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Published by IPC Science and Technology Press Ltd

Fourier Transform Infrared study of mineral matter in coal. A novel method for quantitative mineralogical analysis

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(Received 13 June 1977)

A novel method for the quantitative determination of mineral matter in coal is reported. The low-temperature ash of coal is analysed by means of absorbance spectral subtraction of individual components. The spectra of individual minerals, stored in digital form on computer memory, are multiplied by appropriate weighting factors and subtracted from the spectrum of the low-temperature ash, so that the characteristic bands of the mineral are removed. Provided that the weight of each mineral in the infrared beam is known then the weight fractions can be determined from the weighting factors. Successive subtraction starting with the most strongly absorbing components reveals the minor or less strongly absorbing species, which could not previously be determined by infrared spectroscopy. The analysis of several mixtures and of the low-temperature ash of various coal samples is reported.

Coals are complex mixtures of organic and inorganic species. The inorganic fraction is primarily composed of minerals and to a lesser extent organo-metallic compounds and exchangeable cations¹. The mineral component is usually considered detrimental to many of the processes which utilize coal either for the direct production of energy or as a source of other fuels. The high pyritic sulphur content of many coals is an obvious source of sulphur dioxide pollution in combustion, while in liquefaction processes the presence of minerals leads to problems in filtration, abrasion, reactor solids build-up and catalyst poisoning. Nevertheless, certain minerals are known to have a beneficial catalytic effect in conversion processes. The mineralogical composition of a particular feed coal is therefore a significant variable in process design and in attaining an understanding of the behaviour of coals in these processes.

Direct mineralogical analysis of coal by infrared spectroscopy has until now been severely limited by the overlap of the characteristic mineral absorption bands with the broad bands of the organic phase. Because the mineral concentration is minor it is difficult to use this technique for qualitative identification of constituents, yet alone quantitative analysis. Other analytical methods are similarly limited. A major breakthrough occurred with the development of the low-temperature ashing (LTA) process which removes the organic material with apparently only minimal change in the mineral matter. Estep *et al.*² demonstrated that a number of minerals in an LTA could be identified and determined by classical infrared techniques. O'Gorman and Walker³ used these methods in conjunction with X-ray diffraction and chemical analysis to determine the mineral matter in a number of coals.

Despite the success of this work a number of major problems remain. In the analysis of complex mixtures, infrared spectroscopy has always been restricted by overlap and superposition of bands of the constituents. Curve-resolving techniques can be used but require a prior knowledge of the number of superimposed bands. However,

kaolinite, quartz, gypsum, and calcite have characteristic bands that are usually isolated and resolved, allowing quantitative measurements. In certain cases pyrite can also be measured in the far i.r., but there is a serious overlap with the bands of kaolinite and successful analysis requires the absence of this clay².

Recently, there has been a major advance in infrared spectroscopic instrumentation. The advent of Fourier Transform Infrared (FTIR) spectroscopy has, for example, led to significant improvements in the characterization of polymeric materials⁴. Although the use of an interferometer rather than a system of gratings and slits allows the recording of superior spectra, particularly in the analysis of highly absorbing materials, it is the versatility of the dedicated on-line mini-computer that has proved to be the most useful feature. Spectra can be stored on disc or magnetic tape in digital form and recalled at any time for manipulation. Thus, the spectrum of a material can be recorded before and after a reaction and the two spectra subtracted to yield a difference spectrum that accentuates the chemical changes that have occurred⁵. Bands previously obscured by the absorption of unreacted material are often revealed by this procedure, making available valuable new information.

The success so far achieved in the application of FTIR to a number of analytical problems suggests that the method is potentially a powerful tool for mineralogical analysis. In this communication we describe a novel method for the quantitative determination of mineral matter in coal based on the application of spectral subtraction to the analysis of low-temperature ash. The method is accurate and allows the determination of components previously intractable to infrared analysis.

