NOVEL METHODS FOR FTIR ANALYSIS OF COAL

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FTIR was first applied to the characterization of coal structure during the late 1970's and has now been applied to a range of problems in fuel science. Although the technique can therefore be considered established, in some very fundamental ways it is still evolving. Novel sampling methods, principally diffuse reflectance and photoacoustic techniques, have been applied; in addition, new software with the potential for extracting additional information from the spectrum has been developed. The basic thrust of our research is still the accurate quantitative determination of structural parameters, but in this context we have been studying alternative methodologies. Here we will report an examination of the use of diffuse reflectance methods together with two data processing routines; self-deconvolution and a program that can generate the spectrum of components from the spectra of a series of mixtures.

The application of diffuse reflectance and self-deconvolution to the study of coal has been pioneered by Peter Griffiths and co-workers (1,2). We originally considered the advantages in ease of sample preparation (compared to standard KBr pellets) to be relatively minor, given the greater difficulty in obtaining reproducible quantitative results; band intensities not only vary with particle size but are also affected by packing within the sample cup. If we work with the ratio of various bands, however, such factors can be largely eliminated (particularly for modes that are close in frequency and hence are almost equally affected by scattering factors) and we found that for a particular set of samples we obtained information that could not be determined by standard KBr techniques.

As mentioned above, we are still concerned with the measurement of functional groups, particularly aliphatic and aromatic CH content. We have discussed the difficulties associated with various methodologies in various papers and a recent review article (3). We postulated that if we could obtain a set of samples where most of the hydrogen was tied up in one type of functional group, then it should be a relatively straightforward task to obtain accurate absorption coefficients by relating band intensities to elemental hydrogen. Accordingly, we obtained a set of high rank coals (carbon content > 92%) from the Penn State coal bank, choosing those coals that also had an elemental hydrogen content of the order of 3% or more. To our surprise, we could not obtain spectra using standard KBr pellets, while diffuse reflectance revealed bands characteristic of a coal with a high aromatic CH and very low aliphatic CH content. The region between 2000 and 500 cm^{-1} is illustrated in figure 1 and it can be seen that the spectrum of the standard KBr pellet reveals no coal bands whatsoever. We presume that this is due to scattering factors associated with the difficulty in adequately reducing the particle size of such hard coals. Clearly, diffuse reflectance has overwhelming advantages in the characterization of high rank coals. We are now comparing results for lower rank coals obtained by diffuse reflectance and KBr pellets in order to determine whether the ratio of absorption coefficients for aliphatic and aromatic bands is the same for the two methods.

The infrared spectrum of coal is characterized by a set of broad, overlapping

bands. We could certainly obtain a greater insight into structure if various contributions to specific spectral regions could be separated or deconvoluted. In previous work, we have used second derivative spectra as a starting point for curve-resolving, while Griffiths and co-workers (2) have recently applied a novel self-deconvolution procedure. In refining spectra by improvement of the spectral resolution, deconvolution and derivative analysis can be considered alternative treatments of choice. An asymmetric spectral profile composed of two or more overlapped lines, is resolvable (in principle) into at least two component lines, within the limits imposed by the signal to noise ratio and instrument line shape of the original spectrum. It should be noted that no line in the refined spectrum may be narrower than the instrument line shape, unless continuation of the interferrogram is performed on the spectrum.

The problem that arises in deconvolution is that neither the line shape nor the full width at half height of the overlapped constituent lines is known. To effect deconvolution, a line shape must be chosen which is considered a reasonable approximation to that of the individual overlapped lines. An optimum band width is then selected empirically from a series of deconvolutions of the overlapped spectral region such that ringing in the refined spectrum is reduced to a minimum.

This empirical technique may well be difficult to apply in practice, however, since the effects of over-deconvolution may be misinterpreted as significant spectral information. The sidelobes so introduced, when superimposed upon the residual spectrum, can easily take on the appearance of ligitimate spectral detail, but are in effect artifacts of the technique. This ambiguity in the refined spectrum can be minimized by noting that a symptom of over-deconvolution is the "shifting" of lines in direct relation to the extent of deconvolution.

