STRUCTURAL STUDIES OF BARAPUKURIA COAL BY INFRARED SPECTROSCOPY

BY

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DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma. No other person's work has been used without due acknowledgement.

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Certificate

This is to certify that the research work embodying in this thesis has been carried out under our supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any other University.

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has been accepted as satisfactory in partial fulfilment of the requirements for the degree of **Master of Philosophy** in **Physics** and certify that the student demonstrated a satisfactory knowledge of the field covered by the thesis in an oral examination held on November 30, 1997.

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Abstract

Samples collected from different depth of bore-hole GDH-38 and GDH-39 of Barapukuria coal mine were characterized physically as well as structurally. The physical characterization was done by proximate analysis according to ASTM standards (D3172). The coals were found to have low moisture, low ash and high volatile matter and high calorific values on the basis of which the coals were ranked as high volatile bituminous type.

The average moisture and ash content of the coals of bore hole GDH-38 were about 2.69 wt % and 5.19 wt % respectively with an average volatile matter content of 35 % and Fixed carbon content of 61 % on dry ash free basis The average moisture and ash content of the coals of bore hole GDH-39 were about 3.48 wt % and 6.07 wt % respectively with an average volatile matter content of 34.5 % and Fixed carbon content of 64 % on dry ash free basis. The calorific values of the coals of these two bore-hole were about 15042 and 15044 Btu/lb respectively

Structural characterization was accomplished using infrared (IR) spectroscopy, X-ray diffraction (XRD) analysis and particle induced X-ray emission (PIXE) spectroscopy.

KBr technique was applied and a double infrared spectrophotometer was used to take the IR spectrum of the coal samples. Different organic and inorganic constituents were identified. The coals show considerable absorption in the aromatic ring vibration region at 1600 cm^{-1} and in the aromatic wag region between 900 and 700 cm^{-1}, which signifies that the coals contain

considerable portion of aromatic compound. Large absorption at 1130 cm^{-1} suggests that the coals are siliceous in nature.

From XRD, d-spacing for planes and stack height parameter and layer diameter for crystallite region were calculated and different mineral such as kaolinite, pyrite etc were identified.

IR and XRD analysis were performed on coals carbonized at different temperature upto 900 ^{0}C and structural changes were observed. An increase in absorption in 1600 cm^{-1} band and in the aromatic wag region between 900 to 700 cm^{-1} was observed up to 500 ^{0}C indicating an increase in aromatic condensation. At higher temperatures the coals were found to become opaque to IR so that no further information could be gained at temperatures above 500 ^{0}C. The X-ray diffraction analysis was helpful in this case. The coals exhibited an increase of stack height parameter and layer diameter during carbonization indicating clearly condensation of aromatic ring, which made the coals opaque to IR.

PIXE analysis of the coals samples of bore-holes GDH-38 and GDH-39 of Barapukuria and of bore-holes GDH-45 and GDH-46 of Khalashpir mine were performed using 2.5 MeV proton beam from Van de Graaff accelerator. 19 elements including environmentally hazardous arsenic, bromine, copper, lead, selenium and economically important gallium and germanium along with major elements like iron, calcium, patassium manganese etc were detected and analyzed for their concentration. The concentration of these trace elements in Barapukuria and Khakaspir coals were compared with their respective values in some Canadian coals and in earth's crust. The results were similar with a few exceptions.

List of Abbreviations

ASTM	*American Standards For Testing & Materials*
AECD	*Atomic Energy Centre Dhaka*
AXIL	*Analysis of X-ray Spectra by Iterative Least Square Fitting*
BSU	*Basic Structural Unit*
ECPSSR	*Energy loss, Coulomb deflection, Perturbed Stationary States and Relativistic effects*
d.b.	*Dry Basis*
d.a.f.	*Dry Ash Free*
F. C.	*Fixed Carbon*
HPGE	*High Performance Germanium*
INNA	*Intense Neutron Activation Analysis*
IR	*Infrared*
LMO	*Local Molecular Orientation*
MCA	*Multichannel Analyzer*
PHA	*Pulse Height Analysis*
PIXE	*Particle Induced X-ray Emission*
RFA	*Rodio Frequency Ash*
V.M.	*Volatile Matter*
TEM	*Transmission Electron Microscopy*
XRD	*X-ray Diffraction*
XRF	*X-ray Fluorescence*

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Chapter 1 Introduction to Coal Research

1. INTRODUCTION TO COAL RESEARCH

1.1 Introduction

Coal is an important natural resource and much effort has been given to make the best use of it. Fundamental scientific research has been going on for understanding the structure of coal for augmenting its technical use. The great potential of coal lies in its utilization in power and heat generation and in chemical industries.

Interest in coal as a scientific problem started at the beginning of industrial revolution, about 1700. But coal research as scientific discipline dates back to 1830. In the classical period (1913 -1963), coal petrology and coal chemistry developed as two full grown science. In the mean time understanding of coal structure have developed in terms of aromaticity of coal.

For purely economic reasons coal has been increasingly used in power generation. Sufficient energy supply at bearable cost is an indispensable prerequisite to gain prosperity and welfare and thus to alleviate poverty, hunger, environmental degradation in this world of explosive population growth. There is an increasing energy demand both in the developed and developing countries. The consumption of electric energy has grown since 1930 by a factor of 40 to 12000 $\times 10^9$ KWh. Consequently, the demand for fossil fuel for power generation has also increased tremendously. The emergence of petroleum in the early stage of this century as a plentiful source of primary energy led to demotion of coal as a source of primary combustible energy. In Bangladesh, where petroleum is not yet available, a large amount of foreign exchange is spent every year for importing petroleum fuel. So the recent discovery of huge deposits of coal in the North-Western zone of Bangladesh has given us a scope to exploit it as a source of energy. A large amount of coal estimated to be about 300 million tons is found deposited in an area of 5.25 sq. km. in the shallow basin of Barapukuria. These coals belong to the class of Gondwana and their formation is presumed to be in the period of Permian age. It is of importance to study the properties of these coals and to gain an understanding of its quality as a source of energy.

The coal reserves that are of economic interest to mankind is estimated to last for at least another 1000 years. Although coal alone is incapable of satisfying the energy needs of mankind, coal remains an indispensable factor. Because of the existence of substantial coal reserves and the limited amount of mineral oil and natural gas reserves, it is expected that coal will one day regain its role as an alternative source of energy and raw material and will replace the vanishing mineral oil and natural gas as the energy source.

1.2. Review of Earlier Works on Coal

Infrared spectroscopy has been a useful tool for studying coal structure since the first extensive investigation by Cannon and Sutherland(1). Early Infrared investigation on coal (1-3) used thin section, oil mull and nujol technique. Next work on coal was done at the Pittsburgh spectrometry laboratory of Bureau of Mines(4). Structural assignments to the spectra of coal and their extracts in various solvents were given by Orchin et al.(4). Later Friedel et al.(5) and Storch et al.(6) studied coal and different carbohydrate chars. Cannon and Sutherland(1,2) and Friedel and Pelipetz(5) used thin sections of coal for obtaining IR spectra. Powder suspension in nujol technique was used by Cannon(1,2) and Adams(7). Cannon and Sutherland(1) also studied various solvent extracts of coal by IR technique.

Works on different techniques and band assignments were published by Hadzi(8), Bergmann et al.(9), Friedel and Queiser(10), Roy(11) and Brooks et al(12). Bergmann et al(9) were the first to use KBr pellet technique. Advancement in coal structure research were made by Friedel et al(13), Kasatochkin(14) and Tschmular(15).

An extensive IR study by Brown(16) on coals with wide range of carbon content revealed similar basic carbon skeleton indicated by similarity in the spectra with two well defined changes assigned to substituent groups. One indicated decrease of Hydrogen-bonded -OH group with increase of carbon content upto 89%, which was accompanied by increase in aromatic hydrogen. The other was a reduction in aliphatic material with increase in carbon content which was accompanied by an increase of structureless absorption in the spectra due to electronic absorption of condensed aromatic rings. He observed a pronounced band near 1600 cm^{-1} in spectra of all coals except anthracite which was attributed to aromatic ring vibration enhanced in intensity by polar grouping attached to the aromatic system. Brown also studied behavior of weakly caking and strongly coking coals on carbonization by IR technique(17). He observed that the two types could be distinguished on carbonization to 460 ^{0}C. The hydrogen bonded -OH group formed a significant part in structure of caking coal chars whereas their concentration in coking coal chars were insignificant. Again carbonization at 550 ^{0}C showed a higher level of background absorption for coking coal which he attributed to growth of larger graphitic crystallite size in coking coal.

Peng Chen et al(18) conducted IR study of Yanzhou coal and their solvent extracts on pyrolysis to see the structural changes occurring in coking coals and their extracts after preheating the coals at different temperatures upto 400 ^{0}C. They measured the aromaticity from relative intensity of aromatic C-H stretching band and anti-symmetric methyl stretching band and observed an increase of aromaticity with temperature of pyrolysis. However relative intensity of the absorption bands in the aromatic wag region between 900 and 750 cm^{-1} were found to remain unchanged. This phenomenon was explained by attributing increase in aromaticity to dehydrogenation reaction [of aryl rings]. Chemical and structural changes occurring during heat treatment of coal by IR technique was also studied by A. M. Vassallo et al.[(19)]. They observed that the absorption due to aliphatic C-H stretching vibration did not change much upto 450 °C. The signal intensity of the aromatic C-H out of plane vibration in the region 700 to 900 cm^{-1} increased whereas the 1600 cm^{-1} band due to aromatic ring stretching vibration decreased. This phenomenon was explained by the loss of phenolic –OH groups. They also suggested formation of oxygenated groups such ash carboxylic acids, ketons and aldehydes indicated by the increase of bands between 1650 to 1810 cm^{-1}, the source of oxygen being indigenous.

Painter P. C. et al(20) studied the effect of hydrogen-bonding on frequency shift and intensity changes of absorption band in infrared spectrum using FT-i.r. technique. They observed that there are four types of hydrogen-bonding that contributed to the cross-linking in the macromolecular network of coal structure and the presence of these bonding influence the swelling property of coals. They attributed the increase in swelling property of the solvent extracts of coal to the hydrogen bonding tendencies of the solvents.

Debbie W. Kuehn et al(21) characterized a set of vitrinite concentrates using FT-i.r. by quantitative determination of hydroxyl group and aromatic and aliphatic C-H groups. They observed a decrease in phenolic –OH group with increasing rank of vitrinite concentrates as determined from area of 1770 cm^{-1} band due to acetylated phenolic –OH group. The total –OH content was determined from peak heights of 1770 and 1745 cm^{-1} band. Discrepancies of results of previous work on IR study of coal was removed using curve resolving technique. They used intensity of individual curve resolved bands rather than entire region of the spectrum. Thus they were able to differentiate 7 bands in place of 3 in the aromatic wag region between 900 to 700cm^{-1}.

Painter et al(22) in 1978 worked on quantitative mineralogical analysis of coal using Fourier Transform infrared technique. The low temperature ash of coal was analyzed by subtracting the spectra of individual mineral components stored in digital form in computer memory. Successive subtraction of most strongly absorbing components revealed the less strongly absorbing species. Thus they identified Kaolinite, Quartz, Gypsum, Calcite and other carbonate minerals such as Siderite and Dolomite, Illite, Montmorillonite, Pyrite etc. Qualitative analysis for these components were performed by determining the weight fractions for different components and a good agreement between known and calculated values of weight fraction was obtained.

