

FT. INFRARED SPECTROSCOPIC ANALYSIS OF VARIOUS PAKISTANI COALS

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FT-Infrared spectroscopy has been used for the structural characterization of five Pakistani coals. These include Lakhra coal from Sind Province, Makerwal coal from Punjab Province, Sor-Range and Sharigh coals from Baluchistan Province and Kotli coal from Azad Kashmir. Almost all the peaks observed in the spectra of these coals have been assigned to various functional groups. Important similarities and differences observed in the FT-IR spectra of these coals, point to the similarities and differences between the structures of these coals.

Key words: FT-IR spectroscopy, coals.

Introduction

Pakistan being an energy deficient country needs to exploit all its possible resources for meeting its energy requirements. Since Pakistan has substantial reserves of coal which can be used for energy production, it is desirable to find the chemical composition and structure of various types of Pakistani coals. Significant deposits are mainly found in Sind (Lakhra), Punjab (Makerwal) and Baluchistan (Sor-Range, Sharigh) provinces of Pakistan. In Azad Kashmir, sizable deposits of coal are found near Kotli. The Lakhra, Makerwal, Sharigh and Sor-Range coals are generally classified as lignitic to sub-bituminous while Kotli coal is semianthracitic in nature.

The use of infrared spectroscopy for determination of functional groups in chemical compounds is well known. For coal this technique was first used by Cannon and Sutherland [1,2]. In recent years the use of FT-IR spectroscopy is becoming more popular for functional group determination of coals [4-8]. The mineral matter in coal can be quantitatively and qualitatively determined by FT-IR Spectroscopy [9-11]. The use of FT-IR has certain definite advantages over conventional Infrared Spectroscopy. These include better signal to noise ratio, better resolution and mathematical manipulation of spectra such as subtraction of one spectrum from another is possible by this technique.

By this method overlapping of signals can be greatly avoided and quantitative determination of various functional groups as well as mineral content in a particular coal can be carried out.

In this paper characterization of various Pakistani coals i.e. Lakhra, Makerwal, Sor-Range and Sharigh coals as well as Kotli coal from Azad Kashmir is described.

Experimental

The samples of coals were obtained from Habibullah Mines Ltd., The coal was ground to 60 mesh size and dried in an oven for eight hours at 110° and stored in a desiccator. The

proximate analysis, elemental analysis, sulphur determination, and calorific values were obtained on a Leco MAC-400, Leco CHN-600, Leco SC-132, Leco CV Par Adiabatic Calorimeter respectively. The fourier transform infrared spectra were obtained on a Perkin Elmer Model-1800 infrared spectrometer. The infrared spectra were run as KBr pellets. Three mg. of dried coal was mixed with 300 mg. of potassium bromide and finely milled in a porcelene container for 3 minutes and then pressed into a pellet at a pressure of 10 metric tons. A blank KBr pellet was used as a reference spectrum. The number of scans used was 64 with a resolution of 2 cm⁻¹. The Infrared spectra were recorded in the range of 4000-400 cm⁻¹. During the recording of the spectra the instrument was continuously purged with dry nitrogen. The various conditions for recording the FT-Infrared spectra including the weight of the coal, the weight of the KBr and grinding time were kept strictly identical for all the coal samples. In addition all spectra were obtained in triplicate to ensure that reliable results have been obtained.

Results and Discussions

The proximate and total analysis of various Pakistani coals is shown in Table 1.

The results of the proximate analysis indicate that maximum moisture is present in Sor-Range and Lakhra coals while other Pakistani coals have lower moisture content. The ash content is maximum in Makerwal coal and minimum in Sor-Range coal. The volatile matter is minimum in semi anthracitic Kotli coal while it is quite high in other Pakistani coals.

The ultimate analysis on dry ash free basis showed that Lakhra coal has the highest oxygen and sulphur content. The important parameter, C/H ratio which indicates extent of aromatic ring substitution and condensation is highest in Kotli coal and lowest in Lakhra coal. This indicates that the semi anthracitic Kotli coal has a highly condensed and substituted aromatic ring system while the lignitic Lakhra coal has a

TABLE 1. PROXIMATE AND TOTAL ANALYSIS OF PAKISTANI COALS

Proximate	Lakhra	Makerwal	Sharigh	Sor-Range	Kotli
Moisture	10.6	2.4	4.6	11.3	2.2
Ash	18.4	36.8	13.6	7.9	28.0
Volatile Matter	39.0	32.3	40.7	39.3	16.6
F.C.	32.0	28.4	41.1	41.5	53.2
Sulphur	7.0	5.7	3.7	2.1	3.0
C.V.	7,760	7,890	11,600	10,320	10,275
<i>Total</i>					
on dry ash free basis					
Carbon %	64.5	75.3	72.0	72.5	79.7
Hydrogen%	7.2	7.3	6.6	7.5	4.9
Nitrogen%	2.0	1.5	2.0	2.1	1.3
Sulfur %	9.8	9.4	4.5	2.7	4.4
Oxygen by diff.	16.5	6.5	14.9	15.3	9.7
Atomic C/H	0.75	0.86	0.91	0.80	1.34

minimum content of these polysubstituted aromatic rings.

