THE APPLICATION OF FT-IR AND SOLID STATE ^{13}C NMR
TO THE CHARACTERIZATION OF A SET OF VITRINITE CONCENTRATES

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INTRODUCTION

In a recent review of coal structure Neavel (1) remarked that coal is analagous to fruitcake in that it is an aggregate of different and distinguishable components. Consequently, the characterization of coal structure (or for that matter, fruitcake) demands a recognition and investigation of the separate components, macerals. For most U.S. coals the major maceral type present is vitrinite, so that an understanding of many structure/property relations will ultimately depend on a knowledge of the structure of this maceral. As part of a systematic study of the variability of coal properties within a single seam, a set of vitrinite concentrates has been obtained from samples taken from the Lower Kittaning seam (2). This seam is particularly interesting because of its broad extent and the range of environments by which it is thought to have been affected. However, even though the far from trivial task of obtaining and storing these maceral concentrates under optimum conditions has been accomplished (2), there remains the formidable task of structural characterization.

Because of the heterogeneous, non-crystalline, largely insoluble nature of coal, it is practically impossible to apply the traditional methods of organic and physical chemistry to structural characterization work. Such methods essentially rely on the separation and identification of the constituent simple molecules of a complex system. In fact, for coal it is a notoriously difficult task to obtain reliable data on even the most fundamental property, the average molecular weight and the molecular weight distribution of the macromolecular constituents. Consequently, the most useful information concerning coal structure that we can reasonably expect to obtain is a quantitative identification of the molecular types of hydrocarbons present (eg aromatic and aliphatic carbon) and the type and distribution of specific functional groups (aliphatic CH, CH_2 and CH_3; phenolic OH, alkyl OH, carbonyl etc). It is precisely this information that spectroscopic methods are uniquely capable of elucidating.

Spectroscopic techniques have been widely applied to the study of coal, but have met with only limited success (3-6). Advances in spectroscopic instrumentation however, should allow us to obtain new insights into coal structure. Of particular significance is the recent application of Fourier transform infrared (FT-IR) spectroscopy (7-17) and solid state ^{13}C NMR spectroscopy, using magic-angle spinning in conjunction with cross-polarization and high power decoupling (18-21). In this communication we will consider the initial results of applying these two techniques to the set of vitrinite concentrates mentioned above.

SAMPLE CHARACTERISTICS

A set of 24 vitrinite concentrates were selected for initial study. These samples have been characterized by a number of methods and an extensive body of basic data has been reported (reference 2 and subsequent reports) Space does not permit reproduction of all of this data here. However, Neavel (1) has pointed out the critical importance of reporting reflectance values and the petrographic analysis of coals on which structural studies are performed. Accordingly, a plot

of reflectance as a function of carbon content of the concentrates used in this study is shown in Figure 1. Petrographic analysis of the concentrates demonstrated that most were 95-96% vitrinite with one or two higher (up to 98%) and one odd sample that was significantly lower (88% vitrinite).

TYPE OF INFORMATION THAT CAN BE OBTAINED FROM FT-IR AND ^{13}C NMR

Both FT-IR and ^{13}C NMR have already been used to obtain valuable information concerning coal structure. However, in many ways these techniques are still being developed and it should be possible to obtain new information as instruments and methodology are improved. In this section we will briefly describe the type of complementary information that can be obtained from each method and anticipate areas where we believe advances can be made.

Typically, infrared spectrsocopy is sensitive to specific functional groups. The spectra of three of the vitrinite concentrates, chosen so as to represent samples of different rank, are presented in Figure 2. Four regions of the spectrum have been used to obtain quantitative information; the O-H stretching region near 3400 cm^{-1}, the aromatic C-H stretching modes between 3100 and 3000 cm^{-1}, the aliphatic C-H stretching modes between 3000 and 2800 cm^{-1}, and the aromatic C-H out-of-plane bending modes between 900 and 700 cm^{-1}.

The central problem with infrared spectroscopic studies of coal is the absence of reliable extinction coefficients (relating band intensities to the con-centration of the corresponding functional group). Usually, the integrated in-tensity in an entire region of the spectrum (for example the aliphatic C-H stretch-ing modes) is used and the extinction coefficients of individual bands are thus averaged. Calibration has in the past most often been based on model compound work or on proton magnetic resonance studies of coal extracts. More recently, Solomon (16,17) has equated the concentration of hydrogen containing functional groups to the total hydrogen determined by elemental analysis in order to obtain extinction coefficients. We have previously discussed the problems associated with infrared analysis (22,23), the most critical of which would appear to be the use of entire regions of the spectrum rather than individual bands. It may be that there is no viable alternative to this approach, but one possibility is to use well-defined curve resolving methods. We have previously reported (22,23) the use of such procedures in distinguishing the products of acetylation. This has allowed us to separately determine phenolic OH, alkyl OH and NH groups. We have recently applied these methods to the aromatic C-H out-of-plane bending modes between 900 and 700 cm^{-1}. These results will be considered below in the context of the analysis of vitrinite concentrates.

