

CHARACTERIZATION OF OIL SHALE  
BY FTIR SPECTROSCOPY

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INTRODUCTION

The optical advantages and data handling capabilities of Fourier transform infrared (FT-IR) instruments have led to a resurgence of the use of infrared spectroscopy for the characterization of energy related materials. Most of the work that has so far been reported has involved the characterization of coal. Methods for the quantitative determination of mineral matter (1-5) and various studies of the organic components of coal (6-13) have been published. The only paper (to our knowledge) concerning the application of FT-IR to the study of shale was reported by Solomon and Miknis (14). These authors considered the analysis of both the mineral and organic components. However, they reported a number of problems with the mineralogical analysis of certain shales, particularly the determination of the carbonates present in samples from Colorado. The analysis of the organic component was confined to the aliphatic C-H stretching region of the spectrum near  $2900\text{ cm}^{-1}$ . Unfortunately, these bands are often all that is detectable of the organic component in the infrared spectra of shales.

If FT-IR is to provide further insight into shale structure and composition, some of the problems associated with mineralogical analysis will have to be solved. In terms of the characterization of the organic component, studies of kerogen should provide more information concerning chemical structure than allowed by an analysis of whole shale. In this communication we will consider preliminary results of applying FT-IR to these particular problems.

FT-IR ANALYSIS OF MINERAL MATTER IN SHALE

The qualitative identification of the major mineral components present in a number of shale samples using dispersive infrared techniques was reported by Estep et al (15). In most of the shales considered the major mineral species were carbonates and the clays illite and montmorillonite. Because of the overlap of the bands of these components, a quantitative analysis could not be performed. We have discussed in a number of publications the advantages and utility of FT-IR in the analysis of such complex multicomponent systems (1-5). Essentially, a library of the spectra of mineral standards, stored in digital form on disk or magnetic tape, is used to analyze the shale (or coal low temperature ash) under consideration. The spectrum of the standard is subtracted from that of the shale. The subtraction parameter that results in the complete elimination of the bands of the particular mineral being subtracted then provides a measure of the weight fraction of that mineral present in the shale. There are some subtleties to the method that can be applied, such as the use of least-squares spectral fitting programs (4), but the method is relatively straightforward and will be demonstrated below. However, before proceeding to this illustration it is necessary to emphasize the critical importance of sample preparation.

In initial work (1) we ground samples in a Wig-L-Bug in the presence of 300 mg of KBr, so that standard infrared pellets could be subsequently pressed. Optimum

grinding times were determined for our particular grinding equipment. It is important to note that absorbance values in the final spectra of minerals and shale should be less than 1.0, to ensure a linear relationship between the amount of material in the infrared beam and the intensity of the absorption bands (Beer-Lambert law). This in turn requires the use of an accurate micro-balance, since optimum results are usually obtained with between 0.1 and 0.2 mg of sample for clays and between 0.3 to 0.5 mg for most other minerals. The grinding time was naturally dependant on the type of equipment used and could be as long as 30 mins for old equipment or as little as 45 secs for new, more vicious, instruments.

Recently a problem with this method of sample preparation as applied to the hard minerals has been pointed out to us by Elliott and co-workers (16). The absorption values for minerals such as quartz and dolomite can be dramatically increased by pregrinding the mineral with just a small amount of KBr (25 mg) followed by further grinding with the rest of this alkali halide (275 mg). However, this procedure produced less satisfactory results for the clays, presumably due to agglomeration and subsequent poor mixing of these materials under severe grinding conditions. Consequently, our procedure has been modified to account for these results in the following manner.

- 1) Clays are prepared using the method outlined above. With the new model Wig-L-Bug only 45 seconds of grinding are required.
- 2) Quartz and carbonate samples are prepared by first grinding the mineral with 25 mg of KBr for 30 seconds. The rest of the KBr (275 mg in our procedure) is then added to the capsule and the material is ground for another 30 seconds.