EXPERIMENTAL

Coal samples (Illinois No. 6, Burning Star and Monterey Mines) were provided by Mobil Research and Development

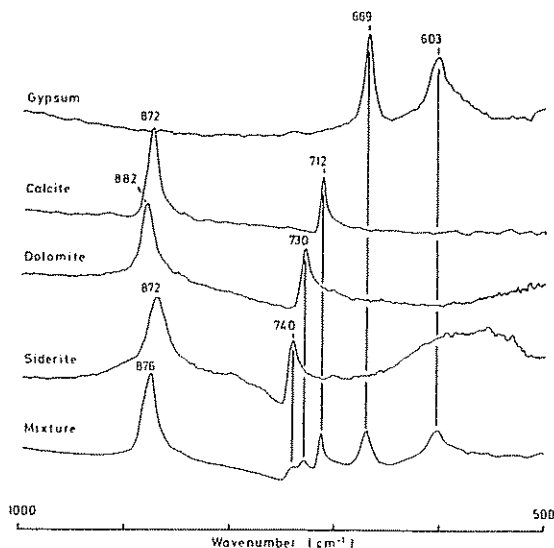


Figure 3 A comparison of the absorbance infrared spectra of (top to bottom) gypsum, calcite, dolomite, siderite and a mixture of equal weights of all four of these minerals

The quantitative aspects of the absorbance subtraction method can be illustrated by reference to a simple mixture of equal weights of gypsum, calcite, dolomite and siderite. The spectrum of the mixture, scale expanded between 1000 cm^{-1} and 500 cm^{-1} , is compared to those of the individual components in Figure 3. Separately resolved bands, which can be assigned to specific minerals, are observed in the spectrum of the mixture in addition to a band at 876 cm^{-1} that is a composite of contributions from calcite, siderite and dolomite. Provided that there is no vibrational coupling among the various constituents, a situation normally observed for simple mineral mixtures and various coal-derived materials such as low-temperature ash, then the absorption of the mixture at any particular frequency, A , is given by a sum of the absorption of the components at that frequency. For the general case of an n component system:

$$A = a_1bc_1 + a_2bc_2 \dots + a_nbc_n \quad (1)$$

where a_n is the extinction coefficient of component n at frequency, b is the thickness of the sample, and c_n is the concentration of component n in the mixture. This equation can be rewritten in terms of the weight fraction x_n of component n and the total weight W of the sample in the prepared pellet as:

$$A = a_1x_1W_1 + a_2x_2W_2 \dots + a_nx_nW_n \quad (2)$$

Figure 4 shows the separate and successive subtraction of the mineral components from the spectrum of the simple mixture described above. First, the gypsum component, characterized by bands at 669 cm^{-1} and 603 cm^{-1} , is eliminated. If we consider the 603 cm^{-1} absorption, then this procedure can be expressed mathematically as:

$$K_A \cdot a_G^{603} \cdot x_G W_M - K_B a_G^{603} \cdot 1 \cdot W_G = 0 \quad (3)$$

The spectra of the mixture (subscript M) and the gypsum (subscript G) are respectively multiplied by K_A and K_B , which are varied until the contribution of gypsum is eliminated from the spectrum of the mixture. It then follows

that the weight fraction of gypsum in the mixture, x_G , is given by:

$$x_G = \frac{K_B}{K_A} \cdot \frac{W_G}{W_M} \quad (4)$$

It should be noted that the extinction coefficient term, a_G^{603} , is eliminated and the procedure holds for all frequencies. This is illustrated in Figure 4 where the composite band at 876 cm^{-1} in the spectrum of the mixture can be observed to shift in frequency with the successive subtraction of calcite and dolomite until in the final difference spectrum this band is at 872 cm^{-1} , characteristic of siderite.

Even though overlapping bands can in certain cases be accurately subtracted (see below), it is usually advantageous to choose as a basis for subtraction a specific band characteristic of a particular mineral, so that values of K_A and K_B can be determined with a minimum of error. Since it is often the case that more than one such band can be directly observed, for example at 669 cm^{-1} and 603 cm^{-1} in the spectrum of gypsum, the method is inherently more accurate than the conventional absorption measurements of a single characteristic band.

The band at 669 cm^{-1} in the spectrum of gypsum does not subtract 'correctly', unlike the band at 603 cm^{-1} . It can be seen that there is both a positive and negative component that is magnified in successive difference spectra. This effect is due to a shift in frequency of the 669 cm^{-1} band during sample preparation, because grinding can induce partial dehydration of gypsum. The spectral subtraction method is extremely sensitive to such small frequency shifts and accurately reflects minor changes in the state of a material.