In most of the solid state ^{13}C NMR results reported to date, including those utilizing magic angle spinning and cross-polarization (18-21), only two broad bands are usually discerned, one for aromatic carbon and one for aliphatic. A careful examination of these spectra reveals the presence of shoulders, but the signal to noise ratio is such that they are not well defined. Nevertheless, the spectra allow useful estimates of the degree of aromaticity, f_a, to be obtained. We have recently applied to coal studies a spectrometer with a static field of 3.5T, approximately 2.5 times the field strength for which most ^{13}C spectra of solid coals have been reported. The resulting increase in sensitivity and potential resolution are considerable, as demonstrated by the spectrum of a vit-rinite concentrate shown in Figure 3. Shoulders are clearly visible on both the aromatic and aliphatic peaks and can be readily assigned using appropriate polymer model compounds. We have previously reported the surprising but satisfying similarities between the infrared spectra of certain phenolic resins and coal (22). These materials should also be an important aid in assigning shoulders in the aromatic and aliphatic resonances of coals. The spectrum of a simple phenol-formaldehyde resin and a phenol/dihydroxynaphthalene-formaldehyde copolymer are also presented in Figure 3. Based on the known structure of these polymers a

number of assignments can be made. For example, in the model compounds aromatic carbons directly attached to hydroxyl groups resonate near 153 ppn and this agrees well with a low field shoulder on the aromatic resonance of vitrinite concentrates. This assignment can also be confirmed by acetylation studies. The ^{13}C NMR spectrum of a coal before and after acetylation is presented in Figure 4, together with a difference spectrum. A negative peak centered near 155 ppm indicates the loss of carbon attached to phenolic OH groups. Furthermore, the carbonyl reson- ance near 170 ppm and the methyl resonance near 22.2 ppm characteristic of the acetyl groups introduced into the coal can be clearly distinguished and used in conjunction with FT-IR studies of the same samples to obtain quantitative data.

The potential of suitable polymeric materials as models for coal is clearly outstanding. However, before proceeding to a discussion of some of the results of the analysis of vitrinite concentrates we wish to draw attention to another procedure that should be extremely useful in resolving shoulders on the broad aromatic and aliphatic resonances of coal macerals. We are presently only just starting to apply this method to coal studies, but preliminary results are sufficiently interesting to report here. It is possible to use pulse sequences to differentiate among carbons contributing to the broad aromatic and aliphatic resonances (21). Figure 5 shows the application of a sequence which incorporates a delay before the beginning of aquisition during which the proton pulse is switched off (24). The protonated carbons dephase preferentially during this period, leaving only the nonprotonated carbons to contribute to the accumulated free induction decay. It can be seen from the difference spectrum shown in Figure 5 that both the aliphatic and the high field side of the aromatic resonance consist of protonated carbons. This type of information should prove extremely valuable in conjunction with FTIR studies, where bands due to various aliphatic groups (CH, CH_2 and CH_3) and aromatic hydrogen arrangements (lone C-H, two adjacent C-H etc.) can be observed. It should be noted that weak spinning sidebands are ob- served in this spectrum. These arise when the magic-angle rotation rate is less than the chemical shift anisotropy, as is almost always the case for the aromatic resonances of coal. The contribution of these sidebands can be accounted for by various methods, but recently a pulse sequence has been introduced which allows elimination of first order sidebands (25). Both this pulse method and a correction based on the observed intensity of the high field aromatic sideband have been applied to coal studies. The aromatic carbon fraction f_a was determined to be the same.

ANALYSIS OF VITRINITE CONCENTRATES

Our initial aim in these studies is to correlate the concentration of various functional groups to rank parameters. In preliminary work we plotted the area of bands assigned to specific functional groups against %C (dmmf). A typical result is shown in Figure 6, where the area of the 1770 cm^{-1} band in the acetylated vitrinite concentrates has been used. This band area is a measure of the concen- tration of phenolic OH groups (22, 23). We found much less scatter when our spectroscopic data was plotted against reflectance, as illustrated in Figure 7. It can be seen that the concentration of phenolic hydroxyl groups drops off in an almost linear fashion with increasing rank of the coal. A band at 1740 cm^{-1} representing alkyl OH concentration (22, 23) displays precisely the same behavior, but its intensity is almost exactly half of the 1770 cm^{-1} band. (In fact, a plot of the 1770 cm^{-1} band against the 1740 cm^{-1} band is linear). Conversion factors relating the intensities of these bands have been determined (26) and total OH concentration,(measured as % O as OH) for the lowest rank coal shown in Figure 7 is about 6%.