Because of the preponderance of 'hard' minerals in most shale samples, the latter method was used in sample preparation. Our initial studies indicate that the problems encountered by Solomon and Miknis (14) in determining carbonates in shale could (at least in part) be due to sample preparation problems. Carbonate minerals have strong bands near  $1400\text{ cm}^{-1}$ , but different species are more clearly differentiated by the characteristic bands near  $880$  and  $720\text{ cm}^{-1}$ . The peak positions of four different carbonate samples are listed in Table 1. Figure 1 compares the infrared spectra of two different shales. The strong bands at  $882$  and  $729\text{ cm}^{-1}$  indicate that the most prevalent carbonate present is dolomite. We originally considered that it would be a straightforward task to subtract the bands of this mineral thereby revealing the presence of other carbonates, which could then be analyzed. However, we found that if the  $729\text{ cm}^{-1}$  band was subtracted out there still remained considerable absorption at  $882\text{ cm}^{-1}$ . Other carbonates have bands in this region, but at different frequencies (see Table 1). One possible explanation is the presence of isomorphous cation substitution in the dolomite. It has been shown that Fe can replace Mg in the dolomite structure in continuously variable proportions to give ankerite. (17) The spectra of ankerite samples we had available, however, showed frequency shifts as well as intensity changes compared to the spectrum of dolomite. Finally, at the moment we were about to abandon this problem in despair, we found that the sample preparation procedure recommended for hard minerals by Elliott et al (16) provided a solution to the analysis of shale. We had already preground our shale samples in the Wig-L-Bug as we had obtained them in the form of large particles. Pregrinding in the presence of the rest of the KBr, resulted in a change of the relative intensities of the  $882$  and  $729\text{ cm}^{-1}$  bands, as shown in Figure 2. The difference spectra obtained by subtracting each of the two dolomite samples from that of the shale are shown in Figure 3. It can be seen that the subtraction of the dolomite prepared according to Elliott et al (16) worked very well leaving carbonate bands that, in fact, corresponded to one of our ankerite standards. Consequently, we believe it is now possible to obtain a good quantitative analysis of mineral matter in shale, but the importance of careful and reproducible sample preparation procedures in such analysis cannot be overemphasized.

FT-IR determination of the mineralogical composition of a set of shale samples (Green River shale, Mahogany Zone) is now being performed. The initial results are presented in Table 2, but are at the time of writing incomplete in that the analysis of the clay component could not be performed. A spectrum of one of the shale samples is shown in Figure 4 and the clay component is characterized by a strong band near  $1040\text{ cm}^{-1}$  and a second weak band near  $470\text{ cm}^{-1}$ . Unfortunately, we could not find an illite or montmorillonite standard in our spectral library that provided a match in terms of band positions and relative intensities. We are presently attempting to separate this clay from the shale in order to obtain the correct "standard".

The necessity of using mineral standards for analysis may at first sight seem a major disadvantage of the FT-IR method. However, all other techniques (eg x-ray diffraction) for quantitative analysis also rely on standards for calibration. At least with infrared subtraction methods subtle differences in the character and composition of a particular mineral in a shale relative to a "standard" can become apparent. For example, the subtraction of the spectrum of a dolomite sample from that of a shale is illustrated in Figure 5. If the  $882\text{ cm}^{-1}$  band is subtracted to the baseline, as shown in the difference spectrum in this figure, the  $725\text{ cm}^{-1}$  band is slightly negative, indicating over subtraction of this band. However, subtraction based on the elimination of the  $882\text{ cm}^{-1}$  band is probably correct, since the very strong  $1450\text{ cm}^{-1}$  band is eliminated by this procedure. The complete difference spectrum is shown in Figure 4 and it can be seen that with the  $1450\text{ cm}^{-1}$  band subtracted a weak absorbance centered near  $1460\text{ cm}^{-1}$  remains and this band can be assigned to  $\text{CH}_2$  bending modes of the organic component. The difference in intensity of the  $728\text{ cm}^{-1}$  band between the spectrum of the dolomite present in the shale and that of the standard is probably due to the presence of a small amount of iron in the dolomite lattice. FT-IR can only be used to quantitatively determine major mineral components, but the sensitivity of the spectrum to such subtle effects indicates the relative ease of selecting the correct standard. Subtraction of the wrong mineral naturally leads to obviously distorted difference spectra. However, the analysis will only be as good as the standards available, and we are presently extending our mineral library to include a number of dolomite and ankerite samples so as to cover a range of compositions.

