survey rock standards, T-1 is a tonalite rock std from Tanganyika, BR a basalt from the Centre de Recherches Petrographiques at Geochemiques, France, NBS97 and 98 are clays from the U.S. National Bureau of Standards and PSOC364 in a coal ash.

Table 3. Comparison of Atomic Absorption* and Plasma Spectrometric* Data from a Coal Ash (PSOC 361)

	d.c. Plasma Spectrometry		Atomic Absorption
	No Internal Standard	Internal Standard (Ge)	Spectrophotometry
SiO_2	61.0% ±.8	60.6% ±.5	57.5% ±5.6
Al_2O_3	27.6 ±.7	26.7 ±.5	27.1 ± .4
Fe_2O_3	4.28 ±.04	4.37 ±.04	4.54 ± .06
CaO	0.794±.008	0.798±.016	0.844± .046
MgO	0.861±.014	0.868±.010	0.875± .014
MnO	0.018±.0004	0.018±.0004	0.018± .002
K_2O	2.69 ±.036	2.65 ±.030	2.58 ± .042
Na_2O	0.767±.050	0.753±.048	0.813± .064

Each value given represents the mean of six sub-samples ± 2 standard deviations.

*Atomic Absorption unit employed was a Perkin-Elmer Model 403, instrumental parameters for A.A.S. were as stated in the Perkin-Elmer manual (3) with the exception of Ca for which a N_2O-C_2H_2 flame was used instead of the recommended air-C_2H_2. The plasma spectrometer was a Spectrametrics Spectraspan III.

TRACE METAL ANALYSIS IN COAL BY MULTIELEMENT ISOTOPE DILUTION SPARK SOURCE MASS SPECTROMETRY

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INTRODUCTION

The use of spark source mass spectrometry for the analysis of environmentally important elements found in coal and fly ash is described. Significant improvement in the accuracy and precision of the method has been accomplished by use of isotope dilution methods for several elements in a sample. As many as 20 elements have been simultaneously determined in certain energy-related samples using multielement isotope dilution SSMS. The precision and accuracy are typically ±5-10% RSD for elements present at greater than 1 part per million in the sample.

For those samples which are difficult to dissolve cleanly, it is not possible to apply the classical isotope dilution technique. Rather, the dry material is mixed with a 'spiked' conducting matrix containing separated isotopes of the elements of interest. This method combines ease of sample handling with certain desirable aspects of separated isotopes—namely their freedom from contamination effects. Here the precision obtained is typically 10-15% RSD and the accuracy depends on the use of appropriate standards.

EXPERIMENTAL

For an isotope dilution analysis, the following steps are taken:

1. Complete dissolution of the sample in a high purity acid (HNO_3, HCl).
2. Addition of accurately standardized separated isotope 'spikes.'
3. Isotopic equilibration by chemical or thermal means.
4. Mass spectrometric analysis.

The important step is number three, because it is assumed that once equilibration has occurred, the separation or concentration steps that follow need not be quantitatively known. It is also assumed that the equilibrated spike and sample isotopes will behave in an identical fashion, both chemically and in the ion source of the mass spectrometer.

Coal and fly ash analysis by this method depends upon sample dissolution. Unfortunately, the acids required to completely dissolve these materials (HF, $HClO_4$, H_2SO_4) are difficult to obtain in a pure form and also produce undesirable molecular ion species in the spark source. High pressure dissolution in a teflon lined pressure bomb (Parr Instrument Co.) using HNO_3 and HCl has been tried, but silicate species are usually not soluble under these conditions. Other methods, such as NaOH fusion followed by HCl treatment produced clear solutions, but these contained an unacceptable amount of NaCl which gave rise to mass spectral interferences.

*Operated for the U. S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

Because of the difficulty of dissolving these materials, a dry mixture technique was developed,[1-3] which involves the use of a 'spiked' matrix material such as high purity Ag or graphite. Separated isotopes of the elements of interest were dried from solution onto the matrix and vigorous shaking in a ball mill ensured homogeneity. This spiked matrix was analyzed alone in order to determine the blank levels and was then mixed with standards (NBS SRM 1632 Coal or 1633 Fly Ash) to determine the amount of each isotope added. This standardization also provided any relative sensitivity corrections which were necessary in this technique.

Table I shows the composition of a spiked Ag matrix (99.9999% pure Ag Cominco American, Inc.) which was used in the analysis of coal (after ashing at 500°C in air to remove the organics) as well as fly ash. The isotopes chosen were usually minor ones in nature which were highly enriched and chosen to be free of spectral interference.

The instrumental operating parameters are summarized below:

Instrument:	AEI MS-702R with photographic plate detection.
Spark conditions:	30 kV rf; 100 pulses per second, 25 μsec pulse length.
Vacuum:	Source <1 x 10^{-4} torr; analyzer 2 x 10^{-8} torr.
Photoplate:	Ilford Q2 or Kodak SWR.
Development:	3 minutes in conc. D-19.

A photoplate data reduction system was used which utilized a minicomputer interfaced with a microdensitometer.[4] The computer accepts digitized optical transmittance data as the densitometer scans over a line. It then computes peak height corrected for background and converts this into relative (ion) intensity using a stored calibration curve (Churchill two-line calibration method[5]). The relative (ion) intensities are employed in the computer code to obtain elemental concentrations according to the Hintenberger[6] isotope dilution equation.

The concentration of the element being measured is obtained from the following equation.

$$x = y \left(\frac{R_t - R_m}{R_m - R_s}\right) \cdot \frac{A_s}{A_t} \cdot \frac{T}{S} \qquad 1)$$

where x = weight of element in the sample.

y = weight of element in the tracer spike.

R_t = isotope ratio of the spike, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

R_m = isotope ratio of the mixture, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

R_s = isotope ratio of the sample, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

A_s = atomic weight of the sample element.

A_t = atomic weight of the tracer.

T = atom % of the spike isotope in the tracer.

S = atom % of the spike isotope in the sample.

The terms: A_s, A_t, T, S, R_s, R_t, and y are usually known in advance, and since R_m can be very accurately measured, it is not unusual to obtain precision and accuracy on the order of 5% for trace element determinations. After equilibrium between spike isotope and sample reference isotope is obtained, quantitative results are assured by isotope dilution even when a low yielding chemical purification is required.

RESULTS AND DISCUSSIONS

Table II shows results for NBS SRM 1632 using the dry spike technique, with SRM 1633 acting as the standard. The results agree within experimental precision for all elements shown. It was possible to analyze a number of other elements by the same technique, provided the concentration in the standard was known with some certainty. In all, twelve elements are routinely reported in coal by this method with a precision and accuracy of about ±15% RSD.

Any analysis of coal or fly ash by SSMS is subject to mass spectral interference arising from the major elements present. These include Si, Al, Ti, Mg, Fe, Na, K and S. Combinations of these elements, oxides, silicates and chlorides, as well as molecular ions from the matrix element (Ag_2^+, AgO^+) must all be considered for their potential effect on the analysis. Certain elements are generally always interfered with (Co^+ by CaF^+ and Sb^+ by AgO^+), while other isotopes are only occasionally affected. Therefore, if a small number of elements is to be analyzed, the analyst should consider using separation and concentration methods to eliminate possible interferents.

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Table I

Spiked Silver for Coal and Fly Ash Analysis

Element	Isotope	Enrichment	Nominal Concentration
Pb	204	99.7	10 ppm
Tl	203	94.9	5
Ba	135	93.6	50
Te	125	91.2	10
In	113	96.4	5
Cd	111	91.3	5
Mo	97	94.3	5
Sr	86	95.7	100
Se	77	94.4	10
Zn	67	89.7	30
Cu	65	99.7	30
Ni	61	99.5	30
Fe	57	93.6	100
Cr	53	96.4	30
K	41	99.4	200

Table II

Analysis of SRM 1632 Using SRM 1633 as Standard

Element	Conc. in μg/g ± RSD	NBS Certified
Tl	0.6 ± 0.2	0.59 ± 0.03
Pb	33 ± 3	30 ± 9
Cd	0.4 ± 0.2	0.19 ± 0.03
Zn	32 ± 8	37 ± 4
Cu	15 ± 3	18 ± 2
Ni	15 ± 3	15 ± 1
Cr	19 ± 3	20.2 ± 0.5

Recent Application of Neutron Activation Analysis to Coal

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The possibility of environmental contamination resulting from current and proposed uses of large quantities of coal for combustion, liquefaction, and gasification has been discussed extensively. In order to evaluate the potential for harm, many studies have been undertaken to determine the trace-element compositions of various coals and the elemental budgets of coal-consuming facilities, such as power plants. Neutron-activation analysis has been used extensively for these studies, because the method has good sensitivity for a large number of elements of interest, is nondestructive, and, when automated, can be used to process samples rapidly and efficiently.

In common with other analysts, the activation analyst strives to reduce interferences and determine the elements of interest. The methods used to discriminate among the large numbers of radioactive nuclides produced by neutron bombardment are listed in Table 1. Such an outline is useful for a general discussion of neutron-activation analysis, but variations of the techniques may deviate from this table. Because of the large numbers of coal samples that must be analyzed, instrumental techniques have been employed whenever possible to avoid time-consuming radiochemical separations and the possibility of loss of volatile elements.

Although all of the techniques in Table 1 are instrumental, with the exception of radiochemical neutron-activation analysis (RNAA), the term instrumental neutron-activation analysis (INAA) is ordinarily reserved for the method in which gamma-spectra are collected using high-resolution gamma-detectors (lithium-drifted germanium or intrinsic germanium) at different decay times following neutron bombardment of the sample. This technique allows the determination of as many as 40 elements in coal and fly ash, and many such multi-element procedures have been reported (1-10). The elements determined include Al, As, Au, Ba, Cr, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, and Zn. However, about seven of these elements (Au, Ba, Ga, Ni, Rb, Ti, and Zn) exist in some coal at concentrations near their limits of detection, and, therefore, the exact number of elements that can be determined depends on the composition of the individual coal sample. The U.S. Geological Survey used INAA to determine many of the elements listed above in eighteen coal samples from various locations in the United States (11) and, more recently, as one of the analytical techniques for routine analysis of 2,000 Eastern U.S. coal samples. However, special emphasis is placed on determining As, Cr, Co, Sb, and Se, because these elements are more difficult to determine by other analytical techniques.

If a sample is surrounded with Cd during neutron bombardment, then activation by epithermal neutrons is enhanced relative to that by thermal neutrons and some selectivity may be achieved. This technique has been used to determine U and Th in coal and coal ash (12, 13). At the U.S. Geological Survey, Rowe and Steinnes made an extensive study of the activation analysis of coal and fly ash that included a comprehensive comparison of thermal and epithermal INAA (10). They found that the sensitivities for Ba, Cs, Ga, Hf, Ho, In, Mo, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, and Zr were improved when epithermal INAA was employed.

Fast neutrons (14 MeV) from a neutron generator may be used to activate light elements. O, N, F, Si, and Al have been determined in coal by this rapid and routine technique (14-17). Because the distribution of O between the organic and mineral components of coal is highly variable and because the other elements are determined by other routine techniques, the fast neutron method is seldom used in coal analysis.

Prompt gamma-counting (PG) involves detecting the gammas emitted immediately after neutrons are absorbed during bombardment. This method has been used to determine Fe, B, and Cd in coal (18, 19).

The delayed-neutron counting technique (DN) is used (20) primarily to determine U and Th. One-minute neutron irradiations are followed by several minutes of counting the neutrons emitted by the fission-daughters of U and Th. Thermal and epithermal neutron irradiations are performed to differentiate between U and Th. At the U.S. Geological Survey, we use automated neutron counters to analyze about 7,000 samples per year by this technique (11, 21). Using 5-g coal samples, the carbon matrix causes neutron thermalization within the sample, so it is important to prepare standards by spiking a suitable coal with U and Th. We maintain good accuracy by intercalibration with isotope dilution-mass spectrometric U and Th standards.

Uranium may also be determined by fission-track (FT) counting (22). This technique is very useful for small samples (<100 mg), such as mineral separates. We have automated this procedure by using spark-counting or more recently, by employing an image analyzer. Fission-track maps of pellets prepared from coal powders indicate whether the U is distributed evenly in the organic matrix or is concentrated in discrete mineral phases such as apatite. Maps of thin sections of coal can be used to find minerals containing high concentrations of U, and these minerals may then be identified by suitable techniques such as electron-microprobe analysis.

Radiochemical neutron-activation analysis (RNAA), in which radiochemical separations are performed after neutron irradiation and prior to counting, has been used to determine As, Br, Cd, Cs, Hg, Ga, Rb, Sb, Se, U, and Zn in coal (23, 24). However, in recent years these methods have been replaced to a great extent by the faster and less tedious instrumental techniques discussed above. RNAA still is used for several elements (e.g., Hg and Cu) for which instrumental methods are not sufficiently sensitive (6, 25), and to calibrate standard materials when the highest levels of precision and accuracy are required.

Table 1. Methods of discrimination employed in various neutron-activation analysis techniques

INAA = Instrumental Neutron Activation Analysis
FNAA = Fast Neutron-Activation Analysis
PG = Prompt Gamma-Counting
DN = Delayed Neutron Counting
FT = Fission Track
RNAA = Radiochemical Neutron-Activation Analysis

Method of Discrimination	NAA Technique						
	INAA						
	Thermal	Epithermal	FNAA	PG	DN	FT	RNAA
Energy of bombarding neutrons:							
thermal (0.1 eV)	X			X	X	X	X
epithermal and resonance (0.1-1000 eV)		X			X		X
fast (14 MeV)			X				
Irradiation time	X	X	X		X		X
Decay time after irradiation	X	X	X		X		X
Emitted particle measured:							
gamma (spectrometry)	X	X	X	X			X
neutron					X		
fission fragment						X	
Chemical properties							X

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A SURVEY OF EMISSION X-RAY ANALYSIS OF COAL

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Measurement of emitted X-rays is finding widespread acceptance as an analytical tool for determining minor and trace elements in coal and coal-related materials. Because the method requires a short time for analysis and can determine concentrations ranging from a few parts per million up to 100% in a single sample, it is a desirable alternative to many other techniques (1).

Following the development of the method of Rose et al. (2), accurate analyses of coal ash have been routinely performed for several years. Methods for X-ray analysis of whole coal, however, despite earlier work by Sweatman et al. (3), have developed more slowly (4,5,6,7). Recent improvements in equipment, especially innovations in detectors and excitation sources, have brought about renewed interest in the technique.

Two types of spectroscopic systems are now available. One is the wave-length dispersive unit which uses crystals with various lattice spacings to diffract and separate the X-rays emitted from excited samples. A goniometer is then used in conjunction with either a gas-flow or a scintillation detector to measure the angle and intensity of the emitted radiation. The second type of system consists of a solid state detector, either lithium-drifted silicon or intrinsic germanium, connected to a multichannel analyzer. A typical detector, with resolution of 140ev to 160ev, produces pulses whose amplitudes can be separated and quantified for most X-rays. These systems, therefore, are capable of simultaneous multi-elemental analyses over a wide range of energies.

The X-ray tube, both with and without filters, is a common excitation source, but a number of other kinds of sources are useful. In systems where portability is desirable, isotope sources are commonly used with solid state detectors. These sources give nearly mono-chromatic exciting radiation which means that background corrections are smaller for effects due to scattered radiation and background. Decay of isotopes limits their useful life, but sources such as americium 241 (used with secondary targets) can provide resonably stable excitation for many years. Excitation by electron probe, ion probe, scanning electron microscopy, etc., is now widely used for X-ray analysis. Energetic protons, also used to induce X-ray emission, have the additional advantage of producing gamma radiation, which increases the number of elements that can be determined (8).

Regardless of the type of spectrometer or the exciting source used, a number of other problems must be solved before accurate analysis of coal and its related products can be obtained. Foremost among these is the problem of adequate standards. At present only two certified standards are available, one for trace elements in coal and one for trace elements in fly ash. This means that each laboratory must produce its own set of standards. Mathematical correction procedures may be applied instead but they are unsatisfactory when there are large variations in matrix. The second major problem is the acquisition of representative samples for analysis. Coal itself, is perhaps the simplest material to sample but still presents problems due to inhomogeneity. Variations within the coal seam or feed stock may limit precision to 5% (9), and the presence of discrete mineral particles may result in even greater errors (10). Coal-related materials - e.g. chars, ashes, residues, and products from liquefaction and gasification processes - vary greatly depending upon temperature,

physical location in the system, processing time, and other factors. These materials may range from nearly totally inorganic minerals to wholly organic liquids; occasionally a very viscous slurry that is almost impossible to homogenize is encountered.

The great variability of these materials causes not only sampling difficulties but also significant analytical problems. X-ray analysis is highly dependent upon matrix variations, which are normally handled in one of three ways. One solution is to prepare a sufficient number of standards so that every conceivable matrix can be very closely matched. Though this is not impossible, it is usually impractical for most laboratories.

A second method of handling the matrix problem is to prepare analytical samples in such a way as to make the variations almost insignificant. This may be done by dilution with an inert material (11), by addition of a heavy adsorber (2), or by preparation of a sample thin enough that all X-rays generated in the material will escape (6,8). The first two technqiues tend to raise the limit of detection of the trace elements in the original sample. Even though the third technique requires great care to prepare a uniform, representative sample, it is being used quite successfully by a number of laboratories.

The third method of correcting for matrix effects employs mathematical procedures. These procedures may be divided into three groups. The first includes various methods for empirically measuring the mass absorption coefficient of the material for the radiations of interest. These methods have been reviewed extensively by Lubecke (12) and Sparks et al. (7). In the second group of procedures, Compton scatter is used to estimate mass absorption coefficients (13,14,15,16,17). In the last group of techniques, all corrections are made mathematically from a knowledge of fundamental parameters (18). This method requires observation of the intensities of the radiation from all of the major elements in the sample.

Although any one of the matrix correction procedures listed above may work for a particular analytical problem, a combination of two or even all three is justified in a laboratory with a wide variety of sample types. All these procedures require the use of a satisfactory background correction. Since the background is due not only to the mass absorption coefficient and to elemental concentrations of the sample but also to the exciting source, the detector, and the analyzing system, it may well be the limiting factor in the precision of analysis, especially for trace elements in most materials. A good discussion of these problems is presented in a recent review by Russ (19).

The coal analyst must be familiar with all of these problems inherent in X-ray procedures. Most of them can be handled satisfactorily with computer programs. When samples are properly prepared, the analyst can handle types ranging from liquids to solids and from almost pure organic materials to totally inorganic minerals. Such samples can be analyzed 'as is' as long as the surface presented to the spectrometer is uniform, representative, and exhibits no particle-size effects. This may require the use of samples with particles of less than -325 mesh down to a few microns in size especially for the determination of elements of low atomic weight.

Precision for modern X-ray systems is approximately 5% to 25% overall, for trace elements, depending upon the optimization of the spectrograph for the elements of interest. For major and minor elements, depending upon the system used, precision may well be less than 1%. The elements with lower atomic numbers, i.e., Na thru Ca, can not be analyzed as precisely as the heavier elements, especially with energy-dispersive systems.

The limit of detection by X-ray analysis, with presently available commercial equipment, ranges, for coal samples, from 100 for sodium to .5 to 4 PPM for the elements iron through cerium (10). For those elements of heavier atomic weight where the L series X-rays are used for analysis, the limit of detection is approximately 10.

While precision and limit of detection do not necessarily indicate accuracy, with good standards and good programs for matrix corrections the results of X-ray analysis compare favorably with results by other methods of analysis. Its simplicity and ease of operation make it the method of choice where a large number of samples are to be investigated for many elements.

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X-ray Fluoresence Analysis of Trace Metals in Solvent Refined Coal

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Introduction

This work was undertaken to ascertain the ability of Energy Dispersive X-ray Fluoresence (EDXRF) analysis to determine trace element content of Solvent Refined Coal (SRC). As a result of recent improvements in the design of solid state detectors for X-ray Fluoresence it is now possible to do very rapid simultaneous quantitative analysis of a large number of elements. In this work some 17 elements are quantitatively analyzed in both raw feed coal and product SRC from the Wilsonville SRC Pilot Plant, Wilsonville, Alabama.

The content of trace metals in SRC product and in feed coal is important for several reasons: Certain metals, particularly iron, catalyze the hydrogenation and hydrodesulfurization reactions that occur in the SRC process. If the SRC product is to be used to fire a gas turbine, then trace metals such as Ca, Na, and V present potential corrosion or fouling problems. When the feed coal has a high oxygen and a low sulfur content, a substantial portion of western, sub-bituminous coal, for example, has a low sulfur (~0.7%) and a high oxygen (~17%) content, trace metals such as Ca react with CO_2 formed in the SRC dissolver and tend to collect in the dissolver, eventually resulting in plugging problems. Trace metals such as As in SRC product present potential environmental problems. Also, metals such as Fe and Al are present in sufficient quantity in the feed coal that the SRC mineral residue represents an attractive source of these metals when current sources have been depleted.

Analysis of trace elements in coal has been the subject of many earlier papers (1,2,3). In fact, analytical methods, specifically, atomic absorption, (4,5) have been presented for determining the content of trace metals in clean coal products such as SRC product. However, because of the large number of analyses required to maintain reasonable quality control of SRC product, etc., alternative methods that are hopefully more rapid and less expensive than those currently available are needed. Application of EDXRF to perform assays of feed coals and SRC products is attractive because it allows simultaneous analysis of trace elements found in feed coals and SRC products. This work demonstrates that EDXRF is an effective method for determining the content of trace metals in coal and coal-derived products.

Experimental

Equipment

All EDXRF analyses were done on a Kevex 0810RW X-ray Fluoresence System (Kevex Corporation, Burlingame, Ca. 94010) consisting of a 0810A X-ray Subsystem, 5100C analyzer, 5100 X-ray Spectrometer Rigaku Gigerflex 3kW X-ray generator, (60 kV and 180 ma) Digital Electronics Corporation PDP 11/03 Computer with RX01 dual floppy disk bulk storage. The system uses a high power X-ray tube (Ag target) to produce X-rays from a series of selectable secondary targets (Ti, Ge, Mo, and Sn). The spectrometer uses a solid state detector of 30 mm^2 active area that has resolution of <165eV @ 1KHz.

Atomic Absorption experiments for iron were done on a Perkin-Elmer Model 305A Atomic Absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut 06856) using an acetylene/air flame and a wavelength setting of 249 nm. Sulfur determinations were made using a Leco model 521-500 sulfur analyzer specially fitted for low level sulfur detection (Laboratory Equipment Corporation, St. Joseph, Michigan 49085).

Procedure

Approximately 10 g. samples of all coals and SRC's were first ground so that the entire sample passed through a 325 mesh screen. The samples were then dried in a vacuum oven at 105°C for at least 3 hours. From these samples 1.25 inch pellets were made using a boric acid backing and were analyzed by EDXRF under a vacuum of 5×10^{-4} torr. Also, fractions of the same samples were used to perform Leco sulfur, C, H and N, and Atomic Absorption analyses.

The raw EDXRF data were analyzed using the Kevex matrix correction program, and adaptation of the shell EXACT (6) program. The EXACT program employs a fundamental parametric method which accounts for matrix interactions due to absorption and enhancement for all the elements in the sample. The EXACT model is basically similar to models presented by Sherman (7), Shiraiwa (8) and Criss and Birks (9) with simplifications.

Results

Table 1 gives a comparison between EDXRF and two methods, Atomic Absorption (AA) and Leco, commonly used in this laboratory for analysis of iron and sulfur, respectively. At the bottom of Table 1 are analyses for three standards (Certified Atomic Absorption Standard, 1000 ppm iron, Fisher Scientific, FairLawn, New Jersey 07410; Calibration Standard no. 764-547 (2.02 ± 0.03% S) and Calibration Standard no. 764-545 (0.31 ± 0.02% S) LECO Corporation, 3000 Lakeview, St. Joseph, Michigan 49085). These standards were purchased for use in calibration of atomic absorption and LECO analysis. In all cases EDXRF gave the best accuracy for the standards analysis.

Table 2 gives the EDXRF elemental analyses for 12 coals and SRC's. As expected smaller amounts of the 17 elements analyzed for were detected in the SRC products than in the respective feed coals.

Little would actually be gained by an element by element comparison of the various coals and SRC's. On the other hand, Figure 1 gives an interesting correlation between ash content of moisture free coal and cumulative weight percent of 15 elements (Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, and Sr) as determined by EDXRF. Least Squares analysis of the data gave a straight line correlation factor (r) of 0.92 at the 95% confidence level. An r value of 0.92 indicates a reasonable fit was obtained and that the resulting correlation can be used to compute the approximate percent ash in feed coals. Most importantly, these data demonstrate that the ash content of a feed coal can be approximated very rapidly in this manner. At this time experiments are in progress to show that the same relationship is also true for SRC product.

Summary and Conclusion

It has been shown that EDXRF is capable of analyzing coals and SRC's for elemental content. These analyses provide simultaneous results for several important elements, namely sulfur, iron and calcium, as well as percent ash. These analyses presently take well over 2 hours per sample to complete, but by using EDXRF this time can be reduced to less than one hour per sample. Furthermore, EDXRF has an added feature in that it may be automated, leading to even shorter analysis times per sample. Thus, EDXRF can be concluded to be an effective tool that can provide very accurate and rapid analyses of coals and SRC product for their elemental content.

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TABLE 1

Comparison of EDXRF to Atomic Absorption and Leco Sulfur

Coal	XRF	A.A.	Leco	Known Value
Western Kentucky				
Fe	0.697	0.800		
S	2.24		2.56	
Wyodak				
Fe	0.265	0.247		
S	0.637		0.764	
Illinois #6				
Fe	0.629	0.526		
S	2.76		2.45	
Pittsburg #8				
Fe	0.561	0.615		
S	2.22		2.87	
Monterrey				
Fe	1.165	0.732		
S	3.07		3.24	
Rosebud				
Fe	0.466	0.270		
S	0.976		1.04	
Bighorn				
Fe	0.267	0.216		
S	0.582		0.620	
Standards				
Fe	0.1072	0.937		0.1000
S	1.995		2.22	2.02
S	0.301		0.278	0.31

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TABLE 2

EDXRF Analysis of SRC and Coal

Element	A	B	C	D	E	F
			wt.%			
Si		1.612		1.813		2.097
P	0.0755	0.183	0.0657	0.186	0.0840	0.251
S	0.723	2.24	1.04	2.22	0.755	2.76
Cl	0.0097	0.0177	0.0053	0.105		
K	0.001	0.0977		0.100		0.112
Ca	0.0087	0.0817	0.0144	0.910	0.0024	0.148
Ti	0.0092	0.0383	0.0088	0.0537	0.0178	0.0549
V	0.0037	0.0089	0.0049	0.0099	0.0036	0.0149
Cr		0.0036	0.0026	0.0025	0.0023	0.0058
Mn	0.0018	0.0022	0.0008	0.0043	0.0026	0.0048
Fe	0.0427	0.697	0.0191	0.561	0.0199	0.629
Ni	0.0002	0.0010	0.0008	0.0038	0.0010	0.0020
Cu	0.0003	0.0012	0.0006	0.0028	0.0014	0.0017
Zn	0.0005	0.0013	0.0007	0.0038	0.0006	0.0015
As	0.0001	0.0008	0.0002	0.0005	0.0001	0.0006
Br	0.0002	0.0003	0.0004	0.0009	0.0003	0.0005
Sr		0.0014		0.0132		0.0014

A Western Kentucky SRC
B Western Kentucky 9/14 Coal
C Pittsburg #8 SRC
D Pittsburg #8 Coal
E Illinois #6 SRC
F Illinois #6 Coal

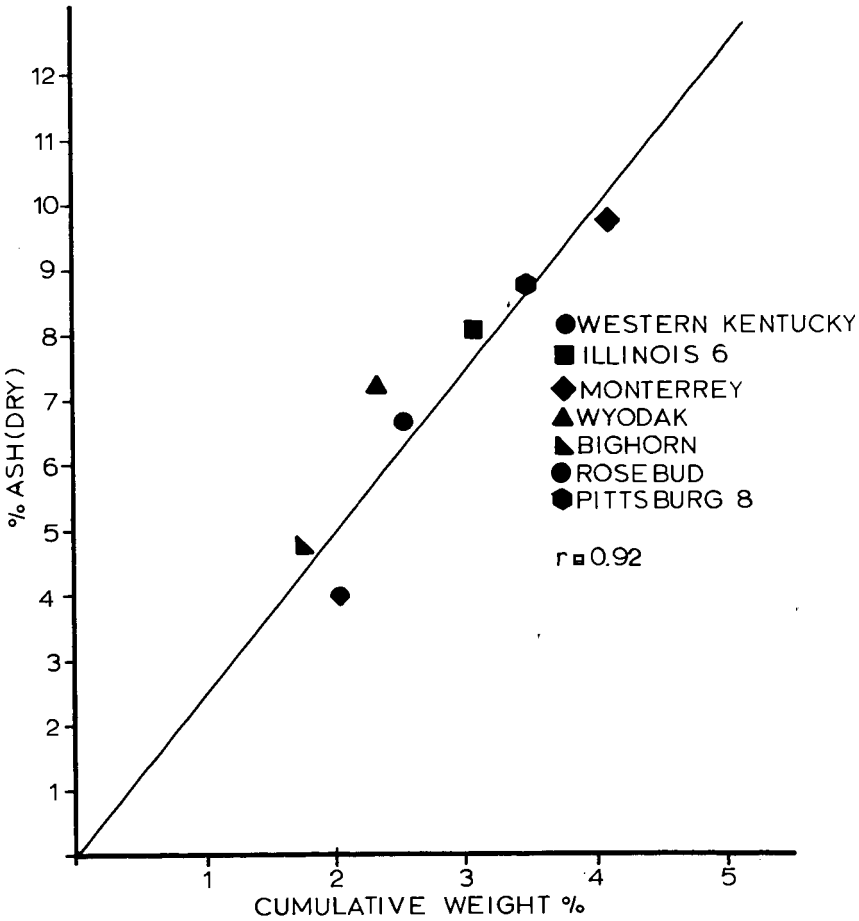
TABLE 2 CONTINUED

EDXRF Analysis of SRC and Coal

Element	G	H	I	J	K	L
			wt.%			
Si		1.073	0.1021	2.578	0.821	0.903
P	0.0306	0.143	0.0953	0.2193	0.122	0.101
S	0.152	0.6371	1.172	3.070	0.976	0.582
Cl	0.0036	0.0536		0.241	0.106	
K		0.0310	0.0040	0.1245	0.0266	0.0204
Ca	0.0162	0.858	0.0022	0.2750	0.557	0.473
Ti	0.0078	0.0585	0.0133	0.0617	0.0352	0.0511
V	0.0023	0.0353	0.0034	0.0104	0.0124	
Cr	0.0017	0.0033		0.0090	0.0110	0.0041
Mn	0.0012	0.0031		0.0087	0.0063	0.0025
Fe	0.0228	0.2615	0.0450	0.1651	0.466	0.2667
Ni	0.0013	0.0006		0.0015	0.0019	0.0014
Cu	0.0017	0.0056	0.0010	0.0201	0.0017	0.0058
Zn	0.0005	0.0020	0.0004	0.0016	0.0004	0.0013
As	0.0001	0.0004	0.0001	0.0006	0.0003	0.0005
Br		0.0002	0.0004	0.0005	0.0008	0.0001
Sr	0.0001	0.0137	0.0007	0.0013	0.0088	0.0074

G Wyodak (Amax) SRC
H Wyodak (Amax) Coal
I Illinois (Monterrey) SRC
J Illinois (Monterrey) Coal
K Rosebud Coal
L Big Horn Coal

FIGURE 1


12
11
10
9
8
7
6
5
4
3
2
1
% ASH (DRY)
1
2
3
4
5
CUMULATIVE WEIGHT %
WESTERN KENTUCKY
ILLINOIS 6
MONTERREY
WYODAK
BIGHORN
ROSEBUD
PITTSBURG 8
r = 0.92

Chemical Constituents In Different Solvent Refined Coals As A Function Of The Feed Coal

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The chemical characterization of the organic constituents in solvent refined coal (SRC) is currently a subject of major concern (1) in terms of understanding present SRC processes and coal processing in general. The heterogeneous semi-solid SRC product obtained from present pilot plants represents a formidable analytical problem for identification and quantification of the organic materials present in SRC solids. Ideally, chromatographic separation of every individual organic compound present in SRC solids would allow relatively easy identification via modern analytical tools, such as, ^{1}H and ^{13}C Fourier transform nuclear magnetic resonance (^{1}H and ^{13}C FT nmr) and mass spectrometry. The feasibility of this approach, however, is questionable even assuming ideal chromatographic resolution could be achieved in light of the enormous time, quantity of material and probably weight losses accompanying each chromatographic separation. These limitations are especially acute for studies which monitor changes in organic composition as a function of a particular coal process variable (e.g., temperature, solvent, feed coal, etc.). An alternate chromatographic approach involves partial separation of the complex coal product mixture into numerous fractions based on either functionality, polarity or effective molecular size. Characterization of chromatographic fractions from this partial separation still has an obvious disadvantage in terms of analytically describing "average" molecular parameters. Although chemical characterization in terms of "average" molecular parameters is certainly a less than ideal approach, it does provide a reasonable method of monitoring processing variables provided that chromatographic fractions of a given size or type (nonpolar, polar, etc.) can be easily separated with nearly quantitative recovery. The established utility of ^{1}H and ^{13}C FT nmr allows a convenient method of deducing important average molecular parameters, such as, H/C aliphatic and aromatic ratios as well as assessing the relative importance of a number of other organic functional groups, (e.g., carbonyl, hydroxyl, phenol, etc.).