X-ray diffractometric study on coal was performed as early as in 1919 by Mahadevan(23). Blayden, Gibson and Riley(24) in 1945 performed extensive X-ray diffraction study on coals, cokes and chars of various organic materials like cellulose, lignin and glycine. They employed powder technique to study the structure of the materials and measure the dimensions of the crystallites present in them. They employed powder technique to study the structure of the materials and to measure the dimensions of the crystallites present in them. They observed nearly a similar kind of growth in crystallite dimension in the chars over the temperature range 400 to 1300^{0}C except that lignin contained a highly condensed aromatic ring system and glycine chars had higher c-dimensions. Their works on a wide range of rank of coals (from peat to anthracite) and their carbonization products showed that various coal fractions had similar structure and that they all consisted of relatively large, more or less, flat molecules. These flat molecules were more or less aromatic in character and stacked to form turbostatic crystallites. They attributed the presence of hydroaromatic and hydro-heterocyclic ring system and alkyl, aryl, carboxylic and phenolic group contributing to γ- band in the diffractograms of less highly aromatic coals. Their study concluded that at least two important chemical changes occurred during coalification. In one some of the original vegetable materials was converted into carbon like crystallites and in the second some or remainder of the material converted into bitumen.

Ludwig Schoening (25) investigated the structural changes that occurred during carbonization of coals at 500 ^{0} and 1000 ^{0}C in argon atmosphere. The growth of total number of atoms in ordered graphitic regions, the crystal perfection and size of these regions were measured. There he introduced a new parameter which was the ratio of number of atoms in graphitic surrounding to the number of atoms in the respective regions. The increase in number of atoms in graphitic region was explained by two processes. One was the volume increase of c-ordered region and the second was greater perfection of these regions. He suggested further investigation to substantiate the usefulness of the crystal perfection parameter he introduced.

M. H. Mazza et al.(26) used powder diffraction technique to characterize feed coals and their combustion products. Minerals in feed coals were identified using low temperature ashing technique. Characteristic peak for illite, gypsum, kaolinite, quartz etc. were identified and analyzed for concentration determination. The samples were then ashed according to ASTM procedure and then scanned to examine the effect of heating.

L. S. Dale et. al.(27) performed accurate quantitative analysis of coal minerals using X-ray diffraction (XRD) in combination with SIROQUANT©, a Reitveld base computer software package. Using their method they determined individual minerals and total organic matter for a number of coals of different ranks. The amorphous content of coal was determined by spiking the coal corundum (Al_2O_3). The results of (XRD) analysis was assessed by comparing the results with radio frequency ash (RFA) and with iron leachate from different coal samples. They also analyzed laboratory ash and fly ash samples and found that XRD technique combined with SIROQUANT© provided accurate data on the concentration of mineral phases in coal ash.

J. A. Cooper et al.(28) worked on the determination of sulfur, ash and trace elements in coal, coke, and fly-ash. They developed a method for multi-element analysis of major and trace elements using energy dispersive X-ray fluorescence spectroscopy with inter-element corrections employing tube excited X-ray. The samples were powdered and pelletized and then loaded directly to the sample chamber. Spectrum was excited with direct bremsstrahlung radiation from Rhodium and Molybdenum anode in different run. About twenty elements were determined in a single run.

L. B. Clarke et. al.(29) worked on distribution of trace elements during coal utilization combustion or gasification. Their work found that during combustion or gasification, coal particles underwent complex changes that lead to vaporization of volatile elements and the trace elements were partitioned into several output streams including solid coal residue and flue gases. They found that the volatile trace elements were enriched in the fine particulate material of flue gas down stream of the combustor or gasifier which were released in the atmosphere.

P. C. Lindhal et. al.(30) worked on development of a rapid analytical method for determination of such trace elements as Beryllium, Chromium, Copper, Lead, Manganese, Nickel, Vanadium and Zinc in coal. Coal samples were combusted in Parr Oxygen bomb and trace metals in the residue from combustion were determined by flame atomic absorption spectrophotometry. They evaluated their method by examining standard reference sample and comparing their results with those of ASTM (D3683) and found that accurate and precise results could be obtained when coal are combusted in Parr Oxygen bomb.

J. Macjanic et. al.(31) worked on analysis of trace elements in coal from various locations of a Croatian coal mine using X-ray fluorescence spectroscopy. They used an X-ray tube with Mo anode for irradiation of samples and Si(Li) detector to detect characteristic X-rays. About 20 elements were detected in all the samples whose concentrations were determined. They also investigated possible correlation between elemental concentration of each pair of elements and found all between V, Cr, Ni, Ga, Se and U.

L. Thorne et. al.(32) analyzed bituminous coals from 84 distinct sources by conventional British Standards (BS) methods for phosphorous, sulfur, chlorine, ash and ash forming elements. The coal samples were also analyzed by wavelength dispersive X-ray fluorescence spectroscopy. The X-ray results were calibrated against those of conventional results and found that accuracy of XRF techniques were adequate or more than adequate for routine analysis of coal.

F. Goodarzi et. al.(33) preformed analyses of major and trace elements on coals from various locations of Canada. Their work included determination of mineral phases in low temperature ash by XRD determination of trace elements in raw coals and High temperature ash by means of intense neutron activation analysis (INAA) and determination of major elements in LTA by X-ray fluorescence spectroscopy. They compared the contents of various elements in coals to the average content for those elements in earth's crust and found that only antimony and selenium are enriched in raw coals. They also observed enrichment of arsenic in lignite and sub-bituminous coals and their depletion in bituminous and anthracite coal. As expected the ash of these coals showed many more instances of enrichment.

1.3. Objectives of the Research

The objective of this research work is to study the quality of Barapukuria coal in terms of organic and mineral matters. Coals which are rich in organic aromatic groups exhibit higher rank. For chemical processing and extraction of organic groups from coal, the detailed structural study is necessary. In this regard infrared spectroscopy is well suited to study the structure of coal because it can be used to identify specific functional groups such as C-H, C=O, and O-H etc. In conjunction with **IR, X-ray diffraction** will be used for crystallite and mineral phase identification and **Proton Induced X-ray Emission Spectroscopy** will be employed for elemental analysis.. The physical characterization of these coals will also be carried out employing **proximate analysis.**

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Chapter 2 Coal Morphology

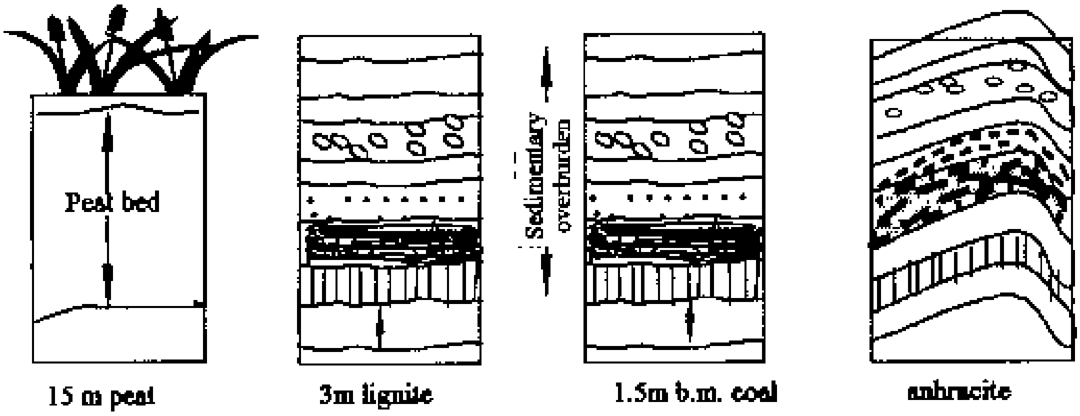
2. COAL MORPHOLOGY

2.1. COAL

Coal is a naturally occurring black organic rock. It is a carbon rich material which has been found to be produced from the decomposition of plant debris under action of temperature and pressure in an anaerobic condition over many geological eras.

Coal is not just another form of carbon as graphite or diamond. It consists of complex mixture of organic chemical substances containing carbon, hydrogen, oxygen together with nitrogen and sulfur in smaller amount in chemical combination. Coal is in fact a fossil formed by the action of pressure and temperature from plant debris.

In certain part of the world there existed, some 300 million years ago, warm and humid climate which favored growth of huge tropical ferns and giant trees which grew and died in vast swamp areas. The dead plants fell into boggy waters where they were partially decomposed under abiotic condition as well as bacterial or fungal attack. This process converted the plant debris into peat like material.



peat ⟶ Lignit → Bituminous coal → Anthracite → Graphite

Figure(2.1.1) : Genesis of coal formation

Vegetation continued to grow for many generations forming vast thick peat bed which became submerged and were covered with sedimentary deposits. A cycle of swamp followed by submersion was often repeated a number of times which resulted in the formation of a sequence of horizontal bands of peat and inorganic sedimentary rocks. Subsequently these bands of peat under went coalification by the action of pressure and temperature caused by overlying sediments during the second or geo-chemical phase forming lignite and thereafter bituminous coals and anthracite.

The elementary composition of debris changes with increasing coalification. The carbon content amounting roughly 55 wt % in peat increases upto 92 wt % in anthracite whereas hydrogen initially at 10 wt % drops below 3 wt % and oxygen initially at 35 wt % drops finally to 2 wt %. Sulfur and nitrogen are present only a few percent and their change during coalification is insignificant. The aromatic portion of the deposits increases with coalification.

The genesis of coal suggests that coal is a non-homogenous material. It is an organic sedimentary rock composed of fossilized plant material which in analogy to minerals are called macerals. Macerals have their origin in different botanical components of debris from which coals have been formed. They are identified microscopically by their form and reflectivity and are differentiated into three main groups based on appearance and physical characteristics [Table (2.1.1)].

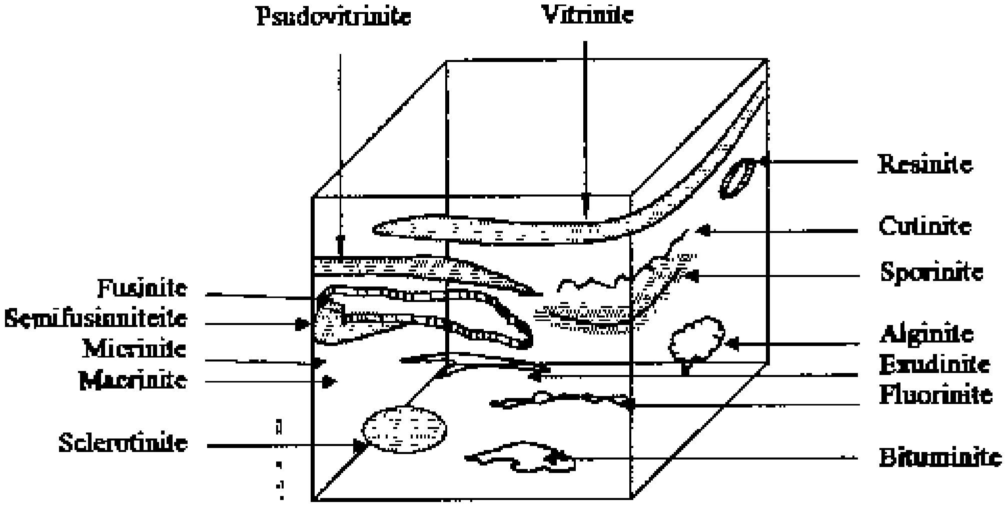


Figure (2.1.2) : Schematic representation of coal macerls[1]

Table (2.1.1) : Maceral and maceral groups of coal[2]

Maceral groups	Symbol	Macerals	Composition/origin
Vitrinite	V	Colinite Telinite	Humic gels , wood barks and cortical tissue
Exinite	E	Alginite Sporinite Cutinite Resinite	Algal bodies Spores Cutins of leaves and needles of plant Resinous constituents of coal
Inertinite	I	Fusinite Semi-fusioite Macrioite Micrinite Sclerotinite	Carbonized woody tissue Unspecified detrial matter , > 10 μm Unspecified detrial matter , < 10 μm Fungal spores and mycelia

Vitrinite may vary from dark to light grey in appearance and may show signs of botanical structure. It appears as brilliant black bands. Two individual macerals belonging to this group are telinite and colinite. Telinite is composed of cell wall materials of original plants and colinite is derived from substances that originally filled cell cavities.

Exinite consists of macerals derived from spores, cuticles, resins and algae. The spores which occurs in tetrads are always compressed and are usually identified as sporinites. Cutins of leaves and needles of plant emerge as another maceral group named Cutinite. The third exinite maceral is Resinite, which includes all kinds of resinous constituents of coal and the resinified oils of lignite and bituminous coal. The fourth exinite maceral, Alginite, is formed from the remains of Algal bodies.