Although deconvolution appears to provide more information than derivative analysis, they are fundamentally related. Cameron and Moffatt (4) have demonstrated that both techniques rely upon the application of a weighting function in Fourier Space. This function is of the form

$$(2kt)^n$$

where n is the order of the derivative. This may be contrasted with the deconvolution weighting function, for a Lorentzian line shape, of the form

$$(e^{bt})$$

Because both procedures rely on such weighting functions, similar limitations exist with respect to discrimination against noise. Deconvolution does have the advantage of retaining the integrated intensity and does not suffer the phase inversion characteristic of the second derivative, but has the disadvantage of more easily introducing artifacts. In this respect it should be kept in mind that coal bands are inherently broad due to the chemical heterogeneity of the material and instrumentally cannot be resolved into a series of sharp overlapping bands. Accordingly, deconvolution should be applied with extreme caution.

The final topic we wish to consider is the application of a routine capable of obtaining the spectra of individual components from those of a mixture. There are a number of approaches to this problem, including factor analysis, that could be useful in the analysis of coal spectra. We have developed a program based on a procedure described by Honigs et al. (5) that is most commonly used in near-infrared analysis of foodstuffs. Essentially, the known concentrations of a particular component in a set of mixtures are used as weighting factors to reconstitute the spectrum of that component from those of the mixtures. The application is illustrated in figure 2, which compares the spectra of three

"mixtures", each represented by a single band. The spectrum of a pure component was easily generated and is shown at the bottom of the figure. This method has several intriguing possibilities when applied to coal. For example, we have obtained the spectra of several coal extracts, where the aromatic and aliphatic hydrogen content is known from proton nmr measurements. Using the aromatic (or aliphatic) CH contents as weighting factors we should be able to generate a spectrum characteristic of those parts of the molecule associated with such groups, a sort of functional group based deconvolution.

The method is promising but preliminary results indicate that a careful choice of samples is required. In initial work we considered the spectra of extracts obtained from PSOC's 785, 801, 1192, 1195, 1196 and 1198. For clarity of illustration just the CH stretching region of the spectra, with the OH bands removed by curve-resolving and subtraction, are illustrated in figure 3. Note that the aliphatic CH stretching bands of the PSOC 785 extract, the top spectrum in this series, are stronger and sharper than those of the other extracts, indicating a higher concentration of long chain alkanes. Accordingly, when the program was applied to these spectra we not only obtained the bands characteristic of the aromatic CH stretching mode, but also negative peaks associated with sequences of CH_2 units, as shown in figure 4. In other words, PSOC 785 did not belong in this set. The character of its CH_2 groups is different to those of the other samples (which were obtained from much higher rank coals) and this resulted in the negative sharp peaks. We are presently obtaining the spectra of a wider range of samples so that we can "clump" similar spectra together for analysis. Nevertheless, this preliminary application illustrates the potential of the technique and also indicates that it might find additional utility in identifying different types of structural features.

References

1. Fuller, M. P., Hamadeh, I. M., Griffiths, P. R. and Lowenahupt, D. E., Fuel, 61, 529 (1982).
2. Griffiths, P. R., Wang, S. H., Hadeh, I. M., Yang, P. W. and Henry, D. E., ACS Fuel Chemistry Preprints, 28(1) 27 (1983).
3. Painter, P. C., Starsinic, M., and Coleman, M. M. in Fourier Transform Infrared Spectroscopy; Applications to Chemical Systems. Vol. 4, p.169, (Edited by J. R. Ferraro and L. J. Basile) Academic Press (1985).
4. Cameron, D. G., and Moffatt, D. J., JTEVA 12, 78 (1984).
5. Honigs, D. E., Hieftje, G. M. and Hirschfeld, T., Applied Spectroscopy, 38, 317 (1984).

