

FUEL

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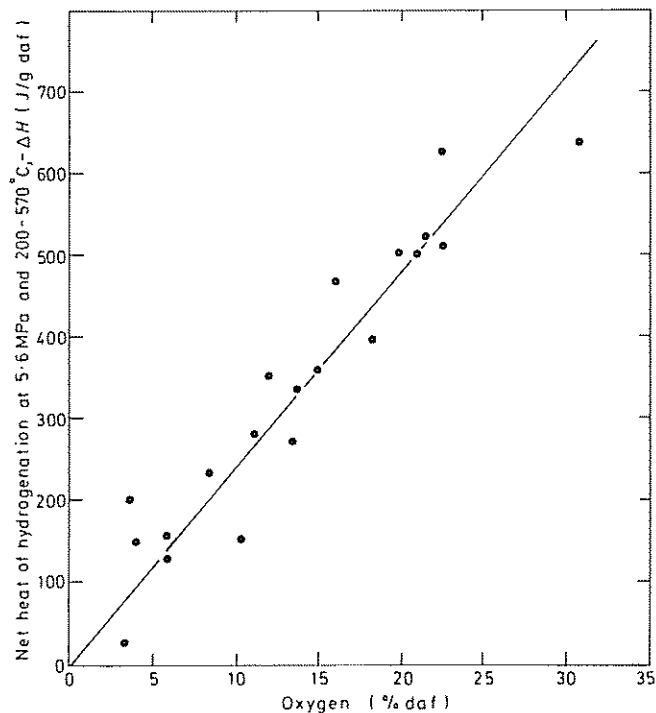


Figure 1 Exothermic heats of hydrogenation as a function of oxygen content of raw coals

their paper, exothermic heats of hydrogenation were correlated with coal rank (% C daf) and less successfully with weight loss (% daf).

One wonders why the authors did not attempt a correlation of exothermic heat of hydrogenation with oxygen content (% O daf). Such a correlation of the authors' data is presented here in Figure 1. One notes that the coefficient of correlation with oxygen content is higher than with carbon content, indicating a better fit.

Mahajan, Tomita, Nelson and Walker suggested that at least part of the exothermic heat of hydrogenation might be due to the reaction of hydrogen with carbon-oxygen complexes in the coal. Carrying their suggestion a step further, one finds that the slope of the correlation of heat of hydrogenation versus oxygen content (about 2400 J/g O) corresponds quite reasonably with the difference in the heats of formation of water and carbon dioxide (about 2800 J/g O), considered as a rough estimate of the heat of reaction of hydrogen with carbon-oxygen complexes. Clearly, such a suggestion grossly oversimplifies a very complex problem in chemical thermodynamics; nevertheless, such a generalization might be of utility for estimating purposes.

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Fourier transform infrared study of acid-demineralized coal

Paul C. Painter, Michael M. Coleman, Robert G. Jenkins and Philip L. Walker Jr

Department of Material Sciences, Pennsylvania State University, University Park, PA 16802, USA

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We have recently reported a quantitative method for the analysis of mineral matter in coal through the application of the subtraction routine of computerized Fourier transform infrared (FTIR) instruments¹. Briefly, the analysis is based on the successive subtraction of the spectra of mineral standards from the spectrum of a mixture, usually the low-temperature ash (LTA) of the coal under investigation. Provided that the weights of the mineral standards and the original mixture are accurately measured, the appropriate weight fractions can be determined from the subtraction parameter required to remove the characteristic bands of each mineral from that of the mixture. The method has a number of advantages over conventional infrared band intensity measurements. Overlapping bands of similar mineral species are readily separated so that in many cases a complete analysis of an LTA can be performed. Previously, only those minerals having prominent, separately resolved characteristic bands could be determined². However, by successively subtracting spectra of mineral standards from that of an LTA, the weakly absorbing species are revealed when the strong bands of the major components are successively removed.

Most of the methods developed for the quantitative measurement of mineral matter in coal are based on an analysis of the appropriate LTA. However, recent work in this laboratory³ has demonstrated that the composition of

an LTA is not always an accurate reflection of the mineral matter in the original coal. In particular, organic sulphur can be fixed as sulphate during ashing. Consequently, the development of a method capable of analysing the mineralogical composition of a coal directly, or at least allowing the determination of the conversion processes that occur during ashing, is of some significance. In this communication we will present the results of an application of FTIR to this problem.