In the present comparison study of the organic constituents in SRC solids as a function of the SRC processing feed coal, we have employed gel permeation chromatography (2,3) for separation of the SRC solids into fractions based on effective molecular size rather than organic functionality or polarity. This approach has the advantage of providing "sized" preparative fractions (0.5-2.0 grams) with nearly quantitative recovery of the injected material from the chromatographic column.

Relatively large quantities of material were necessary for measuring metal content via flameless atomic absorption and for determining the nature and concentration of the organic constituents via ^{1}H and ^{13}C FT nmr techniques (4) in conjunction with elemental combustion and average molecular weight (vapor phase osmometry) data. The five SRC samples derived from different feed coals were obtained from a pilot plant operating at Wilsonville, Alabama. The SRC samples were obtained from eastern feed coals (Pittsburgh #8, and Western Kentucky #9 & #14), Illinois feed coals (Illinois #6 and Monterey), and a western coal (Amax). Preparative separation of the tetrahydrofuran (THF) soluble portion of each SRC sample provided four fractions using Bio-Beads S-X4 as the column packing. The elution volumes were held constant for each chromatographic fraction collected regardless of the SRC sample employed. The weight percent distribution for fractions 10 through 40 which correspond to decreasing effective molecular size along with the THF insoluble fraction (-10) are presented in Table 1. As indicated by the data in Table 1, all the SRC samples are greater than 88% soluble in THF. Although considerable weight changes occur as a function of the SRC feed coal sample between

Table I

Analytical Data For Molecular "Sized" Fractions of Various Solvent Refined Coals*

FRACTION #	PITTSBURGH #8	AMAX	W. KENTUCKY #9 & #14	ILLINOIS #6	MONTEREY
10	19.2[a] (711) [0.82]	23.6[a] (959) [0.79]	28.4[a] (795) [0.81]	39.2[a] (611) [0.83]	33.9[a] (652) [0.85]
20	24.1 (487) [0.92]	16.4 (597) [0.85]	17.1 (408) [0.91]	20.0 (447) [0.88]	22.8 (556) [0.80]
30	47.9 (388) [0.93]	48.6 (547) [0.76]	38.3 (313) [0.90]	30.4 (385) [0.85]	40.7 (479) 0.89]
40	5.9	3.2	4.7	1.6	2.6
-10**	2.9 [0.70]	8.2 [0.62]	11.6 [0.72]	8.8 [0.73]	0

* Average molecular weight data in parenthesis via vapor phase osmometry. Hydrogen to carbon (H/C) total ratio data in brackets.

** THF insoluble fraction, percent solubility determined by suspending 1 gram of the SRC sample in 200 ml of THF and stirring for 3 hours. The resulting solution was filtered through a millipore filter (LWSP) and the residue was dried before weighing.

[a]Fractional weight percentage

fractions 10 and 30, the molecular weight data are relatively consistent for a given fraction. Some variations do, however, occur for the Amax and Monterey SRC samples.

In characterizing the organic constituents for the major soluble fractions, a cursory difference between the eastern coals (e.g., Pittsburgh #8 and W. Kentucky #9 & #14) with the western coal (Amax) is evident. The total hydrogen to carbon ratio (H/C) data obtained from elemental combustion are tabulated in Table 1 with the Amax SRC fractions consistently exhibiting the lowest (H/C) ratios for each fraction. The relatively constant nature of the SRC samples derived from the eastern and Illinois #6 feed coals is indicated by the relatively narrow range of average molecular formulas presented in Table 2. The Amax and Monterey SRC fractions are exceptions in this regard (Table 3) and have consistently larger molecular formulas for a given fraction as previously suggested by the molecular weight data in Table 1.

Table 2

Range of Average Molecular Formulas for Western Kentucky #9 & 14 Pittsburgh #8 and Illinois #6 SRC Fractions *

FRACTION	FORMULA
10	$C_{41-55}H_{35-45}O_{3.7-4.7}S_{0.2-0.4}N_{0.7-1.0}$
20	$C_{27-33}H_{24-30}O_{2.5-3.4}S_{0.2-0.4}N_{0.5-0.6}$
30	$C_{22-27}H_{20-24}O_{1.4-2.2}S_{0.1-0.2}N_{0.4}$

*Values based on average molecular weights and elemental combustion data

Table 3

Average Molecular Formulas For Amax and Monterey SRC Fractions

FUNCTION	MONTEREY	AMAX
10	$C_{43.4}H_{37.0}O_{4.5}$	$C_{67.5}H_{52.7}O_{4.3}$
	$S_{0.3}N_{0.8}$	$S_{0.4}N_{1.0}$
20	$C_{38.0}H_{30.3}O_{2.6}$	$C_{40.0}H_{34.0}O_{4.1}$
	$S_{0.6}N_{0.7}$	$S_{0.3}N_{0.6}$
30	$C_{34.2}H_{30.9}O_{1.5}$	$C_{37.8}H_{34.0}O_{3.0}$
	$S_{0.2}N_{0.5}$	$S_{0.1}N_{0.5}$

*Values based on average molecular weight and elemental combustion data

The ^{1}H and ^{13}C nmr spectra superficially appear very similar for a given SRC fraction regardless of the feed coal. Typical ^{13}C and ^{1}H FT nmr spectra for Amax Fraction 30 are presented in Figures 1 and 2, respectively. Quantitative nmr measurements, however, indicate major changes do occur in the aliphatic and aromatic (H/C) ratios as summarized for fraction 30 samples in Table 4. The unusually low aliphatic (H/C) ratio for the Amax sample is very suggestive of highly condensed cyclic aliphatic networks (e.g., substituted adamantanes) previously suggested by a Mobile group (5).

Further trends and comparisons of the organic constituents will be the major thrust of this presentation with particular attention focusing on the Amax sample.

Table 4

(H/C) Aromatic and Aliphatic Ratios
For SRC Fraction 30 Samples*

SRC	$(H/C)_{ALP.}$	$(H/C)_{ARO}$	F_A(Aromaticity)
Pittsburgh #8	1.66	0.49	0.64
West. Kentucky #9 & #14	2.09	0.44	0.71
Illinois #6	1.35	0.57	0.64
Monterey	2.12	0.46	0.73
Amax	1.15	0.50	0.63

* Values obtained from quantitative ^{1}H and ^{13}C FT nmr measurements.

Acknowledgment: The financial support of the VPI & SU Research Division and the Commonwealth of Virginia are gratefully appreciated.

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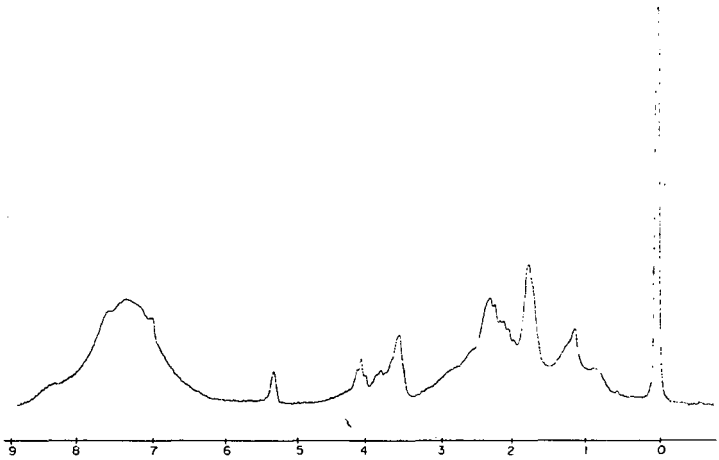
5. D. D. Whitehurst, M. Farcasui and T. O. Mitchell, "Nature and Origin of Asphaltenes in Process Coal", Mobile Research & Development Corporation, Report No. EPRI AF-252, February, 1976.

FIGURE 1

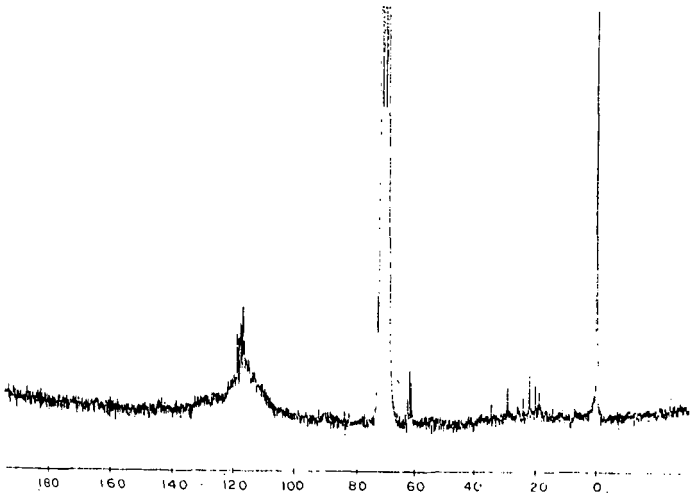
^{1}H Spectrum of Amax Fraction 30



SOLVENT = $CDCL_3$

FIGURE 2

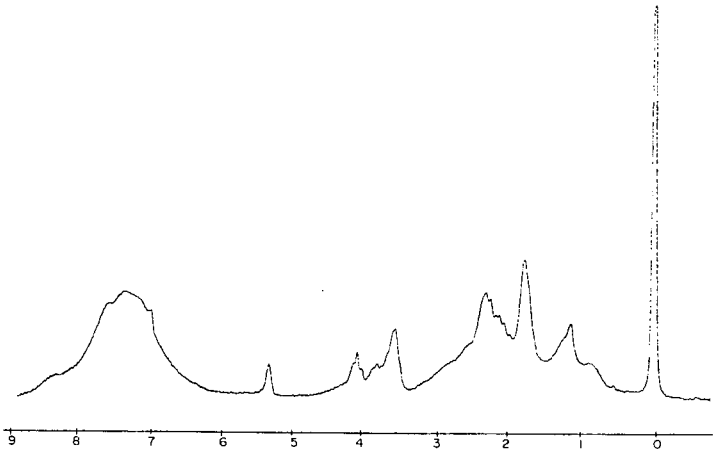
^{13}C Spectrum of Amax Fraction 30



SOLVENT = $CDCL_3$

FIGURE 1

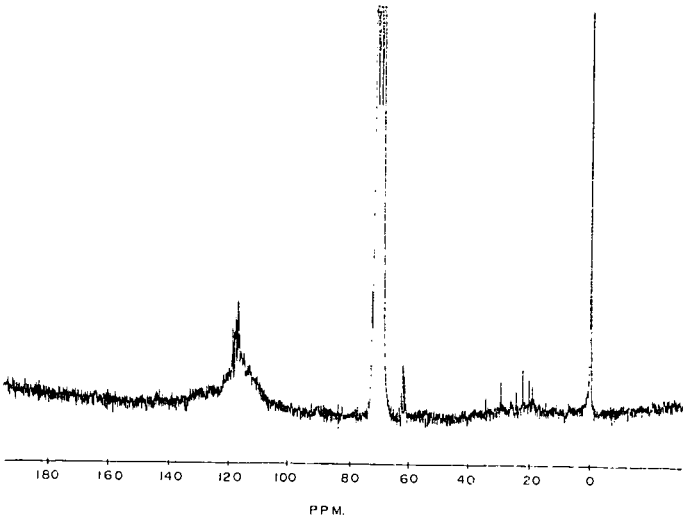
^{1}H Spectrum of Amax Fraction 30



SOLVENT = $CDCL_3$

FIGURE 2

^{13}C Spectrum of Amax Fraction 30



SOLVENT = $CDCL_3$

COMPARISON OF SOLVENT REFINED LIGNITES WITH SOLVENT REFINED BITUMINOUS COALS.

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Comparison of SRL and SRC

Introduction

A considerable amount of work is currently being conducted on solvent refining of bituminous coals. The resulting solvent refined coal (SRC) can be used as a boiler fuel or as a feedstock for further refining. A parallel program on lignite coal is being carried out in our Chemical Engineering Department (Project Lignite). Considering the properties of the starting coals, it was initially assumed that SRC and solvent refined lignite (SRL) would be greatly different and, thus, second stage refining reactions and conditions would have to be developed and "fine tuned" for the different feedstocks. As these programs developed, however, it soon became apparant that SRL and SRC were more similar to each other than the starting coals were. In view of these similarities and because of a lack of definitive evidence to the contrary, it has been generally accepted that the second stage reactions and conditions can be simultaneously, rather than separately developed.

In view of the importance of this tentative conclusion to our work, we have set about examining the similarities and differences between a wide variety of SRL and SRC samples. Our preliminary results (1) were consistent with the conclusion that SRC and SRL were nearly the same within the limits of the experiments and samples we were using. We have now obtained more representative samples of both SRL and SRC produced under more commercial conditions and report their comparison here.

Procedure: Samples refined from lignite, sub bituminous and bituminous coals were obtained. (2,3) In addition, as controls, more deeply hydrogenated samples from a COSteam process and from second stage hydrogenation of SRL were included in the comparison. (3) The method of analysis was similar to that used previously (1) using the whole coal samples. Ultimate analyses, including neutron activation oxygen analysis, nonaqueous titrations, uv, mw, nmr and esr spectroscopy were used to examine these samples. A difficulty rapidly developed. Several of the samples contained unreacted coal and ash. Initially we thought a comparison could be made by correcting for these insoluble materials on the basis of pyridine solubility of the sample. Neutron activation (naa) oxygen analysis showed, however, that oxygen by difference and by naa for maf samples were fairly close, but samples containing ash deviated considerably (Table 1). Thus, the variability of oxygen in the ash and unreacted coal led to large errors in the amount of oxygen in the maf material. Because the oxygen content could be critical to a lignite-bituminous coal comparison, we set out to develop an exact, reproducible laboratory deashing procedure. The deashing procedure was based on pyridine Soxhlet extraction, filtration of the eluate and removal of pyridine under standard conditions. The amount of pyridine remaining in each sample was checked by pmr. Several samples were crosschecked by mass spectroscopy. As little as 0.2% pyridine could have been detected. None was found. Table I shows the percentage of each sample found soluble in pyridine with and without 5 μ filtration. The results show the 5 μ sizing procedure seems desirable, especially in view of the variable amounts of materials obtained from different samples by this technique. For laboratory studies we would like to propose this separatory technique as a standard procedure to define an SRC or SRL (cf Experimental Section).

Discussion of Analytical - Spectroscopic Results.

A. NMR: Proton nmr analysis of samples before and after deashing indicates no gross changes in the samples. Nevertheless, small systematic changes did occur. Samples, both SRL and SRC, initially containing ash and unreacted coal had the same Har/(Hα + Ho) ratio within experimental error before and after deashing.

(Table II). Maf samples showed changes of 0.07-0.26 in this ratio, which is outside the precision of the measurements. Another subtle, but consistent trend for nearly all samples was a decrease in the Hα/Ho ratio on deashing. This was true for initially maf, as well as samples with ash and unreacted coal. Furthermore, this change in ratio was 0.-0.48 for SRL's and larger, 0.36-1.27, for SRC's. Excluding the Amax sample, the range was 1.17-1.27. The Hα/Ho decreased by 0.83-1.17 for two samples when the pyridine insoluble fraction was simply filtered off (nmrs were run with all insoluble material present in non maf material).

Only experience will show if the change in Hα/Ho ratio, caused by laboratory deashing, can be used to identify the coal used for SRC or SRL preparation. whether these small changes are caused by material in the ash or by chemical reaction during the deashing process also remains to be investigated. Our experience with FT carbon-13 determined Car/C total (ie fa) ratios are consistent with a recent report (4) that the ratios determined from proton and carbon-13 nmr are very similar. (eg. for M11A Carbon-13 = 0.815±0.009 and from proton fa=0.813).

B. Molecular Weight: The molecular weights (by VPO) of the samples before and after deashing were also measured. The precision on the single determinations before deashing is much less than for the three concentration extrapolated values determined on the laboratory deashed material. Even so, the two values for each sample were either the same within experimental error or very close to each other (with the exception of Tacoma (maf), which increased significantly). The ranges, in general, both before and after deashing are not grossly different, although the SRC's (before 420-597; after 460-620) are marginally higher in mw than the SRL's (before 400-598; after 428-481).

C. Ultraviolet Spectra: The ultraviolet spectra for these samples was run between 270-400 nm and is plotted vs $E^{1\%}$ in Fig. 1. These and other such samples have remarkably featureless spectra. All samples thus far examined, fall generally within the range shown. These factors make it unlikely that SRL's and SRC's may be distinguished by such data. Comparison to the COSteam and J-1-11-87 samples, indicates that larger reductive changes, however, can be characterized by uv spectra (Fig. 1). There also seems to be a relationship between the integrated uv absorption and both Har and Halip from nmr data (Fig. 2).

D. Acid base properties: non aqueous titration for acidity gave a range of 1.34-2.80 meq/g for SRL's and 1.45-2.95 for SRC's. The basic titer ranged for SRL's 0.30-0.63, and 0.52-0.84 meq/g for SRC's. Where comparisons can currently be made, the oxygen content is marginally lower for SRL's (despite the fact that initially it was much higher in lignite) than for SRC's. Nitrogen content for SRL's is generally lower than for SRC's. Thus, the acidity and basicity of both SRL's and SRC's seem to parallel roughly the percentage oxygen and nitrogen respectively in the sample.

The percentages of C, H are typical (Amax %C is low and is being checked) of other samples with carbon ranging 85-90% (maf) and hydrogen, 5-6% for SRL and SRC samples. The sulfur content ranges somewhat higher for SRC's, 1.30-3.68% (but only a trace for Amax) than for SRL's, 0.85-1.24; probably a reflection of the sulfur content of starting coal.

E. Electron spin resonance: The esr spectra of the samples was measured, with the results given in Table II. The range of g-values was very small for all samples investigated, 2.0026-2.0028. The g values are in good agreement with those reported for coals having carbon contents over 80%. The linewidths for SRL's ranged 3.8-4.8 gauss; for SRC's 1.7 to 7.6. The linewidth appears marginally lower than that expected for a vitrain of comparable hydrogen content. (5)

Summary of Analytical Comparisons: While the comparisons are not yet complete, the gross makeup of the samples indicate that SRL's and SRC's are quite similar. The variations noted in the uv, molecular weight, esr, and nmr analyses may be more a function of reaction conditions than of starting coal. The precentage composition and acid-base characteristics seem to indicate that the starting coal properties, particularly nitrogen, sulfur and oxygen percentages, may be carried over into the solvent refined products, although they are affected also, to a large extent, by reaction conditions.

Furthermore, in cases which we have investigated thus far, hydrotreating of

SRL and SRC have shown similar trends, in that their reactivities and product distributions depend more on how they are made, stored and treated than on the starting coal.

Assessment of Analytical Procedures: Several difficulties have emerged in these analyses for whole solvent refined samples. A standardized laboratory deashing procedure which we have developed, appears necessary. Oxygen analysis on maf samples by difference may be generally acceptable, but should be checked with neutron activation analysis and is absolutely essential with samples containing unreacted coal and ash. A standardized procedure which we are developing needs to be uniformly applied to pulsed carbon-13 nmr analyses.

Future Work in Analysis of Gross Solvent Refined Coal Samples: Application of Carbon-13 nmr techniques have been applied to coal derived samples, but generally only to that portion of the sample soluble in a "desirable" nmr solvent (CS_2, $CDCl_3$, etc.). Whole solvent refined samples containing large amounts of preasphaltenes (like SRL and SRC) are not soluble in these solvents. In order to properly characterize whole samples, either new solvents or new techniques have to be developed. We are working on both.

A second area of critical concern to us is the qualitative way comparisons currently must be made. A critical set of standardized measurements needs to be developed (which we have alluded to above). These measurements should then be reduced to a set of critical structural factors, probably through a computerized technique which will allow direct quantitative comparison of samples. While inroads are being made on this approach, (6) better methods need to be developed.

Experimental Section

Analyses were performed by Midwest Micro and Spang Laboratories. Nmr spectra were measured on an EM-390 and analyzed, as previously described. (1) Titrations were conducted, as previously indicated. (1)

Neutron activated analysis was carried out by Intelcom Rad Tech, San Diego, CA. Uv spectra were measured on a Cary 14 in dimethylacetamide. Esr were determined on a Bruker ER 420. Molecular weights were measured by Spang, and with a Corona Wescan 232 VPO in dimethylformamide, the latter at 74.8° at three different concentrations with extrapolation to infinite dilution. Very little association was noted in this solvent.

Laboratory Deashing Procedure: A Whatman no. 1 Soxhlet thimble was shrunk in acetone, dried at 110°C, cooled in a dessicator and weighed to constant weight. A 3 to 5 g sample of SRL or SRC was weighed into the thimble and extracted with pyridine for 24 hrs under nitrogen. The thimble was dried at 110° for 24 hrs, cooled in a dessicator and weighed. The pyridine solution was filtered through a preweighed 5 μ Teflon filter. The sum of the sample in the thimble and on the filter constituted the undissolved sample by definition. Most of the pyridine in the filtrate was removed at 50° (1mm), then at 50° (0.05mm) for 24 hrs. The sample was scraped into a drying boat and further dried at 56° (0.1mm) for 24 hrs. After grinding in a mortar, the sample was redried at 100° (0.1mm) for 24 hrs more. Less than 1% of pyridine could be observed by nmr in hexamethylphosphoramide. Mass spectrometry indicated less than 0.2% pyridine in several samples.

Table I

Comparison of Deashing Techniques

Sample	Simple Extraction	Filtration Extraction	%O by difference	by NAA**
M11-A*	100	96.8	5.80	2.35
Tacoma II*	99.7	95.4	3.81	3.22
Amax*	99.8	94.1	12.36	3.37
M5-C	80.1	84.2	3.88	7.31
M13-A	86.1	77.6	2.91	5.37
M21-A	75.8	68.0	7.04	5.57
Tacoma I	71.8	69.6	10.7	6.53
Wilsonville	76.4	59.3	8.49	7.71

* maf as received
** neutron activation analysis

Table II

	M11-A	Amax	Tacoma (maf)
%C	89.31	80.57	87.19
%H	5.80	5.50	5.45
%N	1.11	1.57	2.25
%S	0.86	< 0.02	1.3
%O(NA)	2.35	3.37	3.22
MW	497+9	585+7	624+19
Acid meq/mole	2.22	2.95	3.35
Base meq/mole	0.30	0.55	0.84
Pyr. sol. (%)	96.80	94.10	95.38
Har/Hα+Ho	1.07	1.00	0.826
Hα/Ho	2.58	2.22	3.46
fa	0.813	0.797	0.897
σ	0.304	0.399	0.397
Haru/Car	0.707	0.849	0.701
Cl	1.39	1.45	1.29
Ra	5.28	3.41	5.82
Esr ΔH(pp)(G)	4.8		7.6
g value	2.0026		2.0028
Molecular Formula			
C	36.9	39.2	45.3
H	28.8	32.1	34.0
N	0.39	0.66	1.00
S	0.13	—	0.25
O	0.73	1.22	1.26
Acid eq/mole	1.10	1.72	2.09
Base eq/mole	0.15	0.32	0.52

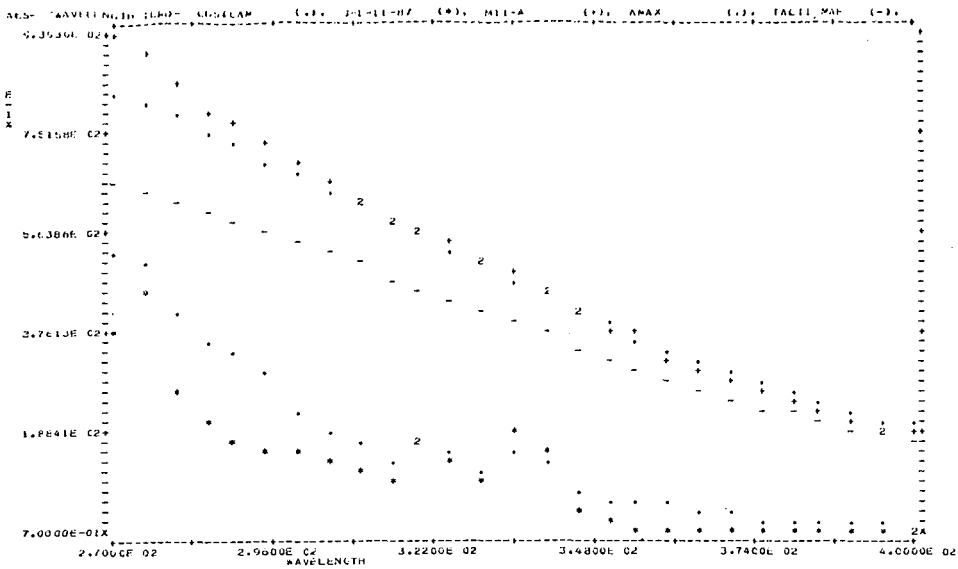

FIGURE 1

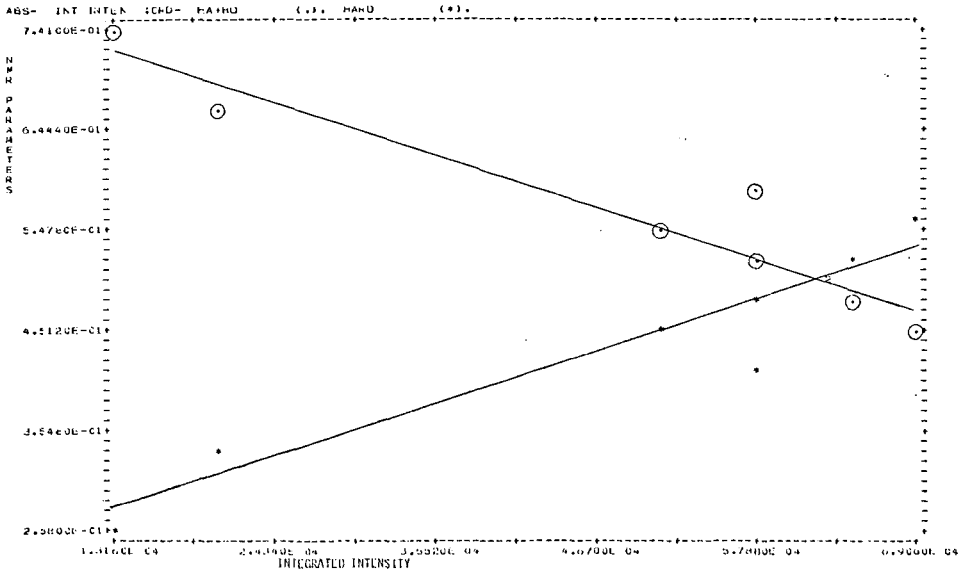

FIGURE 2

References

1. N. Woolsey, R. Baltisberger, K. Klabunde, V. Stenberg and R. Kaba, ACS Fuel Preprints, 2 (7), 33 (1976).

2. Samples were generously supplied by Project Lignite, University of North Dakota and the Grand Forks Energy Research Center.

3. Samples are designated as follows:
   M5-C-(undeashed) Conditions: 2500 psi of 1:1 $CO:H_2$ at 455°C (max).*

   M11-A-(deashed) Conditions: 2500 psi of 1:1 $CO:H_2$ at 479°C (max).*

   M13-A-(partly deashed) Conditions: 2500 psi of 1:1 $CO:H_2$ at 453°C (max).*
   M21-A- (undeashed) Conditions: 2000 psi of 1:3 $CO:H_2$ at 439°C (max).*
   Tacoma I (undeashed): Pittsburgh and Midway Coal Co., Merriam, Kansas (a Gulf subsidiary). From a Kentucky no. 9 and no. 14 blend of bituminous coal from the Colonial Mine. Conditions: PDU, continuous flow, 1500 psi of H_2 (85% min), 450°C (max), using recycle solvent; product not filtered and stored in the open.
   Tacoma II (deashed): Same as Tacoma I except product filtered before solvent distilled. (maf)
   Amax-Southern Services, Inc., Burmingham, Alabama (an ERPI contractor). From a sub-bituminous coal from the Bel Air Mine in Wyoming. Conditions: continuous flow, 2500 psi of H_2 and recycle gases, 460° (max) using recycle heavy in phenols with 1, 2 and 3 ring aromatics.
   Wilsonville-Prepared essentially by the procedure for Amax.
   J-1-11-87: Reduction fraction of KC-SRL. Conditions: batch autoclave, 4500 psi (max) of H_2 at 450° for 2 hrs. using presulfided HT-100 (NiMo) catalyst b.p. 110-180°C (0.4 mm) followed by removal of solid which precipitated on standing in the freezer for ca. month.
   COSteam: Pittsburgh Energy Research Laboratory (an ERDA Lab). N. D. Lignite treated in a tubular reactor with synthesis gas under COSteam conditions. Conditions: continuous flow, 4000 psi of $CO:H_2$. Whole product chromatographed on alumina. This fraction eluted with toluene (aromatics fraction). 126-2 (Separation done in Grand Forks Energy Research Laboratory)

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* Solvent refined N.D. lignite by Project Lignite of the University of North Dakota. PDU operation, FS-120 as make up solvent during recycle operation using ca. 1.8:1 solvent to coal.

ELECTRON SPIN RESONANCE STUDIES OF COALS AND COAL-DERIVED ASPHALTENES

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INTRODUCTION

The discovery of electron spin resonance (esr) absorption in natural carbons by Uebersfeld (1) and Ingram (2) prompted a number of investigators to apply the technique to coal and materials derived from coal. At least three excellent review articles describing the early esr studies of coals have been published (3-5). Although the exact nature of the species responsible for the esr absorption has not been established unambiguously, it is generally thought that the unpaired electrons, at least in non-anthracitic and possibly young anthracitic coals, are associated with organic free radical structures. One group of investigators, however, has proposed that charge-transfer complexes rather than stable free radicals may be responsible for the absorption (6).

During the present investigation, esr spectra were obtained for vitrains and fusains from a large number of coals. For most ranks of coal, samples of both lithotypes were studied. The objectives of the investigation were: 1) to better characterize the immediate chemical environment of the unpaired electrons; 2) to deduce information about the metamorphic changes that occur during vitrinization and fusinization; and 3) to provide needed background information for future studies of the role of free radicals in coal liquefaction. To further pursue the latter objective, esr spectra of asphaltenes, which are considered by many coal researchers to be intermediates in the conversion of coal to liquid fuels, were also obtained. A secondary purpose for examining the asphaltenes was to explore the recent hypothesis (7) that charge-transfer interactions may be important binding forces between the acid/neutral and base components in these materials.