RESULTS AND DISCUSSION

We have applied the absorbance subtraction routine to the quantitative analysis of both mixtures of clays and minerals

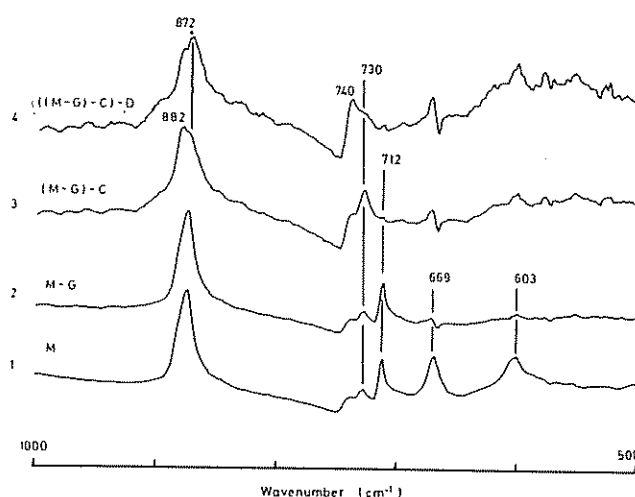


Figure 4 The successive subtraction of the components of the infrared spectra of a mixture of gypsum, calcite, dolomite and siderite.

1. Spectrum of mixture
2. Spectrum of mixture (spectrum 1) after subtraction of the gypsum component
3. Spectrum 2 - calcite
4. Spectrum 3 - dolomite

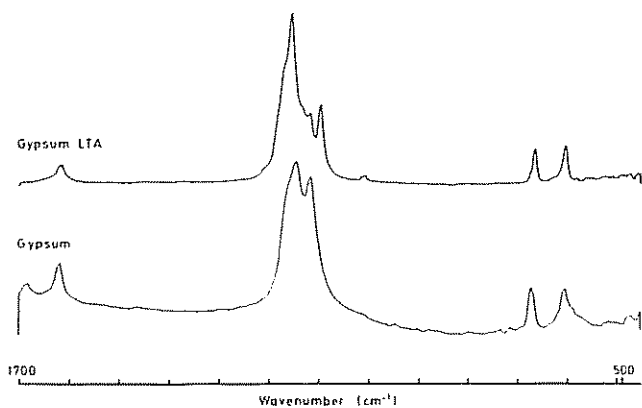


Figure 7 A comparison of the infrared spectrum of gypsum with that of an LTA of the same material

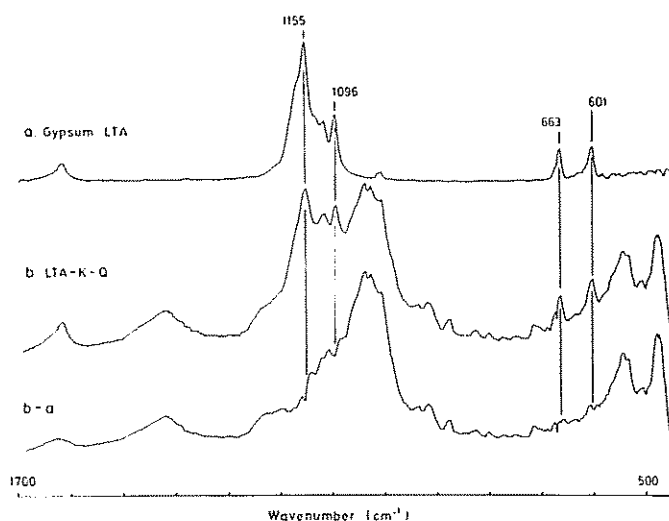


Figure 8 The subtraction of the spectrum of ashed gypsum from the difference spectrum shown in Figure 6.
 a. Infrared spectrum of LTA of gypsum
 b. Difference spectrum LTA - kaolinite - quartz
 b - a. Difference spectrum, LTA - kaolinite - quartz - gypsum

is shown in Figure 8. Even though the subtraction parameters are most easily determined by subtracting the isolated characteristic bands, now observed at 663 cm^{-1} and 601 cm^{-1} , the above considerations demonstrate the importance of performing the subtraction upon the entire spectrum rather than an isolated, scale-expanded portion.