The FT-IR, of various Pakistani coals is shown in Fig. 1. For the purpose of discussion the spectra of organic fraction of coal is discussed first followed by the discussion of spectra due to inorganic fraction (Mineral Matter). The various

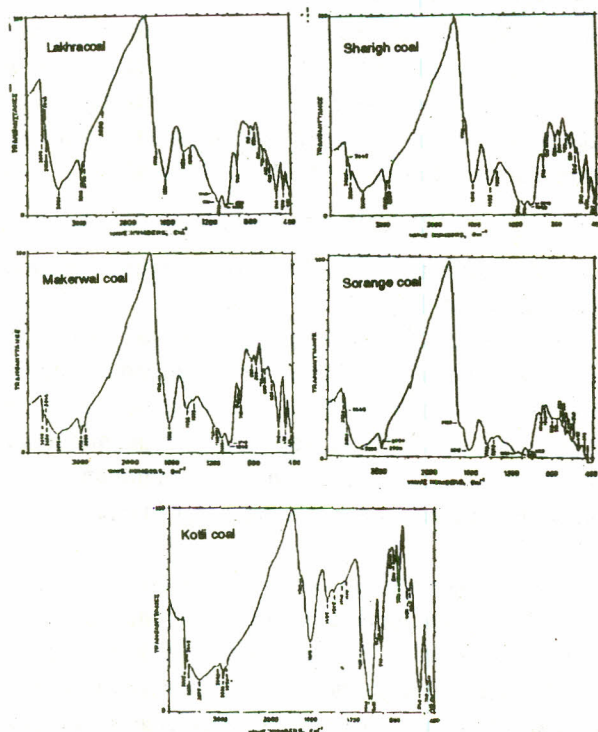


Fig. 1. The FT-IR Spectra of Pakistani Coals.

functional group and their absorption frequencies along with absorption due to minerals observed in Pakistani coals are given in Table 2. It is observed that while Makerwal and Sharigh coals provided sharp and well defined peaks in the infrared spectra, the Lakhra spectrum was less resolved while the Sor-Range coal produced a least well resolved spectrum. This may be due to greater reflectance of the Infrared radiation by the mineral matter in Sor-Range coal.

Organic Structural analysis of coal · A broad absorption band is observed at 3375 cm^{-1} in all the Pakistani coals. This peak is mainly due to hydrogen bonded OH groups. Since this peak is also observed in samples which have been dried at 110° for 6 hours in an oven, the contribution due to H_2O to this

TABLE 2. INFRARED ABSORPTION FREQUENCIES OBSERVED IN PAKISTANI COALS AND THEIR ASSIGNMENTS

Frequency	Assignments
3695	Clay minerals such as kaolinite, illite and montmorillonite group.
3645)	
3620)	
3375	
3040	Hydrogen bonded O-H
2920)	Aromatic C-H stretching
2850)	
	Aliphatic CH_3 , CH_2 and C-H stretching frequencies
1710	Carbonyl group
1615	Aromatic polynuclear, structures, hydrogen bonded O-H electron transfer between aromatic carbon 'rafts'
1435	
1375	
1140)	CH_2 in bridges
1110)	
1100)	CH_3 group on aromatic rings
1040)	
1010)	Clay minerals
940)	
910)	
880)	Clay minerals
810)	
800)	
750)	
690	Aromatic bands
665	C-S stretching
600	Vinylic C=C
540)	Ionic sulphate
470)	
415	Clay minerals
	Iron pyrites

peak is expected to be negligible. The hydrogen bonded NH groups may also contribute to the intensity of this band, although this contribution is expected to be insignificant due to lower percentage of nitrogen in these coals.

A small peak at 3040 cm^{-1} is observed only in Kotli coal which is caused by aromatic C-H stretching frequency. It shows that the Kotli coal has more unsubstituted aromatic carbons than other Pakistani coals. The absence of this band in various Pakistani coals indicates that the ratio of aromatic hydrogen to aliphatic hydrogen is lower in these coals. Usually in lignites this band is absent.