Inertinite originates from plant remains similar to vitrinite but has a stronger role of oxygen during geo-chemical phase. Two predominant inertinite macerals are Fusinite and semifusinite. Fusinite is commonly referred to as fossil charcoal and usually shows well defined structures. Semifusinite is intermediate between fusinite and cellular vitrinite showing well defined structure of wood .

Another maceral of inertinite group is sclerotinite, which is the result of fungal remains. The final two macerals of inertinite group are macrinite and micrinite. Macrinite is composed of grains and is believed to arise from a sediment of inert detritus. On the other hand micrinite is composed of smaller material and is believed to be a maturation product of protoplasm.

2.2. Rank Classification of Coal

Classification by rank progresses from high carbon coal to low carbon coal in conjunction to other properties of coal. The ASTM classifies coal on the basis of proximate analysis. This system of classification indicates degree of coalification with

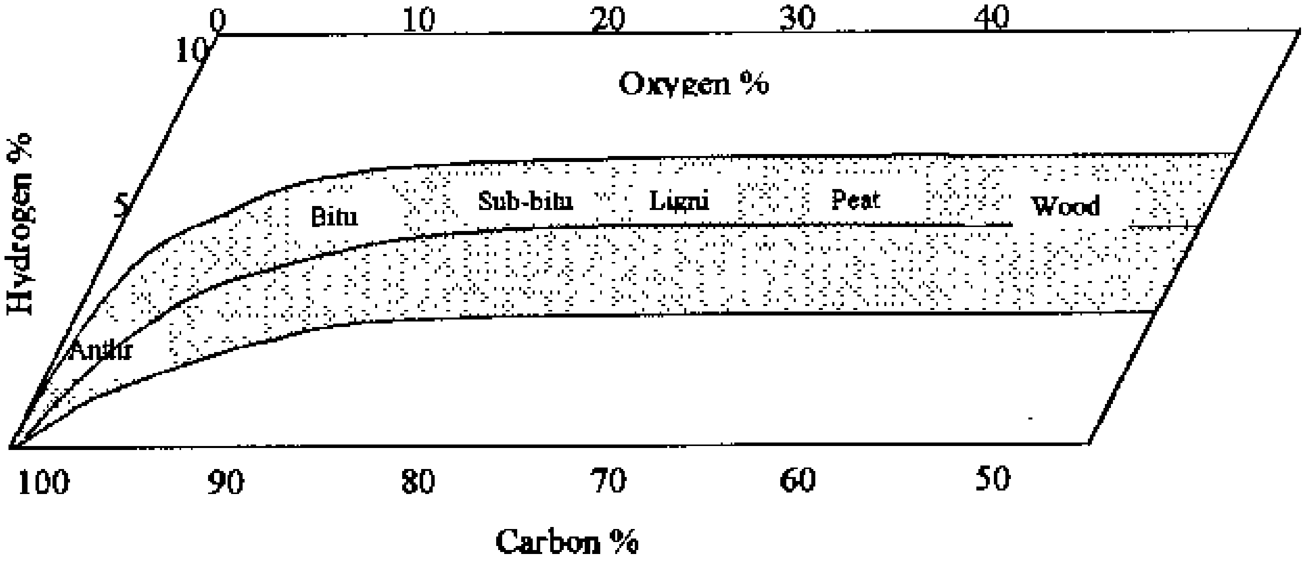


Figure (2.2.1): Classification of coals according to carbon , hydrogen and oxygen contents(2) lignite classed as lowest rank and anthracite as highest rank. Classification of coal according to carbon, hydrogen and oxygen contents is shown in figure (2.2.1). Rank classification of coal is shown in Table (2.2.1).

Lignite marks the transition of peat to coal and form the lowest rank of the true coals. Lignites may be black or brown and early with a pronounced "woody" or fibrous structure The air dried material has a moisture content of 15 to 20%. The dry ash-free contents of carbon and oxygen vary from 60 to 75% and 25 to 20 % respectively.

Table (2.2.1) : Rank classification of coals(1)

Class	Group	Fixed carbon & Volatile matter (db)	Calorific value Btu/lb	Requisite physical. properties
1. Anthracite	a. Meta-anthracite	FC , ≥ 98 %, VM , ≤ 2%		Non-agglomerating
	b. Anthracite	FC , 92 %— 98 % VM , 8% — 2%		
	c. Semi anthracite	FC , 80% — 92% VM , 14% — 8%		
2. Bituminous	a. Low-volatile bituminous coal	FC , 78% — 86% VM , 22% — 14%		Either Agglomerating or Non-agglomerating
	b. Medium-volatile bituminous	FC , 69% — 78% VM , 31% — 22%		
	c. High-volatileA bituminous coal	FC , ≤ 69% VM , ≥ 31%	≥14000	
	d. High-volatile B bituminous coal		13000 - 14000	
	e. High-volatile C bituminous coal		11000 - 13000	
3. Subbituminous	a. Sub-bituminous A Coal		11000 - 13000	Both weathering and Non-agglomerating
	b. Sub-bituminous B Coal		9500 - 11000	
	c. Sub-bituminous C Coal		8300 - 9500	
4. Lignite	a. Lignite		≤8300	Consolidated
	b Brown Coal		≤8300	Unconsolidated

db = dry basis

Sub-bituminous coals are intermediate in rank between mature lignites and the hard bituminous coals. They usually have 10 – 20 % of moisture when air dried. Sub-bituminous coals have 75 to 80 % carbon and 20 to 10 % of oxygen respectively.

Bituminous coals are black, hard and banded in appearance. The moisture content of this type of coal varies widely according to the rank from 13 to 1 %. The carbon contents (daf) vary from 75 to nearly 90 % with a change of volatile matter 40 to 20 %. The calorific value of these coals is high and increases with increasing rank from 14000 to 16000 Btu/lb.(daf). Coking power in this class of coals increases with increasing rank and the bituminous class includes the strongest coking coals.

Anthracite form is the highest rank of coal and is produced from the extreme of metamorphosis of original plant materials. Its carbon content is over 93%, volatile matter is less than 8 % and it is non-coking.

2.3. Chemical Structure of Coal

Coal is an almost non-homogenous, insoluble, highly complex mixture of organic molecules of varying size and structure by origin. It is often defined as organic rock because of an assembly of macerals, minerals and inorganic elements which are held molecularly by organic matter[1]. The coal structure is composed of variously substituted condensed polynuclear systems. The condensed polynuclear systems consist of aromatics and hydroaromatics and increase in size from low rank coal to high rank coal. Figure (2.3.1) depicts the structure of a low rank coal in which the clusters of rings are distributed at random and arranged singly (marked 4) or stacked in parallel arrays (marked 1, 2, 3). The greater portion of the coal is made up of relatively low molecular weight structural units which are connected by various type of bonds such as covalent (alkyl or ether, oxygen and sulfur bridges) and non covalent bonds, hydrogen bonds and Van der Waals' forces.

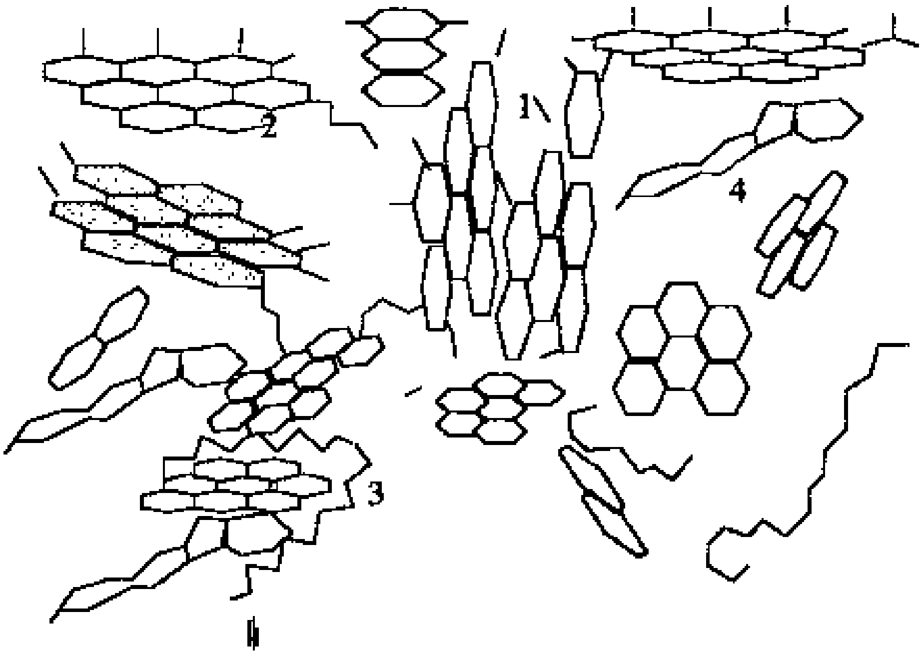


Figure (2.3.1) : Structural model of low rank coal(3)

From high resolution transmission electron microscopic (TEM) studies of numerous coals, other carbonaceous materials and cokes Overlin has defined a basic structural unit (BSU) as an assembly of 2-4 layers staked in parallel arrays, each layer being a planar aromatic structure containing less than 10 – 20 rings[Fig (2.3.2)].

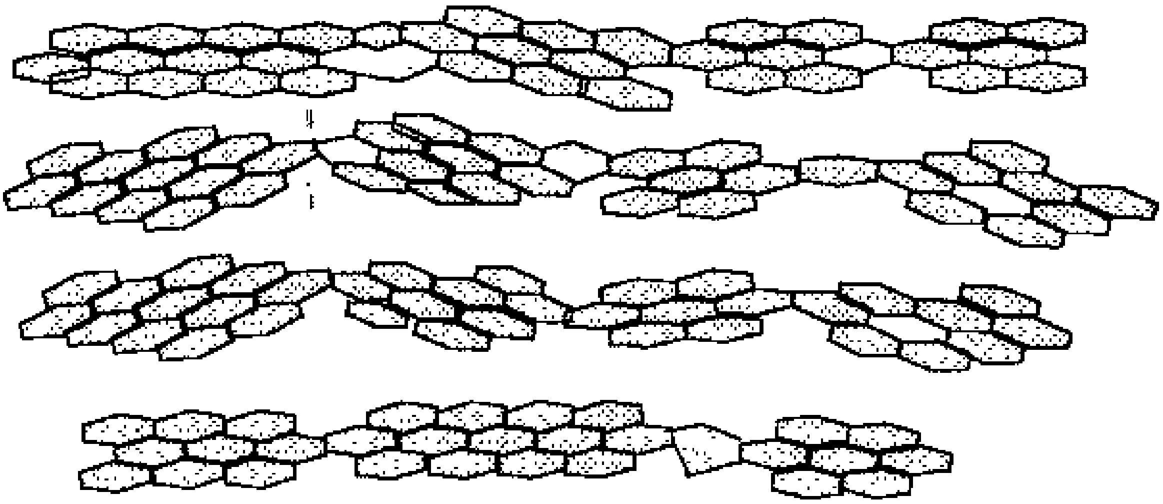


Figure (2.3.2) : Orientation of Basic Structural Unit in Local Molecular Orientation(3)

Two component system
Macromolecular three-dimensional cross-linked network (immobile phase)
Multitudes of relatively small molecules with varying structures embedded there in (10 – 50 %) share.