EXPERIMENTAL

Samples. Most of the vitrains and fusains studied were of high petrographic purity, although several of the vitrains are more appropriately described as vitrain-rich samples. Sixty-three vitrains, including samples from Antarctica, Austria, Canada, Germany, Japan, Pakistan, Peru, the United States, and Yugoslavia, and 30 fusains, most of which were separated from U. S. coals, were investigated. Petrographic characterization and other properties of many of these samples were published previously (8).

The asphaltene samples were derived from products from the Pittsburgh Energy Research Center's SYNTHOIL (9) coal liquefaction Process Development Unit using a recently described solvent separation method (10). The acid/neutral and base components of the asphaltenes were prepared according to published procedures (11).

Spectral Measurements. The esr measurements were made over a period of approximately ten years. The experimental techniques were essentially those published earlier (12) except for minor modifications that were made over the years to facilitate the measurements. All esr measurements were made on evacuated samples (~10^{-6} torr) to prevent line broadening by oxygen in the air. The electrical properties of many of the higher rank samples necessitated that the samples be dispersed in a nonconducting medium to avoid microwave skin effects.

RESULTS AND DISCUSSION

Vitrains and Fusains. ESR data obtained for vitrains and fusains during the present investigation are far too numerous to tabulate here; complete listings of the data are available from the authors upon request. The plots of Figures 1-6 show some of the more significant correlations of the data with coal composition or coal rank.

The concentrations of unpaired electrons in the vitrains, as estimated by comparing the esr intensity of each sample with that of a standard sample of diphenylpicrylhydrazyl, are shown as a function of the carbon contents of the samples in Figure 1. The relationship of Figure 1 is similar to those from earlier studies (3-5, 12), although the scatter of the data points is more pronounced in the present work. These data show that, in general, the concentrations of unpaired electrons increase with increasing coal rank up to a carbon content of approximately 94% after which the spin concentrations decrease rapidly. The initial, crudely exponential increase in spin concentration is generally attributed to the formation of organic free radicals during vitrinization. The free radical electrons are thought to be delocalized over aromatic rings and thus stabilized by resonance. Resonance stabilization of the radicals is greater for the vitrains from higher rank coals since these presumably contain the larger polynuclear condensed aromatic ring systems. The precipitous decrease in spin concentration above 94% C results from the increased conductivity of the samples.

In contrast to the results for vitrains, the spin concentrations of the fusains (Figure 2) exhibit no readily discernable dependence on carbon content. The wide variation in thermal history experienced by fusains during their formation is the most likely explanation for this behavior (13).

The changes that occur in esr linewidths and g values during vitrinization and fusinization are shown in Figures 3-6. The abscissa used in these figures is based on the coalification plots of Schopf (14) with slight modifications by Parks (15) and the present authors. The ranks shown on the plots are those of the parent coals as determined by standard procedures (16).

For the vitrains, an increase in esr linewidth with increasing rank is first observed (Figure 3); this trend is reversed at the low rank bituminous stage. The rate of decrease becomes larger as coalification progresses through the higher rank bituminous stages to the early anthracitic stages. Some of the anthracites and most of the meta-anthracites exhibit very broad lines (not shown in the figure); a linewidth in excess of 60 gauss was observed for one such coal. The linewidth results can be interpreted as follows: Nuclear broadening, i.e., unresolved proton-electron hyperfine interactions, plays an important role in the observed linewidths of peats, lignites, and bituminous coals. The relatively narrow lines observed in the spectra of some of the anthracites probably result from the smaller number of protons in the samples, although exchange narrowing of the esr resonances may also be occurring. The proton line broadening hypothesis is supported by a recent esr study of coals before and after catalytic dehydrogenation (17). The very large linewidths of the highest rank materials are undoubtedly due to the presence of graphite-like structures which form during the latter stages of coalification. The difficulty in differentiating between anthracites and meta-anthracites (18) may be responsible for the apparent lack of predictability of linewidths in vitrains from coals of these ranks.

The esr linewidths for the fusains (Figure 4) are very small, frequently less than one gauss, except for samples from the lowest rank coals. Unlike the results for the vitrains, no evidence was found for the formation of graphitic structures during the latter stages of fusinization. In addition, the gradual decrease in

linewidths of vitrains as coalification proceeds from the low rank bituminous stages to the early anthracitic stages (Figure 3) appears as a very rapid change in the fusinization plot (Figure 4). This is in accord with Schopf's (14) representation of fusinization as a process which has an early inception and progresses rapidly in the peat and lignitic stages, after which the metamorphic changes become nearly imperceptible. Vitrinization, on the other hand, involves a progressive change throughout all stages of rank development.

The relationship between the g values of the lithotypes and coal rank (Figures 5 and 6) also supports Schopf's theories of vitrinization and fusinization. The large g values found for the vitrains from meta-anthracites is in accord with the final step in vitrinization being the fusing of aromatic rings into graphite-like structures. The g value of each of the vitrains and fusains is higher than that of the free electron and lies in the spectral region expected for simple organic free radicals. The only exceptions are vitrains from the more highly metamorphized coals, one of which exhibited a g value of 2.011.

The fact that esr g values of organic free radicals are greatest for radicals in which the unpaired electron is localized or partially localized on atoms having high spin-orbit coupling constants can be used to explain the g value results for vitrains. Since the heteroatom contents of coals decrease with increasing rank, the high g values for peats and lignites can be interpreted in terms of aromatic radicals with some partial localization of the unpaired electrons on heteroatoms, particularly but not exclusively oxygen. As coalification progresses the g values decrease, suggesting that the radicals become more "hydrocarbon-like." The g values of many of the vitrains from bituminous and young anthracitic coals compare favorably with those exhibited by aromatic hydrocarbon radicals. During the final stages of coalification, the g values become quite large as one would expect if continued condensation of the aromatic rings into graphite structures occurs. The observation of a small, but reproducible, anisotropy in the g value of certain anthracites (Figure 7) suggests that some ordering of the polynuclear condensed aromatic rings is occurring.

Coal-Derived Asphaltenes. To better understand the chemistry of coal liquefaction, an esr investigation of coal-derived asphaltenes was initiated. Preliminary results are presented here. Of particular concern was the temperature variation of the esr intensities of asphaltenes and their acid/neutral and base components (Figure 8). The most significant finding to date is that the weighted average of the temperature dependencies of the two components reproduces the temperature dependence of the total asphaltene (before separation) exceptionally well. This suggests that charge transfer interactions, at least in the Mullikan sense, are relatively unimportant binding forces between the acid/neutral and base components of the asphaltenes.

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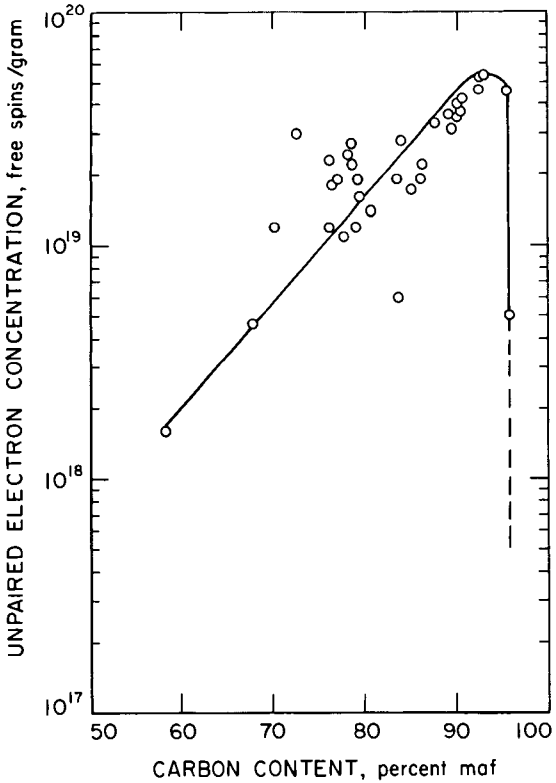

Figure 1–Concentrations of unpaired electrons as a function of carbon content for vitrains from selected coals.

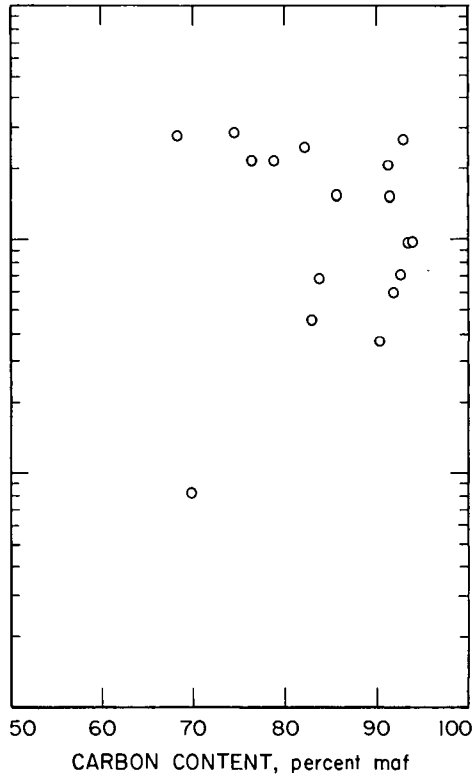

Figure 2–Concentrations of unpaired electrons as a function of carbon content for fusains from selected coals.

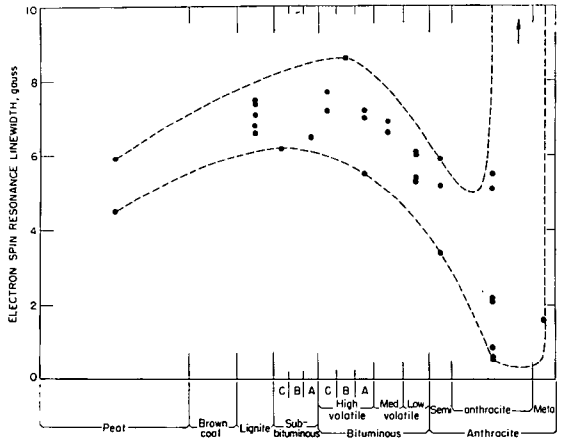

Figure 3 - Electron spin resonance linewidths as a function of coal rank for vitrains from selected coals.

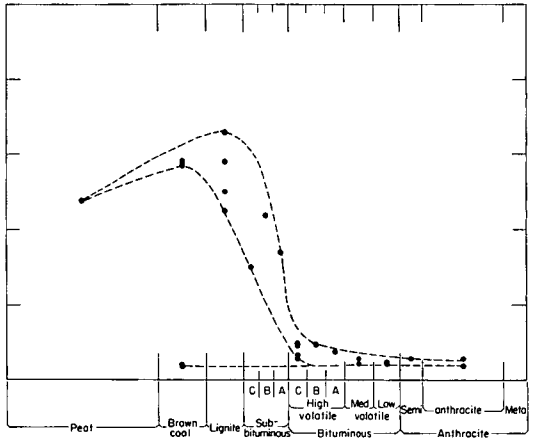

Figure 4 - Electron spin resonance linewidths as a function of coal rank for fusains from selected coals.

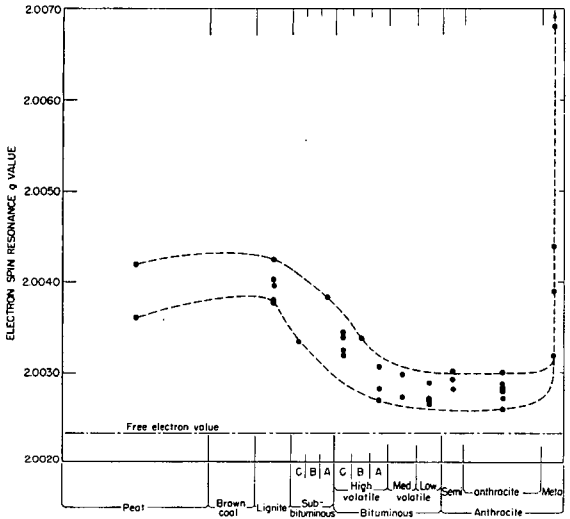

Figure 5—Electron spin resonance g values as a function of coal rank for vitrains from selected coals

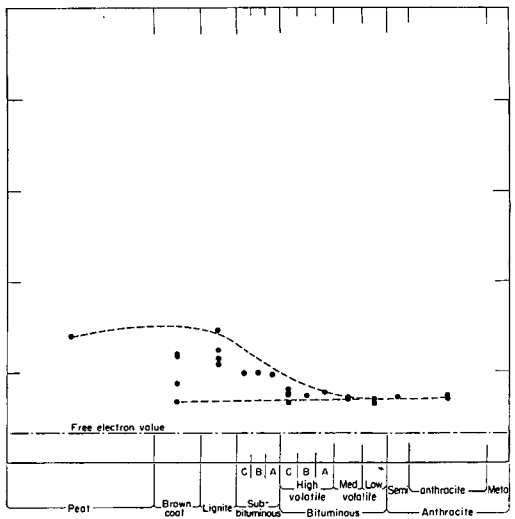

Figure 6—Electron spin resonance g values as a function of coal rank for fusains from selected coals.

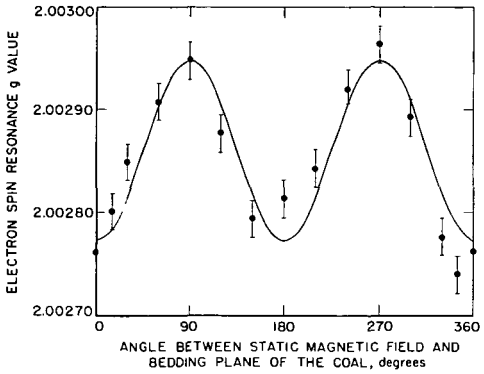

Figure 7 – g Value anisotropy in Huber Mine anthracite

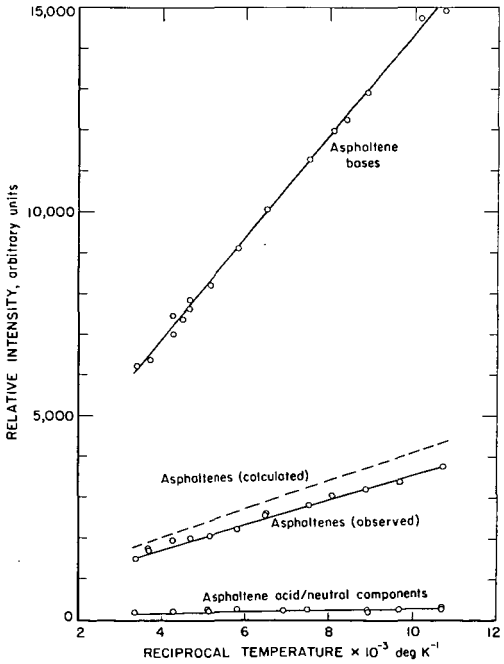

Figure 8 – Variable temperature ESR data for asphaltenes and components.

ISOTOPIC STUDIES OF THERMALLY INDUCED REACTIONS OF COAL AND COAL-LIKE STRUCTURES

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We recently (2) reported that under conditions of coal conversion (tetralin, 400°) several diarylalkanes undergo carbon-carbon cleavage, and that the scission of carbon-carbon bonds must therefore be considered as an important process in asphaltene formation. We also reported (2) that vitrinite (from Illinois No. 6 coal) was a "better hydrogen transfer agent" than tetralin itself for the hydrogenolysis of 1,1,2-triphenylethane to diphenylmethane and toluene. We have now extended these studies to establish a) that vitrinite is indeed a better hydrogen donor than tetralin toward several organic structures; b) that tetralin, in addition to its function as a hydrogen donor, can undergo certain other reactions with coal and with coal-like structures which involve both carbon-carbon bond formation and bond cleavage.

A Comparison of Tetralin and Vitrinite as H-Donors

When 1,2-diphenyl-1-*p*-tolylethane is heated at 400° (either in glass capillaries or in stainless steel tubes) with an excess of tetralin, the major products are toluene and phenyl-*p*-tolylmethane. The same products are obtained when 1,2-diphenyl-1-*p*-tolylethane is heated at 400° in the presence of an excess of vitrinite (handpicked from Illinois No. 6 coal). Given in Table I is a comparison of the

Table I

A Comparison of Tetralin and Illinois No. 6 Vitrinite as Hydrogen Donors

Reactants	Conditions	Percent Reaction
1,2-Diphenyl-1-*p*-tolylethane	400°, 5 min[a] tetralin	2%
"	400°, 30 min[b] tetralin	94%
"	400°, 5 min[a] vitrinite	50%
1,3-diphenylpropane	400°, 30 min[b] tetralin	23%
"	400°, 30 min[b] tetralin & vitrinite	43%
"	400°, 30 min[b] vitrinite	65%

a) The oven was at 400°, but the warm-up time is 15 minutes, thus the actual temperature was considerably less than 400°.
b) 30 min included warm-up time.

extent reaction — as determined by g.c. analysis of the products — after various contact times with tetralin or with vitrinite.

Another diarylalkane which is easily decomposed in the presence of excess tetralin or excess vitrinite is 1,3-diphenylpropane. The major products in both cases are toluene and ethylbenzene, although a multiplicity of minor products are produced. Also given in Table I are comparisons of the extent reaction of 1,3-diphenylpropane (400° for 30 minutes) a) with excess tetralin; b) with excess tetralin and vitrinite; and c) with excess vitrinite. The extent reaction in each case was estimated from the g.c. trace.

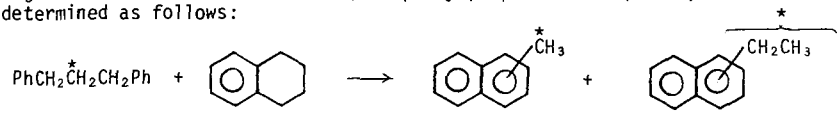
Since the reactions were monitored by g.c., which would detect neither nonvolatile polymeric material, nor high molecular weight products of reaction with vitrinite, it is possible that the vitrinite is acting not as a hydrogen donor, but merely as a catalyst, and that the source of the hydrogen for the hydrogenolyses comes from the 1,2-diphenyl-1-p-tolylethane or from the 1,3-diphenylpropane. To circumvent this problem, we heated benzophenone to 400° for one hour a) in the presence of excess tetralin, and b) in the presence of excess vitrinite. The major products are diphenylmethane and water, with traces of toluene and benzene. The reaction in tetralin proceeded to the extent of only 12%, whereas in the presence of vitrinite 35% reaction had occurred.

Reactions of Tetralin other than Hydrogen Donation

V. F. Raaen (3) showed recently that tetralin-1-^{14}C reacts with Wyodak coal at 400° (1 hour) to the extent that the pyridine-insoluble residue contains chemically bound carbon-14 equivalent to 5% tetralin by weight. Further, when the residue was reheated in normal tetralin (400°, one hour) the reisolated solvent contained no measurable amount of either tetralin-^{14}C or of naphthalene-^{14}C. There were, however, traces of labeled alkylated naphthalenes, which were identified by g.c. retention times as 1- and 2-substituted methyl- and ethylnaphthalenes. These products undoubtedly arise as a result of free radical intermediates. We therefore investigated the possibility that methyl- or ethylnaphthalenes could be produced by the reaction of tetralin with structures containing aromatic moieties separated by two or more methylene groups, or with aryl alkyl ethers. Both types of structure (4,5) are known to be present in different kinds and ranks of coal.

We heated several diarylalkanes and aryl alkyl or aralkyl ethers to 400° in tetralin for varying periods of time. Many of these reactions yielded measurable quantities of methyl- and ethylnaphthalenes in addition to other products. Typical are the reactions of 1,3-diphenylpropane and of phenetole, both of which were investigated with carbon-14—labeled species. The products were analyzed a) by gas chromatography combined with radioactivity monitoring of carbon-14—labeled products; b) by gas chromatography equipped with mass spectrographic analyzers (5); and c) by isolation of specific products using preparative g.c. (6) followed by nmr analysis (Varian XL-100 Spectrometer). Given in Tables II and III are the major products obtained — together with appropriate yields — from the reactions of 1,3-diphenylpropane and phenetole, respectively, with tetralin.

The 1- and 2-methylnaphthalenes were isolated and identified by nmr analysis. Their genesis from the reaction of 1,3-diphenylpropane-2-^{14}C (^{14}C=*) and tetralin was determined as follows:



The mixture of ethylnaphthalenes was identified by g.c. retention times and radioactivity assay by means of the g.c. radioactivity monitor. Traces of methylindane

Table II

Major Products and Yields Obtained[a] on Heating 1,3-Diphenylpropane with Tetralin One Hour at 400°

Toluene	28%
Ethylbenzene	19
1- and 2-(2-Phenylethyl) tetralins	8
1,4-Diphenylbutane	5
1- and 2-Methylnaphthalenes	3
Styrene	1.5
1,3-Diphenylpropene	1.5
Methyldihydronaphthalenes 1,2-Diphenylethane 1- and 2-(2-Phenylethyl) naphthalenes Other	34

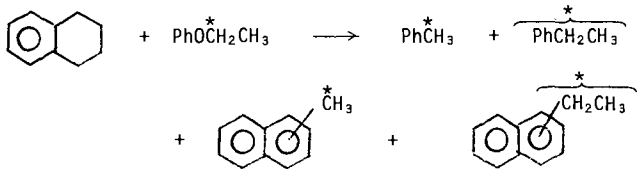
[a]Based on 1,3-diphenylpropane consumed.

Table III

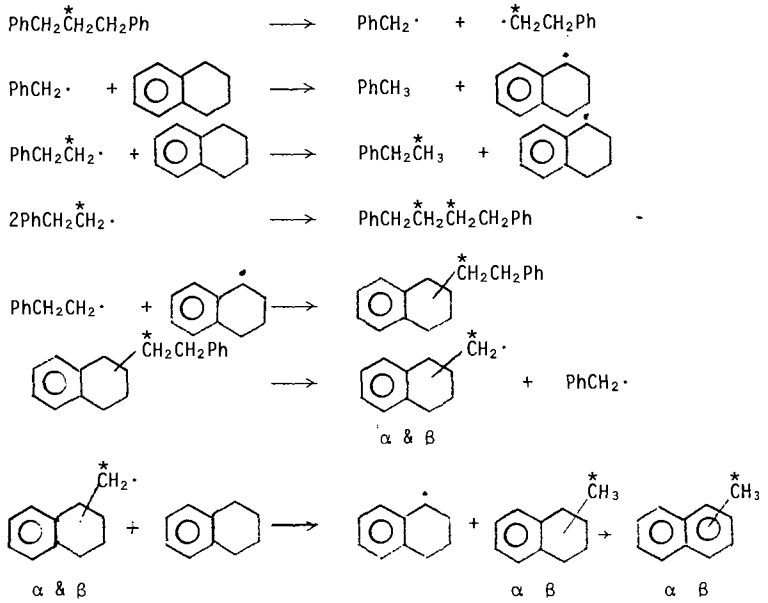
Major Products and Yields Obtained on Heating Phenetole with Tetralin Eighteen Hours at 400°

Phenol	37%
Methylnaphthalenes	13
Toluene	7
Ethylbenzene	7
Ethylnaphthalenes	7
Methyltetralins	4
Ethylphenol	3
Ethyltetralins	3
Ethylmethylbenzene Methylindane Butylbenzene	From Decomposition of Tetralin

and of butylbenzene were always present after reactants were heated with tetralin. That these latter two products were derived from tetralin was demonstrated by the fact that they contained carbon-14 when tetralin-^{14}C was used in the reaction. In like manner, labeled phenetole and tetralin were subjected to the conditions of reaction with the following results:



It is clear from the isotopic labeling experiments that tetralin has entered into the reaction both with 1,3-diphenylpropane and with phenetole. The results are nicely accommodated by the postulation of radical intermediates. A possible mechanism for the reaction of 1,3-diphenylpropane is indicated:



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THE CHEMISTRY OF COAL LIQUEFACTION

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This progress report presents a working hypothesis for our study of coal liquefaction with Illinois No. 6 coal and indicates the kinds of evidence on which our hypothesis is based and which are desirable for its substantiation.

Coal is considered to be mostly a crosslinked high polymer with condensed aromatic aggregates that are difficult to cleave and connecting links that are relatively easy to cleave (scissile bonds). A range of soluble materials is mixed with the predominantly insoluble material. Associated with these primary bond relations are significant interactions between phenolic groups and pyridine-type bases (1). Thus, relatively small polyfunctional molecules, even if not incorporated in the network, need complexing solvents to dissolve them. Our 1976 Coal Workshop paper related the molecular weight, and presumably the functionality, of the fractions that would dissolve in certain solvents (2), as revised and summarized in Table I. Recent experiments indicate that ethylene diamine will extract from coal much more and higher molecular weight materials at 120°C. An effort to relate the amount of soluble material extracted by solvents to the amount of solvent used and to the extent of swelling of the undissolved residue at 100° is in progress.

The extracted coal in the upper series of fractions in Table I is a preferred material for liquefaction studies, uncomplicated by admixed soluble materials. Progress in breaking bonds can be followed by formation of soluble materials and probably also by increased swelling of the insoluble material in a chosen solvent. The pyridine-soluble, toluene-insoluble fractions of both coal extract and SRC are preferred materials for following the upgrading of syncrudes. They have fairly high molecular weights and rather narrow molecular weight distributions. Both the extracted coal and the pyridine-soluble fraction have elementary analyses (dry, mineral free) and nuclear magnetic resonance (nmr) spectra (3) that are very similar; they apparently differ significantly only in molecular size.

Table I

Comparison of Fractions from Extraction and Solvent-Refining of Illinois No. 6 Coal

		Fractions				
	Insoluble extracted Coal	Soluble in Insoluble in	Pyridine Toluene	Toluene Hexane	Hexane	
Coal (78.6% C, 5.1% H, 12.4% O) — Pyridine extraction	78.0	% C	79.5	83.0	84.0	More O
	4.8	% H	5.4	6.3	8.7	
	12.6	% O	10.8	7.3	5.0	
		Increasing C + H, decreasing O →				
Coal — Solvent refining	All soluble	% C	86.1	87.4	89.9	More C + H
		% H	4.9	6.1	6.6	
		% O	5.7	4.0	2.0	
	Common designations		Preasphaltenes, asphaltols, polar Compounds	Asphaltenes	Oils	
	Average moleculer weight		~ 1200	~ 600	~ 300	

Figure 1 summarizes our data on retention times in gel permeation chromatography (gpc) as a function of average molecular weights by vapor phase osmometry (vpo) of fractions derived from both coal extract and the solvent-refined product from the same coal. Even though the SRC fractions contain about 10% more oxygen and 10% less carbon than the extract fractions, the points are well fitted by a single curve. Individual gpc curves show that fractionations into pyridine, toluene, and hexane-soluble fractions give products with fairly narrow and symmetrical gpc peaks. Two pairs of points in Figure 1 correspond to double peaks with special fractions.

Listed below are all the scissile bonds that we now think are important in the liquefaction of bituminous coal under common operating conditions. The same types of bonds are probably involved in scissions under strongly acidic conditions, as with phenol plus boron trifluoride etherate.

$$\mathrm{Ar\text{-}CH_2Ar}$$
$$\mathrm{Ar\text{-}(CH_2)_n Ar}$$
$$\left.\begin{array}{l}\mathrm{Ar\text{-}OAr}\\ \mathrm{R\text{-}OAr}\\ \mathrm{R\text{-}OR}\end{array}\right\}\ \text{and S analogs}$$

We now consider current high-temperature, high-pressure liquefaction processes in terms of Table I and the scissile bonds listed above. The solvent-refining process consists mostly of conversion of insoluble coal to the pyridine-soluble, toluene-insoluble fraction of SRC. The net result approximates loss of some hydrogen and more oxygen, formation of a more aromatic aggregate, and some bond breakage. Because the solubility-molecular weight relations are the same in the extract and SRC series (2), the net phenol-base relations have changed little, and so the required bond breakage appears to be associated with net loss of ethers and some bibenzyl type bonds. The conversion of SRC to "oil" or distillate requires a large hydrogen input and a considerable reduction in molecular weight and heteroatom content. Part of the hydrogen requirement is to cap the fragments left when heteroatoms are removed as water, H_2S, and NH_3, but much of the hydrogen requirement may be to reduce condensed aromatic systems that cannot be cleaved to partially hydroaromatic systems that can be cleaved, especially by reforming catalysts.

Our working hypothesis leads us to suggest cheaper alternative routes to liquefaction. First, there are indications that ether clevage alone, without removal of oxygen or addition of hydrogen, can render coal soluble (4). The alkylation requirement now seems to be associated more with reducing phenol-base interactions (1,2) by O-alkylation (5) than with C-alkylation (4). There should be lower-temperature, low-pressure routes for ether cleavage, as by acids and bases, as well as the alkali metal route. Whether ether cleavage alone will take our coal to preasphaltenes, alphaltenes, or oils, or some of each (Table I) is under investigation (5).

Oxidations of coal models have shown that hydroaromatic rings are likely to be attacked first in free radical chain oxidations. We have therefore tried to dehydrogenate such rings to aromatic rings with two objectives, to direct the oxidation to the scissile bonds and to recover hydrogen for subsequent processing. Our first experiment with ethylene as hydrogen acceptor has given some promise of success.

We are also studying the possibility that selective oxidation will cleave most of the scissile bonds listed above. Oxidation of diarylmethanes should give ketones that can be converted to esters with a peracid. Longer aliphatic chains between aryl groups should be oxidized to pairs of acids. The alkyl ethers should be oxidized to esters. Hydrolysis of esters should then result in cleavage of scissile bonds. Mild oxidations of extracted coal with subsequent base hydrolysis have indeed given marked increases in soluble materials. Oxidation and nmr studies on soluble fractions of coal extract and SRC indicate that the extract is relatively rich in benzyl hydrogen atoms and that these are lost perferentially in oxidation; however, the SRC fractions that have the most aromatic hydrogen are most reactive and this kind of hydrogen is lost preferentially in oxidation.

We have also examined the use of commercial household bleach, $\sim$ 0.8 M sodium hypochlorite, as an oxidizing agent at 30°, where extracted coal is very reactive. By stepwise oxidation, with removal of acids as they form, we have recovered 76% of the carbon reacting as carboxylic acids, mostly black and soluble only in aqueous sodium bicarbonate, with smaller proportions of water-soluble polybasic acids. The susceptibility of some, but not all, substrates to oxidation by sodium hypochlorite is pH dependent.

Acknowledgement: Various portions of this research were supported by the U.S. Energy Research and Development Administration under Contract EF-76-C-01-2202 and by the National Science Foundation under Grants AER74-13359 A02 and AER75-06143.

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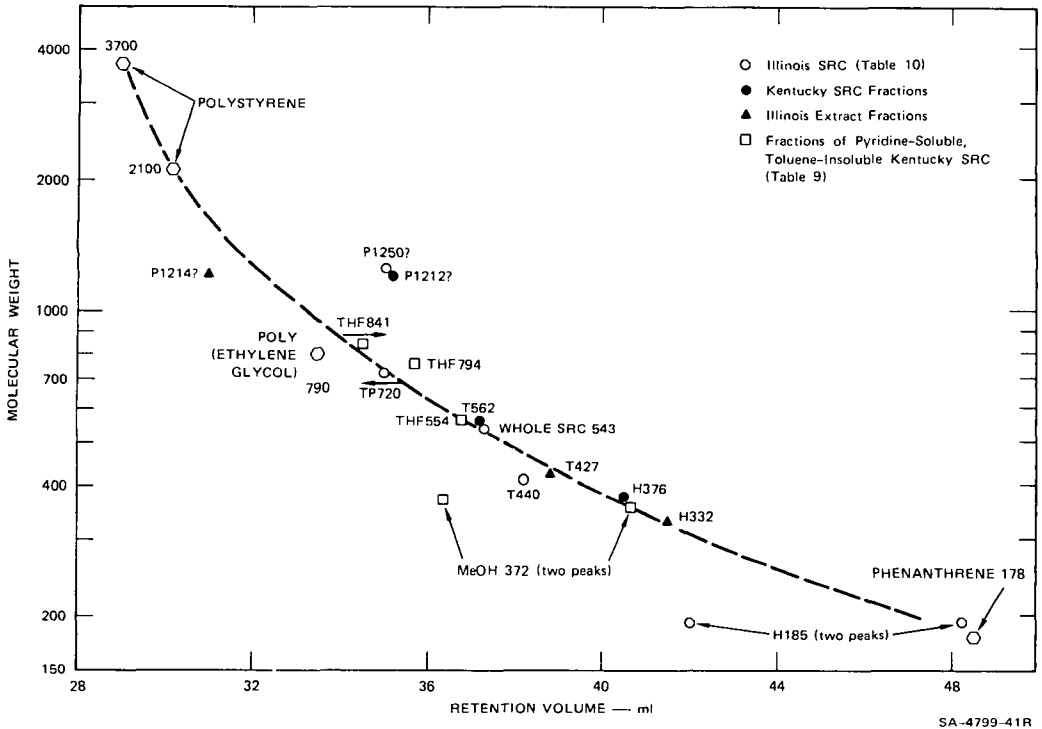

FIGURE 1 MOLECULAR WEIGHTS AND GPC RETENTION VOLUMES FOR FRACTIONS OF EXTRACTS AND SRCs OF ILLINOIS AND KENTUCKY COALS

The letter associated with a point indicates whether the fraction was soluble in pyridine, toluene, or hexane. The number is the $\bar{M}_n$ measured by VPO.