In order to determine the concentration of aliphatic and aromatic CH groups as a function of rank equivalent extinction coefficients need to be determined. Values are available in the literature and we have applied similar calibration procedures. We have little faith in the results, however. There are a number of reasons for

this, the most important of which is that entire areas of the spectrum are used for measuring aliphatic and aromatic areas, as we noted in the introduction to this work. As the bands in these regions may each be independently related to rank parameters considerable scatter in the results can be anticipated. This is precisely what we observe, as shown in Figure 8. The aliphatic C-H stretching and aromatic out-of-plane bending modes (900-700 cm^{-1}) form almost a "scatter-shot" pattern. Of course this behavior could represent incompetent sample preparation and errors in methodology on our part, but the evidence indicates otherwise. The aromatic C-H stretching mode shows a nice consistent trend to increasing values with increasing rank. (Unfortunately, because this band is weak it is not the most useful for quantitative work). Furthermore, if we consider individual bands, carefully curve resolved using precisely defined criteria (22,23), then a relationship to rank of aliphatic and aromatic C-H groups to rank emerges. For example, Figure 9 shows the intensity of the 2853 cm^{-1} mode, representing aliphatic CH_2 groups, as a function of feflectance. The concentration of these groups clearly decreases with increasing rank. Similarly, certain bands in the aromatic C-H out-of-plane bending region increase in intensity as a function of the rank of vitrinite rank, as shown in Figure 10, using the 753 cm^{-1} band (4 adjacent aromatic C-H groups) as an example. Consequently, we can conclude that the scatter in the results observed using integrated intensities of entire spectral regions makes a major contribution to poorly defined behavior as a function of rank. However, if we consider individual bands assigned to specific functional groups, a pattern of behavior emerges.

One other reason for the scatter in the results obtained by plotting the integrated intensity of the aromatic C-H out-of-plane bending modes became apparent from our curve-resolving work. Also shown in Figure 10 is a plot of the intensity of a band near 830 cm^{-1} as a function of reflectance. Clearly, this band behaves differently to the 753 cm^{-1} band. The curve resolved 900-700 cm^{-1} region of the spectrum of a typical vitrinite concentrate is shown in Figure 11. (The initial positions and half widths of the bands were initially well defined using derivative techniques, as discussed previously (22,23), so that we can be reasonably confident that the bands shown in Figure 11 actually exist and are not artifacts of the curve resolving procedure). Bands at 801, 815 and 864 (assigned to 3 adjacent, 2 adjacent and lone aromatic C-H groups, respectively) display the same trend with rank as the 753 cm^{-1} band shown in Figure 10. However, the 785 cm^{-1} band displayed behavior similar to the 830 cm^{-1} band. We suggest that these bands have at least a partial contribution from CH_2 rocking modes that are expected to appear in this region of the spectrum. We are presently synthesizing phenolic resins that will allow us to assign these modes with more certainty. However, if we plot the total intensity of the aromatic out-of-plane bending modes, less the contribution of the 830, 785 cm^{-1} bands, against reflectance, a good correlation to rank emerges, as shown in Figure 12.

One result of these studies is that there is clearly an increase in aromatic C-H and loss of phenolic OH as a function of increase in rank. In fact, these two trends are related, as shown in Figure 13, where the area of the acetylated phenolic OH band (1770 cm^{-1}) is plotted against the total area of the 900-700 cm^{-1} out-of-plane modes (less the contribution of the 830, 785 cm^{-1} bands). Of course, there is not simply a straight replacement of phenolic OH by aromatic C-H with increasing rank, as the ^{13}C NMR results show an increasing degree of aromaticity with reflectance, as shown in Figure 14. (At the time of writing not all of the samples had been characterized by NMR).

Although these results demonstrate the trends in the concentration of specific functional groups in vitrinite concentrates as a function of rank, there is obviously additional work required to convert infrared band intensities to a quantitative measure of specific functional groups. In this respect we are pursuing the use of polymer model compounds and ^{13}C NMR pulse methods, which should provide the necessary data. It was shown above that the contribution of protonated carbons to

the NMR spectrum can be determined by such methods, allowing a quantitative deter-
mination of aromatic C-H. This can then be used to calibrate the intensities of
the aromatic C-H out-of-plane bending modes.