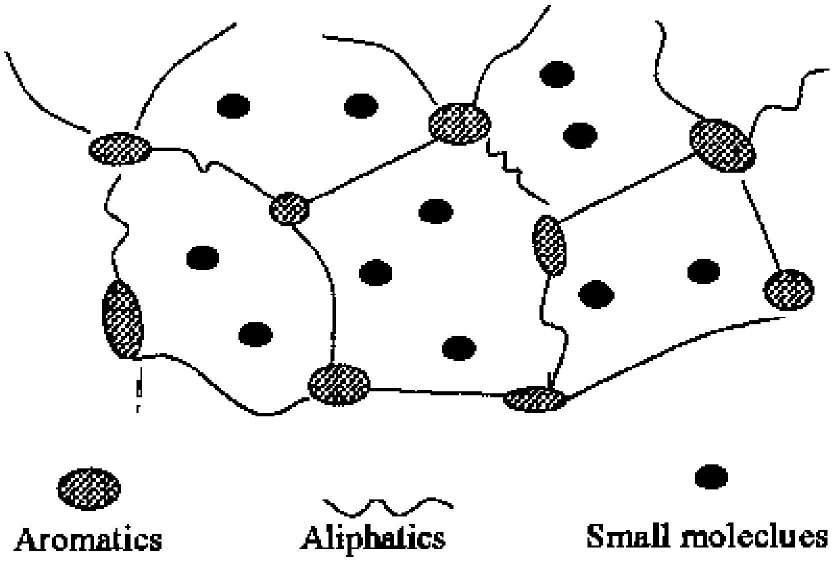


Figure (2.3.3) : Conceptual coal model (Two component system)

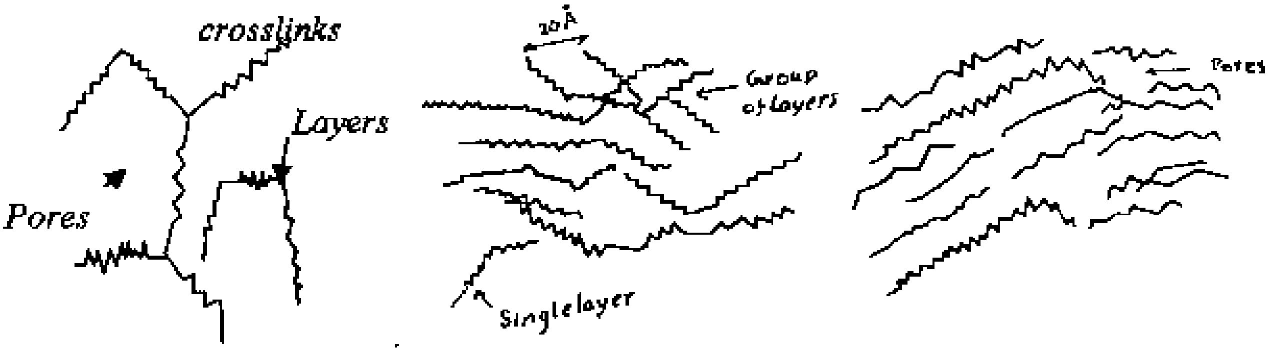
Recent coal models assume that aromatic and hydroaromatic structural units of three to five rings are cross-linked through short aliphatic and ether bridges to form macromolecular aggregates and relatively small molecules with varying structures are embedded in cavities or in pores

The proportion of carbon atoms bond to aromatic units increase with coalification and simultaneously the oxygen and aromatic units is believed to increase only slowly until the region of low volatile bituminous coals and there after to increase rapidly within the range of anthracite coals.

Very recent models abandons the concept of individual structure and view coal as two component system [Figure (2.3.3)]. A macromolecular three dimensional network of coal substance forms the immobile component or phase in which is embedded a multitude of relatively small molecules of varying structures forming the mobile component or phase.

The structural arrangement of coal increases with progress in coalification up to formation of organic macromolecule of flat shape with carbon atoms forming the central part. Every macromolecule consists of several hexagons which make up a planar pattern. There are three structural stages of coalification as shown in figure (2.3.4). (a) Coal with less than 85% carbon has an open structure, lamellae are rarely oriented and are connected by cross-links. (b) Coal with 85 to 91% carbon has a liquid structure ; many cross-links of lamellae are interrupted and lamellae show some orientation. (c) coal with more than 91% carbon has anthracite structure. On the basis of X-ray studies Hirsch[3], Brown and Hirsch[4] determined the dimensions of "coal molecules" the packing of molecules and the dimensions of pores. The inter planar spacing of carbon hexagons decreases from 3.65 Å to 3.43 Å with increasing coalification.

The disordered organic matter of molecules is composed of various organic radicals and groups with linearly polymerized carbon atoms. At higher stages of coalification the carbon embryos arrange themselves into parallel position and come



(80 %C "Open structure") 89 % C "Liquid Structure" 94 % C "Anthracite"

Figure (2.3.4) : Three stages of coalification

closer leading to periodicity in vertical direction. Flat polynuclear aromatic molecules aggregate to form the turbostatic lamellar system (4) as shown in Fig (2.3.5).

The infrared spectra of coals have confirmed its aromatic and also its polycyclic character. The presence of OH groups, aromatic CH groups, aliphatic CH_2 and CH_3 groups, polycondensed aromatic groups and benzene rings have been substantiated. Aromaticity is found to increase with degree of coalification and aliphatic groups become eliminated with 89-93% of carbon in volatile matter.

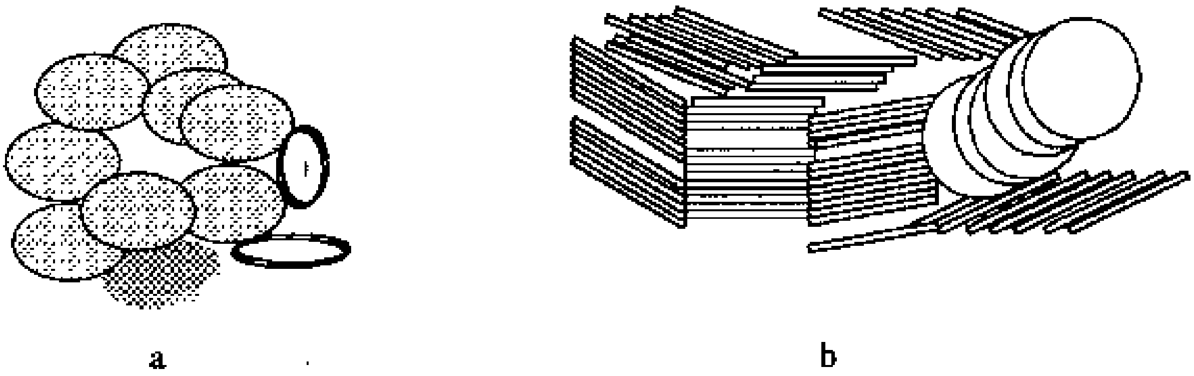


Figure (2.3.5) : Turbostatic Lamellar model of the coal structure (a) less ordered type, (b) more ordered type(4)

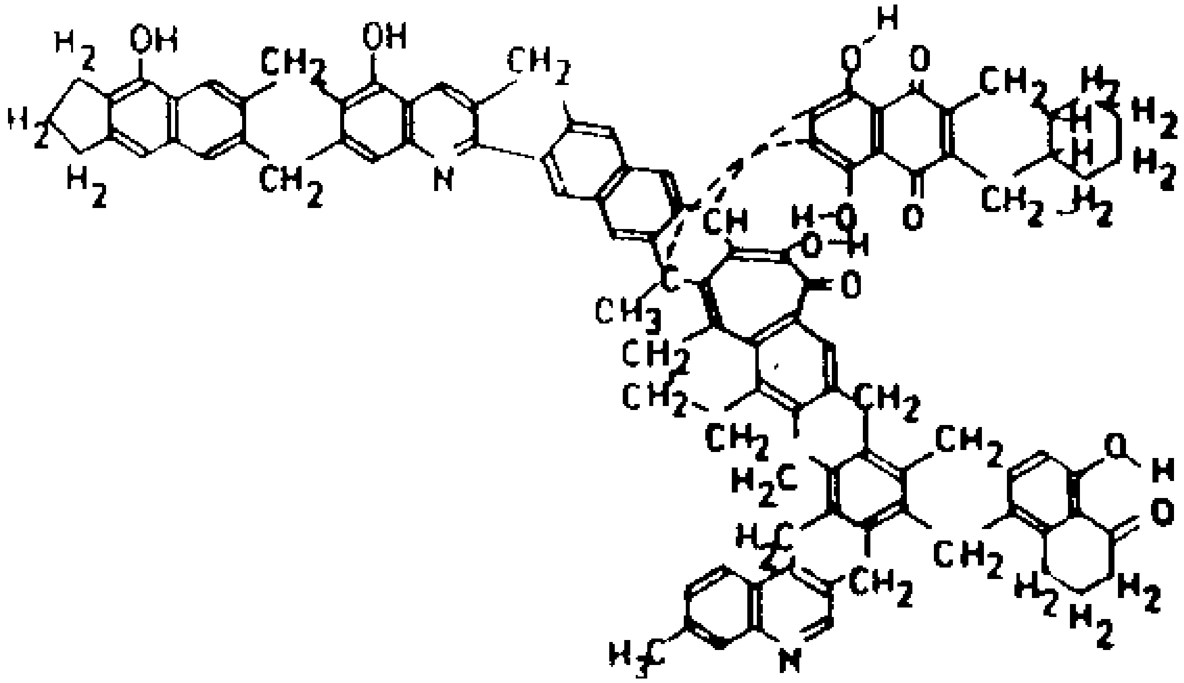


Figure (2.3.6) : Chemical Structure of vitrinite according to Given [4].

Coal molecule can contain its aromatic and aliphatic constituents in various combinations and spatial distribution. A hypothetical typical coal molecule proposed by Given is shown in figure (2.3.6) based on study of vitrinite molecule by infrared spectroscopy.

2.4. Structure Assessment by Infrared Spectroscopy

Spectral information on the structure of coal is obtained by reference to spectra-structure correlation. Structure assignments are included in Fig (2.4.1) and Table (2.4.1). These were reported previously (5, 6, 7, 8, 9).

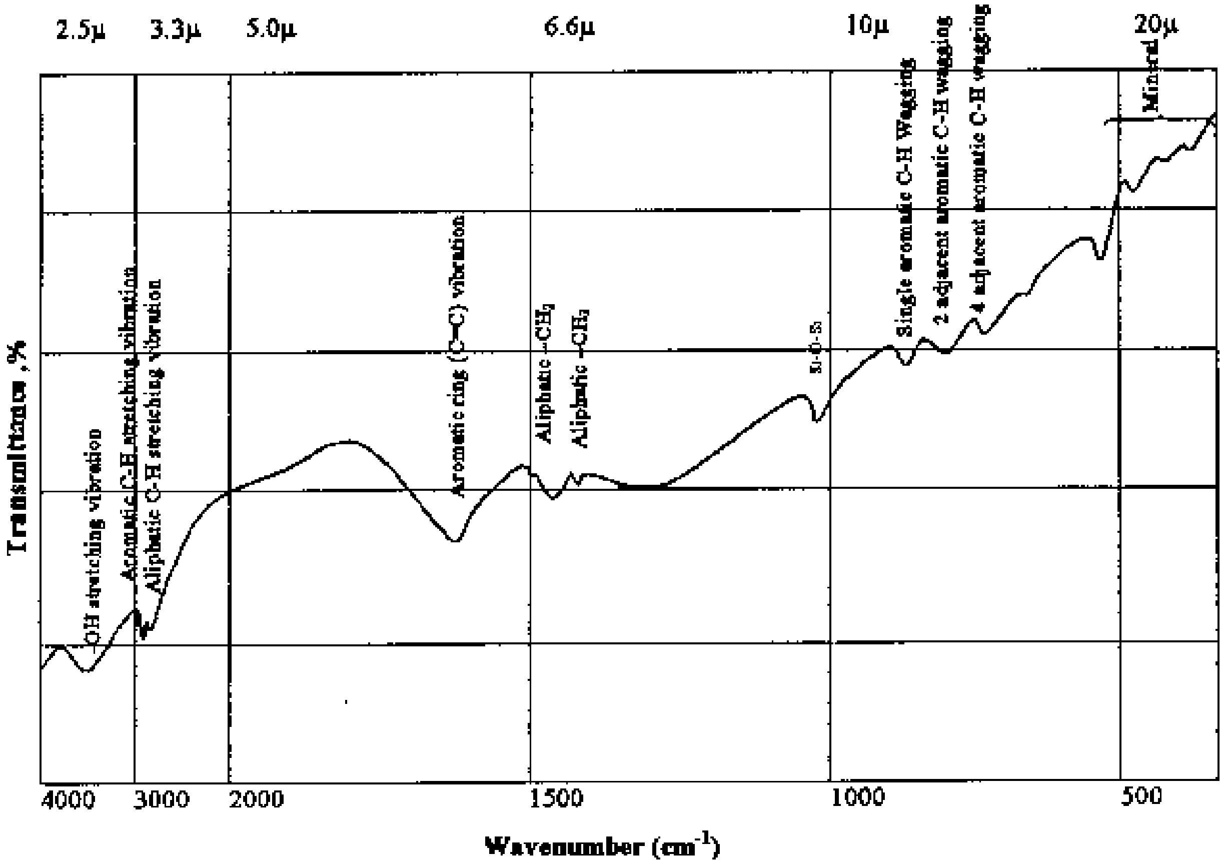


Fig (2.4.1) : Typical Infrared spectra of Coals

Assignment of individual bands are as follows :

3µ *Hydroxyl groups.* The OH group is assigned to phenol. Much of this absorption may also be due to water that is not removable at ordinary temperature. The broad absorption band from 3.5 to 4.25µ is apparently due to -OH (or -NH) groups that are more strongly bonded than the -OH groups contributing to the 3µ band.