Early Stages of Coal-Carbonization: Evidences for Isomerization Reactions*

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At temperatures between ∿350° and 425°C, the molecular structures that characterize coal are rapidly, and very obviously, transformed into more stable carbon configurations through loss of "volatile matter" (as tar and gas). But little is known about possible configurational changes at lower temperatures. Thermograms of coal (1) indicate specific heat effects as endo- and exotherms from ∿200°C up; but because enthalpy changes recorded in this manner include sensible heats as well as heats of reaction, it is difficult to assess the nature of the chemical processes which produce the thermograms. On the other hand, low-temperature chemical changes, if such did in fact occur, should be reflected in the "reactivity" of heat-treated coal - and, in particular in its response to oxidation; and if oxidation could be performed so as to yield identifiable products, it should be possible to detect the major configurational changes in the distribution of oxidation products.

Accordingly, since it was previously shown (2) that sodium hypochlorite oxidation yields relatively simple carboxylic acids of which many could be identified by gas chromatography (GC) and mass spectrometry (MS), we thought it pertinent to determine whether this technique, although involving still not fully understood reaction paths, could also be used to monitor low-temperature changes in coal. The present paper reports the first results of such an exploratory study.

Experimental and Results

For the purposes of this investigation, two coals - a Western Alberta lvb coal with C = 90%, and a Kentucky hvb coal with C = 85% - were used.

10 g samples of these coals, each sized to -60 +115 mesh, were preheated in helium for 2 hr at the desired temperature, cooled, and then stored under pure He until required. No significant weight losses or changes in elemental compositions were observed with either coal up to 375°C, but 5-10% weight losses, and slight (0.5-1.2%) increases in carbon contents, with corresponding reductions in oxygen were noted after preheating at 390-400°C.

For the oxidation experiments, 2 g (preheated) samples were first "activated" by reaction with nitronium-tetrafluoroborate in acetonitrile, and thereafter treated with 125 ml of an aq. 1.6 N sodium hypochlorite solution at 60°C. The pH of the reaction mixture was maintained at 12 by adding NaOH pellets at regular intervals. When reaction was complete, the mixture was acidified; insoluble matter was filtered off; and soluble carboxylic acids were extracted with ether. The residual solution was freed of water by low-pressure distillation at 40°C, and solid material left behind was extracted with anhydrous methanol.

The ether- and methanol-extracts were then combined, converted to methyl esters by reaction with diazomethane, and separated by gel permeation chromatography on a (Water Associates') Poragel column into two fractions with molecular weights >600 and <600 respectively (fractions A and B). Fraction B (mol. wt. <600) was further subdivided into "simple" (B,1) and "complex" (B,2) acids by elution chromatography on a Florisil column. (From this column, methyl esters of "complex" acids could only

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be eluted with 10:1 chloroform-methanol, while esters of "simple" acids could be taken off with pentane, hexane and 2:1 hexane-chloroform.)

The "simple" acids (fraction B,1) were quantitatively analyzed by GC on OV-17/ Chromosorb WHP and reference to peak area vs. concentration diagrams for authentic compounds. Where no authentic compounds were available for methyl esters of toluene carboxylic acids, concentrations were computed from response factors derived from those appropriate for the methyl esters of benzene carboxylic acids.

Detailed study of the oxidation products showed that the raw and variously preheated coals furnished substantially identical amounts of carbon dioxide (Figure 1), but that there were significant, though, complex, variations in the yields of carboxylic acids (Figures 2-6) and that these yields depended on the nature of the coal as well as on the preheat temperature. Thus, while the lvb coal had to be preheated to at least 350°C before it produced greater than the initial amounts of carboxylic acids, the hvb coal needed only to be preheated to 200°C before doing so (Figure 2).

These observations accord well with enthalpy changes recorded by differential thermal analysis (1), and are, in our view, clearly indicative of thermally induced alterations of the initial carbon configurations in the two coals.

Fraction A - composed of acids with mol. wts. in excess of 600 - presumably represents condensed aromatic fragments of the original and heat-treated samples; and if so, the fact that yields of this fraction increase with preheat temperatures suggests that aromatization begins at temperatures as low as 150°C in hvb coal and at ∿200°C in lvb coal (Figure 3).

Fraction B,2 - which represents over 50% of the total acid product from each sample and consists of "complex" acids with mol. wts. <600 - can be tentatively identified as originating in coal fragments that produce "pre-asphaltenes" in coal liquefaction processes (3), and variations of the yield of this fraction with preheat temperature are also interesting (Figure 4). In the case of lvb coal, B,2 yields reach a maximum at 375° and then decline precipitously at 390°C, but the decline is compensated by an almost eqivalent increase in the yield of high molecular weight (>600) material. In contrast, B,2 yields from the hvb coal attain a maximum at 200°C, fall to minimum at 300°C, and then rise to another maximum at 400°C.

The "simple" acids with mol. wts. <600 (fraction B,1), which were completely characterized and invariably accounted for 22-30% of the total acid products, are evidently produced from easily oxidizable open structured coal fragments; and from the lvb coal, the yield of this fraction decreased steadily as preheat temperatures rose. However, in the case of the hvb coal, the yield was found to remain constant up to 300°C, and to fluctuate thereafter (Figure 5).

Finally, some note must be taken of the distribution pattern of penta- and hexa-carboxy benzenes vis-a-vis that of tri- and tetra-carboxy toluenes. Quite generally, maxima for benzenes and almost coincident with minima and maxima of toluenes. But here again, significant differences between lvb and hvb coal are observed. For the lvb coal, maxima of benzenes lie at 175° and 375°C, while for the hvb coal, they appear at 350° and 400°C. Maximum yields of toluenes were obtained from lvb coal after preheating at 300°C, and from hvb coal after preheating at 150°C (Figures 6 and 7).

We believe that these variations in yield and distribution of carboxy acids are best understood in terms of low-temperature intra-molecular isomerization reactions which modify the initial carbon-hydrogen configurations of the coal well before it begins to undergo thermal cracking. Of the two specific processes that could be postulated as effecting such isomerization, one is trans-annular bond

formation (Figure 8) and the other is isomerization of benzylic carbon to methylphenyl derivatives (Figure 8) and more complex ring systems. Either change could readily occur at temperatures as low as 150°C and create structures susceptible to oxidation by sodium hypochlorite.

We note, in this connection, that ether-oxygen also appears to play a major role in the behaviour of coal at elevated temperatures (4); but whether or not isomerization and/or cleavage of ether-linkages also occur at low temperatures could not be determined in this study, since hypochlorite oxidation easily degrades heterocyclic functional elements under acidic as well as basic conditions.

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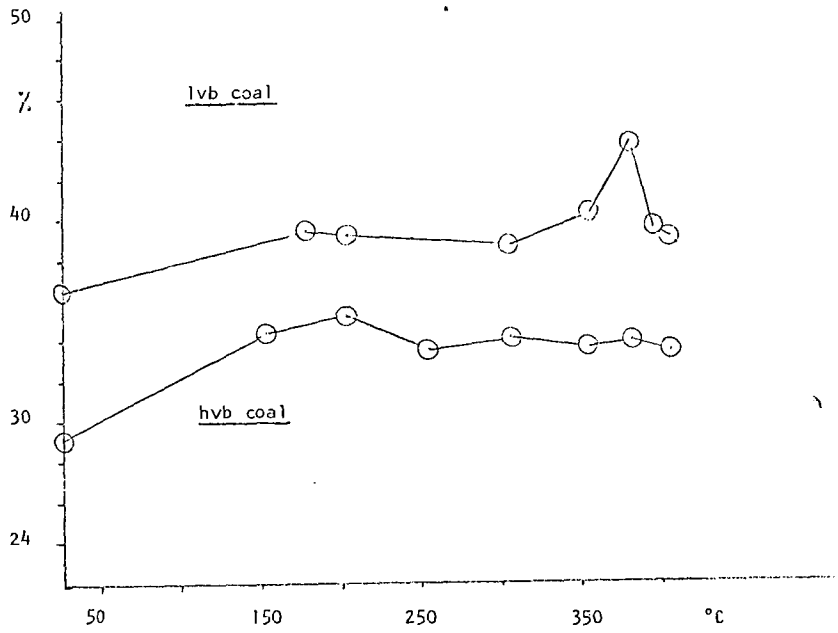


Fig. 1 Yield of CO_2 as per cent of coal-carbon from variously heat-treated samples

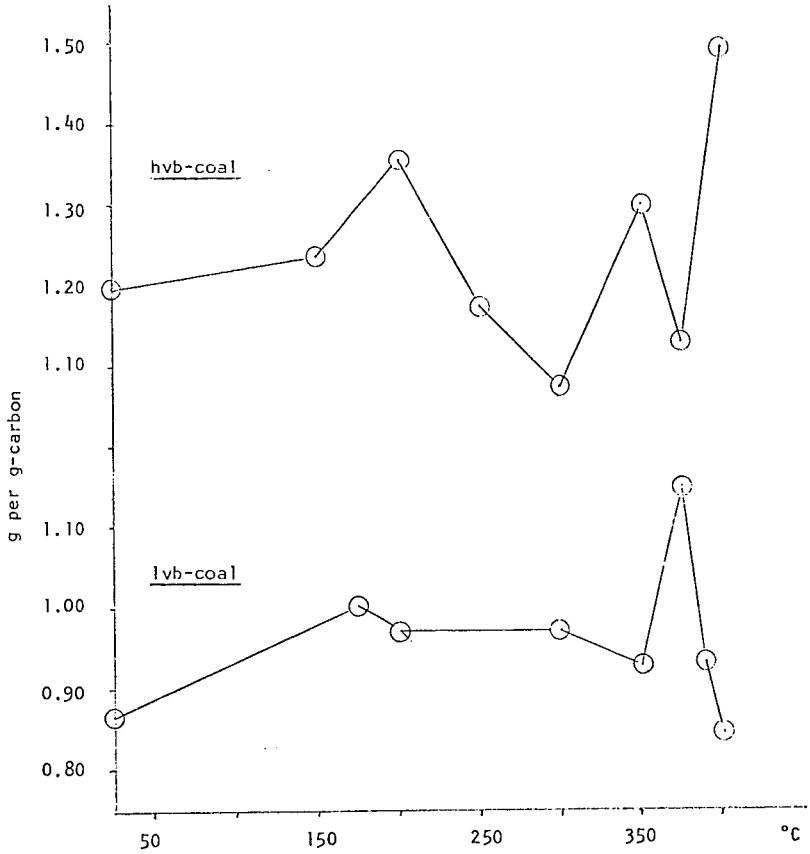


Fig. 2 Yield of total carboxylic acids as methyl esters from variously heat-treated samples.

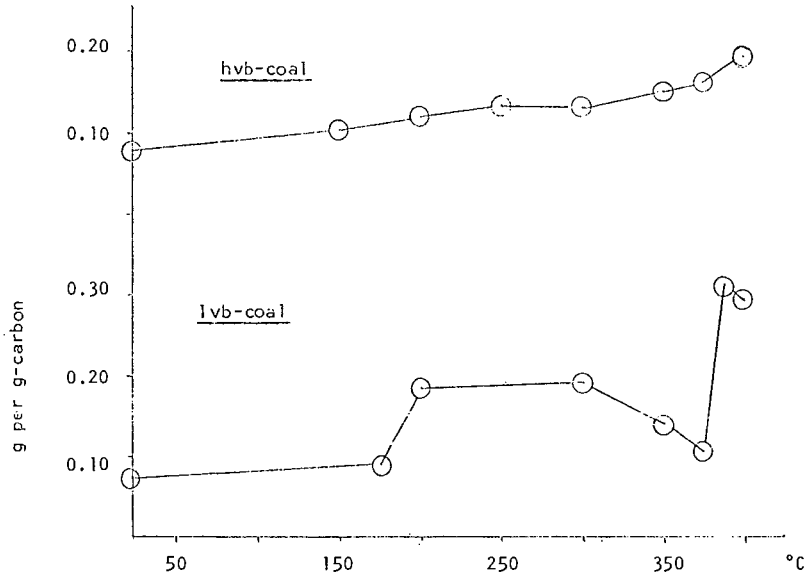


Fig. 3 Yield of 'complex acids' as methyl esters
Mo. Wt. >600

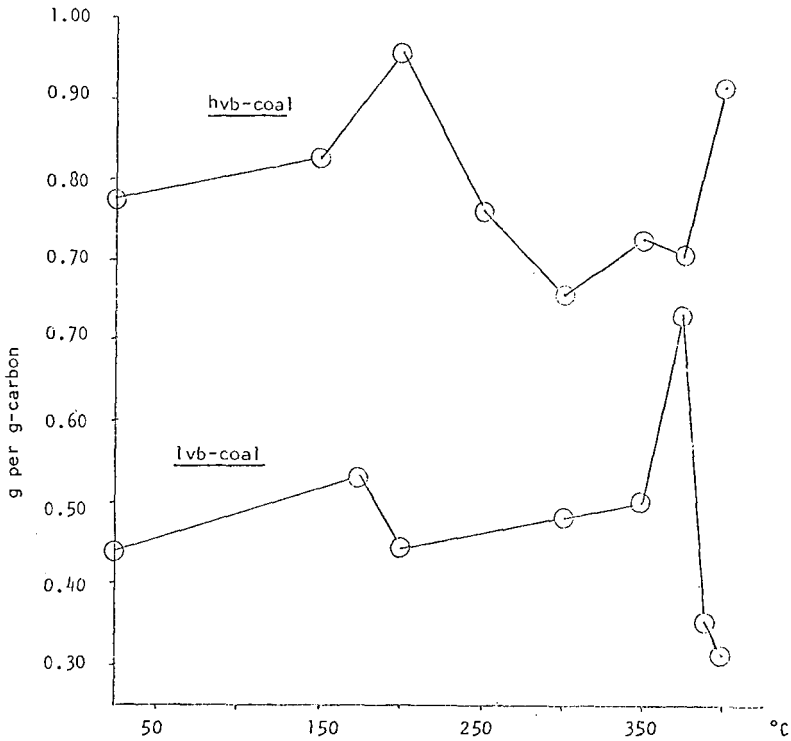


Fig. 4. Yield of 'complex acids' as methyl esters
Mol. Wt. <600

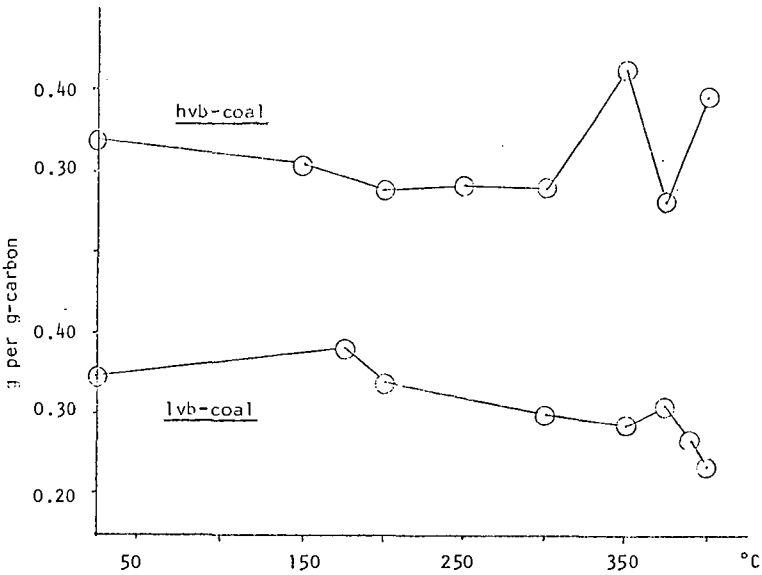


Fig. 5 Yield of 'simple acids' as methyl esters.

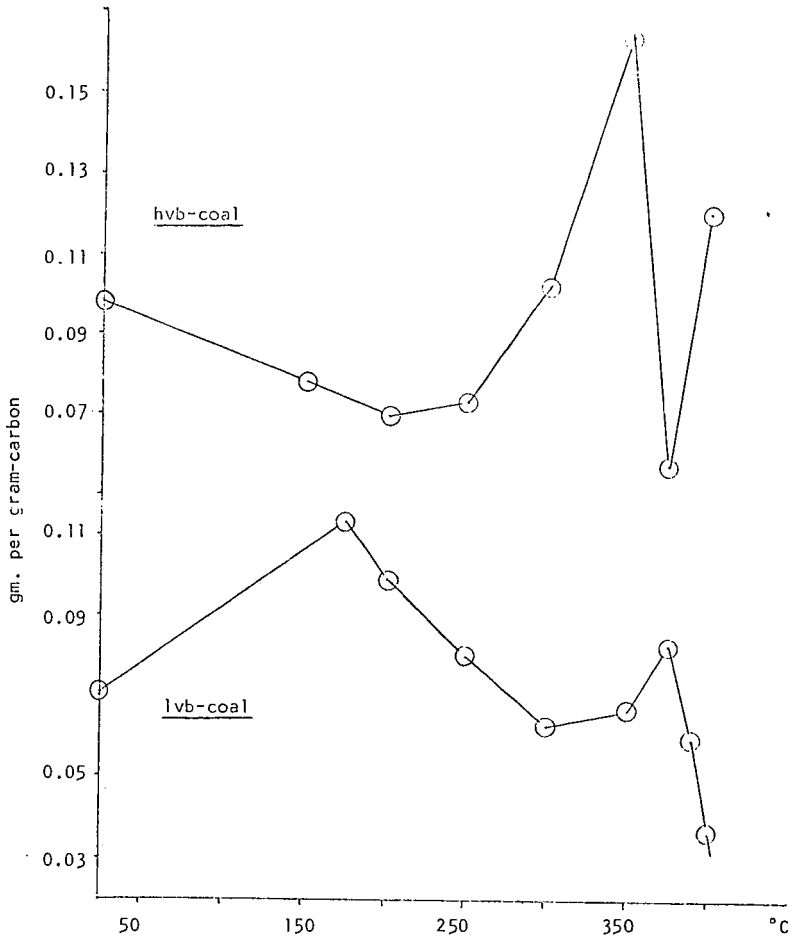


Fig. 6 Combined yield of penta- and hexa-carboxyl benzenes.

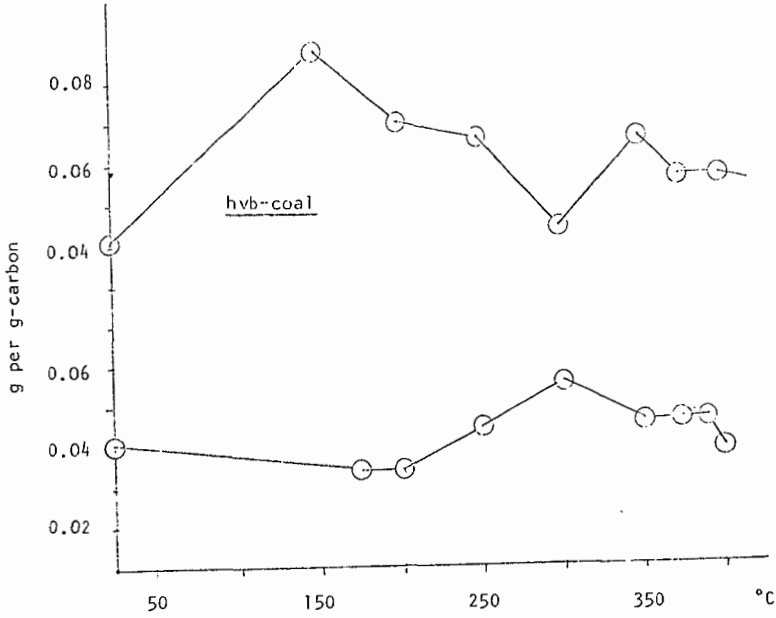
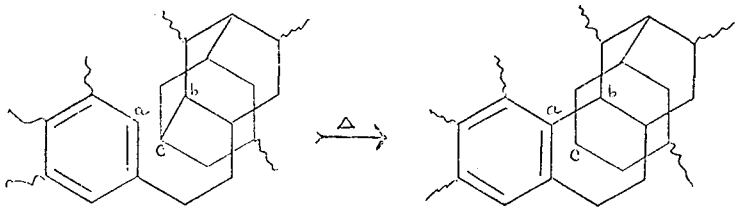


Fig. 7 Combined yield of tri- and tetra-carboxyl toluenes

Scheme 1



Scheme 2

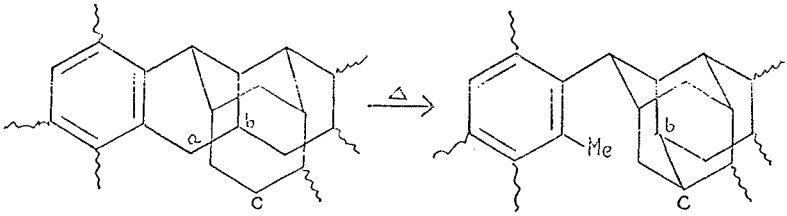


Fig. 8 Possible isomerization path.

SUPERCRITICAL SOLVENTS AND THE DISSOLUTION OF COAL AND LIGNITE

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The use of supercritical media as solvents in coal extraction is of interest because of their unusual solvent abilities. In a review of the general concept of supercritical gas extraction, Paul and Wise (1) discuss the solvent properties of materials above their critical temperatures (T_c). These supercritical vapors display unusual solvent powers when compressed to liquid densities. The solubility of naphthalene in supercritical ethylene (at 320 K), for example, is increased by a factor of 10^3 when the vapor density is increased from about 0.1 to about 0.6 g/cm^3 (2).

Whitehead and Williams applied this principle to the extraction of coal with hydrocarbons in their supercritical state (3). They extracted about 20% of a coal containing 38% volatile matter into toluene at 350°C (T_c for toluene is 318°C), or a quantity of extract that was greater than the tar yield from carbonization of the same coal.

In the work discussed here, we used a number of different solvents as coal dissolution media, all at temperatures above their respective critical temperatures. Our objectives were to investigate a possible structure/solvent-power relationship and to determine if the solvent has to be strictly above its critical temperature to be effective. Our experiments are briefly described below.

Experimental

All experiments were carried out in a 300 cm^3, 316 stainless steel, MagneDrive stirred autoclave from Autoclave Engineers. We used samples of beneficiated Illinois No. 6 coal, and a North Dakota lignite.* Most of the experiments were done at 335°C for 90 minutes.

It was necessary under these test conditions to be able to separate any materials soluble in the media from the material insoluble during the epxeriment. This precaution would eliminate any confusion of results in cases where a significant fraction of the coal was soluble at test conditions but insoluble when the system was brought back to ambient temperature and pressure. Accordingly, we designed a coal filter "basket" for these experiments (Figure 1). Our procedure was to place the starting coal between two sintered glass discs within the autoclave so that any material dissolved under our supercritical conditions would be carried through these discs and found outside the basket after the experiment.

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*The samples were provided by Pennsylvania State University, whose designation for the coal samples was PSOC-26 and for the lignite, PSOC-246.

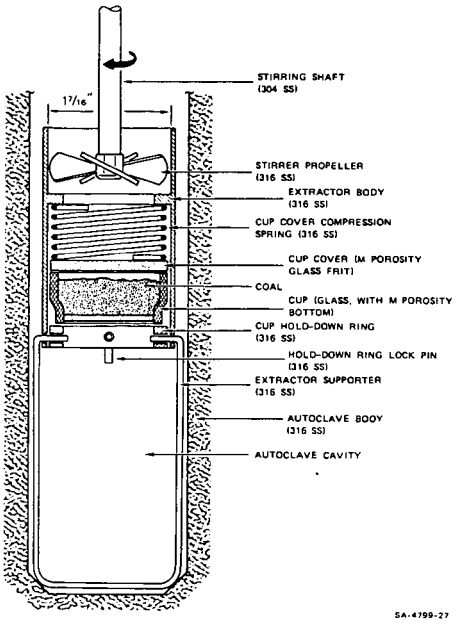

FIGURE 1 SUPERCRITICAL EXTRACTOR (TO SCALE)

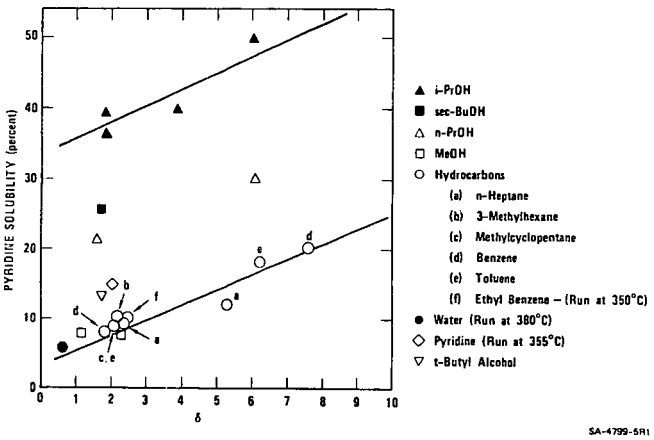

FIGURE 2 HILDEBRAND SOLUBILITY PARAMETER, δ, VERSUS PYRIDINE SOLUBILITY OF COAL PRODUCTS
Experimental conditions were 335°C, 90 min.

Results and Discussion

Supercritical Extraction

We performed a number of experiments with several media, both with and without the extraction apparatus (basket) in the reactor, and under identical experimental conditions. The results in Table 1 show that, first, the degrees of extraction are small, no more than about 13% for the best cases, and second, that the values for material dissolved in each medium after reaction are virtually the same both with and without the basket. Thus, the supercritical media are extracting up to about 13% of the substrate, and that extract in turn is soluble in the respective media at ambient conditions. The extraction for Run 86 is significantly low, perhaps because the lignite tended to agglomerate under the conditions of this experiment, thereby reducing circulation of i-propanol through the basket.

Clearly, filtration under supercritical conditions was not necessary to obtain the maximum dissolution, and the promise of supercritical extraction appeared diminished in view of the low extraction values. To confirm these findings, we made several additional runs with coal in a wide range of solvents without the basket at several different solvent densities.

We found it useful to consider all our extraction data in terms of the Hildebrand solubility parameter of the respective solvents. This parameter is a measure of the cohesive forces in a solution and is expressed by the relation $\delta = a^{1/2}/V$, where a is van der Waal's intermolecular term and V is the molar volume (4). In addition, the solubility parameter has been considered in terms of polar and nonpolar contribuions [4(c)]. The application of the solubility parameter to coal processing has been discussed by Angelovich et al. (5), who concluded that solvents with a nonpolar solubility parameter of about 9.5 appeared to be most effective in coal dissolution.

Giddings et al. (6) found a correlation between solvent capabilities and δ values of a number of supercritical fluids at liquid densities. Their expression defining the parameter is

$$\delta = 1.25\ P_c^{\frac{1}{2}}\rho_r/\rho(\mathrm{liq}) \qquad 1)$$

where P_c is the critical pressure in atmospheres, ρ_r is the reduced density, and $\rho(\mathrm{liq})$ is the reduced density of liquids, assumed to be about 2.66. We can thus vary the δ value for a given medium simply by varying the experimental density.

The pyridine solubition of our starting coal is 13%. Figure 2 compiles all our extraction data and plots the total pyridine solubilities of the coal products versus the Hildebrand solubility parameter value for each medium, as determined by Equation 1. Each experiment yielded both a filtrate soluble in the reaction medium and a filterable residue. All filtrates were pyridine-soluble, and the solubilities in pyridine of each of the residues were determined at room temperature. The values used in the figure are the total solubilities, obtained by summing the fraction of the starting coal represented by the filtrate, and the pyridine-soluble fraction of the starting coal in the residue.

Table 1

SUPERCRITICAL EXTRACTION OF ILLINOIS NO. 6 COAL AND NORTH DAKOTA LIGNITE (at 335°C for 60 min)[a]

Run No.		Supercritical Medium Type	(g/ml)	Mode	Recovered in medium[b] (%)	Mass Recovered (%)
Coal	55	iPrOH	0.3	Basket	11	97
	38	iPrOH	0.3	No Basket	11	97
	82	Benzene[c]	0.6	Basket	12	95
	60	Benzene[c]	0.6	No Basket	13	92
	58	MeOH[d]	0.4	Basket	12	97
	76	MeOH[d]	0.4	No Basket	8	94
Lignite	84	Toluene	0.2	Basket	3	87
	66	Toluene	0.2	No Basket	4	88
	86	iPrOH	0.1	Basket	5	86
	65	iPrOH	0.1	No Basket	12	85

[a] 5 g coal or lignite; reactor volume, 280 ml.

[b] Room temperature solubilities of the starting coal and lignited are less than 1% in all the test solvents.

[c] 1 g coal, for 3 hr.

[d] 1 g coal.

Table 2

EXPERIMENTS ON ILLINOIS NO. 6 COAL WITH TOLUENE BELOW AND ABOVE ITS CRITICAL TEMPERATURES FOR 90 MINUTES

Run No.	Solvent	Experimental Conditions P (g/ml)	Temp[a] (°C)	psig[b]	Filt[c]	Solubility (%) THF	Pyridine
45	Toluene (subcritical)	0.65	305	2400	8	12	13
49	Benzene (supercritical)	0.70	305	2400	8	11	13
27	Toluene (supercritical)	0.65	335	3400	13	21	24
16	Benzene (supercritical)	0.70	335	4100	10	22	20

[a] The critical temperatures for toluene and benzene are 320°C and 288°C, respectively.

[b] The critical pressures of toluene and benzene are 630 psi and 720 psi, respectively.

[c] The "Filt" values are the fraction of the product coal which is soluble in the test medium at room temperatures.

The plot may be roughly split into two regions. The upper region of relatively high pyridine solubilities represents data from previously discussed work with alcohols as H-donor solvents (7). The bulk of the data falls about the lower line. Most of the solubilities are below 13% or less than the solubility of the untreated coal itself in pyridine.

We used pressure ranging from about 700 psi for the lower δ values to about 4000 psi for the highest. Within the range of solvents studied, and with the exception of the H-donor alcohols, no gross differences are apparent between solvent types. For example, all the hydrocarbons (○), both aliphatics and aromatics, cluster well about the line, as does the single point for water (●). Methanol (□) is also close to the line and apparently does not serve as an H-donor* under these conditions. The two solvents a little above the line are pyridine (◇) and t-butyl alcohol (▽). Pyridine is a well known solvent in coal work; its extraction capability is apparently not enhanced by high pressures and temperatures and its supercritical state. The alcohol, on the other hand, cannot operate as an H-donor, and yet, unexpectedly, the plot shows it to be a better solvent than methanol.

The roughly linear correlation displayed by the data suggests that the dissolution process is not a function of the solvent type, but rather, is sensitive to the density (i.e., pressure) of the medium. Perhaps what we observe is an initial, reversible thermal fragmentation of a critical link in coal.

$$\sim\sim C\text{-}C\sim\sim \longrightarrow 2C\cdot$$

followed by some means of stabilization by solvent (S)

$$\sim\sim C\cdot + S \longrightarrow \text{stable product}$$

The nature of the stabilization process remains in question.