#### FT-IR ANALYSIS OF KEROGEN

Solomon and Miknis (14) demonstrated that the aliphatic C-H content, as measured by the intensity of the C-H stretching mode near  $2920\text{ cm}^{-1}$ , correlated reasonably well with oil yield. We have determined similar results in initial studies. Figure 6 shows the aliphatic CH stretching region of three shale samples. The plots have been made on the same absorbance scale, although the baselines have been offset for clarity. The oil yield of the samples decreased in the samples going from the top spectrum A to the bottom C, the values being 33.6, 20.3 and 14.2 gallons per ton, respectively. Not surprisingly, the intensity of the CH stretching modes is proportionally higher in the samples yielding the largest quantity of oil. A plot of the peak height of the  $2920\text{ cm}^{-1}$  bands against yield or, as shown in Figure 7, organic carbon content, shows a roughly linear relationship (more scatter is observed in the plot of absorbance against oil yield, and our results are similar in this respect to those obtained by Solomon and Miknis (14)). Since Kerogen is a multi-component system we would anticipate some variations in the width at half height of the bands from sample to sample. Consequently, we are also in the process of determining peak areas (from curve-resolved spectra). Determinations of this type should certainly prove a useful tool for assaying oil shales, but in terms of structural characterization it necessitates the use of careful, well-defined curve resolving techniques and we have discussed such methods in terms of the analysis of coal(18). Derivative methods are used to determine the number of curves in a spectral profile and also provide initial estimates of the values of various band parameters (peak position, width at half-height) used in the subsequent curve resolving process. If these procedures are followed we can have a high degree of confidence in the results. The resolution of the C-H stretching region into five bands is shown in Figure 8. All

of these bands can be readily identified from well-established group frequencies. The bands at 2924 and 2855  $\text{cm}^{-1}$  are the asymmetric and symmetric stretching modes (respectively) of methylene units; the bands at 2956 and 2872  $\text{cm}^{-1}$  are the asymmetric and symmetric stretching modes of methyl groups; the 2895  $\text{cm}^{-1}$  band has a contribution from lone C-H groups, but overtone and combinations of bending modes near 1450  $\text{cm}^{-1}$  also absorb at this frequency. Curve resolving of the C-H stretching region has proved very successful, with a standard deviation of  $\pm .2$  for the initial set of oil shale samples.

If we obtained values of the extinction coefficients, relating individual band intensities to the concentration of the corresponding functional groups, then we would have at our disposal useful structural information. It has been shown that paraffin standards can be used to obtain extinction coefficients for the analysis of petroleum fractions (19,20). However, in order to be able to use extinction coefficients from long chain paraffins (which can be readily prepared as KBr pellets, unlike the shorter chain material), we must determine whether the kerogen is sufficiently saturated and contains sequences of  $\text{CH}_2$  units, so that extinction coefficients can be transferred with minimal error.

This knowledge can be determined from the 700 to 900  $\text{cm}^{-1}$  region of the spectrum, where characteristic bands can be assigned to aliphatic  $\text{CH}_2$  rocking modes and aromatic C-H out-of-plane bending modes. This region of the spectrum of a kerogen obtained from one of our Green River shale samples is shown in Figure 9, where it is compared to the spectrum of a kerogen obtained from a Rio Blanco shale. These samples were prepared at Gulf R&D by consecutively washing the whole shale with HCl, HF and HCL acids to remove the mineral components. The spectrum of the kerogen from Green River shale is dominated by a band at 724  $\text{cm}^{-1}$ , characteristic of the  $\text{CH}_2$  rocking mode of sequences of four or more methylene units (21). Consequently, we can have a high degree of confidence in applying extinction coefficients determined from various paraffins to the analysis of this shale. However, the Rio Blanco shale also displays overlapping bands near 730, 745 and 820  $\text{cm}^{-1}$  characteristic of 3,2 and lone  $\text{CH}_2$  groups, respectively. This shale would not seem to be a candidate for analysis based on extinction coefficients determined from long chain paraffins. Incidentally, the bands at 820  $\text{cm}^{-1}$  and 745  $\text{cm}^{-1}$  could have a small contribution from aromatic bending modes, and more work is necessary to sort out such relative contributions. We are still in the process of applying the extinction coefficients determined from paraffins to the analysis of our Green River shale samples, but these results clearly demonstrate a number of important points. The most important of these is that an examination of the  $\text{CH}_2$  rocking region of the spectrum of shale reveals important structural information. In addition, the differences in the spectra of various shales in this region of the spectrum suggests that a single set of extinction coefficients will probably not prove adequate for analysis of all shales. Instead a range of values will probably have to be determined according to the sequence distribution of  $\text{CH}_2$  units and the presumably corresponding degree of branching of the aliphatic structure present.