Table (2.4.1): Spectral Assignments for Infrared Spectra of Coals[1]

Wave numbers (cm^{-1})	Wavelength (μ)	Assignments
3300	3.00	-OH (Stretching), –NH (Stretching)
3030	3.30	Aromatic -CH
2962	3.38	Aliphatic C-H stretching
2925 to 2850	3.42 to 3.50	$-CH_3$ (stretching), $-CH_2$ (stretching)
2780 to 2350	3.60 to 4.25	More strongly hydrogen bonded -OH than at 3.0 μ
1900 to 1780	5.25 to 5.60	Aromatic bands, 1, 2-di and 1, 2, 4-tri substitution
1700	5.90	C=O (stretching)
1610	6.20	C=O….-OH and /or aromatic CC with -O- substituent
1590 to 1470	6.19 to 6.80	Aromatic C=C (stretching)
1450	6.90	$-CH_3$ (asymmetric deformation), $-CH_2$ (scissors deformation)
1380	7.25	$-CH_3$ (symmetric deformation), Cyclic $-CH_2$
1300 to 1000	7.70 to 9.00	Phenolic and alcoholic C-O stretching C_{ar} - O - C_{ar} C_{al} - O - C_{al} C_{ar} - O - C_{al}
1040 to 910	9.60 to 11.0	Clay minerals such as kaolinite, some phenoxy structures
860 815 750	11.60 12.30 13.30	Aromatic HCC (rocking) in single and condensed rings
873 816 751	11.50 12.30 13.30	Substituted benzene rings with isolated or two neighbouring H- atoms ; O - substituted benzene rings
893 758	11.30 13.20	Angular condensed ring system , mono substituted benzene rings ; condensed system
690 to 400	14.50 to 25.0	General absorption ; mineral bands

<u>3.25 to 3.5μ Region.</u> Absorption in this region are mainly due to aromatic C-H stretching (3.3μ) and aliphatic C-H stretching (3.4μ).vibration.

5.9µ Carbonyl Groups. In medium and high rank coals absorption at this wavelength is very weak, if present. This band develops due to oxidation of coal during handling.

6.2 µ Condensed Polynuclear Aromatic groups. A pronounced absorption band near 1600 cm^{-1} is observed in all coals except in the anthracite. It is probably due to aromatic ring vibration that is enhanced in intensity by polar grouping attached to the aromatic system. Another possibility is that the absorption band arises from carbonyl groups which form part of aromatic system.

6.9 µ Band. The usual assignment of this band is due to aliphatic CH vibration of CH_2 and CH_3 groups. Aromatic ring (C-C) vibration is another possibility.

7.5 to 9.0µ Region. This region is assigned to aromatic ethers and phenols.

9.0 to 11.0µ Region. some of the broad absorption band from 9.0 to 10µ is probably due to C-O groups. But bands at 9.67 and 10.0µ are principal bands in the spectra of kaolin and other clay minerals. Kaolinite also produces weaker bands at 10.7 and 11.0µ which are found in spectra of coals with appreciable mineral contents. Other minerals identifiable in various spectral region include carbonates and silica.

11.0 to 14.0µ Aromatic bands. These bands has always been assumed to be aromatic structures.

2.5. Low Temperature Carbonization of Coal

Coals undergo a variety of physical and chemical changes when heated to a temperature at which thermal decomposition occurs. Carbonization generally means a process of thermal decomposition in which chars or cokes are produced when coal is heated at temperature above 500 ^{0}C. Carbonization is a complex process in which polymerization plays a dominant role during which elements usually oxygen, nitrogen or sulfur as well as some carbon constituents are removed as temperature rises.

However there are some changes that occur before the onset of thermal decomposition at around 350 ^{0}C. Water evolves and adsorbed methane and CO_2 is released below 100 ^{0}C. In low rank coals (lignite) CO_2 is evolved from decarboxilation reaction. At further higher temperature ("pre-carbonization" stage, from 200 to 370^{0}C) some bond breaking reaction and reduction of hydrogen binding occurs which may lead to melting. Coal loses some low molecular weight organic species which are mainly aliphatic compounds and some low molecular weight aromatics and condensation and molecular stripping also takes place.

In the second intermediate phase of "active decomposition" (between ~400 and ~650 ^{0}C)further bond breaking occurs, leading to evolution of organic matter as tar and gases and thereby condensation reaction result in the formation of residual carbon. In this phase coking coal passes through a plastic stage in which aromatic condensation takes place leading to greater ordering due to the development of progressive alignment of aromatic layers or lamellae in groups which form "crystallites".

In the third phase of "secondary degasification" (~650 to 900 ^{0}C), and there after re-solidification reactions take place principally in the solid state. The carbonaceous product may evolve secondary gases, mainly CO and H_2, while undergoing condensation. Figure (2.5.1) depicts a hypothetical picture of three phase of pyrolyzed organic coal structure.

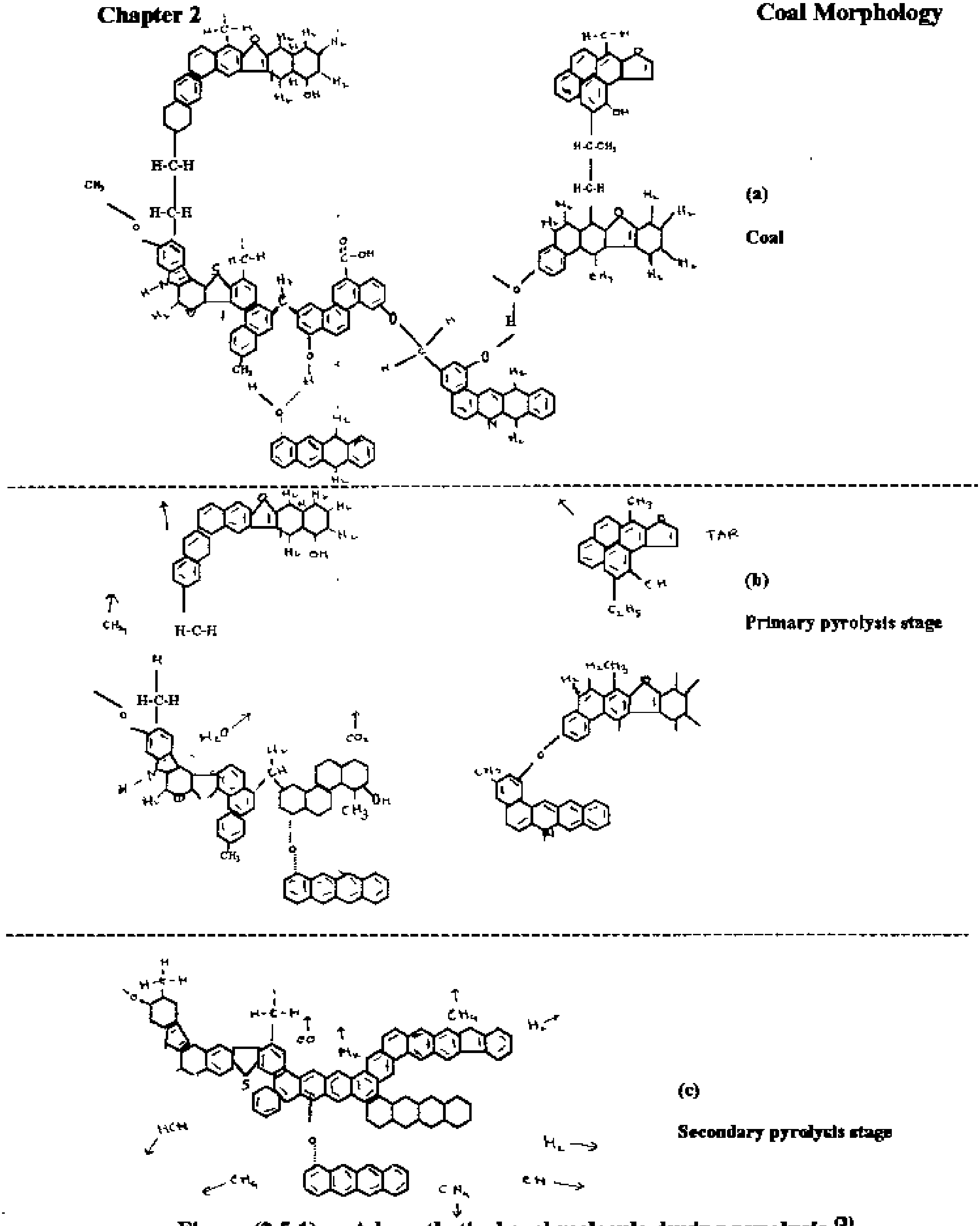
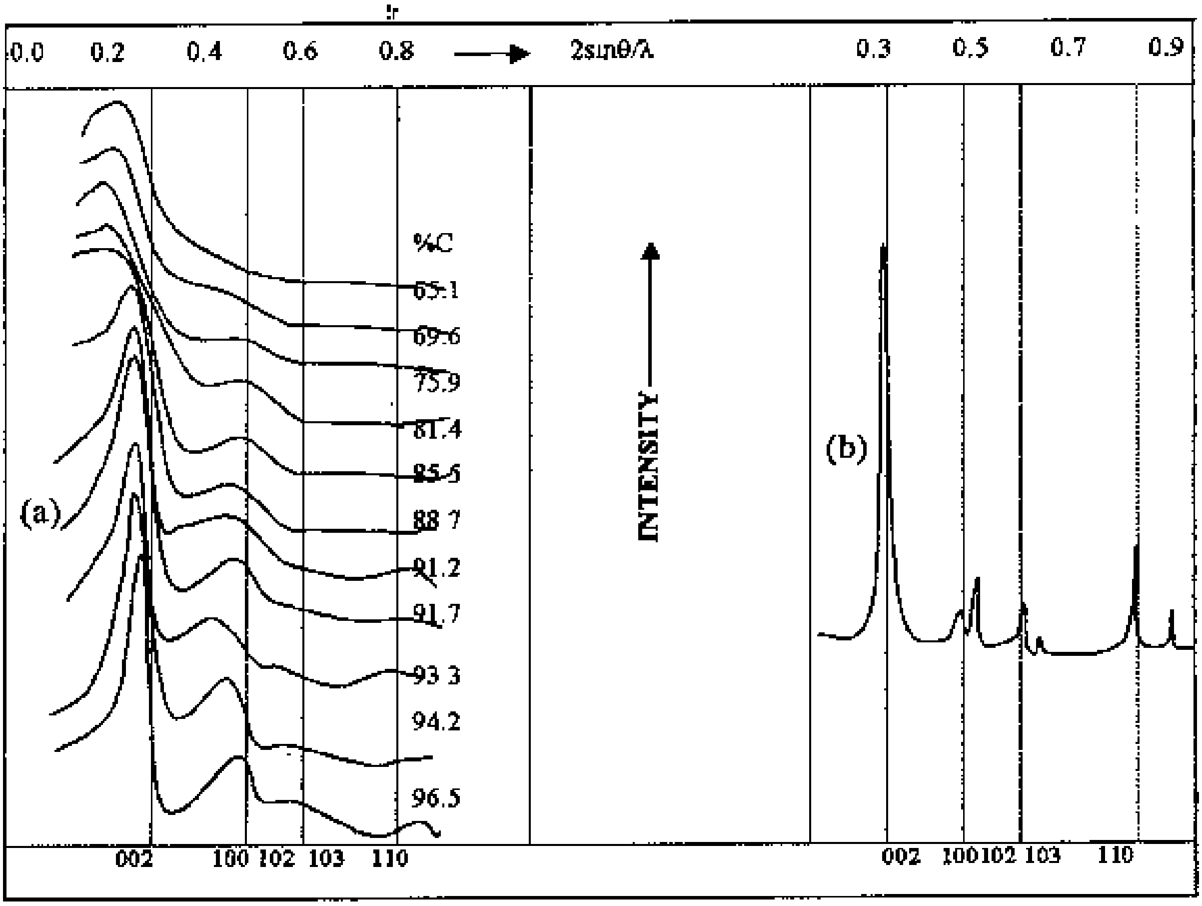