The positive slope of the lower line in Figure 2 suggests that greater degrees of extraction might be possible at higher δ values. The point labeled d in the figure is for a δ value of 7.5 and is taken from an experiment with benzene at 4100 psi. If we make the appropriate simplifying assumptions regarding liquid compressibility, we can calculate that for a δ value of 10, where by extrapolation we would expect a pyridine solubility of 25%, a pressure in excess of 7800 psi would be required. Clearly, extractions at thse pressure would not be practical.

Effect of Supercritical State

Finally, to determine if the supercritical state is stictly necessary to obtain the small extractions discussed here, we compare the results of using toluene and benzene at 305°C and 335°C. These temperatures are above the T_c of

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* We have recently found that with some bases present, methanol operates very well as an H-donor alcohol.

benzene (288°C), but below and above, respectively, the T_c of toluene (320°C). The results of this series of runs are presented in Table 2.

The benzene in Runs 49 and 16 is supercritical. With increasing temperature, a small increase can be seen in the tetrahydrofuran (THF) and pyridine values. Similar changes can be seen for toluene in Runs 45 and 27 over the same temperature range, where toluene is below and above its T_c, respectively.

The changes observed are due to temperature differences alone. These conversions are thus due to the presence of a dense medium at high temperatures. We conclude, therefore, that whether an extraction medium is strictly supercritical, that is, above the critical temperature, is of little consequence.

Acknowledgement

We acknowledge the support of the U.S. Energy Research and Development Administration of the work.

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HETEROATOM SPECIES IN COAL LIQUEFACTION PRODUCTS

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INTRODUCTION

An assessment of the nitrogen and oxygen heteroatom species in coal-derived products is a complex yet important analytical problem in fuel chemistry. Principally, this is because the system is a multifarious molecular mixture that does not easily lend itself to direct analysis of any one component or functional group. Albeit this problem is not new, the characterization of these heteroatoms is of immediate importance to further processing of these fuels. We shall detail the methods and techniques used to rapidly isolate and/or characterize both nitrogen and oxygen heteromolecular species. Utilization is made of solvent separations, functional group type separation, chemical derivatization, HCl salt formation and the use of chromatographic and spectrometric analytical methods to quantitate our results. Specifically, we ascertained the kind and distribution of nitrogen and oxygen heteromolecules in a coal liquefaction product and in a recycle solvent used in solvent refined coal (SRC) processing. The coal liquefaction product was first solvent separated into oils, asphaltenes, preasphaltenes and ash, while low boiling oils (light oils) trapped from knock-out tanks and the SRC recycle solvent were treated directly. Nitrogen bases were complexed as HCl adducts or separated on ion-exchange resins. Hydroxyl-containing species from the separated fractions were quantitated by infrared spectroscopy or by formation of a trimethylsilyl ether (TMS) and subsequent analysis by ^{1}H NMR and mass spectrometry. Hydroxyl species were also isolated on ion-exchange resins or by selective gradient elution from silica gel.

EXPERIMENTAL

Solvent Separation

Coal liquefaction products were solvent separated[1] by first freezing the coal liquids in liquid nitrogen and grinding them to fine particles. This frozen oil can be easily transferred to a stainless steel centrifuge tube. Pesticide grade solvents were then used to solubilize specific fractions--oils (pentane), asphaltenes (benzene), preasphaltenes[2] (tetrahydrofuran) and coal-derived ash (insoluble in all solvents used). By starting with a 3-4 gram sample, one (1) liter of each solvent in four or five 200 ml portions was usually sufficient to extract the solubles. Insolubles were removed by centrifugation at 10^4 rpm at 6°C for 10 minutes. Solvents were removed by nitrogen flush on a Rotovap using a water bath (65-85°C). Asphaltenes were treated differently at the final solvent removal step; a 20 ml solution of benzene/asphaltenes was swirled in a flask and flash frozen in liquid nitrogen, and the solvent was sublimed at 10^{-1}-10^{-2} torr for 2-3 hours.

HCl Treatment

The objective of this procedure was to separate and/or concentrate both nitrogen heteromolecules and hydroxyl-containing species from coal-derived material.[3] Gaseous HCl was bubbled through a benzene or pentane solution of the coal product to form an insoluble HCl adduct with molecules containing a basic nitrogen atom. The adduct, after being washed free of other components, was back titrated with dilute NaOH solution to free the base nitrogen into an organic phase, usually diethyl ether, methylene chloride or benzene. The two fractions recovered contain acid/neutral and nitrogen base material, respectively.

Hydroxyl Silylation

Oils, asphaltenes and preasphaltenes were treated with hexamethlydisilazane (HMDS) to form a trimethylsilyl ether (TMS) of active hydroxyl groups.[4,5] A 50 mg sample of coal-derived product was dissolved in 25 ml of benzene containing 50 µl of pyridine-d_5. To this solution 500 µl each of HMDS and N-trimethylsilyldimethylamine were added. This mixture was maintained as a closed system except for a small Bunsen valve and mildly refluxed for one hour with occasional swirling of the flask. After the reaction was completed, solvents and unreacted reagents were removed under nitrogen flush on a Rotovap and finally freeze dried from 5 ml of benzene for 30 minutes. A portion of the final product was checked by infrared spectroscopy (IR) for disappearance of the OH band at 3590 cm^{-1}.[6] The remaining sample was dissolved in benzene-d_6 and its proton NMR spectrum taken and integrated. From the relative areas of the peaks in the proton NMR spectrum, a percent H as OH was calculated (Equation 1).[7]

$$\frac{\left(\frac{\text{TMS Area}}{9}\right)}{\left(\frac{\text{TMS Area}}{9}\right) + (\text{Remaining Proton Area})} \times 10^2 = \%\ \text{H as OH} \qquad (1)$$

From an elemental analysis of the original sample, one can calculate the weight percent oxygen as OH on a moisture and ash free basis (MAF).

Combined Gas Chromatography-Mass Spectrometry (GCMS):

The combined GCMS analyses were performed using a Dupont 490 mass spectrometer* interfaced to a Varian 1700 Series gas chromatograph, equipped with an 80:20 glass splitter and a flame ionization detector. The spectrometer was also coupled to a Hewlett-Packard 2100A computer used for spectrometric data storage and reduction. The mass spectrometer was operated at a resolution of 600 and an ionizing voltage of 70 eV. The ion source, jet separator and glass line from the chromatograph to the mass spectrometer were held at 275°C. The chromatographic effluent was continuously scanned at a rate of four seconds per decade by the mass spectrometer.

The gas chromatographic separations were effected using a variety of conditions. The nitrogen bases and acid fractions from the coal liquefaction product were chromatographed on a 10' x 1/4" OD glass column packed with 100-120 mesh Supelcoport coated with 3% OV-17. Bases from the SRC product were chromatographed on a 10' by 1/8" OD glass column packed with 100-120 mesh Chromasorb-G coated with 2% OV-17. Gas chromatographic separation of bases from the light oil was achieved using a 10' x 1/8" OD glass column containing acid washed and silyl treated 100-120 mesh Supelcoport coated with 3% Carbowax 20M. In each case the He flow rate was 30 cc/min and the analyses were performed using appropriate temperature programming conditions.

Column Chromatographic Separation

Coal-derived liquids, soluble in pentane, were separated into five fractions: acids, bases, neutral nitrogen, saturate hydrocarbons and aromatic hydrocarbons. Acids were isolated using anion-exchange resins, bases with cation-exchange resins, and neutral nitrogen by complexation with ferric chloride adsorbed on Attapulgus clay. Those pentane soluble hydrocarbons remaining were separated on silica gel to give the non-adsorbed saturates and the moderately retained aromatics. This method is commonly referred to as the SARA technique.[8]

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*Reference to specific makes or models of equipment does not imply endorsement by the U. S. Energy Research and Development Administration.

RESULTS AND DISCUSSION

The centrifuged coal liquid product (CLP) was produced using Ireland Mine, Pittsburgh seam, West Virginia coal in the 1/2 ton per day SYNTHOIL Process Development Unit (PDU).[9] Operating conditions for this experiment were 4000 psi hydrogen pressure, 450°C and no added catalyst. The light oils were derived from a catalytic experiment (Harshaw 0402T) using Homestead Mine, Kentucky coal, under 4000 psi pressure and 450°C.

The coal liquefaction product was solvent separated by the method previously described to yield the distribution of fractions given in Table 1. Figure 1 gives the atom weight percent distribution of nitrogen and oxygen in the solvent separated fractions listed in Table 1. The pentane soluble oils were subsequently separated into five fractions using the SARA chromatographic scheme. Table 2 lists the weight percents of the individual fractions. The asphaltenes were treated with HCl to form acid/neutral and base subfractions, 63 and 37 weight percent, respectively.

The acid and base fractions from the SARA separation of the oils were subjected to analysis by combined GCMS and low voltage low resolution mass spectrometry (LVLR). Figures 2 and 3 reproduce the gas chromatograms of the base and acid fractions, respectively. The oxygen containing species shown in Figure 3 have been classified as alkylated phenols, indanols/tetralinols, phenyl phenols, and cyclohexyl phenols. Table 3 lists the carbon number range and tentative compound type assignments for the nitrogen heteromolecules in the acid and base fractions as determined by LVLR mass spectrometry.[10] Table 4 lists the compound types assigned to the base fraction of the oils by GCMS.

Table 5 lists the carbon number range data from the HRMS analysis of the asphaltenes and their acid/neutral and base subfractions. It must be noted that at the operating conditions of the solids inlet, 300°C, 10^{-6} torr, less than 50% of the these materials could be volatilized. These preliminary studies have also indicated the presence of a limited number of diaza-species from Z# = 8-18.

The SYNTHOIL PDU contains several knock-out traps that condense low boiling components, light oils.[11] Nitrogen bases in the light oils were isolated by their precipitation with gaseous HCl and back titrated with NaOH into diethyl ether. These nitrogen bases constituted 3% by weight of the light oils. The gas chromatographic profile of these bases is given in Figure 4. An earlier study of these light oils characterized the saturates, aromatics and acidic components separated by Fluorescence Indicator Analysis (FIA).[12] The present investigation has resulted in the first quantitative analysis of pyridines and anilines in an oil produced by the hydrogenation of coal.

Table 6 summarizes the quantitative results from the chromatogram of Figure 4. It is of interest to point out that during this investigation, though numerous substituted pyridines were quantitated, no evidence for the parent was found. Because the techniques employed recovered components with boiling points near that of pyridine it is suggested that this observation may be significant. If free pyridine was trapped within the coal macromolecular structure it surely would have been found in either the light oils or the pentane soluble oils. If, on the other hand, pyridine was attached exo-, via a single C-C bond, to a more complex molecular network, the hydrogenation process should have freed it intact. But if the nitrogen heteroatom was an integral part of the original coal macromolecule, then hydrogenation would have cleaved a number of C_α-C_β bonds to produce a wide distribution of methylpyridines. Table 6 shows this methyl substitution trend. Quantitative results indicate that 2,3,6-trimethylpyridine is seven times more abundant than 2,3-dimethylpyridine and approximately twice as abundant as any other methylpyridine.

The source of anilines and, in particular, the observation of both the parent and the methyl substituted anilines are of interest. Anilines can arise from hydro-

genation of the heteroring in a fused ring system followed by breaking of the bond between nitrogen and an aliphatic carbon.[13] Therefore quinoline and its alkyl derivative could be a source of the anilines. Table 4 lists seven quinolines found in the oils that could be the precursors. The presence of the parent aniline, that should readily be hydrodenitrogenated,[13] is significant. If dealkylation was the same for all species, why didn't we see any of the parent pyridine? It could mean that the potential aniline moieties are located near the periphery of the coal macromolecule in contrast to the pyridines. The quantitative results indicate that methylanilines (toluidines) are in abundance in the order meta > ortho >> para > parent aniline, and all are greater than the dimethylanilines. These interpretations are based upon the more detailed analysis of the light oils. To date direct evidence for the presence of significant amounts of alkylated anilines and pyridines in the pentane soluble oils from the CLP have not been reported.

To complete this initial investigation of nitrogen species we chose to look at the nitrogen compounds present in the recycle solvent used for SRC processing and compare them with those found in coal liquefaction product oils. After extracting the gross benzene solubles, they were treated with HCl to isolate nitrogen bases. This particular sample had a slight residue that was benzene insoluble. Figure 5 gives the gas chromatographic profile of these nitrogen bases and summarizes the prominent structural isomers. The base fraction from the SRC solvent was less complex than the nitrogen bases found in the liquefaction oils, but the same principal molecular species were found in both samples.

The presence of hydroxyl groups in coal-derived materials has long been established. Our present interest is to define quantitatively the OH as a percentage of the total oxygen. The separation methods described concentrate a high percentage of the hydroxyl groups by anion exchange resin chromatography (acids) or the HCl treatment (acid/neutral). Once the separation/concentration has been made the sample is treated with a derivatizing reagent to form a trimethylsilyl ether, Ar-O-$Si(CH_3)_3$.

It has been shown that all of the hydroxyl groups contributing to the 3590 cm^{-1} infrared band can be quantitatively removed with the derivatizing reagent.[6] The TMS ethers are next examined by proton NMR. The signals near 0 ppm represent the trimethylsilyl $(CH_3)_3$ protons from each of the hydroxyl derivatives. By integrating the area under the total proton spectrum and allowing for the 9-fold intensity enhancement for the TMS area, the percent H as OH can be calculated. Table 7 lists some representative determinations of hydroxyl content from oils and asphaltenes. The silyl derivatization quantitation of hydroxyls in asphaltenes has been compared to the infrared spectroscopic method of standard additions.[14] Our results agreed to within 10%.[15] Infrared data, and those from others working on similar fractions indicates that there is little if any carbonyl oxygen (C=O) present in coal liquefaction products produced in the SYNTHOIL PDU. Therefore, we conclude that substantially all of the oxygen exists as either hydroxyl (phenolic or benzylic) or in an ether linkage (e.g. furan).

A useful corroboration of the NMR data and of characterizing the acid fraction of the oils is its mass spectrum before and after TMS derivatization. Figure 6 A and B shows the acid components from the pentane soluble oils before and after TMS derivatization, respectively. Note that the mass peaks are shifted 72 amu to give a nearly identical mass distribution. Table 8 lists those hydroxyl containing compounds that definitely formed a TMS ether. From the mass spectral data there was also evidence for trace amounts of indenol, naphthol and phenanthrol derivatives.

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Table 1. Solvent Separation Weight Percent Distribution.

Solvent Fraction	Wt. % of CLP
Oil	68.0
Asphaltenes	26
Preasphaltenes	4
Ash	2

Table 2. SARA Chromatography Fractions, Weight Percent Distribution.

Chromatography Fraction	Wt. % of CLP
Saturates	4.1
Aromatics	37.3
Acids	6.3
Bases	10.2
Neutral Nitrogen	3.9
Loss	7.4
Total Oil	68.0

Table 3. Carbon Number Distribution for the Acid and Base Fractions From SARA Chromatography Separation.

	Bases		Acids	
ZØ	LRLV CØ Range	Typical Structural Nitrogen Analogs	LRLV CØ Range	Typical Structural Nitrogen Analogs
- 5	6-12	Pyridines, Anilines	--	—
- 7	8-13	Azaindans	--	—
- 9	9-15	Dihydroquinolines, Indole	--	—
-11	9-15	Quinolines	—	—
-13	11-17	Phenylpyridines	--	--
-15	12-19	Azafluorenes	12-20	Carbazoles
-17	13-19	Acridines	14-20	Phenylindoles
-19	14-21	Benzo[ghi]azafluorenes	14-22	Benzo[def]carbazoles
-21	15-21	Azapyrenes	16-24	Benzocarbazoles
-23	17-26	Benzacridines	18-24	Phenylcarbazoles
-25	17-26	Benzo[ghi]azafluoranthenes	--	—
-27	19-26	Benzazapyrenes	20-29	Dibenzocarbazoles
-29	21-26	Dibenzacridines	22-29	Naphthylcarbazoles
-31	21-26	Azaanthanthrenes	22-29	Naphthobenzo[def]carbazoles
-33	23-26	Dibenzazapyrenes	24-29	Anthracenocarbazoles
-35	23-27	Azacoronenes	26-29	Anthranylcarbazoles
-37	--	--	28-29	Anthracenobenzo[def]carbazoles
-39	--	--	28-30	Dinaphthocarbazoles

Table 4. Compounds found in the nitrogen base fraction of Figure 2.

PEAK NUMBER	COMPOUND
1	SOLVENT (CARBON DISULFIDE)
2	PHENOL
3	CRESOL
4	CRESOL
5	TETRAHYDROQUINOLINE
6	QUINOLINE
7	6-METHYLTETRAHYDROQUINOLINE
8	METHYLQUINOLINE
9	ISOQUINOLINE
10	METHYLQUINOLINE
11	METHYLQUINOLINE
12	C_2-QUINOLINE
13	C_2-QUINOLINE
14	OCTAHYDRO-N-3-RING (OCTAHYDROACRIDINE)
15	METHYLOCTAHYDRO-N-3-RING (METHYLOCTAHYDROACRIDINE)
16	PHENANTHRIDINE + ACRIDINE
17	MEHTYLACRIDINE
18	AZAPYRENE
19	METHYLAZAPYRENE

Table 5. Carbon number range data for nitrogen heteromolecules in asphaltenes.

Z[a]	Asph	Asph A	Asph B	Possible Structural Types
	Carbon Number Range			
- 5	5-7	6,8,9	6	Pyridines
- 7	8-11	9-12	8-12	Azaindans
- 9	8-14	9-15	8-14	Dihydroquinolines; Indoles
-11	9-14	9-15	9-14	Quinolines
-13	11-16	11,12,14-17	11-16	Phenylpyridines
-15	11-19	11,12,14-19	11-17	Azafluorenes; Carbazoles
-17	13-20	14-20	13-18	Acridines
-19	14-20	14-21	14-19	Azabenzo[ghi]fluorenes
-21	15-21	15-22	15-20	Azapyrenes; Benzocarbazoles
-23	17-21	18-23	17-21	Benzacridines
-25	17-21	19-22	17-21	Azabenzo[ghi]fluoranthenes
-27	19-23	20-23	19-22	Azabenzopyrenes; Dibenzocarbazoles
-29	21-23	21-23	21	Dibenzacridines
-31	21-23	21,22	21,22	Azabenzoperylenes
-33	23,24			Azadibenzopyrenes

Formulas derived by HRMS represent isomers and fragment ions as well as molecular ions.

Table 6. Identification and quantitation of selected peaks from nitrogen bases in light oils.

Peak #	Compound	Wt. % of Base Fraction
1	2,6-Dimethylpyridine	0.5
2	2,4-Dimethylpyridine	2.2
3	2,3,6-Trimethylpyridine	3.5
4	3,5-Dimethylpyridine	1.5
5	Aniline	6.4
6	2-Methylaniline	12.8
7	4-Methylaniline	8.1
8	3-Methylaniline	15.1
9	Quinoline	7.6

Table 7. Hydroxyl distribution in solvent separated fractions determined by TMS derivatization.

Fraction	% H as OH ±5%	% O as OH ±10%
Oils	1.2	67
Asphaltenes	2.0	43
Asphaltenes Acid/Neutral	2.0	44
Asphaltenes Base	1.5	49
Preasphaltenes	3.0	35

Table 8. TMS derivatized hydroxyl species in acid components from SARA separation.

Phenol Series Molecular Weights	TMS Ether	Indanol Series Molecular Weights	TMS Ether
94	166	134	206
108	180	148	220
122	194	162	234
136	208	176	248
150	222	190	262
164	236		276

Acenaphthenol Series Molecular Weights	TMS Ether	Fluorenol Series Molecular Weights	TMS Ether
170	242	196	268
184	256	210	282
198	270	224	296
212	284	238	310
226	298	252	324
240	312	266	338
254	326	280	352

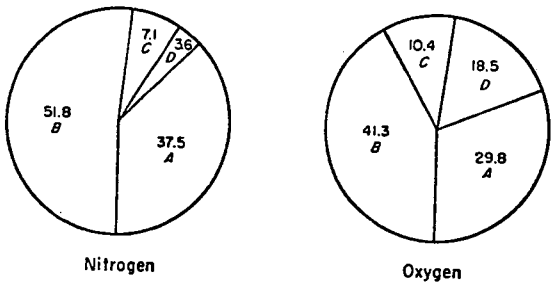

Figure 1. Atom weight percent distribution of heteroatoms. A) Oils, B) Asphaltenes, C) Preasphaltenes, and D) Ash.

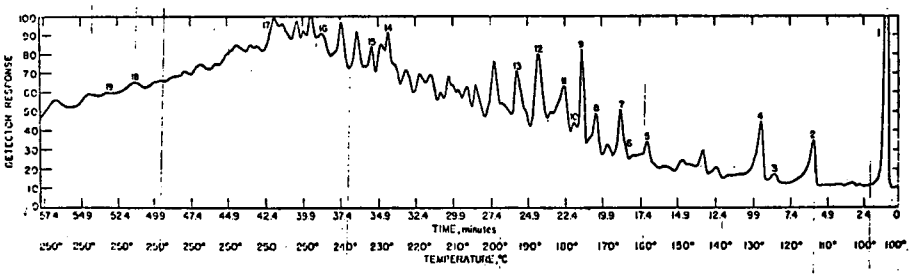

Figure 2. Gas chromatogram of base fraction from a coal liquefaction product. Table 4 identifies major components.

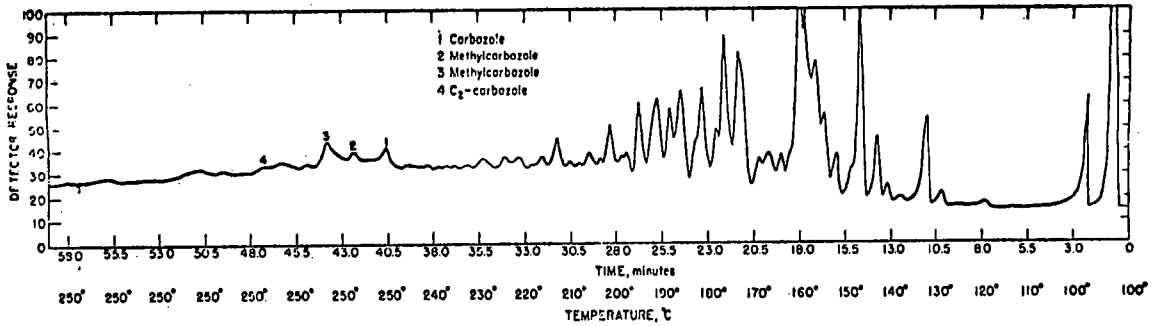

Figure 3. Gas chromatogram of acid fraction from a coal liquefaction product.

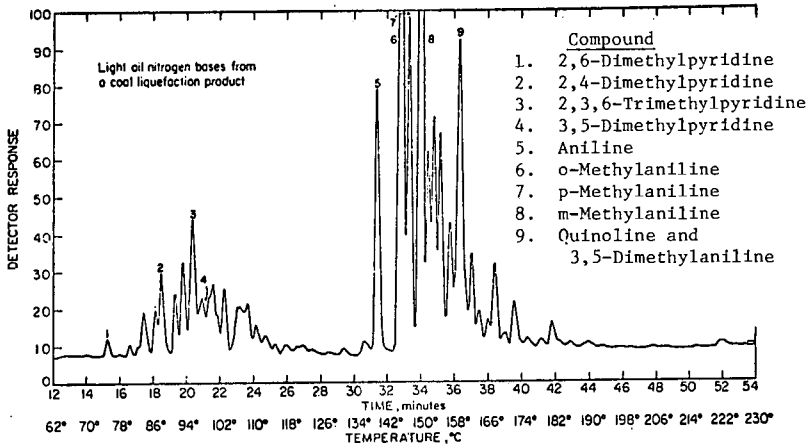

Figure 4. Gas chromatogram of nitrogen bases from a light oil.

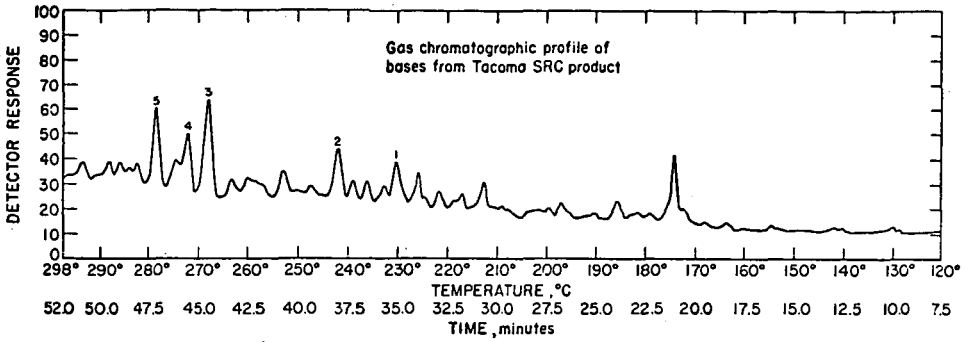

Figure 5. Gas chromatogram of nitrogen bases from an SRC recycle solvent. 1) N-3 ring, e.g. acridine, 2) methyl-N-3-ring, 3) azapyrene, 4)and 5) methylazapyrene.

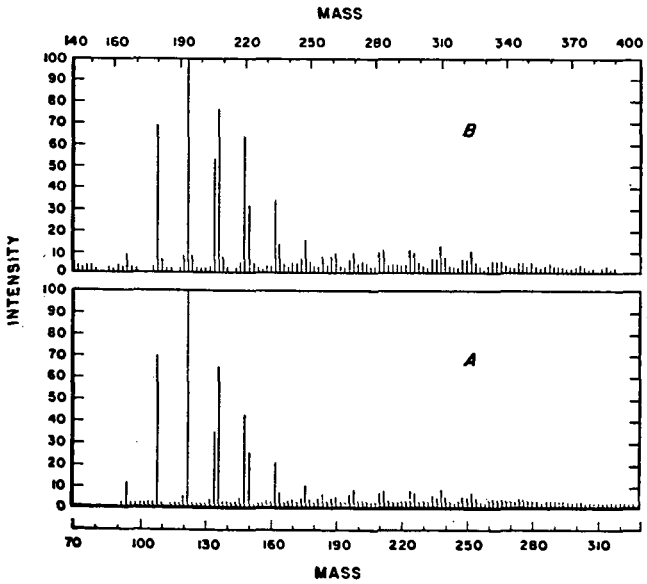

Figure 6. Mass spectrum of acids before (A) and after (B) TMS derivatization. Note change in mass scale.

Characterization of Coal Products by Mass Spectrometry

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I. Introduction and Background

In studies on the organic chemistry of coal, the researcher, unfortunately, is unable to examine a complete coal molecule. He must instead be content to analyze bits and pieces of coal molecules produced by solvent refining, liquefaction, pyrolysis, or extraction. Knowledge of the composition of these pieces helps in understanding the organic chemistry of coal and is vital for the development of coal liquefaction processes and the further upgrading of the liquefaction products.

Mass spectrometry is the prime technique used in our laboratories (1,2) and in other laboratories (3) to determine the composition of the very complex mixtures derived from coal. Petroleum fractions have been analyzed by mass spectrometry (MS) for over 30 years. As heated inlet systems evolved (4,5) and instrumental resolving power increased, MS was applied to higher boiling ranges and more complex mixtures. When research in coal liquefaction began in our laboratories about 10 years ago, we had well-developed instrumentation, data handling procedures, and quantitative analyses for petroleum (6,7). Extension of these techniques to coal products required only minor changes and extensions (8,9). In this paper we describe some of the MS procedures we use and give some typical examples of analyses.

II. Equipment and Data Handling Procedures

A very repeatable low resolution instrument is used for streams in which the major components have been previously identified. The unseparated naphtha boiling range, separated saturate fractions, and mid-boiling range samples (when detailed knowledge of the hetero-atom components is not required) fall in this category. For mid-boiling and high-boiling fractions requiring more complete breakdown of aromatic, hydroaromatic, and aromatic hetero-compounds, spectra are obtained on a high-resolution double focusing instrument.

Both of the instruments are automated. A digital readout system senses peaks and converts analog signals to digital signals, records digital data on printed paper tape and on magnetic tape, and a larger computer reads the data from the magnetic tape and further processes it employing proprietary computer programs. A list of the equipment is shown below:

Item	Manufacturer	Model
Low Resolution MS	Consolidated Electrodynamics Corp.	21-103C
High Resolution MS	Associated Electrical Industries, Ltd.	MS50
MS Readout System	Columbia Scientific Industries	CSI-260
Printer	Mohawk Data Systems	2016
Computer	International Business Machines	370

III. Methods and Results

A. Naphtha Boiling Range

High ionizing voltage, low resolution spectra are adequate to determine paraffins, naphthenes, 2-ring naphthenes, C_6-C_{11} benzenes, C_9-C_{10} indanes and

tetralins, C_9-C_{10} indenes, C_{10}-C_{11} naphthalenes, and C_{10}-C_{12} phenols in the C_5 to 450°F boiling range. The calibration data were derived primarily from scans of pure compounds and assembled in a 20 component matrix. A summary analysis is given in Table I.

Table I

Component	Wt.%
Total Saturates	76.6
Total Benzenes	13.9
Indanes/Tetralins	2.3
Indenes	0.1
Naphthalenes	0.0
Total Phenols	7.1
Total	100.0
Wt.Pct. Carbon	85.80
Wt.Pct. Hydrogen	13.09
Wt.Pct. Oxygen	1.11

With some assumptions regarding the molecular weight distributions of the paraffins and naphthenes, a useful elemental analysis can be readily calculated.

Occasionally more detailed data for the saturated components is desirable. A 42 component combined MS and gas chromatographic procedure determines the aromatic and phenolic components listed previously and further breaks down the paraffins into iso- and normal types by carbon number and the naphthenes into cyclohexanes and cyclopentanes by carbon number. Calibration data were obtained from pure compounds and from concentrates separated by molecular sieve and gas chromatography.

B. Higher Boiling Range Saturate Fraction

Fractions boiling above the naphtha range can be separated into saturate, aromatic, and polar fractions employing a modified version of the clay-gel adsorption chromatographic method, ASTM D-2007. The saturate fraction is analyzed by the high ionizing voltage MS method, ASTM D-2786. A typical analysis of a 430-950°F saturate fraction from a Synthoil product (10) is given in Table II.

Table II

Compound Type	Wt.%
Paraffins	34.2
1-Ring Naphthenes	18.4
2-Ring Naphthenes	16.3
3-Ring Naphthenes	14.6
4-Ring Naphthenes	10.3
5-Ring Naphthenes	3.0
6-Ring Naphthenes	1.1
Monoaromatics	2.1

Normal paraffins generally comprise the major part, 80-90%, of the total paraffins in coal liquefaction products and a lesser part in coal extracts. When a split between iso- and normal-paraffins is desired, gas chromatography rather than mass spectrometry is normally the method of preference in higher boiling

fractions. Iso-paraffins are not usually identified. However, we have recently identified the isoprenoid paraffins pristane, 2, 6, 10, 14-tetramethyl pentadecane, and phytane, 2, 6, 10, 14-tetramethyl hexadecane in coal extracts and liquefaction products. These components were separated and identified by gas chromatography, corroborated by MS (10).

Isoprenoid paraffins are used in organic geochemistry to group oils into "families" (11). It is possible that coals from different seams or deposits might be differentiated by the relative ratios of these isoprenoids or by the isoprenoid to n-paraffin ratio. Pristane is thought to be derived from the diterpenic alcohol phytol (12), that comprises about 30% of the chlorophyll molecule, and its presence and concentration might be related to the environment of the marsh in which a particular coal bed or seam was formed.

C. Higher Boiling Range Aromatic and Polar Fractions

If data on the saturate portion are not required, the aromatic and polar aromatic components are determined on the unseparated sample. This is done with a high resolution instrument operated in the low ionizing voltage mode (13). The same procedure can be applied to separated aromatic and polar fractions, and this is preferred if there is a significant concentration of polar components.