ACKNOWLEDGEMENTS

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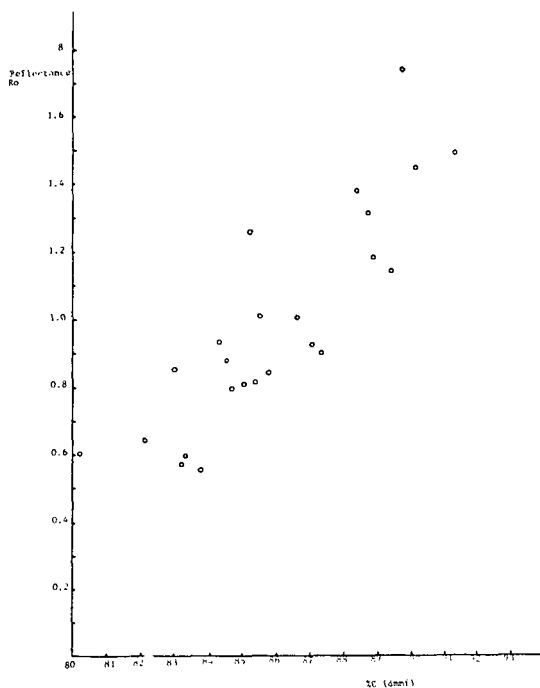26. Snyder, R.W. and Painter, P.C. (to be published).

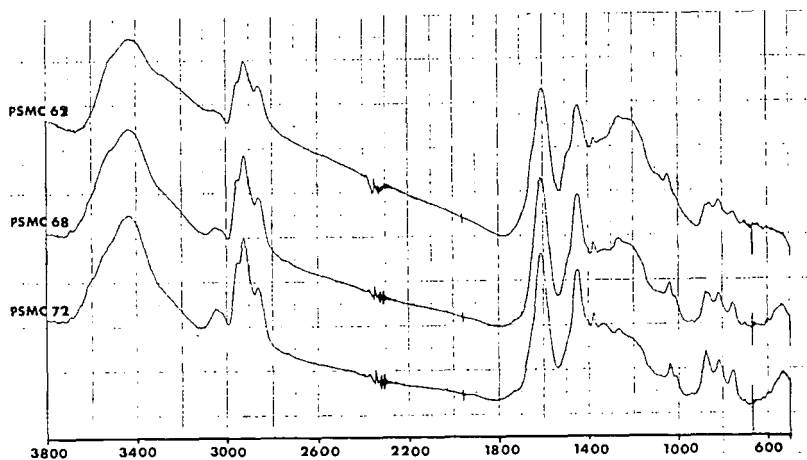Figure 1. Plot of reflectance (Ro) values vs % C (dmmf) for a set of vitrinite concentrates.