Figure (2.5.1) : A hypothetical coal molecule during pyrolysis (3)

2.6. X-ray Diffraction of Coal

Coherent scattering of X-rays by matter causes interference pattern that reflects the geometry of scattering material. The diffraction pattern of coal, a relatively highly aromatized amorphous solid, is a continuous scatter curve on which only more or less grossly broadened maxima appear. These scattering curves bears a distinct resemblance to diffraction spectra of 'macro-crystalline' graphite as shown in figure (2.6.1). The most prominent [002] band and less intense [100], [004] and [110] band corresponding to hexagonal graphite crystal has been identified in coals of different ranks(10,11). The spectral data are interpreted in terms of ordered regions which formed through localized parallel staking of aromatic units.



Figure(1) : X-ray diffraction curves of vitrinites and graphitte
(a) The coalification series ; (b) Graphite [100%C]

Figure (2.6.1) compares the X-ray powder diffraction of various coals and graphite(12). The [002] reflection of graphite is essentially attributed to diffraction at equidistant graphite layers. In case of coal anthracite (96 wt % carbon) shows a diffractogram in which the reflections of graphite can be recognized. With decreasing the carbon content, the diffraction pattern becomes more and more diffuse and the 002 line shifts slightly toward smaller diffraction angle.

The d-spacing and crystallite dimension calculation(11) indicates slow progressive ordering and aromatization during metamorphic development toward higher anthracite. This is observed in the sharpening and shifting of [002] band toward higher Bragg angle as shown in figure (2.6.1). The average layer diameter $\bar{L}$ is determined from the [100] and/or [110] band.

A band with d-spacing 4-5 Å overlapping the [002] line in the diffraction pattern of coals is called the γ-band and is attributed to low molecular weight materials responsible for coking properties of coal(10). Some workers(12,13) proposed that exinite inclusion in coal produce this γ-band.

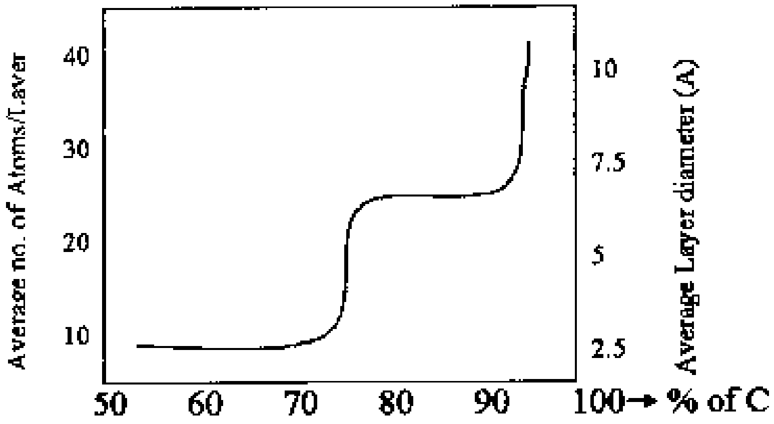


Figure (2.6.2) : Variation of layer diameter and no of atoms per layer with rank

Moreover X-ray pattern of coals with over 84% carbon display a band with d-spacing of 20 Å. Since electron density of scattering units may be above or below the band at 20 Å, this band may be due either to pores or to lamellae. The 20 Å band appears to be mainly due to ordering (on a scale of 20 Å) parallel to the bedding plane.

2.7. Trace Elements in Coal

Study of mineral matter in coal is an essential part of coal evaluation. Coal mineral matter originates from inorganic constituents of the vegetation that acts as precursor to coal and from the mineral matter that has been transported into coal bed from a remote site. Less than 12 elements constitutes the inorganic or mineral in coal which are found in coal ash [Table(2.7.1)]. There are many individual mineral elements in coal which are classified as trace elements. A trace element is that element which occurs in concentration less than 0.1% (<1000 ppm) in earth's crust. The concentration of some rare trace elements are of geochemical importance. Major trace elements in coal are summarized in table (2.7.2).

Coal contains most naturally occurring elements at least in trace concentration. Many of the elements are thought to be toxic to plant and animal life if present in sufficient quantities. Goldscmidt(18) was the first to apply spectrographic analysis to the study of trace elements and study their distribution in coal. In modern time, Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence Spectroscopy (XRF) and Particle Induced X-ray Emission (PIXE) Spectroscopy are used for analysis of trace elements.

The coal itself is the primary source of trace elements in coal fired combustion and gasification system. The elements are present as inclusions in coal particles or as discrete minerals and rock fragments. During combustion or gasification coal particles undergo complex changes, including formation of char, agglomeration of melted inclusions and vaporization of volatile elements. As the combustion or gasification product leave the combustor or gasifier, they cool and volatilized trace elements begin to condense.

Trace elements have been classified into three broad groups(19) according to their partitioning behavior during coal combustion [Figure (2.7.1)]. Group (1) elements are concentrated on coarse residue or equally partitioned between coarse residues and finer particles. Group (2) elements are volatilized in combustion or gasification but condense down stream. They are concentrated in the finer particles which may escape the particulate control systems. Volatile elements preferentially condenses on the surfaces of smaller particles in the flue gases as cooling occurs. Group (3) elements are most volatile elements and are depleted in all solid phases. In both combustion and gasification systems, the most volatile element Hg and Halogens may remain in the gaseous phase during passage through the plant. There is considerable overlapping between the groups due to wide variation in operating condition especially temperature that control elemental volatility

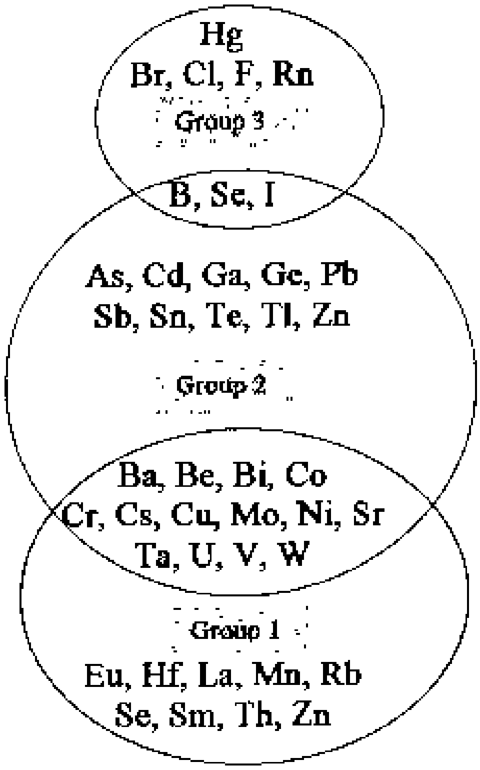


Figure (2.7.1) : Classification of trace elements according to volatility

The concentrations of different trace elements like Na, Rb, Co, Mg, Si, Cr and Mn are lower in coal than earth's crust. The elements like Li, Sr, Ag, As, Bi, B, Ga, Ge, La, Hg, Pb, Sb, Sn and Zn are found to be enriched in coal ash 10 to 185 times.

Table (2.7.1) : Major inorganic constituents of coal ash[1]

Constituents	Representative percentage
SiO_2	40-90
Al_2O_3	20-60
Fe_2O_3	5-25
CaO	1-15
MgO	0.5-4
Na_2O	0.5-3
K_2O	0.5-3
SO_3	0.5-10
P_2O_5	0-1
TiO_2	0-2

The accumulation and concentration of elements are the result of different geochemical processes, which may be divided into two groups

(A) Accumulation of elements as a result of living activity of plant and partly of animals : C, N, P, S, Fe, V, I, Ca, Mg, Al, Sn, Zn, Pb and others;

(B) Accumulation of elements after death of organisms :

(a) In mechanical way -- Minerals and rock fragments supplied during the coal formation : Si, Al , Ca , Mg , Fe , Mn , Na , K and others ;

(b) In chemical way -- by incorporation into organic compounds : Ge, U,V, etc.

-- by precipitation as sulfides : Fe, Cu, Pb, Zn, etc.

-- by reduction -- Ag and others ;

(c) By physical adsorption -- U, Th, Ge, V and others.

Table (2.7.2) : Major Trace Elements in Coal[20]

Constituent	Range (ppm)
Arsenic	0.50 — 93.00
Boron	5.00 — 224.00
Beryllium	0.20 — 4.00
Bromine	4.00 — 52.00
Cadmium	0.10 — 65.00
Cobalt	1.00 — 43.00
Chromium	4.00 — 54.00
Copper	5.00 — 61.00
Fluorine	25.00 — 143.00
Gallium	1.10 — 7.50
Germanium	1.00 — 43.00
Mercury	0.02 — 1.60
Manganese	6.00 — 181.00
Molybdenum	1.00 — 30.00
Nickel	3.00 — 80.00
Phosphorous	5.00 — 400.00
Lead	4.00 — 218.00
Antimony	0.20 — 8.90
Selenium	0.45 — 7.70
Tin	1.00 — 51.00
Vanadium	11.00 — 78.00
Zinc	6.00 — 5350.00
Zirconium	8.00 — 133.00
Aluminium*	0.43 — 3.04
Calcium*	0.05 — 2.67
Chlorine*	0.01 — 0.54
Iron*	0.34 — 4.32
Potassium*	0.02 — 0.43
Magnesium*	0.01 — 0.25
Sodium*	0.00 — 0.20
Silicon*	0.58 — 6.09
Titanium*	0.02 — 0.15
Sulphur*	0.42 — 6.47

* Quantity given in percentage

According to their assignments to the organic coal matter or inorganic coal components the elements are classified as follows :

(A) Elements associated almost completely with the organic coal matter : Be, Ge, U, Zr, Cu, Cr ;

(B) Elements associated predominantly with organic coal matter : Cu, Cr, Pb, Ag, Au, Sb, Mo, Ga, V, Ni, Sn, As, Ti, B ;

(C) Elements bound predominantly to the external ash substances : Ga, V, Ni, Sn, Co, As, Ti, B, Li ;

(D) Elements bound almost completely to the external ash substances : Mn, Ba, Sr

The concentration of trace elements depending on their concentration in plant is feasible. The elements present in the plant bodies were liberated during decomposition processes and enriched the waters of coal forming basin to be resorbed in the early stages of organic matter coalification.

Concentration of trace elements in coal may be influenced as by contact metamorphism so by regional metamorphism. Contact metamorphism is usually produced by intrusions of younger volcanic rocks and is often accompanied by mineralization. Regional metamorphism pronouncedly affects the concentration of many trace elements (Be, Ge, etc.) which decrease with rise of metamorphism. During coalification mineral components (carbonates, oxides and salts) are liberated from humates and other soluble compounds like GeO_2 or Na_2GeO_3 are washed away from the seam by circulating water.