The direct mineralogical analysis of a coal sample depends upon the ability of FTIR to produce a high signal-to-noise ratio difference spectrum. Our approach was to first obtain a high quality infrared spectrum of the whole coal. This sample was then acid demineralized by treatment with HCl and HF under nitrogen. The procedure is similar to that described by Radmacher and Mohrhauer⁴ and Bishop and Ward⁵. (The treatments used in this study were for longer periods of time at lower temperatures, in order to minimize modification of the organic components.) The spectrum of the demineralized coal was then obtained. Subtraction of this spectrum from that of the original coal should then be characteristic of the mineral matter, or more precisely the mineral components that are removed by acid treatment. The spectra of an Illinois No. 6 coal (Burning Star Mine) and this sample subsequent to demineralization are compared in Figure 1A. Spectra were re-

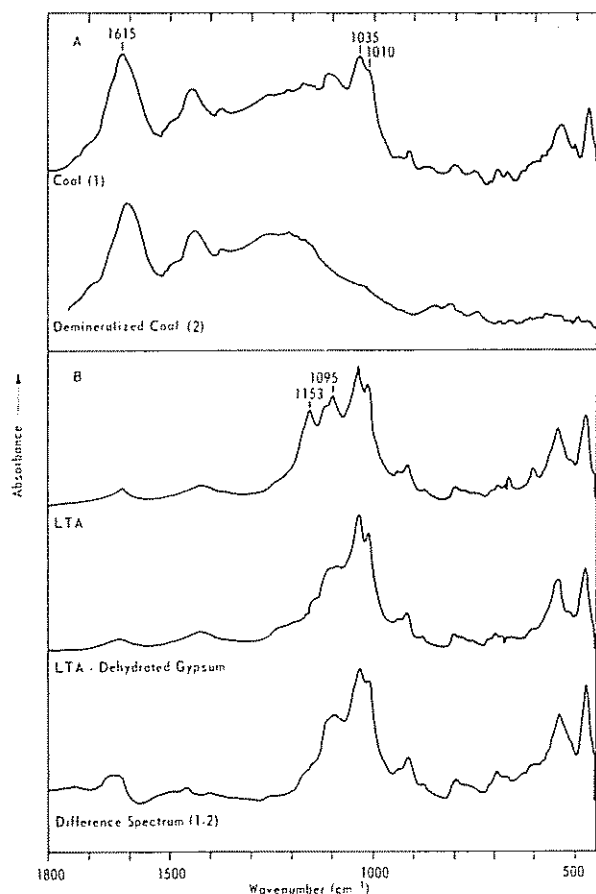


Figure 1 (A) Top: Infrared spectrum of Illinois No. 6 coal, Burning Star Mine. Bottom: Infrared spectrum of this sample demineralized by acid treatment
(B) Top: Infrared spectrum of the low-temperature ash of this coal. Middle: Difference spectrum obtained by subtracting the spectrum of dehydrated gypsum from that of the LTA. Bottom: Difference spectrum obtained by subtracting the spectrum of the acid-demineralized coal from that of the original coal

corded on a Digilab FTS 15/B instrument using 400 'scans' at a resolution of 2 cm^{-1} . The absence of any new bands near 1700 cm^{-1} ($\text{C}=\text{O}$ stretching region) in the spectrum of the demineralized sample indicates that no significant oxidation of the organic component occurred during acid treatment. A difference spectrum was obtained by subtracting the bands of the organic component to the baseline, and is shown in *Figure 1B*. This spectrum can be com-

pared to that of the LTA of this coal, shown in the same Figure. The most prominent difference in the two spectra is the presence of bands near 1153 cm^{-1} and 1095 cm^{-1} , characteristic of dehydrated gypsum, in the spectrum of the LTA. If the spectrum of this latter mineral is subtracted from the LTA, then it can be seen from *Figure 1B* that the resulting difference spectrum is very similar to the difference spectrum obtained from the original and demineralized coal. The results are a direct demonstration of calcium sulphate formation during the LTA process.

In principle, this method can be used to analyse the mineral matter in coal directly, without resorting to any form of ashing. The difference spectrum produced by the procedure described above can be quantitatively analysed by successive subtractions of the bands of mineral standards, as in the analysis of the spectrum of LTA described previously¹. However, depending upon the particular coal under consideration, the method is not always as accurate as the analysis of an LTA. Even though the signal averaging capability of FTIR can be used to obtain extremely high quality spectra of whole and demineralized coal, the noise-level of the resulting difference spectrum will always be inferior to that of the corresponding LTA obtained by co-adding an equal number of interferograms (spectra). Consequently, unless the mineralogical composition of a particular coal is high, we have found that a more accurate determination can be achieved by analysing the LTA of a coal and using the acid-demineralization method to ascertain the type and degree of conversion of mineral species during ashing.

ACKNOWLEDGEMENT

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ANNOUNCEMENT

A short course on **FIRE AND EXPLOSION** will be held at the University of Leeds, England, on 4-6 April 1978.

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