With low ionizing voltage electrons only those components containing double bonds, such as aromatics and olefins, are ionized and only the molecular ion is produced. Thus, the spectra, the spectral interpretation, and the calibration data are simplified, as there is no interference between components.

A full discussion of high resolution mass spectrometry is beyond the scope of this paper, so the technique will be described here only briefly. Different combinations to form molecules of the atomic species found in coal products will have different molecular weights. For example, from the atomic weights of the most abundant species given below one calculates the molecular weight of methyl

Atomic Species	Atomic Weight
Carbon	12.000
Hydrogen	1.0078
Oxygen	15.9949
Nitrogen	14.0031
Sulfur	31.9721

acenaphthene, $C_{13}H_{12}$, to be 168.0939, and the molecular weight of dibenzofuran, $C_{12}H_8O$, to be 168.0575. The high resolution MS resolves these two peaks having the same nominal molecular weight and the resolving power required is 4615 ($Mass/\Delta Mass = 168/0.0346 = 4615$). Other molecules require even greater resolving power to separate, particularly those containing nitrogen or sulfur (14). The MS and its auxiliary apparatus must also provide data from which precise mass measurements can be calculated. By measuring the time at which each peak occurs in a repeatable logarithmic scan of the spectra and by introducing compounds having peaks at known masses, the masses of the sample peaks can be determined very precisely, and the mass determines the molecular formula.

The scheme we use from mass spectrometer to final quantitative analysis is given in the data flow scheme shown below. The MS, MS readout system, printer, computer, computer programs, and people are required.

Sample and reference compounds charged to high resolution MS

Peak heights and times printed on paper tape → Reference peak times recognized and cards punched by hand

Peak height and times written on mag tape → Mag tape read and cards punched by computer

Cards read, masses calculated, molecular formulas assigned, output printed, cards punched by computer

Formulas checked and correction cards punched by hand

Cards read, quantitative analysis, average molecular weight, carbon number, and ring distributions, elemental analyses, distillation characteristics, predicted composition of narrow cuts calculated and printed by computer.

The most detailed information calculated from the high resolution spectra is the quantitative amount of each compound type at each carbon number. This tabulation is printed on 6 pages, 50 rows and 12 columns per page. This is more data than most engineers care to examine; therefore, summary tables, distributions, and other items are calculated from these detailed data. Excerpts from the compound type summary of a Synthoil product (10) are given in Table III. This is the initial summary made from the detailed data.

Table III

Compound Type	Wt.%	Average Mol.Wt.	Average Carbon No.	C Atoms in Sidechains
Alkyl Benzenes	1.74	160.8	11.9	5.9
Naphthalenes	11.02	176.4	13.5	3.5
Dibenzothiophenes	0.33	210.9	13.9	1.9
Fluorenothiophenes	0.16	241.2	16.4	2.4
Benzofurans	0.56	210.9	14.6	6.6
Dibenzofurans	2.55	255.0	16.1	4.1

The distribution of aromatic rings is a further summary which may be of value in refining of coal products. The ring distribution for the same product of Table III is shown in Table IV normalized to 100%, but the program also calculates and prints the same distribution normalized to the percent aromatics in the sample.

Table IV

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Nonaromatics	0.0	0.144	0.0	0.144
1 Ring Aroms	20.960	0.517	2.235	23.712
2 Ring Aroms	36.919	0.611	3.465	40.996
3 Ring Aroms	15.644	0.153	2.202	17.999
4 Ring Aroms	12.388	0.067	1.470	13.925
5 Ring Aroms	1.997	0.020	0.208	2.225
6 Ring Aroms	0.856		0.084	0.940
7+ Ring Aroms	0.068			0.068
Totals	88.832	1.512	9.664	100.008

Additional calculated items, such as distillation characteristics (15), can be of great value to a researcher. If there is insufficient sample available for actual distillation, say from a bench-scale experiment, a few milligrams will suffice for a high resolution MS run. The calculated MS values, GC distillation, and 15/5 distillation are in good agreement.

The same high resolution scheme can also be applied to the polar fractions from the clay-gel separation. But the analysis of polars can become very tedious - the composition is much more complex as the polars contain many of the same hydrocarbon species as the aromatic fractions in addition to the polar hetero-aromatic oxygen, nitrogen, and sulfur compounds. In addition, our computer programs for some of these classes of components are not yet fully integrated into the final quantitative analysis program, and separate programs must be run and the results meshed. An indication of the complexity of the polar components in coal products is provided by a very small portion of spectra of the polar faction of a Synthoil product given in Table V, in which some typical multiplets resolved by the high resolution MS are shown. The data were obtained at a resolving power of about 40,000.

Table V

Mass	Formula	Intensity	General Formula	Possible Structure
254.0764	$C_{16}H_{14}SO$	230	$C_nH_{2n-18}SO$	C_2-Hydroxythiophenoacenaphthene
254.1306	$C_{17}H_{18}O_2$	822	$C_nH_{2n-16}O_2$	C_4-Dihydroxyfluorene
254.1671	$C_{18}H_{22}O$	511	$C_nH_{2n-14}O$	C_6-Hydroxyacenaphthene
381.1517	$C_{29}H_{19}N$	337	$C_nH_{2n-39}N$	C_2-Dibenzoperylenide
381.1729	$C_{26}H_{23}NO_2$	219	$C_nH_{2n-29}NO_2$	C_5-Dihydroxybenzochrysenide
381.2092	$C_{27}H_{27}NO$	363	$C_nH_{2n-27}NO$	C_7-Hydroxydibenzcarbazole
381.2456	$C_{28}H_{31}N$	267	$C_nH_{2n-25}N$	C_9-Chloranthridine
394.1357	$C_{30}H_{18}O$	110	$C_nH_{2n-42}O$	C_2-Hydroxybenzocoronene
394.1569	$C_{27}H_{22}O_3$	225	$C_nH_{2n-32}O_3$	C_5-Trihydroxybenzoperylene
394.1933	$C_{28}H_{26}O_2$	275	$C_nH_{2n-30}O_2$	C_6-Dihydroxybenzochrysene
394.2295	$C_{29}H_{30}O$	507	$C_nH_{2n-28}O$	C_9-Hydroxybenzopyrene

III. Conclusions

The national need to develop liquid fuels from coal to augment diminishing petroleum fuels is a challenge to the coal chemist. Analytical characterization of these coal liquids is a challenge to the analytical chemist. We believe that mass spectrometry, both low resolution and high resolution, plays an important role in responding to this challenge, and have given examples of the application of the technique to various coal product samples.

More detailed information on the use of high resolution mass spectrometry to analyze hetero-compounds in coal extracts and liquefaction products is given in our paper in the "Symposium on Refining of Coal and Shale Liquids," Division of Petroleum Chemistry, National ACS meeting, Chicago, 1977.

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FIELD IONIZATION AND FIELD DESORPTION MASS SPECTROMETRY APPLIED TO COAL RESEARCH

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Mass spectrometry offers a unique way to characterize coal liquefaction products. Molecular weight profiles of such complex mixtures of organic materials may be considered as the first step in the understanding of their nature in molecular terms. Molecular weight profiles may be produced by nonfragmenting mass spectrometry, which almost exclusively yields molecular ions. Field ionization produces molecular ions from most organic compounds (1). When a complex mixture is analyzed by this mass spectrometric technique, we obtain a single peak for each constituent or for a group of constituents that shares the same nominal molecular weight. By repeated multi-scanning, we can obtain a quantitative molecular weight profile of complex mixtures (2).

The detailed molecular weight profiles attainable by field ionization mass spectrometry are much more informative than molecular weight profiles obtained by gel permeation chromatography (GPC). Moreover, GPC is subject to artifacts caused by associations of solutes or by solute-solvent complex formations. The average molecular weight profiles obtained by vapor phase osmosis (VPO) contain minimal chemical information and are useful mainly in conjunction with prior chromatographic separation. The cost per mass spectrometric analysis is higher than by these two techniques, but the information obtained on each individual constituent or group of constituents would cost much more if obtained separately by other techniques. The advantage of the mass spectrometric technique is its universality; for the same sample, the same molecular weight profile will be obtained by different investigators using different mass spectrometers.

Low energy electron impact ionization, which induces relatively little fragmentation, has been proposed as an appropriate alternative technique for the analysis of complex organic mixtures (3,4) including fuels(5). However, an excellent systematic study by Scheppele et al (6), has shown that field ionization is by far superior for this purpose. This recent study has shown that the relative ionization efficiencies by field ionization of many different classes of organic compounds are very similar, ranging only over a factor of two. This can be compared with a range of over an order of magnitude for low energy electron impact on the same substrates. Moreover, it was shown (6) that once corrected for the small differences in ionization efficiencies, which can be programmed and calculated for known homologous series, the analysis of complex mixtures, like fuels, can produce quantitative results with a significantly lower variance than obtainable with low energy electron impact, following an identical computational correction.

Without such a correction, when dealing with unknown constituents, field ionization is by far a superior technique for obtaining semiquantitative information on the composition of highly complex mixture.

Field ionization is facilitated by the high field gradient that can be produced with very high curvatures. A cathode with a radius of curvature of about 0.1 μ requires less than 1000 V to produce field ionization. Such a configuration is readily attainable in a reproducible manner by the appropriate technology. At SRI, we have developed a novel field ionization source, the preactivated foil slit type source (7). This source is superior to the now classical SRI multipoint source (2,8) because of its lower sensitivity to deactivation in the presence of oxygen-, sulfur-, or halogen-containing compounds. The new source comprises an activated tantalum foil on which carbonaceous dendrites are deposited from pyridine vapor at high temperature under a high electrostatic field (7).

The mass analyzer used by us for multicomponent analysis is a 60° sector, 25 cm instrument and has been described before (9). The temperature of the sample can be controlled independently of the temperature of the source. The temperature of the source is maintained constant and higher than the maximum temperature the sample is subjected to; this prevents memory effects and results in more controlled ionization conditions. This ionization source, which may be operated up to $400^{\circ}C$, may thus handle thermally stable compounds of very low volatility (9).

The ionization efficiency of our sources is 5×10^{-4} or higher, (10) which is comparable to that of advanced electron impact sources. However, owing to the relatively large area of our ionization source, the high energy of the ions produced, and their divergence, less than 10^{-4} of the ions produced are detected after mass separation. The overall efficiency of the present generation of field ionization mass spectrometers is about 2×10^{-8} ions/molecule for instruments with a magnetic sector analyzer and a resolution of 700.

Since most organic compounds have similar field ionization efficiencies (6), the molecular weight profile obtained by integrating all the spectra while evaporating the sample to completion truly represents the composition of the mixture. A number of examples of molecular weight profiles of different coal liquefaction products have been presented elsewhere (9). These spectra were obtained on our mass spectrometric system before it was interfaced with a PDP-11 computer. In this mode of operation, the mass range of interest was scanned repeatedly and synchronized with a 4096-multichannel analyzer operating in the multiscaler mode (8). The instrument integrates the spectra produced in each scan into a composite mass spectrum. The integration over time is necessary because the sample is evaporated slowly and the composition of the vapor phase changes because of the wide range of volatility of the different components. This field ionization mass spectrometric system thus facilitates the quantitative analysis of molecular weight profiles of mixtures that may contain constituents varying in their vapor pressure by many orders of magnitude (estimated range, 10^{10}) over a mass range up to 2000 amu with a resolution of $M/\Delta M = 800$.

Computer Controlled FI Multicomponent Analysis

The published field ionization spectra of coal liquefaction products (9) are just the first step in the full utilization of field ionization mass spectrometric multicomponent analysis. These are chart recordings from a 4096-channel analyzer and, although the information in each channel is digitized, these spectra give us only a means of visual inspection of the gross feature of the spectra. Accurate mass assignment and the integrated ion counts under each peak are lacking, and these are necessary for any detailed quantitative interpretation of these complex spectra.

We would also like to know the "history" of each peak--the actual rate of accumulation of the ions of a given nominal molecular weight as a function of time and temperature of the analyzed sample. This information is necessary for estimating the number of materials of the same nominal molecular weight that contributed to a given peak. Moreover, from the temperature profile of a given peak, it may be possible to deduce whether some of the contributing ions originate from a chemical process (e.g., pyrolysis, dehydrogenation) that took place in the sample while the sample probe was being heated. Obtaining, for instance, a material with a molecular weight of only 150 when the probe temperature reaches 300°C suggests that it may be a secondary pyrolytic decomposition product. The temperature profile analysis may help us to distinguish between these two possibilities and even determine the activation energy for the appearance of the given species.

To achieve these goals, we have interfaced our mass spectrometric system with a PDP 11/10 dedicated computer (Fig. 1). The computer controls the magnet scan of the mass spectrometer by means of the 12-bit digital-to-analog converter (DAC). The data acquisition program increments the input to the DAC at precisely controlled time intervals so that each channel is receiving ions counted for exactly the same amount of time. At the end of each time interval, the computer causes the ion counts accumulated by the 10-MHz counter to be transferred to the 12-bit buffer register. The counter is cleared and restarted in less than one microsecond, so the interface has a negligible dead-time and no ion counts are missed. The DAC input is incremented by one unit, and the ion count in the buffer is transferred to the computer and added to the previous ion counts for that channel. The time spent at each channel, or in other words, the scan rate of the mass spectrometer, is variable and is controlled by the operator through the data acquisition software. Actual time intervals are measured within the computer by a programmable clock based on a very stable quartz crystal oscillator.

The output from the DAC is a linear voltage ramp, since each of the 4096 possible channels is active for an equal amount of time. Since the mass of the ions focused on the mass spectrometer's detector varies as the square root of the magnet current, the magnet scan control unit is used to convert the linear voltage ramp into a signal that drives the magnet power supply to produce a linear mass scan.

The 12-bit analog-to-digital converter (ADC) is connected to a temperature programmer for the solids probe. At the end of each mass spectrometer scan, the temperature of the probe is recorded for later use in the printed reports or data analysis. Since the temperature programmer is digitally driven, a given temperature program can be very precisely reproduced to allow meaningful comparisons between samples. Our experience indicates that most pure compounds are volatilized over a narrow temperature range of 10-30°C. Thus, separate peaks will be observed in

the temperature profile of a single mass if there is more than one component of the sample with that particular molecular weight. It is possible to distinguish between genuine low molecular weight components of a sample and those resulting from the thermal decomposition of much larger molecules because these two different types of species appear at very different temperatures. Our experiments show no indication of significant pyrolysis of coal liquefaction products or of crude oils.

The report program produces reports listing the masses and total ion counts for each peak in the spectrum. Two different formats are available: one is a simple table of the peak mass and intensity, and the other is the same information arranged in a fixed format with 14 masses in each row. The advantage of this second format is that homologs are all listed in the same column, making it easy to pick out groups of peaks that may have similar chemical structures.

The plotting program produces simple bar graphs of the mass spectra on the X-Y recorder. Full-scale intensity is arbitrarily chosen as 50 and the entire spectrum is automatically scaled, if necessary, by dividing all peak intensities by an integer. Figure 2 is an example of a spectrum plot obtained in this manner. These spectra are evidently superior in quality to those obtained with the multichannel analyzers (9).

Additional programs are available for performing simple but useful data handling tasks. These include programs for listing on the terminal the ion counts in each channel of a raw data file and a program for summing the data in several files into a composite spectrum. The latter program is useful for obtaining the molecular weight profile of a complex multicomponent mixture by adding together all the spectra obtained from a sample.

Additional examples of the types of information currently available from the combination of FIMS and the PDP 11/10 computer are shown in Figs. 3a and 3b. The sample was fractions 1 and 2 of basic compounds from an H-coal product and was provided to us by the Atlantic Richfield Company. The evolution of this spectrum as a function of temperature is presented in Figs. 3a and 3b. This figure presents the plotted spectra integrated within the different temperature ranges during the evaporation of a single sample.

The first three spectra in Figure 3a show volatile components of the sample that came off as soon as the sample was introduced into the mass spectrometer. When the signal produced by these volatile materials began to decrease, the operator started the temperature program, heating the sample at about 2°C per minute. The heating rate was increased twice during the run to maintain a reasonably high signal as the less volatile components were being analyzed. Finally, three spectra were recorded at 325°C, (Figure 3b) which was the final probe temperature for this sample. Weighing the sample before and after analysis showed that 94% of this material was volatilized.

These results illustrate the vast amount of information to be obtained by combining chemical separations with nonfragmenting FIMS in the analysis of coal liquefaction products.

Figure 4 is an example of a spectrum of a crude oil analyzed by the computer in the same manner as the samples presented in Figures 2 and 3. The only difference was that the crude oil sample was "weathered" in the probe at room temperature to remove the most volatile constituents. The same sample was analyzed 5 times to assess the variance of the analytical procedure. Figure 5 presents the standard deviation of each of the mass peaks as a function of molecular weight. One can see here that the constituents below 250 amu have a high variance due to irreproducible preevaporation ("weathering") but in the mass range 250 to 550, the standard deviation is in the range of 3 to 6%, which is very satisfactory for such a complex analysis. It should be noted that even the most abundant constituents in our complex mixture amount to just about 0.6% of the total. At higher molecular weights, there is an increase in the variance predominantly because of the lower abundance of these constituents and possibly also because of some irreproducible pyrolysis or polymerization of such minor components. The effect of abundance on the variability of the individual constituents can be seen in Figure 6 which also presents the theoretical lower limit of variance due to statistical fluctuations of the ions counted. The two lines "200" and "800" designate the theoretical limit for these two extreme cases of molecular weights. The limits are different because of the difference in the monitoring time per amu during the magnetic scanning. The actual variance is about 2 to 3 times higher than the theoretical lower limit. This is fairly satisfactory in view of the complexity of the sample and the analytical procedure.

Field Desorption Experiments

Two years ago, we developed at SRI a novel type of field desorbing source that used a broken metal tip (11). We have also shown that ionic and other polar substances field desorb more readily when dissolved in an appropriate nonvolatile matrix. Our preliminary tests on low molecular weight hydrocarbon polymers were highly encouraging (9). Recently, we have extended our experiments, using broken graphite rods and bundles of graphite rods and bundles of graphite fibers as field desorbing sources, with evan greater success. We applied these sources to the analysis of asphaltenes. Figure 7 shows a field desorption spectrum (obtained on a multichannel analyzer) of the asphaltenes of SRC produced from Illinois No. 6 coal. The spectrum was obtained from a graphite fiber field desorbing bundle at 205°C.

An example of a computer handled FD spectrum of asphaltenes (produced from Kentucky coal) is presented in Fig. 8. In order to provide a direct comparison of the characteristics of FD and FI spectra currently available, Figures 8-12 show the raw data as it was acquired by the computer, rather than the normal bar-graphs. The resolution of the FD spectrum is inferior to that obtained by FI of the same sample (Fig. 9), probably due to the wider energy spread of the field desorbed ions, as well as to the fluctuating nature of the FD ion beam. Note, however, the significant mass peaks at about 395 amu in the FD spectrum which are absent in the FI spectrum. This feature appears again at somewhat higher temperatures (157-158°C) as shown in Figure 10. Figure 11 a-d present FD spectra in the temperature range 160 to 187°C. Comparison of these spectra with the FI spectrum over the same temperature range (Fig. 9) and over a higher temperature range (Fig. 12) shows that under FD, one ionizes the same constituents, or other compounds of comparable molecular weight, at significantly lower temperatures. The reproducibility and resolution obtained by FD are, however, major limiting factors in the application of

this technique as a quantitative way to characterize coal products. Some of these limitations could be overcome by focal plane simultaneous ion collection techniques (e.g., photoplate mass spectrography).

Summary

We have shown that mass spectrometric multicomponent analysis techniques are ideal for the characterization of coal liquefaction and fuel products. These include the capability of determining molecular weight profiles up to 1000 amu with unit amu resolution and the ability to obtain and record molecular weight profiles as a function of sample temperature during a temperature programmed evaporation of the analyzed sample.

Combined with appropriate liquid chromatographic separation techniques or certain fast and quantitative derivatization procedures to separate coal liquefaction products into families of compounds, advanced FIMS offers an unprecedented, precise and meaningful analytical methodology for the characterization of coal products.

The field ionization technique described in this paper is not yet perfect, and it requires some further development in the areas of instrumentation, sample pretreatment, and data handling. However, there is sufficient evidence that this technique can provide the basis for one of the most comprehensive analytical methodologies ever available to coal research.

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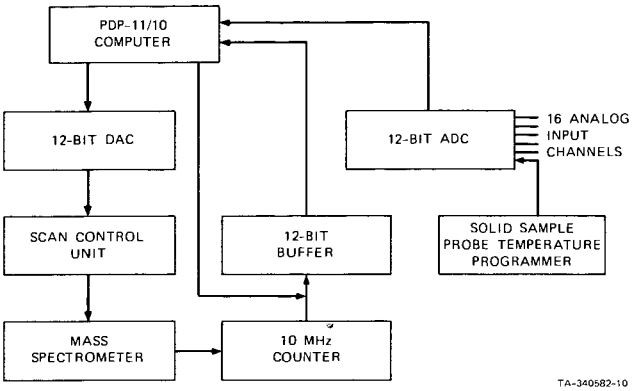

FIGURE 1 MASS SPECTROMETER-COMPUTER INTERFACE

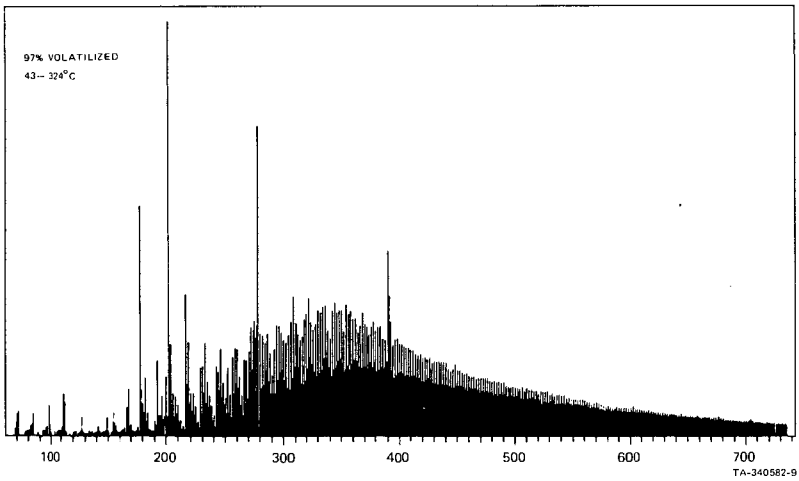

FIGURE 2 KENTUCKY 9/14 SRC, OILS FRACTION (SOURCE: ARCO)

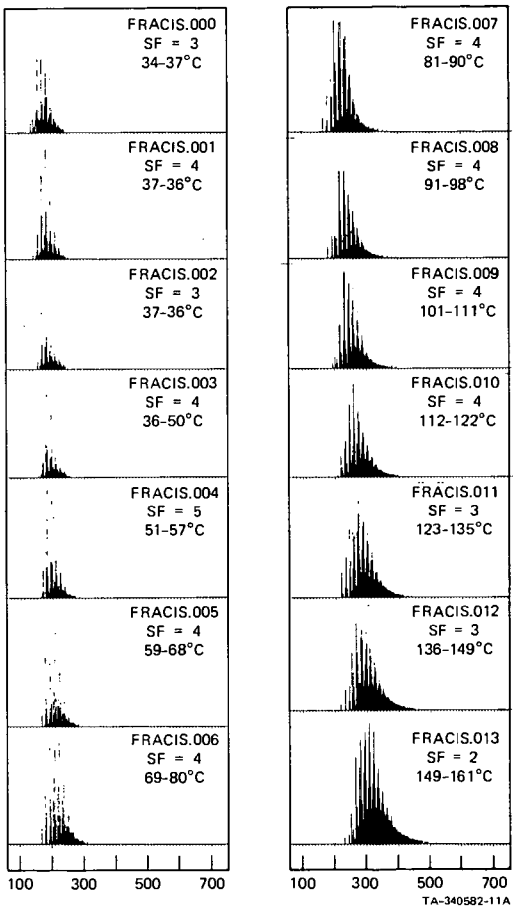

FIGURE 3A FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)

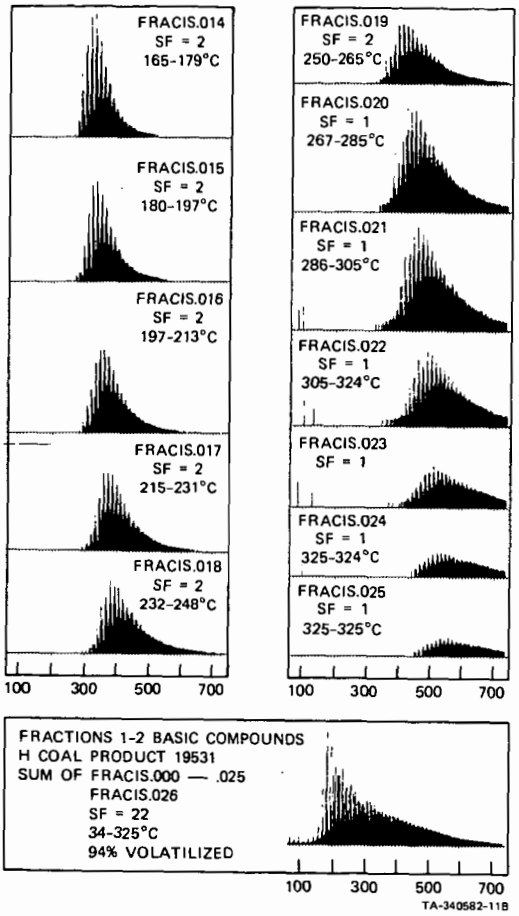

FIGURE 3B FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)

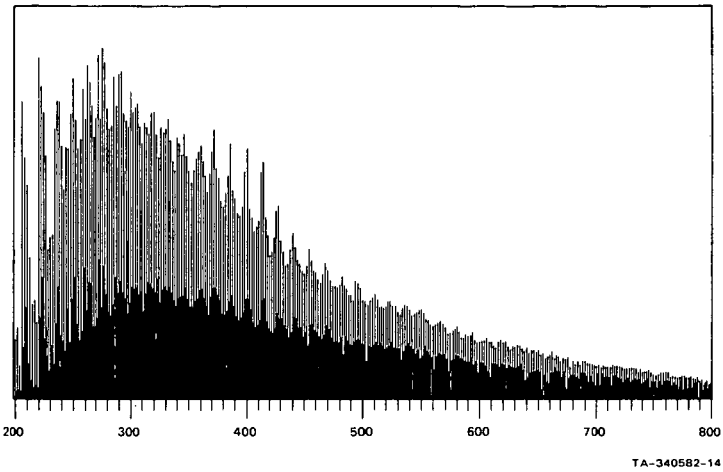

FIGURE 4 VENEZUELAN OIL WEATHERED IN MASS SPECTROMETER

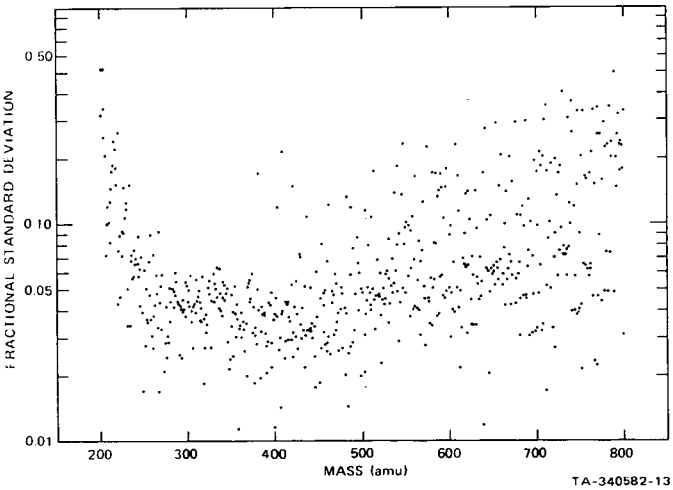

FIGURE 5 STANDARD DEVIATION OF EACH OF THE MASS PEAKS AS FUNCTION OF MOLECULAR WEIGHT

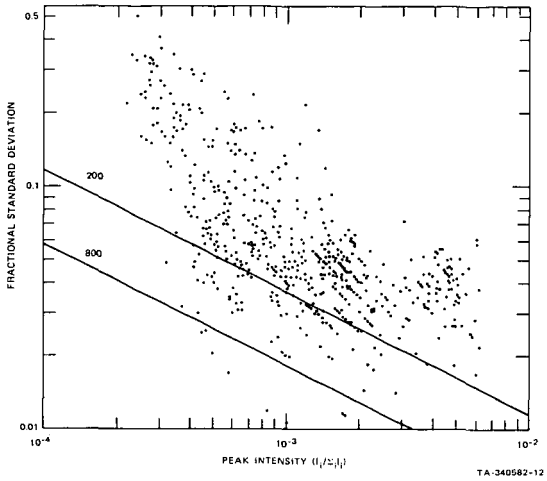

FIGURE 6 EFFECT OF ABUNDANCE ON VARIABILITY OF INDIVIDUAL CONSTITUENTS

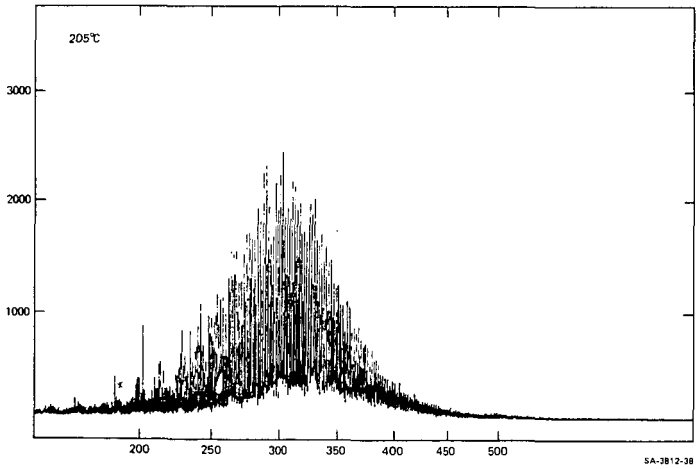

FIGURE 7 ASPHALTENES FROM ILLINOIS NO. 6 COAL, SRC PRODUCT, ARCO SAMPLE NO. 9634, GRAPHITE FIBERS SOURCE - FDMS

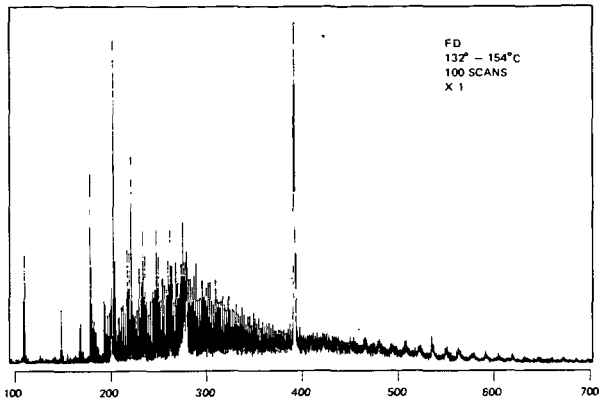

FIGURE 8 FIELD DESORPTION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 132°-154°C

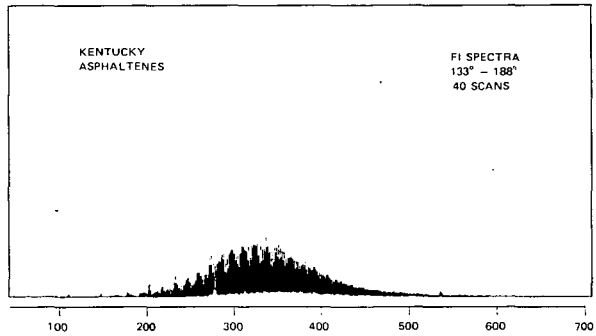

FIGURE 9 FIELD IONIZATION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 133°-188°C

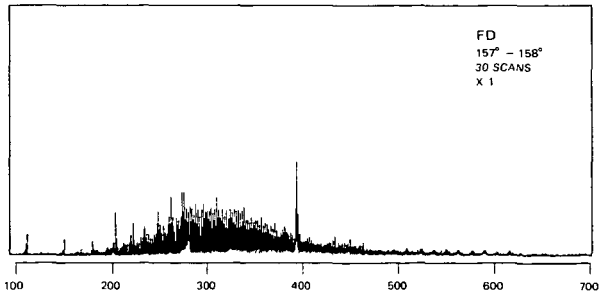

FIGURE 10 FIELD DESORPTION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 157°-158°C

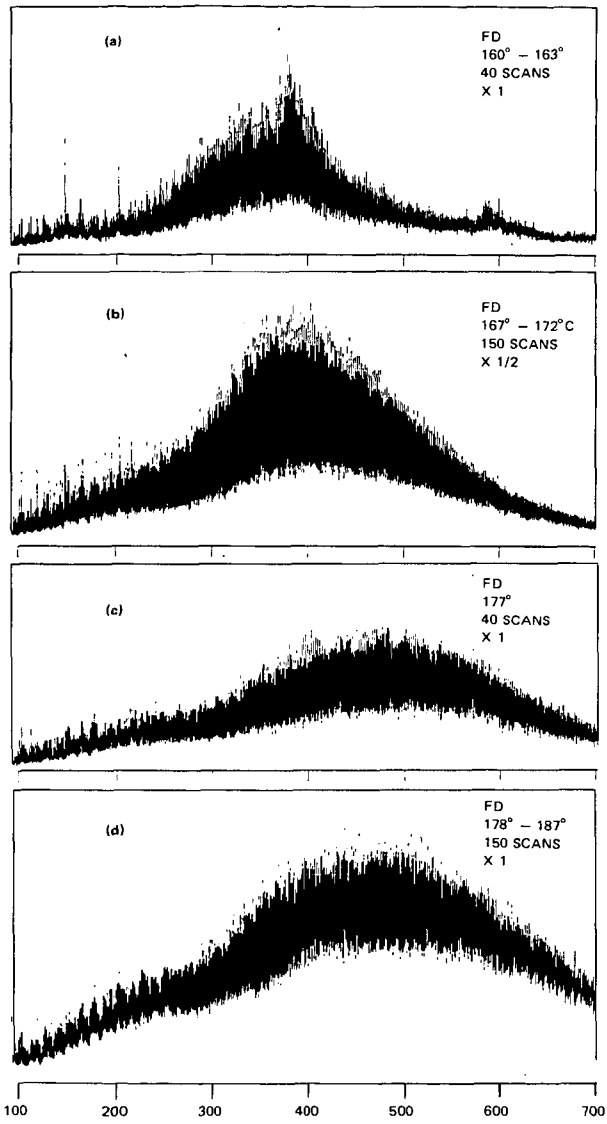

FIGURE 11 FIELD DESORPTION MASS SPECTRA OF KENTUCKY SRC ASPHALTENES, 160°-187°C

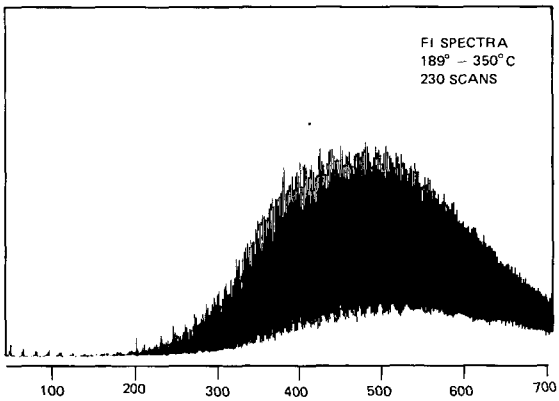

FIGURE 12 FIELD IONIZATION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 189°-350°C

OXIDATIVE DEGRADATION STUDIES OF COAL AND SOLVENT REFINED COAL

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INTRODUCTION

The bulk of the organic matter in coals consists of a macromolecular material of complex and variable composition. Many workers have attempted to degrade coals to smaller molecules which could be identified and interpreted in terms of coal structure. Oxidation has been one of the more important degradation methods. To date a number of oxidizing agents have been used. Among these were HNO_3, HNO_3-$K_2Cr_2O_7$, $KMnO_4$, O_2, H_2O_2-O_3 and NaOCl, all drastic oxidants. Because these reagents in general result in extensive ring degradations, with benzene carboxylic acids the only aromatic compounds identified, they have been of limited usefulness. Our approach has been to compare the products from drastic oxidants with more selective ones designed to break up the macromolecules into identifiable units with a minimum of chemical change so that units indigenous to coals can be identified. We have found aqueous $Na_2Cr_2O_7$ to be selective and have reported a number of polynuclear aromatic units which resulted from the dichromate oxidation of a bituminous coal and which we believe to be indigenous to the coal (1). We have explored a number of oxidizing agents using the samples listed in Table 1.