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Chapter 3 Experimental Details

3. EXPERIMENTAL DETAILS

3.1. METHODS USED IN COAL STRUCTURE RESEARCH

Coal structure is heterogeneous, non-crystalline and largely insoluble in nature and it is practically impossible to apply traditional methods of organic and physical chemistry for its structural characterization. The most useful information concerning coal structure that can be expected to be obtained is a quantitative determination of the molecular types of hydrocarbons present (i.e. aliphatic and aromatic) and distribution of specific functional groups (aliphatic CH, CH_2 and CH_3, phenolic –OH, alkyl –OH, carbonyl group etc.). For elucidating this kind of information spectroscopic methods are applied. The methods that are used in this investigation to characterize Barapukuria coals are summarized below.

i) Proximate Analysis of Coal

Proximate analysis is done to characterize coal physically and involves the determination of moisture content, ash content, volatile matter content, fixed carbon content, calorific value and bulk density.

ii) Infrared Spectroscopy of Coal

Infrared Spetroscopic study is done to characterize coal in terms of organic and inorganic species present in coal.

iii) X-ray Diffraction of Coal

X-ray diffraction is another useful method to structurally characterize coal by identification of different crystallite and mineral phases.

iv) Particle Induced X-ray Emission Spectroscopy of Coal

Particle induced X-ray Emission Spectroscopy is an useful method for elemental analysis by which major and minor (Trace) elements are detected and their concentrations are determined.

3.2. COAL SAMPLING

Coal samples have been collected systematically from different depths of bore holes GDH-38 and GDH-39 of Barapukuria coal mine with the help of Geological survey of Bangladesh (GSB). Barapukuria coal mine is in Parbatipur thana of Dinazpur district. The latitude of this land is $25^0\ 31'\ 45''$ to $25^0\ 33'\ 5''$ N and longitude is $88^0\ 57'\ 48''$ to $88^0\ 58'\ 55''$ E. Figure (3.2) shows the coal sampling location. Total area covered by this coal deposit is about 5.25 sq. km. Depth of coal-deposit ranges from 387 to 1600 feet below the surface. The total in-situ geological reserve is estimated to be about 300 million metric tons. Twenty samples were collected from each bore-hole of GDH-38 and GDH-39 at different depths (from 400′ to 1400′). The samples have been reserved in air-tight polythene bags.

3.3. PROXIMATE ANALYSIS OF COAL

The proximate analysis involves the determination of moisture content, volatile matter content, ash content, and fixed carbon content by heating coal under a set of standard conditions. It is essentially an examination of suitability of coal for combustion or cooking purpose. Proximate analysis of coal was carried out according to ASTM standard D3172(1)

3.3.1. Sample Preparation

The collected coal samples have been first broken-up into small pieces and spread on trays for drying . The dried samples are ground to fine powder by mortar

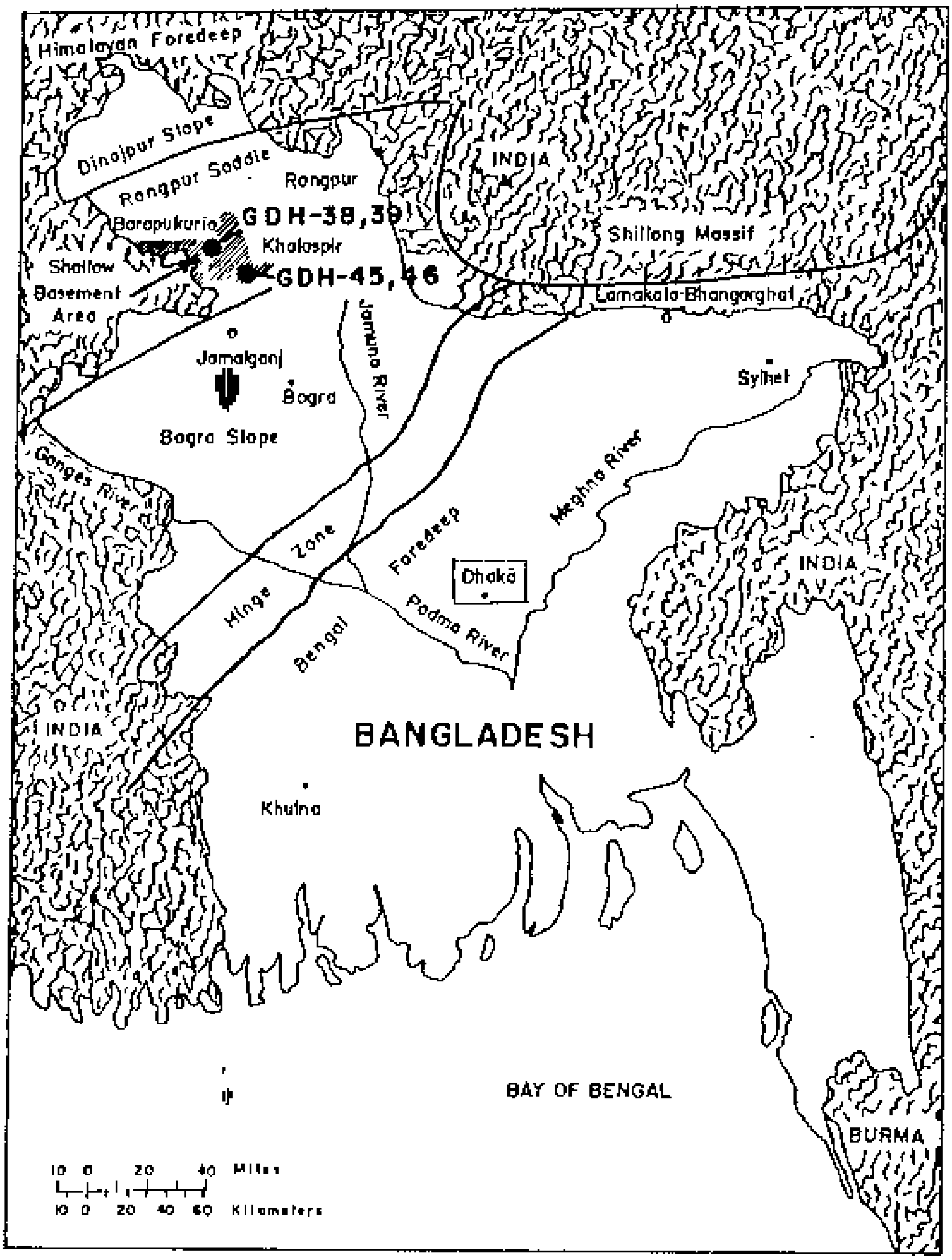


Figure (3.2) : Map of Bangladesh showing sampling location and pestle and passed through a 60 mesh sieve (Tyler). The powder have been immediately stored in an air tight container .

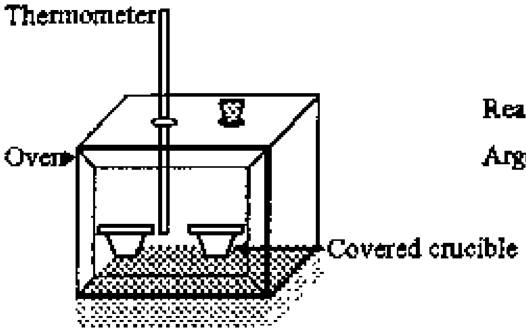


Fig. (3.3.1) : Setup for moisture determination

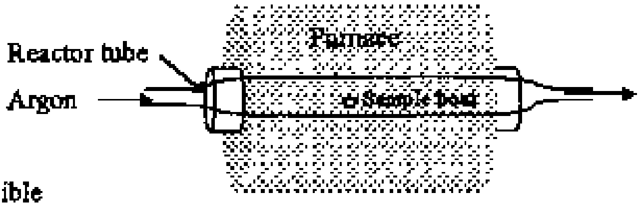


Fig (3.3.2) : Setup for VM Determination

3.3.2. Moisture Content Determination

The moisture content of coal is conveniently determined according to ASTM standard D3173$^{(1)}$ by measuring the percentage of weight loss of 60 mesh (250 μm) size sample when heat treated at 107 ± 3^0 C. The sample is heat-treated under controlled condition [Figure (3.3.1)] in an inert atmosphere for 1 hr. The moisture content is then determined by the following formula

$$Moisture\ content,\% = \frac{w_1 + w_2}{w} \times 100 \quad --- \quad --- \quad --- \quad --- \quad --- \quad --- \quad --(1)$$

Where, w_1 = weight loss in air,

w_2 = weight loss in oven,

w = weight of the sample before heating

3.3.3. Volatile Matter Determination

The volatile matter content of coal has been determined as per ASTM standard D3175$^{(1)}$. About ~1g of moisture free sample is put into a reactor tube and air is expelled by flowing argon for 10 minutes. The air free reactor tube is then placed inside a tubular furnace [Figure (3.3.2)] which has been preheated to ~950 °C. After 20 minutes, the reactor tube is removed from the furnace and cooled under argon flow. Volatile matter content was then calculated from the following equation,

$$Volatile\ matter,\% = \frac{w - w_1}{w} \times 100 \quad \text{--- --- --- --- --- --- ---} \quad (2)$$

where, w = weight of the sample before experiment

w_1 = weight of the sample after experiment

3.3.4. Ash Content Determination

Ash is the residue derived from mineral matter during complete incineration of the coal. The ash of coal is determined according to ASTM D3174(1). A porcelain crucible containing ~1g of moisture free coal sample is placed in the tubular furnace of figure (3.3.2) with free flow of air through the tube and heated gradually to redness. The ignition has been continued until a constant weight is reached at temperature between 700 and 750 °C. The crucible is then allowed to cool in a desiccator and weight is taken as soon as it becomes cold. Ash content is determined using the following formula,

$$Ash\ content,\% = \frac{weight\ of\ ash}{weight\ of\ moisture\ free\ coal} \times 100 \quad \text{--- --- --- ---} (3)$$

3.3.5. Fixed Carbon Content

Fixed carbon is a measure of the solid combustible material after expulsion of volatile matter. Fixed carbon is determined as per ASTM D3172(1) by subtracting from 100 the resultant summation of moisture, volatile matter and ash with all percentage on the same moisture reference base ,i.e.,

$$Fixed\ Carbon,\% = 100 - (ash,\% + volatile\ matter,\% + moisture,\%) \quad \text{--- ---} (4)$$

3.3.6. Calorific Value

The calorific value or heating value of coal is a direct indication of the energy content. It is an important property for determining the usefulness of coal. The calorific value has been determined as per ASTM standard D3286$^{(1)}$ using a Parr bomb calorimeter (Model 1261). About ~5 mg weighed coal sample is taken in the platinum crucible which is then placed in the bomb. The bomb is then charged with oxygen at 300 psi and submerged in water of the calorimeter. The system have automatic firing and calculation of the result facility.

3.3.7. Bulk Density

Bulk density is dependent on the degree of packing of the coal matrix. Bulk density of coal samples have been determined by mercury displacement method. A solid coal sample of suitable size is weighed and then volume determined by a mercury porometer (Ruska Instr. corp., Houston, Texas, Model 1051-801). Bulk density is then determined from the equation below

$$Bulk\ density = \frac{w}{v} \quad \text{---- ---- ---- ---- ---- --(5)}$$

Where, w = weight of coal sample

v = volume as determined by mercury porometer.

3.3.8. The results of Proximate analysis standardized by the following equations

i) $$F.C._{daf} = \frac{F.C.}{100-(M+A)} \times 100$$

ii) $$V.M._{daf} = 100 - F.C._{daf}$$

iii) $$Moist, dry\ ash\ free\ Btu. = \frac{Btu}{100-(M+A)} \times 100$$

Where, M = moisture content of the coal sample

A = ash content of the coal sample

3.4. INFRARED SPECTROSCOPY OF COAL

3.4.1. Introduction

The infrared radiation lies between visible and micro-wave region of electromagnetic spectrum. It is an important tool for studying organic substances by which a wealth of information can be obtained about its structure and constituent.