The peaks at 2920 cm^{-1} and 2850 cm^{-1} which appear as sharp peaks of medium intensity may be assigned to aliphatic and alicyclic CH_3 , CH_2 , and CH , groups although the major contribution is expected to be due to CH_2 groups. The intensity of peak at 2920 cm^{-1} is always greater than the peak at 2850 cm^{-1} indicating the presence of long aliphatic chains in all the coals. In Sor-Range coal the intensity of peak at 2920 cm^{-1} is greater than the peak at 3375 cm^{-1} while reverse is true for other coals which indicates that there is more wax content in Sor-Range coal than any other Pakistani coal.

The peak at 1710 cm^{-1} appears only as a small shoulder in all Pakistani coals which indicates that the carbonyl content is very small. Thus it could be concluded that most of the oxygen in these coals is present as -OH groups. The strongest peak in all the coals is observed at 1615 cm^{-1} which is due to aromatic C=C, vinylic C=C and due to other oxygen containing functional groups. We did not observe any peak at 1500 cm^{-1} which is due to C=C in benzene rings in any of these coals. This may be explained by two factors:-

(i) Increase in substitution of benzene ring is known to weaken this band.

(ii) As the degree of condensations the benzene ring increases this band is displaced to smaller wave numbers and may finally disappear in the strong absorption at 1435 cm^{-1} .

We have observed a strong band at 1435 cm^{-1} in all Pakistani coals which is mainly due to CH_2 groups in bridges but may also be partly due to aromatic C=C and strongly hydrogen bonded OH groups. This absorption band is strongest in Sharigh coal than in other Pakistani coals. This indicates that the length of aliphatic chains is longest in Sharigh coal which may also account for its higher coking properties. The band at 1357 cm^{-1} is mainly due to CH_3 groups while CH_2 group in cyclic structure may also partly contribute to this band. The intensity of this peak is much lower than the absorbance at 1435 cm^{-1} indicating that the number of methyl groups is much smaller than the methylenes present as long side chains.

In all these coals no etherial oxygen is observed an indicated by the absence of any absorption at 1270 cm^{-1} .

However in Kotli coal there is a weak absorption at 1300 cm^{-1} which may be due to C-O (phenols) C-O (alcohols) and C-O-C (aliphatic and aromatic). The bands between 880 cm^{-1} to 750 cm^{-1} have been assigned to aromatic structures. On the basis of report in the literature these bands have been ascribed as follows:-

- $870\text{-}872\text{ cm}^{-1}$: Aromatic HCC rocking (single and condensed ring) with isolated H.
- $800\text{-}805\text{ cm}^{-1}$ and shoulder at $778\text{-}780\text{ cm}^{-1}$: Substituted benzene ring with two neighbouring H and or angular condensed ring systems.
- $750\text{-}758\text{ cm}^{-1}$: O-substituted benzene rings mono substituted benzene rings and condensed ring systems.

These bands are most useful in determining the aromatic ring structure of a coal. The band at 880 cm^{-1} appears only as a weak shoulder in Lakhra, Makerwal, Kotli coal while it is strong in Sharigh coal and of medium intensity in Sor-Range coal. This indicates that in Sharigh and Sor-Range coals there is a greater percentage of substituted aromatic carbons than the other coals. The band at 800 cm^{-1} appears as a weak absorption in Lakhra, Makerwal, Sor-Range coals while it is strongest in Kotli coal and of medium intensity in Sharigh coal. This indicates a higher percentage of angular condensed aromatic rings in Kotli coal. The band at 750 cm^{-1} is strongest in Kotli coal, is of medium intensity in Lakhra, Makerwal and Sor-Range coals while is quite weak in Sharigh coal which indicates that in Sharigh coal there is a smaller percentage of ortho substituted benzene rings and mono substituted benzene rings, while in Kotli coal these structures are present in maximum amount.

A weak band at 690 cm^{-1} is observed in all the Pakistani coals except Kotli coal. This may be due to C-S bond. Relatively this band is more intense in high sulphur coals such as Lakhra, Makerwal and of lower intensity in low sulphur coals such as Sharigh and Sor-Range coals. A weak absorption at 660 cm^{-1} which is due to vinylic C=C in organic structures is also present in all Pakistani coals. This band is relatively of strong intensity in Sharigh and Kotli coals and weaker in other coals.

