

## INFRARED SPECTROSCOPIC STUDIES ON COALS OF PAKISTAN

AZHAR M. SYED

*PCSIR Laboratories, Karachi*

M.Z. PIRZADA and ZAHID RAZA

*PCSIR Fuel and Leather Research Centre, Karachi*

(Received June 5, 1974; revised September 24, 1974)

**Abstract.** IR studies on four lignites, from two different regions of Pakistan, have been made and compared with the Sharigh lignite having good caking properties. A close correlation of caking properties of the lignite to the appearance of out-of-plane bending vibrations of aromatics in the region  $745\text{--}875\text{ cm}^{-1}$  has been used to classify these lignites. Minerals have been detected by the spectrum of ash from the lignite for a preliminary study.

IR spectroscopic investigation of coal and coal products was started by Cannon and Sutherland.<sup>1,2</sup> They assigned some of the absorption bands in coals to chemical groupings and showed that carbon in aromatic systems formed a major part of the chemical constituent of coal. Cannon<sup>3</sup> made further assignments such as oxygen-containing groups,  $\text{CH}_2$  and  $\text{CH}_3$  groups, and both single ring and condensed aromatic structures. He also discussed the spectra of different ranks of coal and interpreted the decrease of oxygen-containing group to the increase in rank.

Brown<sup>4</sup> carried out a more detailed study of coals by investigating the spectra of vitrains and examined the changes in the spectra of heated coals up to  $800^\circ\text{C}$ . Between  $400\text{--}500^\circ\text{C}$ , a loss of aliphatic CH and phenolic OH groups was indicated. Physical properties of heated coals at different temperatures were also discussed.

Friedel and Queiser<sup>5</sup> compared the spectrum of anthraxylon from bituminous coal with the spectra of sucrose and cellulose chars and observed marked similarities in both the structures. They also explained that it was not necessary to presume the presence of polynuclear condensed aromatic structure in coal for explaining the IR spectra.

Low rank coals, classified as lignites have not been studied in detail. A survey reveals that Pakistan has about 440 million ton coal reserves and the major part is lignite. Berkowitz and Schein<sup>6,7</sup> first observed that hard black lignite from Sharigh had the same caking properties corresponding to a free swelling index (FSI) of 5–5.5, belonging to coal of high carbon-contents.

The purpose of the present study had been (i) to obtain the IR spectra of a few varieties of lignites and to compare them with the spectrum of Sharigh lignite, and (ii) to study the minerals of different lignites by their ash spectra.

The presence of minerals in any coal is very common and the knowledge of associated minerals is necessary for the recovery and utilization of these fuel resources. For example, carbonate minerals have been shown to increase the retention of sulphur during coal combustions.<sup>8,9</sup>

### Experimental

The lump coals were finely powdered and dried at low temperature for 24 hr in vacuum. Pellets for IR spectra were prepared by transferring 1 mg pre-ground coal in an agate-mortar and again ground for 20 min with 300 mg KBr powder. The mixture was pressed in a die at 24,600 psi, for 10 min during which the air around the sample was pumped out. The resulting 13 mm dia pellet was scanned immediately on a Perkin-Elmer 137 IR spectrophotometer. A blank KBr pellet, prepared under similar conditions was kept in the reference beam. The only objection to the KBr technique was the production of OH absorption during the preparation of pellet, even if extreme precautions were used. This OH absorption could not be compensated completely by a blank.

Coal ash was prepared by standard British methods and the spectra were recorded in KBr pellets.

### Results and Discussion

Table 1 shows the frequencies observed in the spectrum of Sharigh lignite. These frequencies are almost the same as assigned for the spectra of vitrain<sup>4</sup> and high volatile bituminous coals,<sup>5</sup> except that the following frequencies have not been observed clearly; (i) An absorption band near  $1160\text{--}1300\text{ cm}^{-1}$  due to C—O stretching of phenols or aromatic ethers has not been observed. This may be due to the large amount of minerals, interfering in that region. (ii) The weak C—H aromatic frequency at  $3030\text{ cm}^{-1}$  has not been detected in Deghari lignite, others show very weak shoulder (Fig. 1).