Finally, it is important to briefly indicate that other types of structural information can be obtained from the infrared spectrum of kerogen. Figure 10 shows the spectrum of a kerogen from Green River shale and it can be seen that there is a complex of bands between 1800 and 1500  $\text{cm}^{-1}$ . The band near 1700  $\text{cm}^{-1}$  is almost certainly due to carboxylic acid groups, but high frequency shoulders due to other carbonyl structures are apparent (possibly esters) and a strong band near 1630  $\text{cm}^{-1}$  is also intriguing. By analogy with the spectrum of coal (13) this band could be due to aromatic structures, a highly conjugated hydrogen bonded carbonyl or COO groups. FT-IR studies of acid and alkali washed material and methylated samples (to convert COOH groups to esters) should clarify these assignments and allow further structural information to be obtained.

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TABLE 1

CHARACTERISTIC BANDS IN THE FTIR SPECTRA OF CARBONATES.

<u>Mineral</u>	<u>Origin</u>	<u>Bands cm<sup>-1</sup></u>
Ankerite	Hancock County, Illinois	876 727 713
Dolomite	Eiginvin Twp., Ontario	882 729
Siderite	Nova Scotia	873 741
Calcite	Unknown Origin	877 713

TABLE 2

MINERALOGIC ANALYSIS OF GREEN RIVER SHALE SAMPLES  
WEIGHT % OF WHOLE SHALE

<u>GRDC Sample</u>	<u>Microcline</u>	<u>Quartz</u>	<u>Dolomite</u>	<u>Calcite</u>	<u>Aragonite</u>
13	10	15	22	15	15
14	15	15	35	-	-
15	8	15	25	10	9
16	10	16	30	9	14
17	15	15	20	15	11
18	12	15	27	8	14
19	12	17	35	7	10
20	10	16	34	9	15
21	5	16	28	15	11
22	10	18	35	10	-

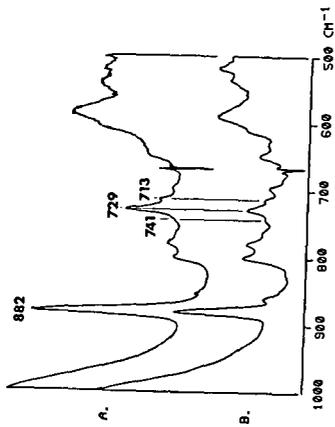


Figure 1: FT-IR spectra in the region 1000 to 500  $\text{cm}^{-1}$  of two shale samples A. Piceance Basin Shale. B. Green River shale (Spectra recorded on Digilab FTS-15B, 400 scans, resolution 2  $\text{cm}^{-1}$ ).

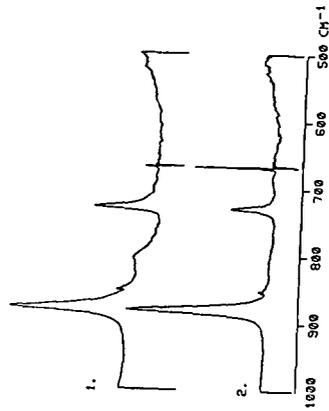


Figure 2: FTIR spectra of dolomite samples 1. Prepared using old grinding method. 2. Prepared according to Elliott et al (ref. 16).

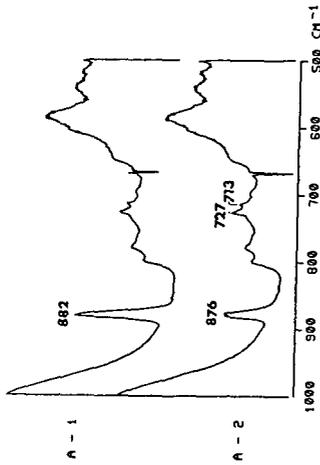


Figure 3: Difference spectra; A-1. Piceance basin shale - 'old' dolomite. A-2. Piceance basin shale - 'new' dolomite.

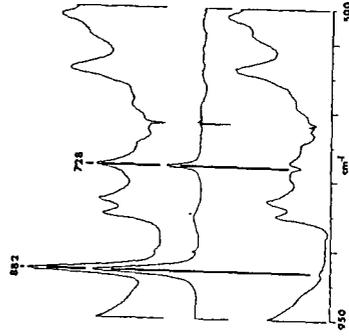


Figure 4: Top FT-IR spectrum of Green River shale, Mahogany zone sample. Middle. FT-IR spectrum dolomite. Bottom. Difference spectrum obtained by eliminating 882  $\text{cm}^{-1}$  band.