Mineral Matter in Coal. The minerals usually found in coals along with their infrared frequencies are given in Table 3. Most of the peaks in infrared spectra of coals can be assigned to clay minerals such as kaolinite, illite and montmorillonite group. The distinct peaks at 1100 cm^{-1} , 1040 cm^{-1} , 1010 cm^{-1} , 940 cm^{-1} , 915 cm^{-1} , 540 cm^{-1} and 470 cm^{-1} can all be due to kaolinite. In kaolinite group which have the formula $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, one of the silicate anions is replaced by a sheet of hydroxyl group and the various layers are linked by hydrogen bonding. The high frequency strong absorption at 3700 cm^{-1} and 3620 cm^{-1} and a weak shoulder at

TABLE 3. THE MINERALS USUALLY FOUND IN COAL AND THEIR I.R. ABSORPTION FREQUENCIES

S. No.	Minerals	Formulae	Frequencies
1.	Koalinite	$Al_4 [Si_4O_{10}](OH)_8$	3695, 3665, 3650, 3620, 1108, 1025, 1000, 910, 782, 749, 690, 530, 460, 422, 360, 340, 268.
2.	Illite	$K_1-1.5 Al_4 [Si_7-6.5 Al_1-1.5O_{20}](OH)_4$	3620, 1640, 1070, 1015, 920, 820, 750, 510, 460.
3.	Sodium Mon-morillonite	$(1/2Ca, Na) 0.7 (Al, Ng, Fe)_4 [(Si, Al)_4 O_{20}](OH)_4 \cdot nH_2O$	3625, 3400, 1640, 1110, 1025, 915, 835, 790, 515, 460.
4.	Calcite	$CaCO_3$	1782, 1420, 871, 842, 710, 310.
5.	Dolomite	$CaMg(CO_3)_2$	1435, 875, 730, 390, 355, 310.
6.	Pyrite	FeS_2	411, 391, 340, 284.
7.	Quartz	SiO_2	1160, 1065, 790, 770, 687, 500, 450, 388, 362, 256.
8.	Gypsum	$CaSO_4 \cdot 2H_2O$	3605, 3550, 1615, 1150, 1110, 1090, 1010, 660, 595, 450.

3640 cm^{-1} may be due to these inner O-H groups. In dioctahedral silicate the perpendicular Si-O vibration causes peaks at 1100 cm^{-1} . The Si-O-Si stretching vibration causes absorption at 1040 cm^{-1} and 1010 cm^{-1} . The Si-O bending vibration contribute to the strong absorption at 540 cm^{-1} and 470 cm^{-1} . Both these peaks can also be due to presence of ionic sulphates. The presence of gypsum is indicated by peaks at 1100 cm^{-1} , 1010 cm^{-1} , 600 cm^{-1} and 470 cm^{-1} . A weak absorption at 1160 cm^{-1} can be ascribed to the presence of the mineral quartz (SiO_2). Since the range of the infrared spectra measured in this study has been 4000-400 cm^{-1} , a weak absorption due to iron pyrites at 415 cm^{-1} can also be observed clearly in all the Pakistani coals.

Conclusions

Important conclusions concerning the structure of various Pakistani coals made in this study are listed below:

The proximate analysis results of various Pakistani coals showed a wide range of values for their moisture, ash, volatile matter, fixed carbon and calorific values.

(ii) The ultimate analysis showed Kotli coal having highest C/H ratio while the Lakhra coal the lowest value. This indicates that in Kotli coal the aromatic rings are most

highly condensed.

(iii) The FT-Infrared spectra provided an insight into the organic as well as mineral matter content of these coals. Extensive hydrogen bonding between OH groups was observed in all the coals. In the Kotli coal an aromatic C-H absorption at 3040 cm^{-1} which is absent in all other coals indicates that in this coal there is a higher percentage of unsubstituted aromatic carbon.

(iv) Most of the oxygen in these coals is present as OH groups.

(v) The absorption at 1435 cm^{-1} is strongest in Sharigh coal indicating that longest aliphatic chains are present in this coal which may account for the observed coaking properties of these coals.

(vi) The bands between 870 cm^{-1} and 750 cm^{-1} provide useful information concerning the aromatic ring structure of these coals. Thus it is concluded that the Sharigh coal has the highest percentage of polycondensed aromatic rings while Lakhra and Makerwal coal have much lower percentage of these type of rings. The percentage of angular condensed aromatic rings is highest in Kotli coal as shown by an intense absorption at 800 cm^{-1} . The Sharigh coal has the lowest percentage of monosubstituted aromatic rings as shown by a minimum absorption at 750 cm^{-1} .

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