The infrared spectra of other minerals containing bound water, such as kaolinite and montmorillonite, were determined to be unaffected by the ashing process.

4. Calcite

The spectral subtraction of calcite from the LTA difference spectrum is shown in Figure 9. The procedure is straightforward and based on the elimination of the characteristic bands near 1420 cm^{-1} , 872 cm^{-1} and 712 cm^{-1} . There was no evidence for any other carbonate minerals in this particular sample.

5. Other carbonate minerals

Calcite can be distinguished from other carbonate minerals such as siderite and dolomite by the characteristic frequencies of the bands near 700 cm^{-1} . A mixture of such minerals can be analysed in a straightforward manner by

spectral subtraction, as illustrated in Figure 4 for a simple mixture.

6. Illite and montmorillonite

Subsequent to the spectral subtraction of kaolinite, quartz, gypsum, and calcite, the only bands remaining in the final difference spectrum (between 1700 cm^{-1} and 450 cm^{-1}) can be identified as being due to illite and montmorillonite. The infrared spectrum of these two clays is compared to the final difference spectrum in Figure 10. It is apparent that the spectra are very similar, making an accurate analysis of the individual components difficult. We determined two methods that gave good results with mixtures of known composition. The first is based on the difference in the observed frequency of the strongest band,

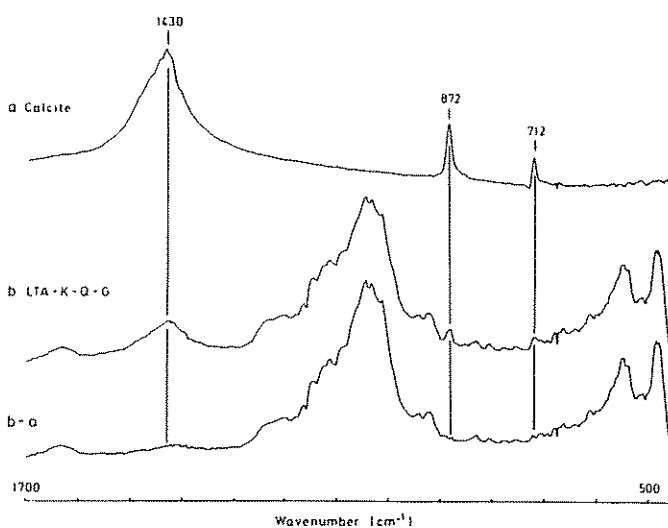


Figure 9 The subtraction of the spectrum of calcite from the difference spectrum shown in Figure 8.
 a. Infrared spectrum of calcite
 b. Difference spectrum, LTA - kaolinite - quartz - gypsum
 c. Difference spectrum, LTA - kaolinite - quartz - gypsum - calcite

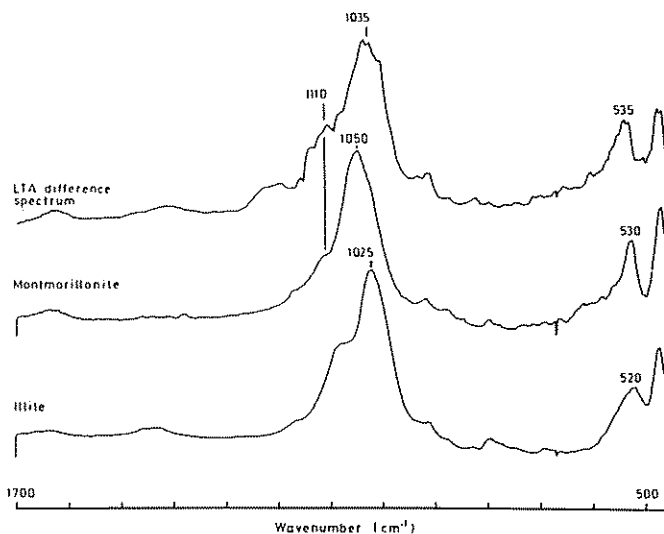


Figure 10 A comparison of (top to bottom) the difference spectrum shown in Figure 9 with the infrared spectra of montmorillonite and illite

Table 1 A comparison of the weight fractions of mineral mixtures determined by FTIR with known values