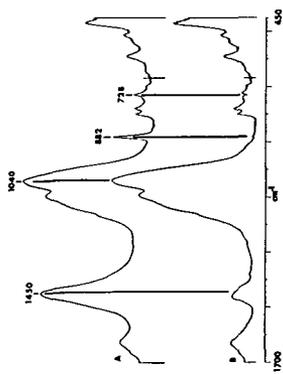


Figure 5: A. FT-IR spectrum Green River shale sample. B. Difference spectrum after subtraction of spectrum of dolomite.

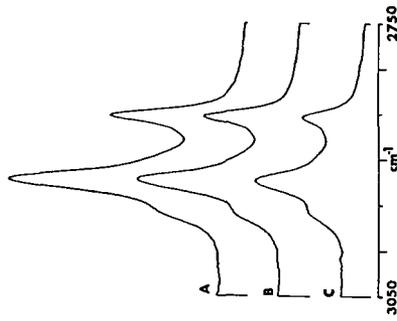


Figure 6: FTIR spectra of samples of Rio Blanco shale. A. 33.6 C.P.T. B. 20.3 C.P.T. C. 14.2 C.P.T.

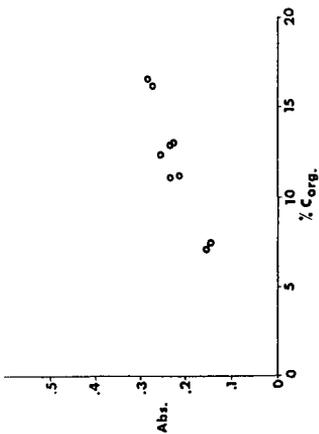


Figure 7: Plot of peak height 2924  $\text{cm}^{-1}$  band against % organic carbon for Green River shale samples.

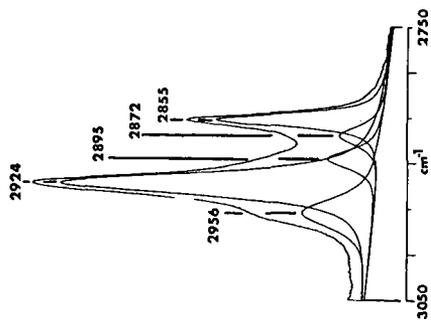


Figure 8: Curve resolved aliphatic C-H stretching region of FT-IR spectrum of shale sample.

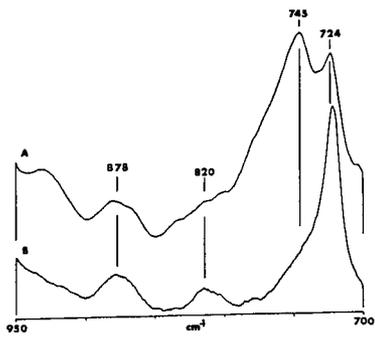


Figure 9: A. FT-IR spectrum (950-700  $\text{cm}^{-1}$ ) of kerogen from Rio Blanco shale. B. FT-IR spectrum of kerogen from Green River shale.

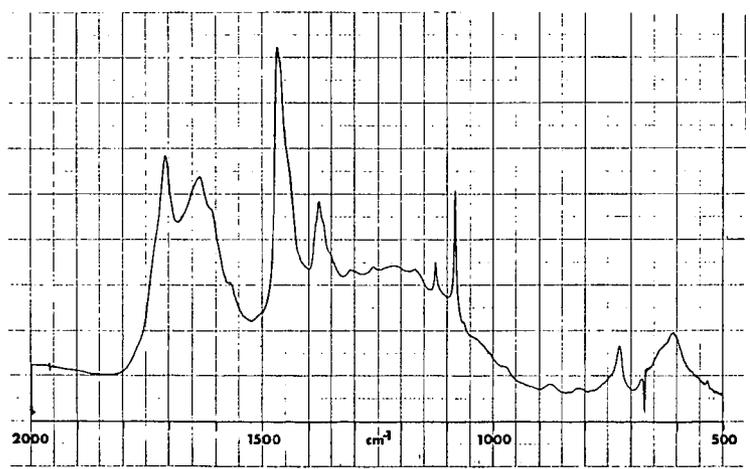


Figure 10: FT-IR spectrum of kerogen from Green River shale.