The structure of coal has already been discussed in detail by several authors and is not mentioned here. The only important topic to discuss is, the changes of spectra arising from low-rank and high-rank coals. Brown<sup>4</sup> has shown that the hydrogen-bonded OH frequency near  $3300\text{ cm}^{-1}$  increases in intensity as compared to the CH frequency, with the decrease in carbon contents. This has been observed in all the four lignites (Fig. 1), and it has been estimated by comparing the IR spectra of coal<sup>4</sup> that the carbon contents in these lignites may not exceed more than

75%. The other substances present may be high sulphur, moisture and ash-contents. The average sulphur contents in these lignites has been estimated to be about 5.5% by chemical methods.

Another characteristic feature of high rank coal is the appearance of three absorptions (860, 820 and 750  $\text{cm}^{-1}$ ), associated with out-of-plane deformation vibrations of one, two and four adjacent CH groups, respectively. These absorptions in the normal lignites are absent and is an indication that, in these lignites the aromatic rings are heavily substituted and cross-linked. Therefore, heating of coal does not produce plasticity and related swelling. In a semicoking lignite, such as the one found in the Sharigh region

the presence of these absorptions (Fig. 1) indicates that, despite its low carbon-contents, the aromatic rings are free of cross-linking to give a product which is thermoplastic and, therefore, having good caking properties. The lignite has almost all the absorptions which have been observed in coals of high carbon-contents.<sup>4</sup> The lignites from Jhimpir (Sind) and Deghari (Baluchistan) show one weak absorption in the long wavelength region. The third lignite from Sor-Range (Baluchistan) does not show any absorption in that region. It may, therefore, be predicted that two lignites having slight appearance of absorption in the long wavelength region have better caking properties than the one which does not show any absorption.

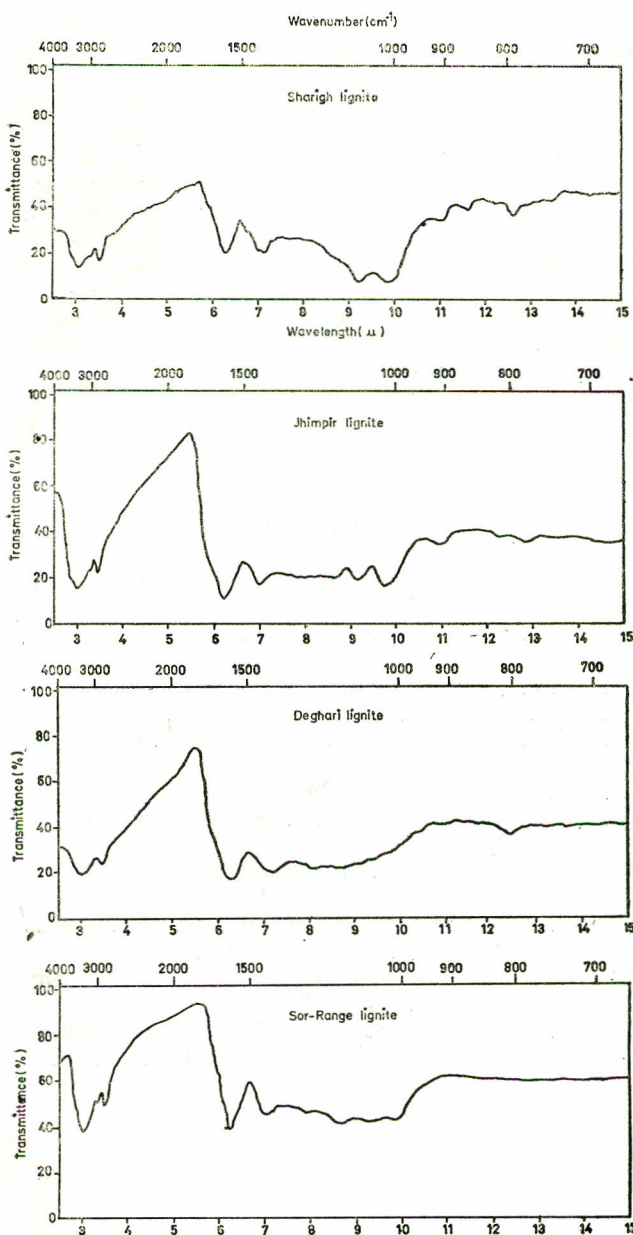


Fig. 1.