Table 1

Elemental Analyses of Samples (maf %)

No.	Sample	C	H	N	S	O (by diff)
1	Lignite (Sheridan Wyoming)	64.4	5.3	1.1	1.1	28.1
2	Bituminous (Illinois Seam #2)	77.8	5.4	1.4	2.1	13.3
3	Bituminous (Pittsburgh Seam #8)	82.7	5.5	1.3	2.8	7.7
4	Anthracite (Pennsylvania PSOC #85)	91.3	3.9	0.6	1.1	3.1
5	SRC (from Pittsburgh Seam #8)	87.2	5.5	1.8	1.2	4.3
6	SRC benzene-methanol ext.*	86.2	5.6	1.8	0.7	5.7
7	Char	84.9	1.7	---	---	---
8	Synthetic Polymer (from Fischer-Tropsch) (2)	80.0	5.1	1.3	0.0	13.6
9	Polymeric Material (from Murchison Meteorite (2))	76.1	4.6	2.8	1.3	15.2

*The SRC was fractionated into 3 fractions on the basis of solubility: hexane (4.5%), benzene-methanol mixture (82.3%), pyridine (11.8%) and a small residue (1.4%).

In addition to four coals, a solvent refined coal (SRC) and two completely abiotic samples, the synthetic Fischer-Tropsch polymer, and the polymer from the Murchison meteorite, were used for comparison and to test the oxidation methods.

RESULTS AND DISCUSSION

Identification of products: In general the products of oxidation were chiefly carboxylic acids which were esterified with diazomethane to increase their volatility for easier analysis by time-of-flight mass spectrometry (TOFMS), a variable temperature solid inlet, GC-TOFMS and high resolution mass spectrometer (HRMS).

Nitric Acid Oxidation: All samples of Table 1 except #6 were refluxed with 70% HNO_3 for 16-24 hours yielding a clear orange colored solution. The acid solutions were evaporated to dryness under reduced pressure and the residue weighed. The methylated acids were analyzed by GC-MS, HRMS and the solid probe. Fragmentation patterns and precise mass determination of both molecular ions and fragments, in particular $(M-OCH_3)^+$, were used for identification. In Figure 1 are summarized the data for benzene carboxylic acids (as their methyl ester). The synthetic sample had been prepared by heating CO, H_2 and NH_3 with an Fe-Ni catalyst at 200°C for six months (2). It was a macromolecular material insoluble in organic solvents, HCl, HF and KOH. Despite the drastic nature of the nitric acid oxidation it appears that useful information can be obtained by the procedure. For example the yield of total acids and the number of carboxylic acid groups per benzene ring seem correlated with the degree of condensation of the original material. The spectra from the synthetic sample from the Fischer-Tropsch reaction, and from char are relatively simple consisting primarily of the benzene carboxylic acid esters with from two to six ester groups. The coal samples and coal derived products (except for char) are more complex and contained nitro substituted esters and pyridine derivatives. Note the similarity between the synthetic sample and the char prepared from Illinois bituminous coal by heating under vacuum to 800°C. The abundance of the benzene hexacarboxylic acids for these two suggest a high degree of condensation in the original samples. The similarity in distribution of the oxidation products from the two bituminous coals (the Illinois and Pittsburgh) is striking. The solvent refined coal derived from the Pittsburgh #8 coal is shown later (Figure 3, Table 2) to have a higher degree of aromatic ring condensation than its feed coal. Thus it is surprising to see the shift to fewer acid groups for SRC. This may mean that many aliphatic crosslinks were destroyed in the SRC process and evolved as light hydrocarbons.

The results from the meteoritic polymer (not shown in Figure 1) were very similar to those of the synthetic polymer.

Sodium dichromate oxidation: In general 1-3 g of sample was heated at 250°C for 36-40 hours with excess $Na_2Cr_2O_7$ (60-120 ml of 0.4 M - 0.6 M) with stirring. This procedure oxidizes side chains and alicylic appendages to polynuclear aromatic systems with a minimum of degradation of aromatic rings (3). We have found that model compounds are oxidized in high yields (78-95%) to their corresponding carboxylic acids. Samples 1, 2, 3, 4, 6, and 9 were oxidized with $Na_2Cr_2O_7$ with a high degree of conversion to soluble or

volatile compounds (70-100%). The yields of soluble compounds were 50-70% of the weight of the original samples. The anthracite also yielded 17% of a humic acid type material of high molecular weight soluble in alkaline solution. In Figure 2 are shown graphically the relative abundances of aromatic and heteroaromatic units produced by the dichromate oxidation of three coals (samples 1, 2 and 4). It is obvious that the degree of aromatic condensation increases with rank of coal from lignite to bituminous to anthracite. The $Na_2Cr_2O_7$-aq oxidation procedure has been questioned because of the possibility that major structural rearrangement with pyrolytic formation of polynuclear aromatic compounds might occur during the reaction at 250°C (4). The fact that no polynuclear aromatic compounds with more than two fused rings were detected in the oxidation products of lignite (sample 1) and that the degree of condensation increases with rank of coal is internally consistent and suggests that condensation during oxidation with $Na_2Cr_2O_7$ is minimal. In a blank experiment bituminous coal (sample #2) which had been extracted with an organic solvent to remove trapped compounds was heated at 250°C for 40 hours with water. An insoluble residue 96.2% and inorganic salts 2.9% were obtained. Mass analysis of the residue was indistinguishable from that of the original coal and the H/C ratio was unchanged. Furthermore, detailed pyrolysis studies of the coal showed no evidence of significant thermal decomposition until heated above 250°C.

The gas chromatograms of the oxidation products (as methyl esters) from the Pittsburgh coal (sample 3) and its SRC (benzene methanol extract-sample 6) are shown in Figure 3. The numbered peaks are identified in Table 2. A greater degree of aromatic condensation of the SRC extract over that of its feed coal is observed. For example, naphthalene and phenanthrene rings are much more abundant in the SRC. The dibenzofuran ring is the most abundant heterocyclic to have survived the SRC process.

Fifteen aromatic ring systems were identified in the $Na_2Cr_2O_7$ oxidation product of the meteorite polymer: benzene, biphenyl, naphthalene, phenanthrene, fluoranthene (or pyrene), chrysene, fluorenone, benzophenone, anthraquinone, dibenzofuran, benzothiophene, dibenzothiophene, pyridine, quinoline or isoquinoline and carbazole (2). These data support the generally accepted idea that the polymeric material in meteorites has a highly condensed aromatic structure (2, 5, 6) and gives us confidence in the dichromate oxidation procedure.

Photochemical oxidations: Oxidation by air bubbling through an aqueous HCl solution while irradiating with ultraviolet light from a high pressure mercury lamp was investigated. In Table 3 are shown the results obtained with model compounds. From the results with the model compounds it appears that aromatic hydrocarbons are readily oxidized to benzene carboxylic acids. On the other hand N-heterocyclics resist oxidation. In Table 4 are listed the aromatic carboxylic acids isolated from a bituminous coal (sample 2) after photochemical oxidation. The products from lignite (sample #1) were primarily benzene carboxylic acids with only traces of pyridine tricarboxylic acids and xanthone di- and tricarboxylic acids. Several aliphatic carboxylic acids were identified (after methylation) in the photo-oxidation product of bituminous by TOF variable temperature solid inlet and HRMS. They are methyl esters of malonic acid, succinic acid, glutamic acid and saturated monocarboxylic acids (CH_3-$(CH_2)_n$-$COOCH_3$ n = 1-7). The fragments for 3-methyl

Table 2

Aromatic Acids Found in the Oxidation of SRC and Its Feed Coals[a] Identified as Methyl Esters

C Peak Number		Number of $-COOCH_3$	Relative Abundance (± 15%)[b]	
			SRC Extract	Coal
1	Benzene	2	100	100
5		3	58	29
10		4	9	10
4	Biphenyl	1	3	9
2	Naphthalene	1	47	30
8		2	82	29
16		3	24	8
		4	*7*	*3*
13	Phenanthrene	1	82	28
20		2	8,*15*	*8*
		3	*5*	*7*
		4	*1*(T)	---
19	Pyrene/Fluoranthene	1	7	*3*
		2	*4*	*2*
11	Fluorenone	1	4	8
		2	*3*	*2*
		3	*3*	---
14	Anthraquinone	1	26	4
		2	*3*	---
7	Dibenzofuran	1	32	21
17		2	9	4
		3	*10*	*4*
15	Xanthone	1	4	9
		2	*6*	*7*
		3	*2*(T)	*3*
3	Benzothiophene	1	---	4
12	Dibenzothiophene	1	*2*	8
		2	---	*5*
	Pyridine	3	---	*5*(T)
	Carbazole	1	*4*	*3*
		2	*3*	*4*
18	Benzoquinoline/Acridine	1	3	7
		2	*5*	*4*
		3	*2*	*2*
6[c]				11
9[d]				22

Table 2 (Footnotes)

[a]92% of the extract was oxidized and the yield of total acidic and non-acidic less volatile compounds was ≈59%. For the feed coal, 84% of the coal was oxidized; Yield of totals was ≈58%.

[b]Benzene dicarboxylic acid methyl ester is normalized to 100.

[c]Peak no. 6 is tentatively identified as trimethoxyxanthone.

[d]Peak no. 9 shows prominent mass ions at 216 and 215. HRMS shows their elemental composition corresponding to $C_{12}H_{10}O_3N$, $C_{12}H_9O_3N$ or $C_9H_{12}O_6$, $C_9H_{11}O_6$. Identification has not been made at this present time.

T = identification tentative; --- = not detected; x = peak consists of more than one component which are difficult to identify by GC-MS.

Italics indicate that identification and estimation of relative abundances were made by TOF variable temperature solid inlet and HRMS, because of difficulty of identification by GC-MS.

Table 3

Photochemical Oxidation of Model Compounds*

Compound	Unreacted† (%)	Major Oxidation Products§
p-cresol	0	unident. small species, polymer
anisole	0	unident. small species, polymer
naphthalene	8	phthalic acid
1,4-diMe-naphthalene	5	phthalic acid
2,6-diMe-naphthalene	7	benzene-1,2,4-tricarboxylic acid
indane	3	phthalic acid
fluorene	8	fluorenone
acenaphthene	10	phthalic, naphthalene-1,8-dicarboxylic acids
phenanthrene	24	phthalic acid, phenanthrene-9,10-diketone
pyrene	12	benzene tri- and tetracarboxylic acids
dibenzofuran	32	styrene, salicyclic acid
xanthone	78	unidentified chloro compounds
dibenzothiophene	43	styrene, thiophenol
carbazole	78	polymer
N-Et-carbazole	83	polymer
poly(2-vinylpyridine) -polystyrene polymer	8	pyridine-2-carboxylic, pyridine-2-aldehyde, benzoic, malonic, and succinic acids

*The oxidation was carried out in 10% aq. HCl solution for 6-10 days.
†Values are accurate to ±10%.
§After preliminary separation into acidic, neutral, and basic fractions, products were identified by TOFMS with variable temperature solid inlet. Except for the first two samples and the two carbazoles, all identifications were checked by high-resolution MS. For the italicized samples, GC-MS was used as well, after esterification of the product.

All major products were accompanied by lesser amounts of their monochloro derivatives.

Table 4

Aromatic Acids Found in the Photochemical Oxidation of Bituminous Coal: Identified as Methyl Esters[a,g,h]

Nucleus	Number of $-COOCH_3$	Precise mass $(M-OCH_3)^+$ elemental composition	observed	Dev. x 10^3	Relative Abundance[b] ± 15-20%
Benzene	2	$C_9H_7O_3$	163.0388	-0.7	42
	3	$C_{11}H_9O_5$	221.0457	0.8	100
	4	$C_{13}H_{11}O_7$	279.0510	0.6	97
	5	$C_{15}H_{13}O_9$	337.0555	-0.3	29
	6	$C_{17}H_{15}O_{11}$	395.0593	-2.0	4
Cl-benzene[c]	2	$C_9H_6O_3Cl$	196.9990	-1.5	24
	3	$C_{11}H_8O_5Cl$	255.0066	0.6	31
	4	$C_{13}H_{10}O_7Cl$	313.0125	1.1	26
	5	$C_{15}H_{12}O_9Cl$	371.0124	-4.4	2
Fluorenone	2	$C_{16}H_9O_4$	265.0494	-0.6	9
Anthraquinone	2	$C_{17}H_9O_5$	293.0451	0.2	3
	3	$C_{19}H_{11}O_7$	351.0520	1.6	1
Phthalan	2 (T)	$C_{11}H_9O_4$	205.0478	-2.2	2
	3 (T)	$C_{13}H_{11}O_6$	263.0572	1.8	1
Xanthone	2	$C_{16}H_9O_5$	281.0461	1.2	9
	3	$C_{18}H_{11}O_7$	339.0510	0.6	7
Dibenzofuran[d] and/or naphthofuran	2	$C_{15}H_9O_4$	253.0477	-2.3	3
	3	$C_{17}H_{11}O_6$	311.0560	0.6	2
Pyridine	2	$C_8H_5O_3NCl$[e]	197.9974	1.6	3
	3	$C_{10}H_8O_5N$	222.0408	0.5	3
	4	$C_{12}H_{10}O_7N$	280.0488	3.2	3.5
Quinoline and/or isoquinoline	1	$C_{10}H_6ON$	156.0412	-3.7	0.5
	2	$C_{12}H_8O_3N$	214.0468	-3.5	2
Carbazole[f]	1	$C_{13}H_8ON$	194.0598	-0.7	4
	2	$C_{15}H_{10}O_3N$	252.0660	-0.0	2
	3	$C_{17}H_{12}O_5N$	310.0708	-0.6	2
Acridone	1	$C_{14}H_8O_2N$	222.0525	-2.9	5
	2	$C_{16}H_{10}O_4N$	280.0592	-1.8	2
	3	$C_{18}H_{12}O_6N$	338.0635	-2.8	1

Table 4. Footnotes

[a]Some preliminary results were reported earlier (1). Identification based on TOF variable temperature solid inlet, GC (Carbowax 20 M)-TOFMS and high resolution MS.

[b]Benzene tricarboxylic acid methyl ester is normalized to 100. Relative abundances were estimated from the GC and an integration of the base peak of each compound during the time that the sample was completely volatilized in the MS.

[c]Monochlorobenzene carboxylic acids were always obtained when coal or model compounds were oxidized in 10% HCl aq. solution. Chlorocarboxylic acids of other aromatics were also observed in very low yield.

[d]Relatively large amounts of dibenzofurans were found to be produced by $Na_2Cr_2O_7$-oxidation (1), while photo-oxidation produced dibenzofuran carboxylic acids in low yield. Perhaps this shows the photochemical procedure destroyed most of the dibenzofuran ring.

[e]For pyridine dicarboxylic acid, only chloroderivatives were found.

[f]The previous estimates of relative abundances (1) were somewhat high.

[g]The products of lignite photo-oxidation in 5% KOH aq. solution were very similar to those shown in this Table. In addition some mono- and dimethylbenzene carboxylic acids were identified.

[h]Polynuclear aromatic carboxylic acids such as naphthalene and phenanthrene found in the $Na_2Cr_2O_7$ oxidation product (see Fig. 2) are not observed in this product. From our model experiments, we have found that these aromatic compounds are oxidized by the present procedure.

T = identification tentative.

and 3,3-dimethyl aliphatic carboxylic acid methyl esters were also seen in the mass spectra. A similar observation was made for the oxidation product of lignite.

Hydrogen Peroxide-Acetic Acid: It is probable that in the oxidation experiments described above aromatic units with phenolic groups would have been destroyed. Schnitzer et al. (7) have shown that an acetic acid-H_2O_2 mixture under mild conditions oxidizes humic acids while preserving phenols. Using this procedure we have oxidized lignite (sample #1) and bituminous coal (sample #2) with over 80% conversion to methanol soluble acids and have methylated the acids produced.

The gas chromatogram of the aromatic portion of the methylated product from lignite is shown in Figure 4. The identification of individual compounds was made by coincident MS and HRMS of the mixture. The methyl esters identified gave the following approximate distribution: 36.1% benzene, 7.6% methyl-benzene, 22.1% methoxy-benzene, 15.9% furan and 18.2% dibasic aliphatic. For the bituminous coal the methoxy derivatives were half as abundant. These results suggest that the lignite has twice the phenolic content of the bituminous coal. It is interesting to note that methyl furan

tetracarboxylate has been identified and other furan derivatives have been tentatively identified.

It appears that the coals are acting as catalysts for this oxidation. If 2,6-dimethylnaphthalene is reacted with H_2O_2 under the same conditions as used for the coals, only 2,6-dimethylnaphthaquinone is isolated in essentially quantitative yield. With the addition of a small amount of lignite to the reaction, 5-methyl phthalic acid is obtained as the major product. Also no hydroxylated benzene carboxylic acids were isolated which indicates that this procedure does not hydroxylate aromatic rings. Transition metals are known to catalyze reactions of hydrogen peroxide. Part of the catalytic effect may be due to the mineral matter in the coal.

No polyhydroxyl benzene carboxylic acids have been observed in the products from either coal. It is expected that these species would undergo ring oxidation and subsequent degradation. However, the concentration in coal of these species is probably small. These compounds are expected to be very reactive and probably would not survive the coalification process. We have examined aqueous NaOH extract of the Wyoming lignite. Numerous hydroxylated aromatic hydrocarbons and aromatic acids were identified, but no polyhydroxylated species were detected.

Sodium Hypochlorite Oxidation: On the basis of results of oxidation of coal with NaOCl, Chakrabartty et al. have suggested that coal has a non-aromatic "tricycloalkane or polyamantane" structure (8). They pointed out that no evidence for aromatic compounds other than benzene derivatives was found in their oxidation product. The specificity of NaOCl as an oxidant has been questioned (9) and is still in dispute (10). We are attempting to resolve the question and have oxidized samples 6, 9, and 2,6-dimethyl naphthalene under conditions described by Chakrabartty et al. (8, 10, 11). Of particular interest is the oxidation of the polymeric material from the Murchison meteorite (sample 9). Numerous studies have shown this material to be a highly condensed aromatic structure. All samples were nitrated according to the method of Chakrabartty et al. When nitration was followed by NaOCl oxidation at 60°C for 3-4 hours almost no oxidation was observed for nitrated samples 6 (SRC) or 9 (meteorite) while 26% of nitrated dimethyl naphthalene was converted to benzene carboxylic acids and their nitro and/or methyl derivatives. No naphthalene acids were detected. When the reaction was continued for 15 hours, at 65-70°C 57% of sample 9 and 42% of sample 6 were oxidized to water soluble acids. Polynuclear aromatic and heterocyclic acids were not detected in the oxidation products of either sample although both are highly aromatic. Benzene carboxylic acids were the major products (nitro and/or methyl derivatives and a methyl chloro dicarboxylic acid). Apparently polynuclear aromatic systems were destroyed and the product distribution closely resembled that from a nitric acid oxidation. Obviously more work is needed to clarify the role of NaOCl in the oxidation of coal.

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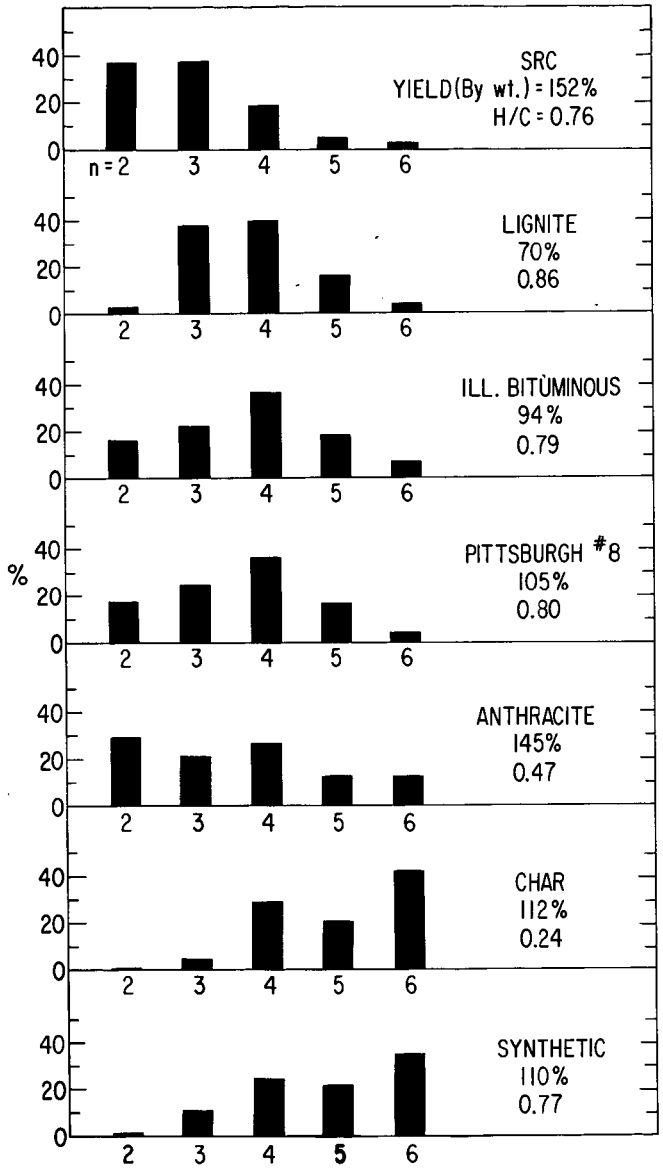

Figure 1. Abundances (%) of benzene carboxylic acids, determined as their methyl esters, produced by nitric acid oxidation. n = number of ($COOCH_3$) groups per benzene ring.

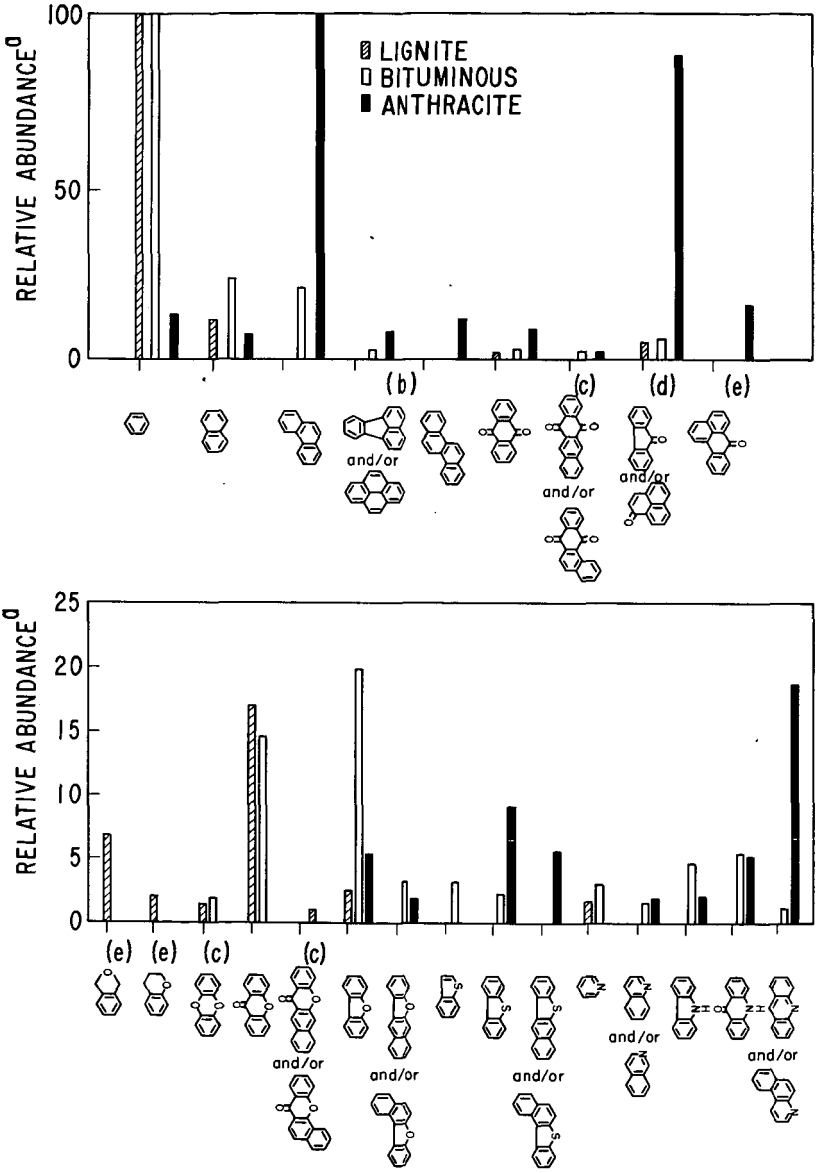

Figure 2. Relative abundances of aromatic and heteroaromatic units produced by sodium dichromate oxidation of lignite, bituminous and anthracite coals.

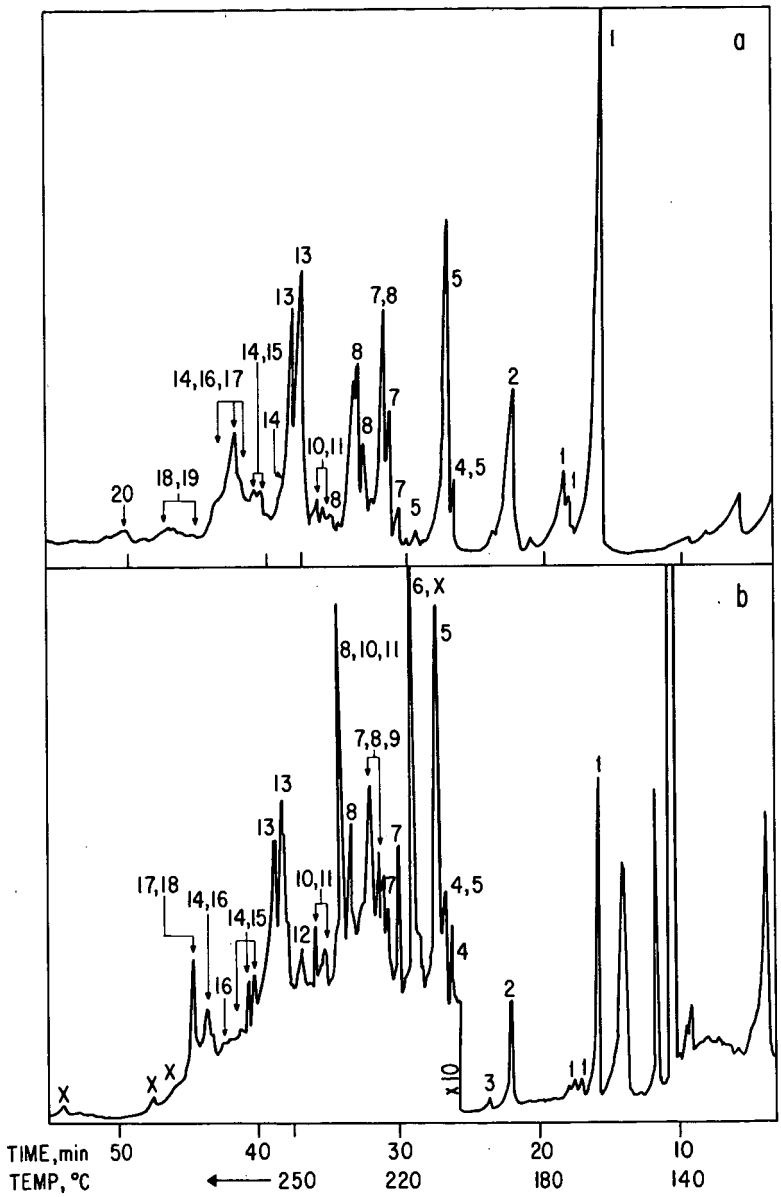

Figure 3. Gas chromatograms of methylated $Na_2Cr_2O_7$ oxidation products of SRC benzene-methanol extract (a) and its feed coal, Pittsburgh #8 (b). Separations were made on an OV-101 SCOT column.