Figure 2. FT-IR spectra of three vitrinite concentrates obtained on a Digilab FTS 15B instrument (400 scans at 2 cm⁻¹ resolution). Top to bottom, PSMC 67 (83.2% C dmmf), PSMC 68 (87.04 %C dmmf, PSMC 72 88.74%C dmmf).
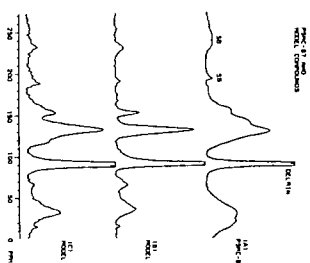
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Figure 3. ^{13}C spectra of PSIC 67 (A) and model compounds. B: phenol-formaldehyde resin. C: phenol/dihydroxynaphthalene-formaldehyde copolymer (Spectra recorded on a Nicolet ND 150 instrument).
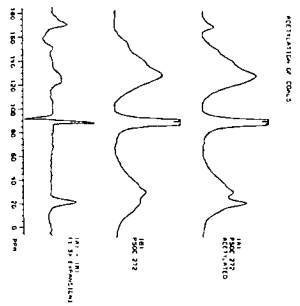
Figure 4. Spectra illustrating changes occurring in ^{13}C NMR spectra of acetylated coals.
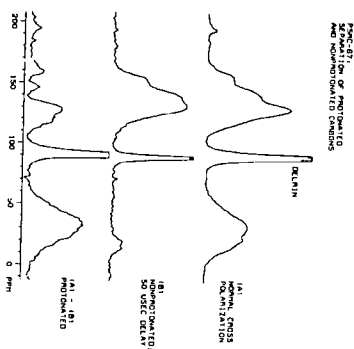
Figure 5. Spectra showing the isolation of protonated and nonprotonated carbons for a maceral, PSNC-67. Spectrum (B) is obtained by allowing the carbon spins to dephase for 50 μsec by coupling to nearby protons before the beginning of acquisition. Digital subtraction is then performed to isolate the protonated carbons.
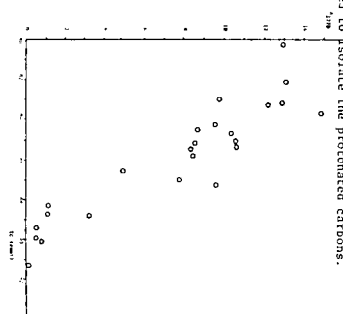
Figure 6. Plot of area of 1770 cm^{-1} band in acetylated vitrinites (proportional to phenolic OH content) vs % C (dmmf).
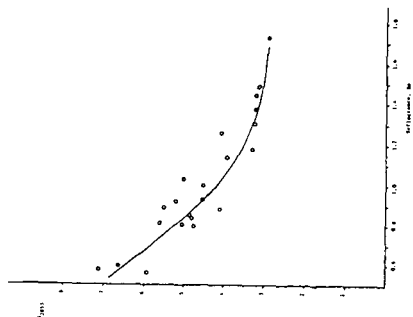
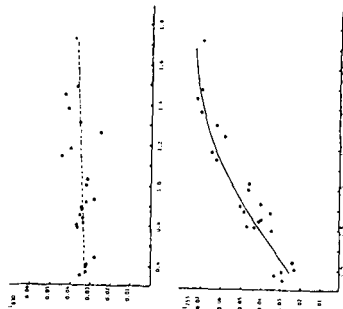Figure 9. Plot of area of 2853 cm^{-1} band (aliphatic CH$_2$ mode) vs reflectance (Ro).

Figure 10. Top: Plot of peak height of 830 cm^{-1} band vs reflectance. (Ro)
Bottom: Plot of peak height of 753 cm^{-1} band vs reflectance. (Ro)

Figure 7. Plot of area of 1770 cm^{-1} band in acetylated vitrinites vs. reflectance (Ro).

Figure 8. Plots of (top to bottom) integrated area of aliphatic C-H stretching modes; integrated area of aromatic C-H out-of-plane bending modes; integrated area aromatic C-H stretching modes vs reflectance (Ro)

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Figure 13. Plot of area 1770 cm^{-1} band in acetylated vitrinites (a measure of phenolic OH content) vs area of aromatic C–H out-of-plane bending modes (excluding 830, 785 cm^{-1} bands)

Reflectance R$_o$

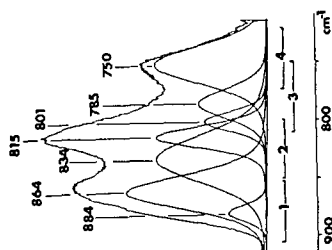Figure 14. Plot of aromaticity f$_a$ vs reflectance for vitrinite concentrates.

Figure 11. Curve resolved bands in the 900 to 700 cm^{-1} region of the FT-IR spectrum of a vitrinite concentrate.
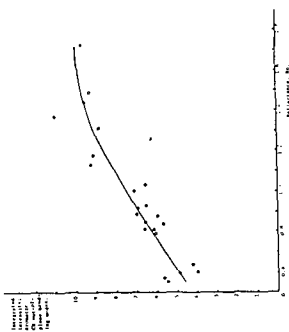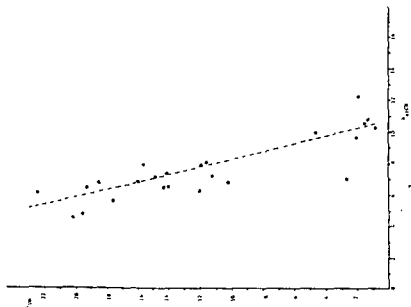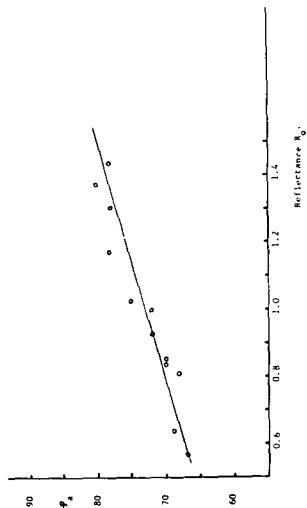

Figure 12. Plot of integrated intensity of aromatic C–H out-of-plane bending modes (excluding the 830, 785 cm^{-1} bands) vs reflectance (Ro).

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