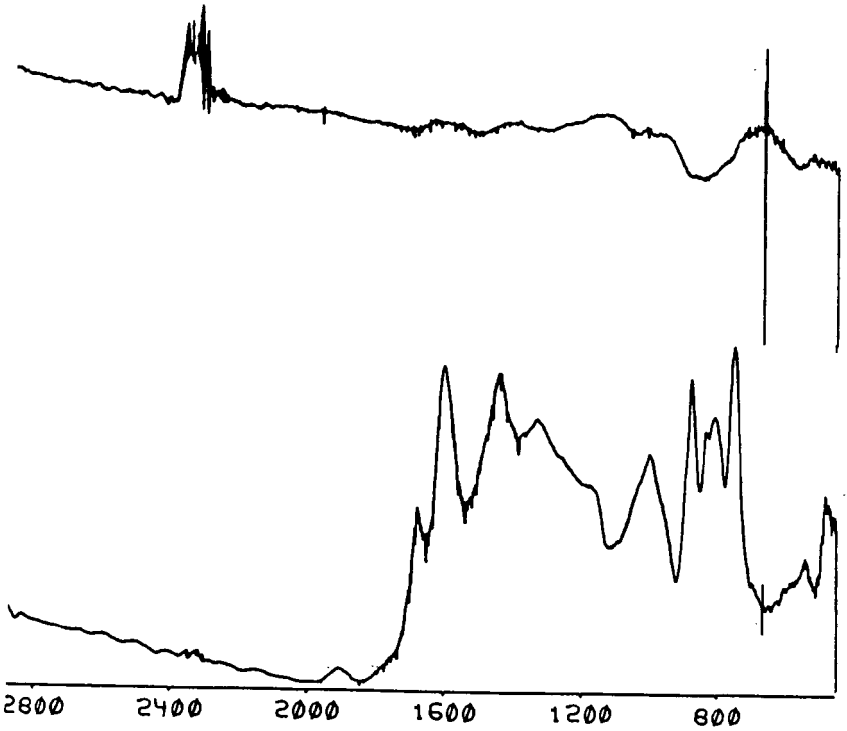

Figure 1. Top; Spectrum of PSOC 161 (92% C) prepared as a KBr pellet. Bottom; same sample run in diffuse reflectance.

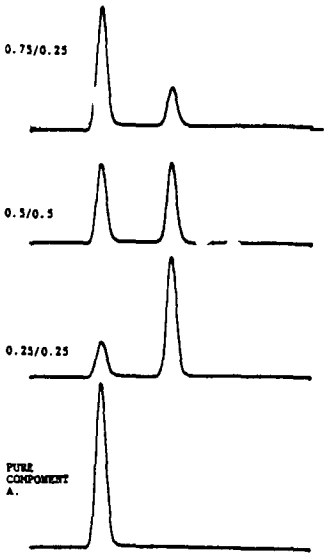

Figure 2. Top to bottom, spectra of a mixture of two components and the generated spectrum of the pure component.

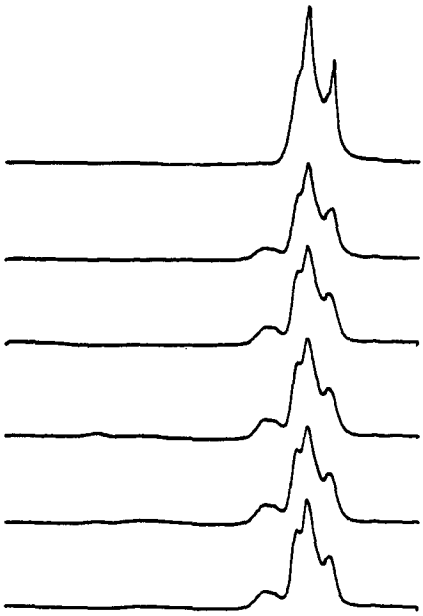

Figure 3. Top to bottom, CH stretching modes of pyridine extracts of PSOC's 785, 801, 1192, 1195, 1196 and 1198.

Figure 4. Generated spectrum of aromatic CH component.