Mineral or clay	Weight fraction (%) as prepared	Weight fraction (%) by FTIR	Weight fraction by X-ray diffraction (quartz, calcite) and conventional i.r. (kaolinite)
Analysis of Mixture I			
Kaolinite	6	5 ± 1	5
Gypsum	17	15 ± 2	
Quartz	46	45 ± 5	68
Calcite	10	14 ± 2	13
Illite	11	11 ± 2	
Montmorillonite	11	10 ± 2	
Total	101	103	
Analysis of Mixture II			
Kaolinite	9	9 ± 1	10
Gypsum	16	15 ± 2	
Quartz	20	18 ± 2	38
Calcite	14	18 ± 2	15
Illite	29	32 ± 5	
Montmorillonite	12	14 ± 3	
Total	100	104	

Table 2 Analysis of kaolinite and pyrite by FTIR

Mix		Wt fraction (%) as prepared	Wt fraction (%) by FTIR
Mix 1	Kaolinite	15	16 ± 2
	Pyrite	40	36 ± 6
Mix 2	Kaolinite	25	26 ± 2
	Pyrite	30	27 ± 5
Mix 3	Kaolinite	35	33 ± 3
	Pyrite	25	23 ± 5

Quantitative analysis of low-temperature ash

The weight fractions of the major mineral and clay components, measured by FTIR, of the LTA of four different Illinois No. 6 coals are listed in Table 3. Samples (a) and (b) were both from the Burning Star mine and consisted of different size fractions of the ground material. The analyses of these samples were apparently complete (total 100%) and the determination of calcite and pyrite was in good agreement with X-ray results. As above, X-ray analysis of quartz did not agree with FTIR measurements while absorbance measurements at 910 cm^{-1} for kaolinite consistently gave weight fractions that were slightly above the values determined by spectral subtraction. In view of the possible intensity contribution of illite and montmorillonite at this frequency we consider the FTIR values to be more accurate.

Sampling can be a major problem in the analysis of coals since the distribution of minerals in a seam may not be random and in addition various minerals have different grinding characteristics. However, considering these variables there is a fair agreement between the calculated weight fractions of these two samples of different size range. A

second problem is the possibility of chemical change in the LTA process. Sample (c) is another LTA of Illinois No. 6 coal, Burning Star mine, prepared under different conditions. It can be observed that there is good agreement with the analysis of minerals in samples (a) and (b) apart from gypsum. There is apparently no gypsum in this sample. Under the conditions encountered in the low-temperature asher it is possible to fix sulphur from the organic fraction by reaction with calcite. In the case of low-rank coals containing large amounts of exchangeable calcium cations, gypsum will always be formed in the low-temperature asher. Thus the analysis of this mineral performed on LTA does not always accurately reflect the composition of the original coal. Obviously, care must be taken to set the conditions of ashing to ensure that gypsum is not formed.

Sample (d) is yet another Illinois No. 6 coal, but from the Monterey mine. Apart from calcite the mineralogical composition of this material is very similar to samples (a) and (b).

Table 3 Analysis of LTA by FTIR

	Wt fraction by FTIR	Wt fraction by conventional i.r. and X-ray diffraction
(a) Illinois No. 6, Burning Star (<45 μm)		
Kaolinite	12 ± 1	16
Gypsum	6 ± 1	
Quartz	23 ± 2	16
Calcite	6 ± 1	6
Illite	13 ± 3	
Montmorillonite	6 ± 2	
Pyrite	32 ± 5	27
Total	98%	
(b) Illinois No. 6, Burning Star (45–70 μm)		
Kaolinite	10 ± 1	16
Gypsum	10 ± 1	
Quartz	18 ± 2	34
Calcite	9 ± 1	10
Illite	18 ± 3	
Montmorillonite	9 ± 2	
Pyrite	29 ± 5	30
Total	101%	
(c) Illinois No. 6, Burning Star, HRI 3689 sample		
Kaolinite	11	
Gypsum	Trace	
Quartz	18	
Calcite	10	
Illite	13	
Montmorillonite	14	
Pyrite	Not determined	
(d) Illinois No. 6, Monterey		
Kaolinite	9 ± 1	
Gypsum	11 ± 1	
Quartz	22 ± 2	
Calcite	Trace	
Illite	11 ± 2	
Montmorillonite	12 ± 2	
Pyrite	18 ± 2	