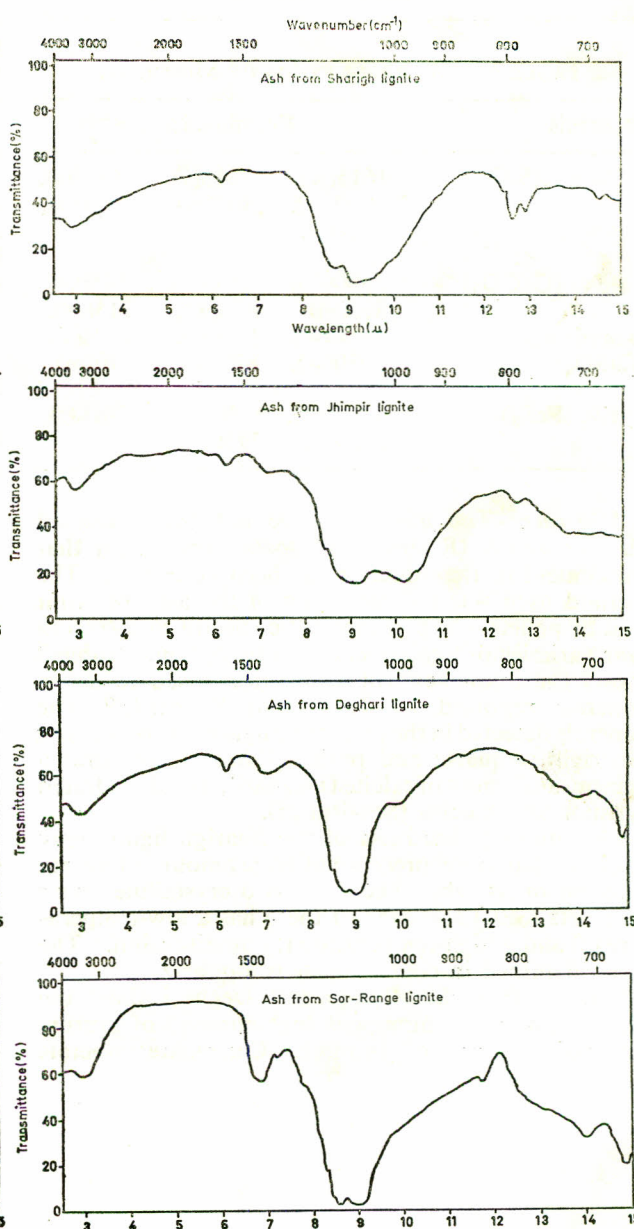


Fig. 2.

TABLE 1. ASSIGNMENT OF FREQUENCIES OBSERVED IN THE SPECTRUM OF SHARIGH LIGNITE.

Frequencies (cm <sup>-1</sup> )	Assignment
3300 (s)	Hydrogen-bonded OH
3030 (w.sh.)	Aromatic C—H stretching
2925,2850 (w)	Aliphatic CH <sub>2</sub> and CH <sub>3</sub> stretching frequencies
1600 (s)	Aromatic ring frequency
1700 (w.sh.)	C=O group may be present
1430 (m)	CH <sub>2</sub> groups
1070 (s)	Mineral absorption
1035 (m)	Aromatic C—O, intense in aromatic ethers
860,820,750 (w)	Aromatic C—H out-of-plane deformation frequencies

TABLE 2. IR FREQUENCIES OF MINERALS.