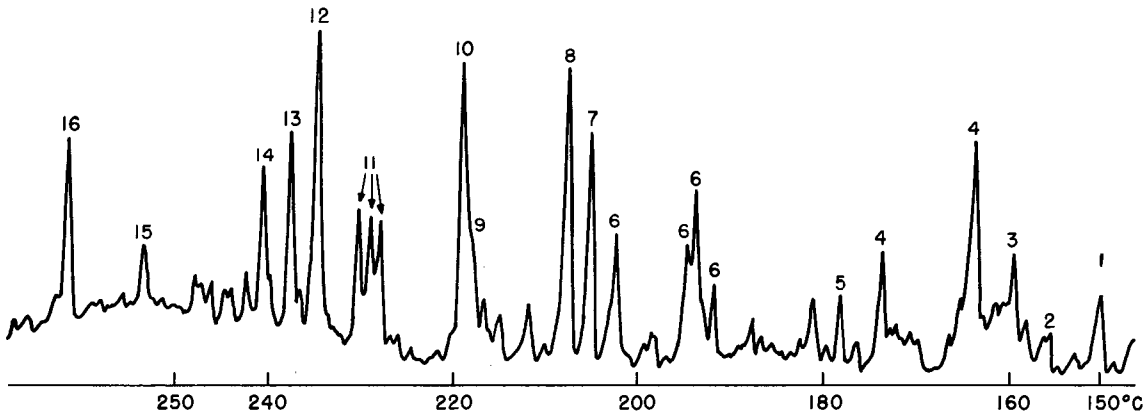

Figure 4. Methyl esters from hydrogen peroxide-acetic acid oxidation of lignite separated on an OV-101 SCOT column. Numbered compounds: 1. methyl o-methoxybenzoate; 2. methyl m- or p-methoxybenzoate; 3. methyl methylfurandicarboxylate; 4. methyl benzenedicarboxylate; 5. methyl carbomethoxyphenylacetate; 6. methyl methoxybenzenedicarboxylate; 7. methyl 1,2,3-benzenetricarboxylate; 8. methyl 1,2,4-benzenetricarboxylate; 9. methyl methoxybenzenetricarboxylate; 10. methyl furantetracarboxylate; 11. methyl methoxybenzenetricarboxylate; 12. methyl 1,2,3,4-benzenetetracarboxylate; 13. methyl 1,2,4,5-benzenetetracarboxylate; 14. methyl 1,3,4,5-benzenetetracarboxylate; 15. methyl methoxybenzenetetracarboxylate; and 16. methyl benzenepentacarboxylate.

PHENOLS AS CHEMICAL FOSSILS IN COALS

by
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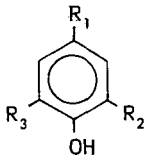
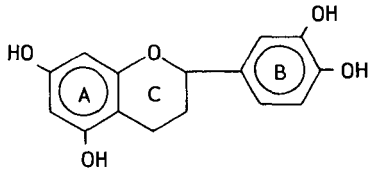
Introduction

It is generally considered that vitrinite, the principal maceral in most coals, represents coalified, partly decayed wood. Hence lignin should be one of the important precursors to the vitrinites in coals. Accordingly, it would be interesting to know whether any chemical fossils related to lignin could be found in coals. The purpose of this paper is to report what we believe to be a successful search for such fossils. The experimental approach exploited a degradation reaction developed in a study of soil humic acids by Burges et al.[1]

This reaction involves a reduction degradation with sodium amalgam and hot water. Thin layer chromatography of the ether soluble part of the product (yield, about 20%) showed the presence of a number of phenols and phenolic acids, most of whose structures bore obvious relationships to known microbial and chemical degradation products of lignin (I) but some to the A ring of flavonoids (II).

I 

II 

where R_1 = COOH, CHO, -CH=CH-COOH, -CH-CO-COOH, etc.; R_2 = H or OCH_3 or OH; R_3 = H or OCH_3 or OH. The R_1 group may represent a side chain of 1, 2 (rarely) or 3 carbon atoms, in various states of oxidation. Burges et al. therefore concluded that the humic acids they studied were condensates of phenolic compounds from the degradation of plant products with amino acids (see also Flaig[2]).

Humic acids can be extracted from peats and lignites but not from bituminous coals. However, oxidation of bituminous coals with aqueous performic acid generates in high yield (80-110% by weight) materials that closely resemble humic acids[3]. In preliminary studies performed some years ago by one of us (J.B.) while on leave of absence from his Institute, the Burges reductive degradation was applied to humic acids extracted from some peats and lignites, and produced by oxidation of a number of bituminous coals. A number of identifications of products were made by gas chromatography with co-injection of standards, but at that time facilities were only rarely available to permit confirmation by mass spectrometry. Such confirmation has been more fully obtained recently by another of the authors (S.R.), who also studied a wider range of coals (totalling 43 samples).

It is proposed in this preliminary publication to describe the experimental procedures and to give a sufficient selection of the data to show what was found by co-injection and later confirmed by mass spectrometry.

The major coal measures of the United States were laid down either in the Carboniferous era (ca. 300 m. years B.P.), or in the Cretaceous and Tertiary (130-60 m. years B.P.). Between these two eras a great deal of evolution occurred in the plant kingdom; associated with this were some changes in the nature of groups R_2 and R_3 in structure I above. However, having stated the fact, we need not pursue this matter here.

Experimental

Humic acids were extracted from peats and lignites with 0.5N sodium hydroxide following standard procedures.

The oxidation of coals with aqueous performic acid is highly exothermic. Five gm of coal was dispersed in 50 ml of anhydrous formic acid, and 50 ml of 30% hydrogen peroxide was added in 2 ml portions at such a rate that the temperature did not exceed 55°C (however, in the earlier phase, the coal/formic acid suspension was cooled in ice during the addition of H_2O_2). The mixture was then allowed to stand at room temperature with stirring for 24 hours. The washed and dried solid product was extracted with 1N NaOH under nitrogen and centrifuged. The extract was precipitated by acidification to pH 1. The washed and dried humic acids were redissolved in alkali and, following the procedure of Burges et al.[1], treated with 3% sodium amalgam while the solution was heated in an oil bath at 110-115° for 4-5 hours.

After removal of mercury, the resulting solution was acidified to pH 1 and centrifuged; the supernatant was carefully removed and the residue extracted twice by centrifugation with ether and twice with methylene chloride. Solvents were removed and the residues mixed. The residues were treated with Sylol HTP reagent (Supelco, Inc., Bellefonte, Pa.) under the conditions recommended for converting phenols to trimethylsilyl ethers and carboxylic acids to the corresponding esters.

Experiment showed OV 101 column packing (3% on 80/100 mesh Supelcoport) to be the most effective for gas chromatography of the six packings tested. GC analyses, with and without co-injection of standards, were performed with a Hewlett-Packard No. 5750 instrument, equipped with flame ionization detectors. GC/MS analyses in the later phase were made by Mr. David M. Hindenlang, using a Finnegan model 3000 instrument under the charge of Dr. Larry Hendry of the Chemistry Department of this University. OV 101 columns were again used. The GC/MS instrument was provided with a data system, and this was used to subtract the mass spectrum at the foot of each peak just before it began to elute, or just after it had done so, from the spectrum recorded as the maximum of the peak was eluted. Such a procedure is certainly arbitrary, but disc space could not be monopolized for continued storage of our data while other procedures were tested and interpretations worked out. Consequently, the raw MS data, massaged as described above, were reported for standards and unknowns as printouts tabulating m/e values and relative intensities, and comparisons were made by visual inspection of the printed data.

Results

On the dry basis the weight of crude oxidized coal was usually 85-105% of the weight of raw coal. The yields of daf humic acids were in the range 65-90% of dmmf coal. Within the range of rank studied (78-87% C dmmf), the yield tended to increase with increasing rank. Petrographic studies of the

oxidized products of three coals (by Dr. Alan Davis and Mr. Harrey Zeiss, to whom we are indebted) showed that the vitrinites were greatly altered compared with their appearance in the raw coals, while sporinite and the inert macerals had changed little or not at all. These apparently unaltered macerals could still be recognized in the NaOH-insoluble materials. Thus the humic acids were derived very largely from the vitrinitic macerals. The yields of ether soluble products from the reductive degradation were in the range 10-40% of the weight of humic acids taken; yields when the reaction is applied to soil humic acids were about 20%.[1] Yields from humic acids from the younger Western coals tended to be somewhat higher than those from Carboniferous coals of the eastern U.S.

Chromatograms obtained in the earlier phase of the work are shown in Figures 1 and 2, where the names of compounds identified, mostly by co-injection, are entered against the corresponding peaks (trivial names are used in the figures because they are usually shorter; a list of equivalent systematic names is given in the Appendix. Comparison of the structures with I and II above will show which may be biologically related). It will be seen that resolution is moderately good but that even so a number of major peaks are unidentified.

These curves are typical of what was found for products from the six coals studied. All 3 dihydroxy-benzenes were commonly found and 2 of the trihydroxy-benzenes. 2,6-Xylenol was frequently found in both the earlier and later work, and was the only one of the six xylenols to be identified. Several of the compounds frequently encountered (vanillin and vanillic acid, syringic aldehyde and acid, p. hydroxy-benzoic acid) are well known as degradation products of lignin. A peak is seen in Figure 1 labelled 2,5-dihydroxy-benzoic acid (2,5-DHBA), and another labelled 2,4-, 3,4-, 3,5-dihydroxy-benzoic acid. Experiments with known compounds showed that the latter three isomers could not be resolved under the conditions used. Later work, using GC/MS, showed that of the three only the 3,4-isomer was in fact present, and this is lignin-related. However, the 2,5-isomer is not, though it could be derived from the A ring of flavonoids, 2,3,4-Trihydroxy-benzoic acid has no obvious biological associations, though the 3,4,5-isomer (gallic acid) occurs widely in the plant kingdom (both isomers were identified).

When, later, a wider range of samples was studied (with somewhat more severe conditions of oxidation), some very poorly resolved chromatograms were obtained; the products evidently often represent very complex mixtures of substances. Surprisingly, the products from nearly all of the younger western coals were resolved poorly or very poorly, while the resolution of those from the Interior and Eastern provinces ranged from mediocre to good. Representative examples of each type are shown in Figures 3 and 4. The resolution in Figure 3 is so bad that one might question whether any identifications are possible. In Table 1, we have assembled details of the mass spectra of four substances alleged to be identified from the GC/MS run shown in Figure 3, with details of the spectra of the standards. The agreement is surprisingly good, and the identifications are, taken with matching of retention times, reasonably secure. When resolution is better, as in Figure 4, one can surely be confident in the identifications; examples of the correspondence of mass spectral data are shown in Table 2.

It should be added that even when the GC/MS system is used, many prominent peaks remain unidentified. However, many of these showed fragments of m/e=73 in the corresponding mass spectra, so that they evidently contained the trimethylsilyl group and were therefore phenols or acids or both.

In considering the origin of the substances shown as identified in Figures 1-4, one must assume with bituminous coals that carboxylic acid groups result entirely from the performic acid oxidation. There is every reason to suppose that some of the hydroxyl groups were present as such in the raw coals, but one must necessarily enquire to what extent is new OH introduced by the oxidation (performic acid is a known reagent for converting alkenes to epoxides and cleaving them; this process occurs by a concerted electrophilic mechanism. However, the mechanism of attack on coals could be quite different and might, for example, follow a free radical mechanism).

The substances named in Figures 1-4 can be arbitrarily classified as follows: (1) "non-committal" substances - those like phenol, p. cresol and benzoic acid, whose structures are relatively simple and contain no obvious clues to origin, (2) those whose structures could obviously be related to biological precursors, such as vanillic, syringic, ferulic and other substituted cinnamic acids, (3) those whose structures are relatively complex but do not display any obvious association with biological precursors, such as the dimethyldihydroxybenzene shown in Figure 1 (isomers not identified). Of these classes, (1) requires no further comment here, while (3) presumably may include - or consist largely of - compounds whose OH groups are an artefact of the oxidation process. This leaves open the question, to what extent are the compounds of class (2) chemical fossils or artefacts?

Many of the substances identified have methoxyl groups in the 3-position or the 3,5-positions, as in lignins. These groups could hardly have been introduced by the performic acid oxidation, and therefore indicate a chemical fossil status for the substances. On the other hand, Blom et al.[4] state that methoxyl groups are eliminated by metamorphism in the subbituminous range. We must admit that the structures we identify as methyl phenyl ethers represent a small weight fraction of the whole coals: but can also point out that Blom et al. present no evidence that the Zeisel procedure, which they used in their analyses, was completely effective (the reagent HI may not have penetrated the pore structure fully), or even that it produced with coals the results found with simple compounds. Whatever the mechanism of the performic acid oxidation with coals, one would expect that if it introduces new OH groups, more than one isomer would usually be produced. Therefore, where a peak in the chromatograms was identified as due to a lignin-related substance like vanillin or caffeic acid, the mass spectra corresponding to neighboring chromatographic peaks were carefully examined to determine whether they could represent spectra of position isomers. Such isomers were rarely detected. On the other hand, some of the relatively complex substances not obviously related to biological precursors evidently did have isomers present.

We conclude that some of the OH groups in the products may well have been introduced by the performic acid oxidation, but that most of the substances of structure related to lignins were probably not artefacts.

The question, to what extent do the findings reported here relate to the composition of whole coals, must be left for discussion in a later paper when a more complete set of data can be presented. In concluding this paper, we

should draw attention to some implications of the findings, if the provisional assumption can be made that the findings do indeed have relevance to the structure of vitrinite macerals in coals:

1. o-Dihydroxybenzenes, and still more trihydroxybenzenes, are notoriously easily oxidized. This, if such structures are indeed present in vitrinites, we could explain why it is so difficult to nitrate or sulfonate coals, even with mild reagents, without accompanying oxidation[3], and also why coals so readily oxidize in weathering. Partially methylated polyphenols are less reactive, but still quite readily susceptible to oxidation.

2. *Ortho* - dihydroxybenzene derivatives are capable of chelating boron and other elements. Less information is available about o.hydroxy-methoxy derivatives, but there seems no reason why they should not be capable of chelation.

3. During catalytic hydrogenation of coals of any rank to liquid fuels, under conditions that give high conversion, a substantial fraction of the oxygen is removed. However, in interactions of coal with hydrogen donor solvent alone, or in applications of the SRC process, oxygen removal is less complete and the products may retain o.dihydroxybenzene structures, a point perhaps worthy of note by those concerned with the composition of coal liquids.

It is worth noting here that in a study of the products of laser pyrolysis of coals in the ionization chamber of a time-of-flight mass spectrometer, homologous series of what appeared to be dihydroxybenzenes were noted[5]. The technique could not distinguish positional isomers, but the finding is suggestive when taken with the data in this paper.

Acknowledgements

The authors are indebted to Mr. David Hindenlang and Dr. Larry Hendry for assistance with obtaining GC/MS data. They are also grateful to Dr. William Spackman for fully characterized coal samples from the Penn State/ERDA Coal Sample Base assembled under his direction.

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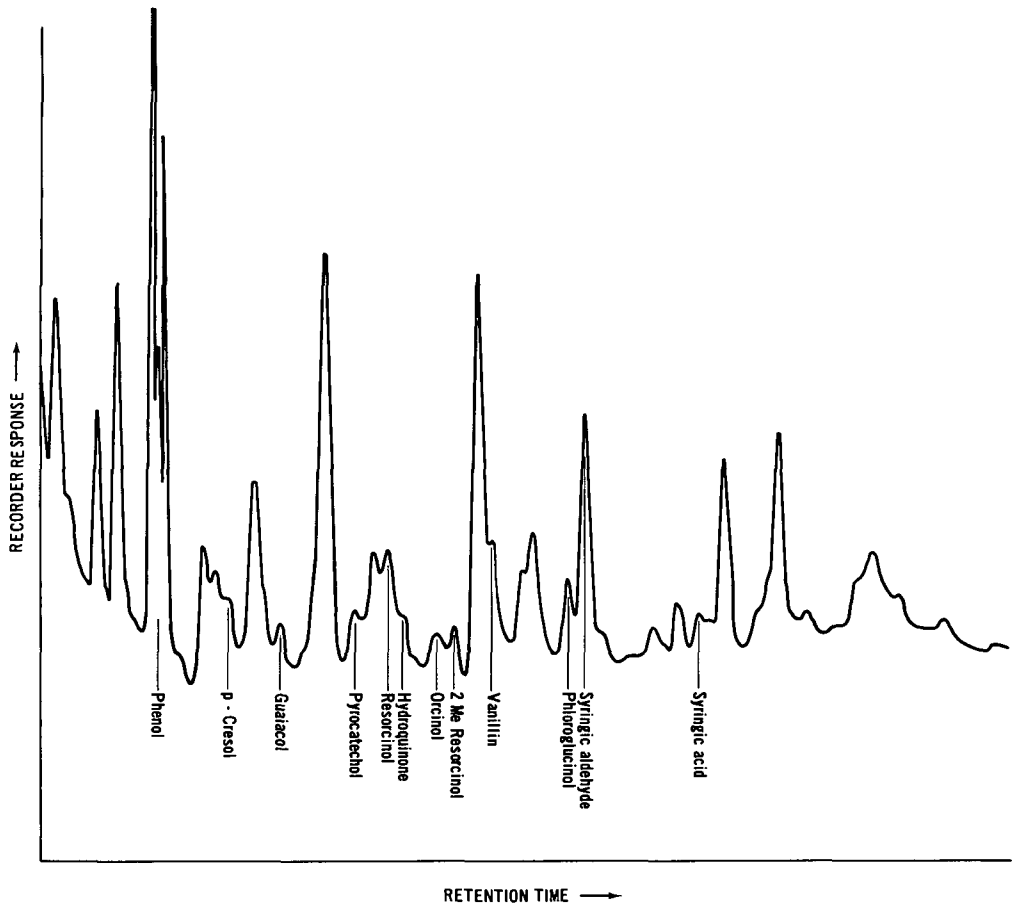

Figure 1. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM C SEAM COAL, BENHAM, KENTUCKY (HVA, PSOC 13)

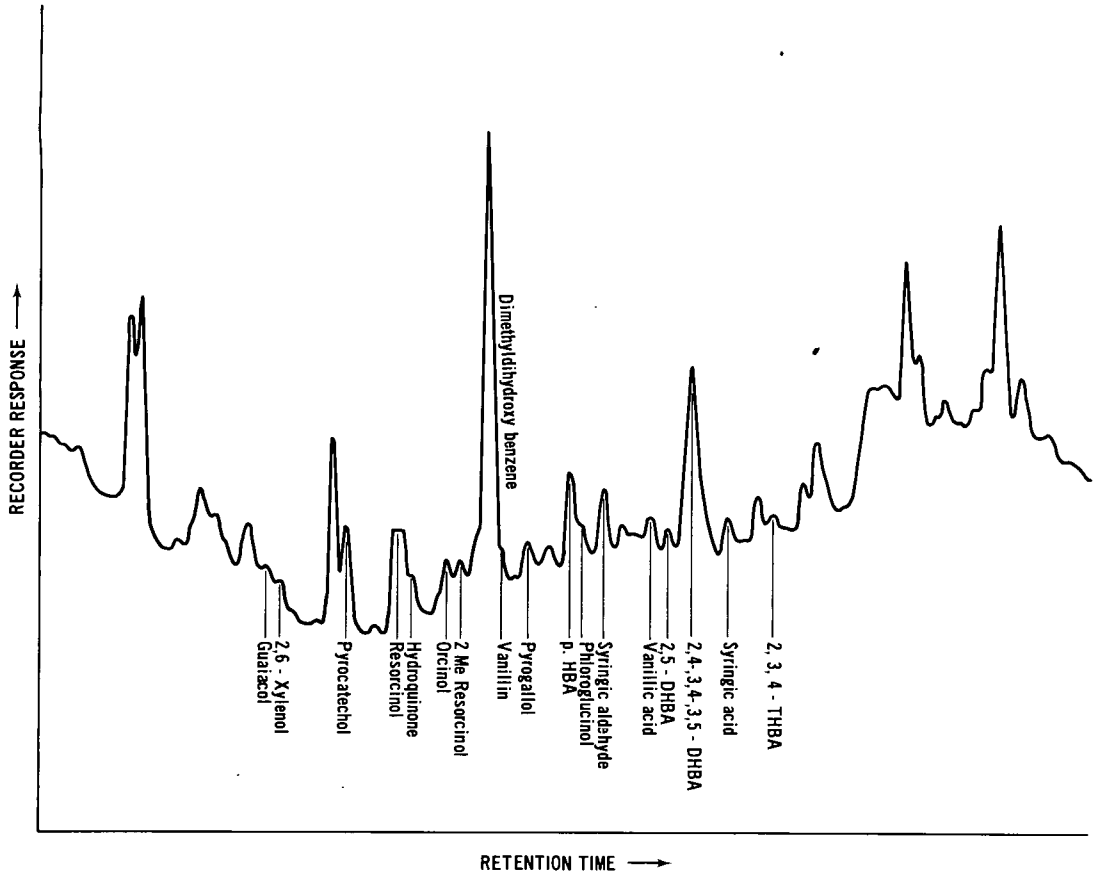

Figure 2. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM WYODAK SEAM COAL, GILLETTE, WYOMING (sbb., PSOC 100)

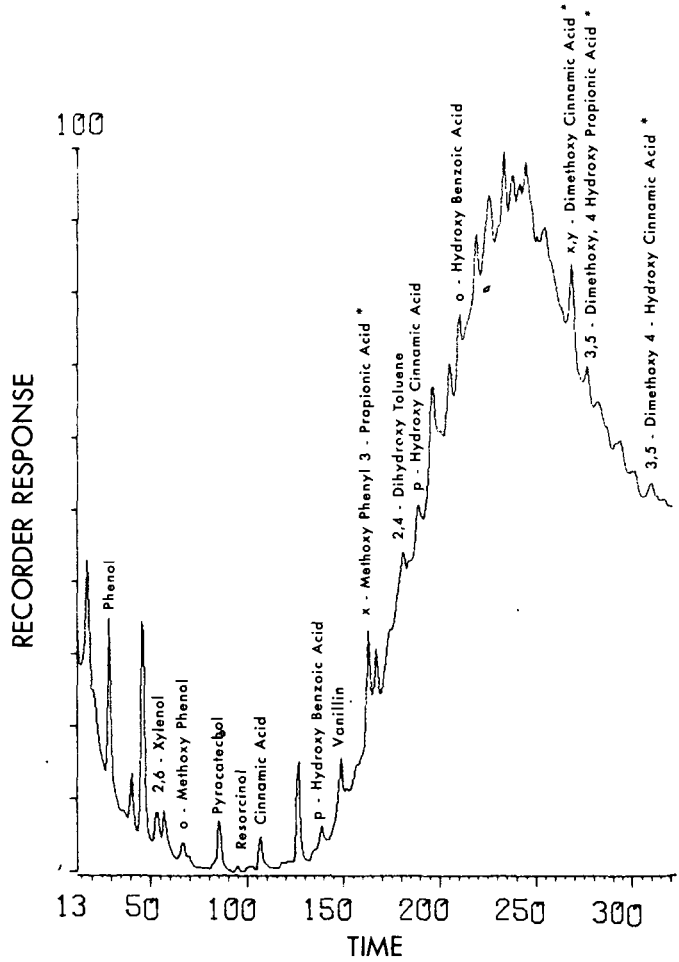

Figure 3. TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM RED SEAM (HVC), KAYENTA, ARIZONA (PSOC 312)

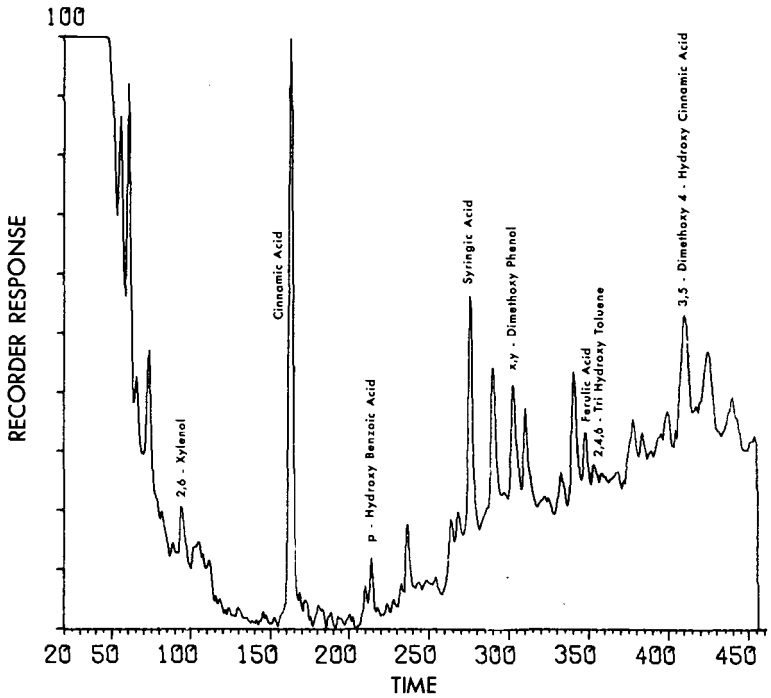

Figure 4. TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM OHIO NO. 1 SEAM (HVC), JACKSON, OHIO (PSOC 202)

Table 1

Data for MS Identification of Substances in Degradation Products of Coal from Black Mesa, Arizona (HVC)(PSOC 312)

Cinnamic Acid		
m/e	Standard	Unknown
p/p+1	3.98	4.13
205	100	100
57	82	86
45	48	39
145	27	23
55	25	20
89	20	16
67	18	14

p. Hydroxybenzoic acid		
m/e	Standard	Unknown
p/p+1	3.28	2.73
73	100	100
193	45	63
267	44	59
223	42	56
45	21	41
75	15	23
126	13	17

Vanillin		
m/e	Standard	Unknown
p/p+1	6.95	5.15
194	100	88
23	83	100
193	53	45
209	37	60
151	29	38
45	27	33
165	9	17

p. Hydroxycinnamic acid		
m/e	Standard	Unknown
p/p+1	6.00	5.27
13	100	83
219	76	100
235	61	79
293	32	41
191	21	39
45	16	25
75	15	19

Table 2

Data for MS Identification of Substances in Degradation Products of Coal from Ohio No. 1 Seam (HVC)(PSOC 202)

p. Hydroxybenzoic acid		
m/e	Standard	Unknown
p/p+1	3.28	3.18
73	100	100
193	45	52
267	44	48
223	42	41
45	21	34
75	15	19
126	13	14

Syringic acid		
m/e	Standard	Unknown
p/p+1	3.72	3.15
73	100	100
45	18	29
141	15	23
327	12	19
312	10	13
89	10	15
297	9	10

Ferulic acid		
m/e	Standard	Unknown
p/p+1	2.71	2.93
73	100	100
75	48	49
117	38	35
225	24	32
181	22	30
129	22	25
297	20	31

Appendix. Trivial and Systematic Names of Relevant Phenolic Substances

resorcinol	1,3-dihydroxybenzene
pyrocatechol	1,2-dihydroxybenzene
phloroglucinol	1,3,5-trihydroxybenzene
pyrogallol	1,2,3-trihydroxybenzene
orcinol	3,5-dihydroxytoluene
2-methyl resorcinol	2,6-dihydroxytoluene
guaiacol	2-methoxyphenol
vanillin	3-methoxy-4-hydroxybenzaldehyde
vanillic acid	3-methoxy-4-hydroxybenzoic acid
syringic acid	3,5-dimethoxy-4-hydroxybenzoic acid
cinnamic acid	phenyl-3-propenoic acid
ferulic acid	3-methoxy-4-hydroxyphenyl-3-propenoic acid
caffeic acid	3,4-dihydroxyphenyl-3-propenoic acid

SEARCH FOR A NEW COAL TECHNOLOGY. Frank C. Schora, Institute of Gas Technology, 3424 South State Street, Chicago, Illinois 60616.

Since the beginning of a coal industry, technology — other than for combustion — has evolved through the steps of devolatilization, gas production by the reaction of hot cokes with steam, and lately, coal hydrogenation for the production of both liquids and gaseous fuels. Much of the research today in the United States is dedicated to improving these present concepts and to the development of supporting steps necessary for commercialization. In the midst of these activities, one should not overlook the need for intensive research to uncover better techniques for conversion of coal — techniques which will take advantage of the structure and chemistry of coal so as to yield useable products without undergoing the severe conditions which have been the basis of our technology in the past. New coal technology should seek to allow production of liquid and gaseous hydrocarbons by controlled reactions which avoid the rapid and uncontrolled polymerization of intermediate products to coke.

FREQUENCY OF CROSS-LINKS AND MOLECULAR WEIGHT DISTRIBUTIONS IN COALS. Jeffrey Kovac and John W. Larsen, University of Tennessee, Chemistry Department, Knoxville, Tennessee 37916

Coals may be mixtures of cross-linked macromolecules. Information on the average molecular weight of the chain segment between cross-links can be obtained from equilibrium solvent swelling measurements using the Flory-Rehner equation as well as from the plastic deformation properties of coals using the Gaussian model for the elastic modulus of polymer networks. Attempts to develop a simple non-Gaussian theory of a polymer network which should be a more reasonable model for coal will be described. The average molecular weight per cross-link calculated using the above techniques will be compared with data obtained from solubilized and depolymerized coals. The implications for various coal structure models will be discussed.

GASIFICATION AT VERY HIGH HEATING RATES. C. W. von Rosenberg, Jr., D. B. Northam and R. E. Gannon, AVCO Everett Research Laboratory, Inc., 2385 Revere Beach Parkway, Everett, Massachusetts 02149

Large yields of volatile matter and high throughput for gasifiers are two notable benefits of subjecting well-dispersed aerosols of pulverized coal to large rates of heating (>10^5°K/sec) to high temperatures (>1500°K). This central theme forms the basis of several investigations at AERL which seek to explore this frontier, understand the basic processes involved and apply this approach to gasifier development. Recent experimental data from our "controlled explosive gasification" program are given and related to prior work on rapid heating entrained bed reactors and to our concurrent "shock heating studies." In a single pulse/batch process reactor of 12 litre volume we dispersively premix −200 mesh HVA bituminous coal in suitable mixtures of H_2-CO-O_2. Ignition leads to explosive combustion of the gas mixture which provides a background of hot H_2O, CO_2 and attendant radicals which then heat the coal, stabilize the evolved volatiles, and react with the nascent char. Large yields of stabilized volatiles at high solids mass loading have been achieved. Proposed gasification processes based on this approach will be discussed.

RISER CRACKING OF COAL TO OIL AND GAS. Dennis A. Duncan, Justin Beeson, Donald Oberle, Institute of Gas Technology, 3424 South State Street, Chicago, Illinois 60616.

A four-year program is under way at IGT under ERDA/FE sponsorship to develop a practical hydrocarbonization or hydropyrolysis processing scheme based on an entrained-flow reactor similar to the Riser reactors used in refinery catalytic cracking. The reaction products are gasoline, gas, fuel oil and char.

Hydrogen and coal are reacted in entrained flow at pressures in the 1000 to 2000 psi range and at temperatures up to 1500°F. Such parameters as hydrogen concentration, hydrogen preheat temperature, coal particle size, reaction temperature history, residence time and the use of other carrier gases, will be explored to establish their effect on product yields and overall economics.

A bench-scale unit is being operated now to obtain engineering design parameters. A 100 pound per hour process development unit (PDU) will be designed, fabricated, and operated later in the program.