Minerals	Frequencies (cm <sup>-1</sup> )		
$\alpha$ -Quartz (SiO <sub>2</sub> )	1615(w), 1010(w), 695(m).	1315(s), 800(m),	1085(s), 780(m),
Calcite (CaCO <sub>3</sub> )	2500(w), 875(m),	1820(w), 850(w),	1450(s), 715(m).
Dehydrated-gypsum (CaSO <sub>4</sub> )	1450(w), 1010(w),	1150(s), 875(w),	1100(s), 670(m).
Pyrite (FeS <sub>2</sub> )	1125(m), 915(m),	1030(s), 795(w).	1010(s),

*Minerals.* The minerals have not been detected directly by the IR spectra of coals, because for that enrichment of the minerals has been necessary. The method used was the recording of the ash spectrum in KBr pellets. Fig. 2 shows the spectra of ash from four varieties of lignites under examination. Table 2 shows the frequencies of absorptions used to detect minerals reported by Hunt and Wisherd.<sup>10</sup> The minerals detected in the respective lignites were  $\alpha$ -quartz (Sharigh),  $\alpha$ -quartz and pyrite (Jhampir), dehydrated gypsum and traces of calcite (Deghari), and dehydrated gypsum and calcite (Sor-Range).

The unusual hardness of the Sharigh lignite may be attributed to the presence of large amount of quartz detected in its ash. There are two crystalline forms of quartz (SiO<sub>2</sub>) and each of these has a low-temperature ( $\alpha$ ) and a high-temperature ( $\beta$ ) modification. The form identified in coal samples is  $\alpha$ -quartz.

Lignites from Sor-Range and Deghari show the presence, of calcite alongwith high contents of gypsum the main source of sulphur. Carbonate minerals

occurring in coals play a significant role in many of its uses. As mentioned earlier, carbonate minerals increase the retention of sulphur during combustion of the coal. These type of coals are of great interest in air-pollution research. Sprunk and O'Donnell<sup>11</sup> have shown that variation of calcite-contents in coal can affect ash yield as well as fusion temperature. Carbonate minerals can also affect the yield of volatile matter which is an important determination in coal analysis, and is used as a parameter for evaluating coals for combustion and carbonisation.

Lignite from Jhampir shows the presence of pyrite alongwith quartz. This lignite has been selected from an area which is geographically different from the area of other three lignities.

The method of making ash used in this work, may not give the original amount of minerals present and, therefore, the enrichment of minerals by low-temperature ash formation under 150°C in oxygen plasma produced by an r.f. field, is very essential. This technique removes all the organic matter and unaltered mineral residues of coal are left for analysis. This type of work has been under consideration for future studies on these coals, which may easily be used for quantitative analyses of minerals. The minerals detected by a less accurate method of ashing have only been included to make a complete preliminary study on these lignites.

*Acknowledgements.* Authors would like to thank Mr. M. Aslam, Director, PCSIR Laboratories, Karachi for providing facilities and encouragement to carry out this work. We are also indebted to Mr. A.H. Chotani, Head, Fuel and Leather Research Centre, Karachi for providing coal samples and for his interest in this work.

## References

1. C.G. Cannon and G.B.B.M. Sutherland, *Nature*, **156**, 240 (1955).
2. C.G. Cannon and G.B.B.M. Sutherland, *Tans. Faraday Soc.*, **41**, 279 (1945).
3. C.G. Cannon, *Nature*, **171**, 308 (1953).
4. J.K. Borwn, *J. Chem. Soc.*, 752 (1955).
5. R.A. Friedel and J.A. Quieser, *Anal. Chem.*, **28**, 22 (1956).
6. N. Berkowitz, *Fuel*, **29**, 138 (1950).
7. N. Berkowitz and H.G. Schein, *Fuel*, **31**, 19 (1952).
8. W.H. Ode and F.H. Gibson, *Bureau of Mines Report 5931* (1962), pp. 11.
9. G. Whittingham, *Brit. Coal Util. Res. Assoc. Monthly Bull.*, **18**, 581 (1954).
10. J.M. Hunt, M.P. Wisherd and L.C. Bonham, *Anal. Chem.*, **22**, 1478 (1950).
11. G.C. Sprunk and H.J. O'Donnell, *Bureau of Mines, Technical Paper 648* (1942), pp. 67.