Infrared spectroscopy has played an important role in the investigation of coal structure since the first extensive investigation by Cannon and Sutherland(4,5) on thin sections of coal and on its various solvent extracts. Since then IR spectroscopy has been widely used for identification of functional groups and mineral matter in coal.

3.4.2. Principles of Infrared Spectroscopy

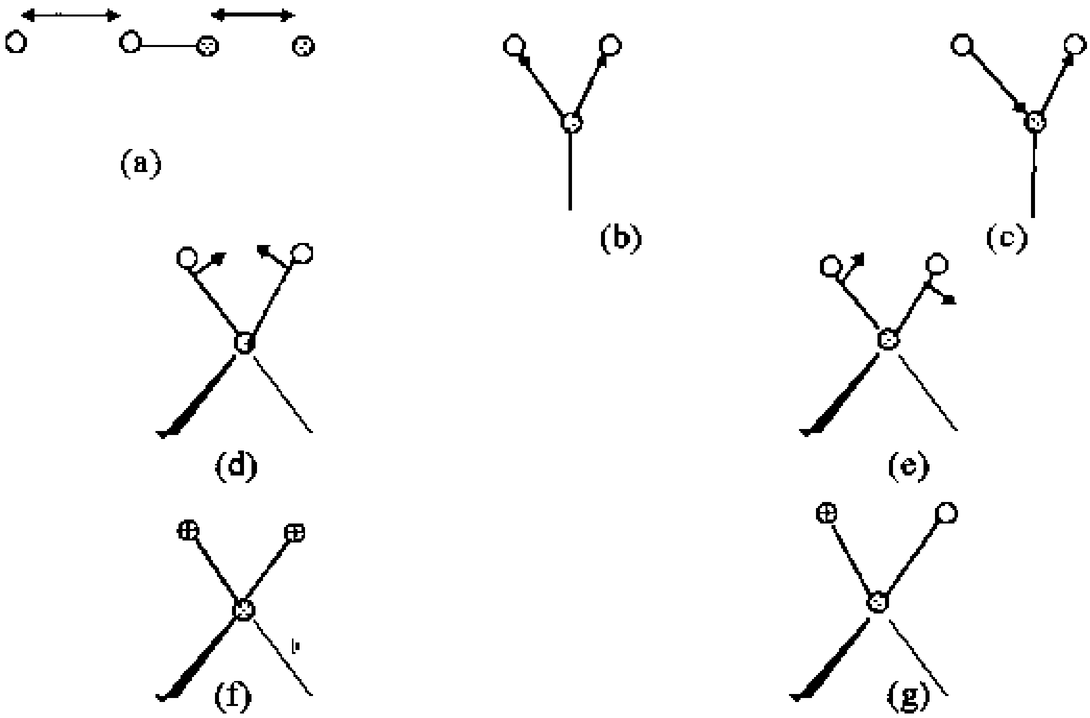
Infrared spectroscopy is based on the absorption of infrared radiation by molecules. It has been found that all chemical compounds show marked selective absorption in the infrared. However infrared spectroscopy is widely used for identification of organic compounds.

The infrared radiation encompasses the region between 14000 cm^{-1} and 200 cm^{-1} (0.7μ - 50.0μ). The region of interest for analytical purpose lies between 4000 cm^{-1} and 666 cm^{-1} (2.5μ - 15.0μ). The 14000 cm^{-1} to 4000 cm^{-1} region is called the near infrared region and the 700 cm^{-1} to 200 cm^{-1} region is called far infrared region.

The absorption of radiation occurs due to vibration of atoms within the molecules and rotation of molecules themselves. The absorption of infrared radiation within the range of wavelength 1μ - 100μ may set the molecule as a whole rotating or cause vibration of atoms relative to one another. The vibrational and rotational energy levels of a molecule are quantized and each vibrational level has associated with it a number of rotational levels. Thus a vibrational spectra results when absorption of radiant energy takes place thereby changing the vibrational energy of the molecule. Vibrational spectra appears as bands rather than as lines, because a single vibrational energy change is accompanied by a number of rotational energy changes. The frequency or wavelength of absorption depends on the relative masses of atoms, the force constant of the bond and the geometry of the atoms. Band position in infrared spectra are presented in terms of wave numbers ($\bar{\lambda}$) or wavelengths (λ). The wave number unit is mostly used because it is directly proportional to energy of vibration. Wave number is often referred to as frequency since it differs from frequency (ν) by a constant factor of 1/c i.e. $\bar{\lambda}=\nu/c$.

Band intensities are expressed either as Transmittance (T) or Absorbence (A). Transmittance is the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Absorbance is the logarithm to the base 10, of the reciprocal of transmittance i.e. $A = \log_{10} (1/T)$.

The IR spectra of polyatomic molecules are complex in nature because of multitudes of vibration that can occur in a molecule containing several atoms and



Figure(3.4.1) : Different types of molecular vibration (a) Stretching (b) Symmetrical stretching (c) Asymmetrical stretching (d) Scissoring(e) Rocking (f) Wagging (g)Twisting

several bonds. There are two types of molecular vibration, stretching and bending. Stretching vibration is a rhythmical movements of atoms along the bond axis such that the bond length increases or decreases at regular intervals. A bending vibration may consist of change in bond angle between bonds with a common atom or movement of a group of atoms with respect to remainder of the molecule without movement of atoms within the group with respect to one another. For example scissoring, rocking, wagging and twisting involve a change in bond angle with reference to a set of co-ordinate system arbitrarily set-up within the molecule. Figure (3.4.1) illustrates different modes of vibration that can occur in a polyatomic molecule.

3.4.3. Instrumentation

Infrared spectra of the coal samples are taken using a IR-470 Shimadzu double beam spectrophotometer having 400 to 4000 cm^{-1} Wave number with its beam line O, transmission expansion - 5 and scan time 7 minutes. Schematic diagram of such a spectrometer is shown in figure(3.4.2) and the optical layout is shown in figure(3.4.3).

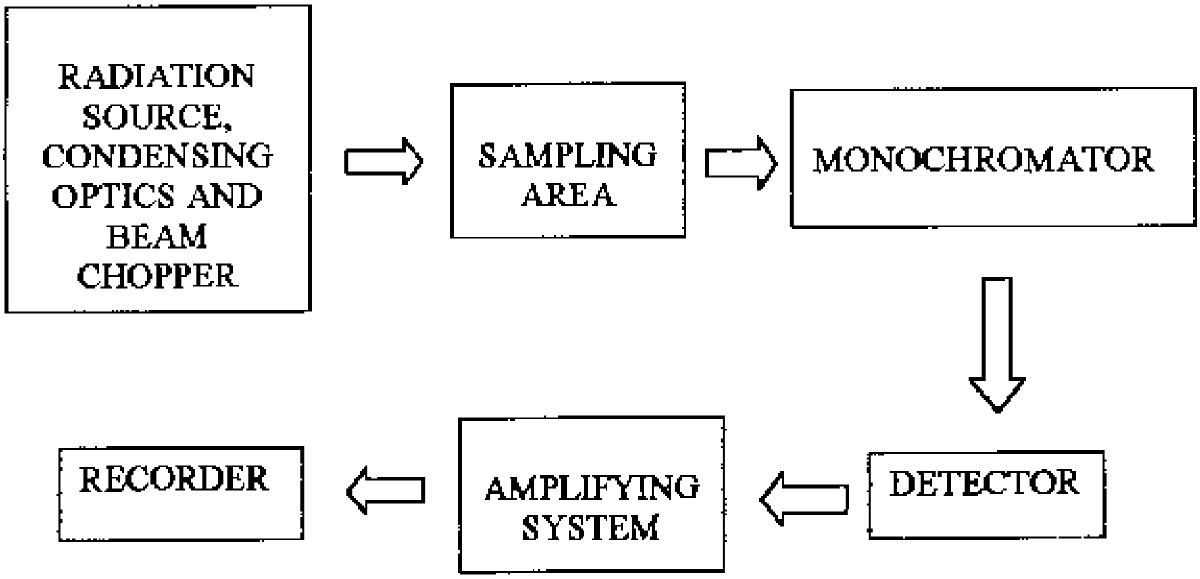


Figure (3.4.2) : Schematic diagram of a double beam infrared spectrometer

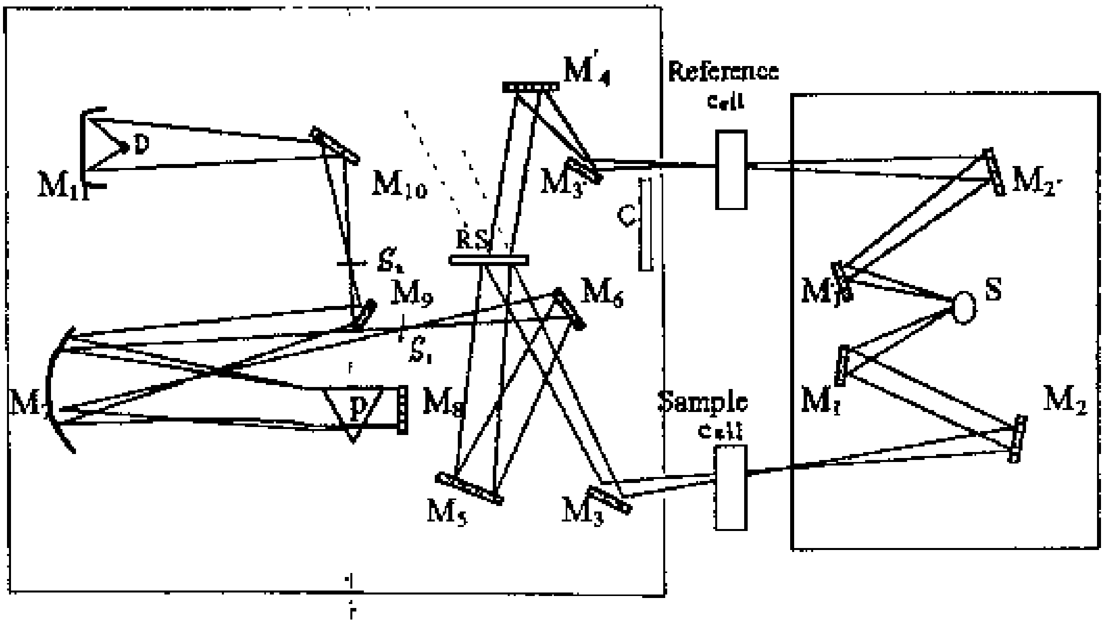


Figure (3.4.3) : Optical layout of a double beam Infrared spectrophotometer

In figure(3.4.3) S is a Nernst glower which acts as source of infrared radiation. Two beams are picked up by two mirrors M_1 and M_1'and rendered convergent by means of concave mirrors M_2 and M_2'. The beam are then allowed to traverse the sample and reference cells. These two beams are then directed by a series of mirrors onto opposite sides of a rotating sector (RS) enclosed in the photometer housing. The RS passes the reference beam and reflects the working beam on the focusing mirror M_5. The light then passes through the slit S_1 into the monochromator where it is dispersed by doubly passing through the prism P. One of the beam is selected by the mirror and focused on the detector D (a thermopile). An alternating potential which is signal from the detector is converted into frequency. The frequency can be determined from the rate of rotation of the RS . The signal is amplified which is used to drive a comb shaped attenuator across the reference and a recording pen. The recording pen and a paper drive synchronized with automatic rotation of the wavelength mirror plots the resulting IR spectrum .

3.4.4. Sample Preparation

KBr technique developed by Scheidt[4] has been employed to take IR spectrum of the coal samples. KBr pellets are prepared by mixing ~3 mg of finely powdered raw coal with ~300 mg of potassium bromide. The mixture is then milled in an agate mortar for 5 minutes and then pressed into pellet of 13 mm dia under 15000 psi pressure in a hand press pellet maker. The resulting pellets are thin and transparent. Since KBr is hygroscopic, the pellets have been dried over-night in a vacuum oven at 105 °C and then stored in a desiccator to avoid further moisture absorption.

3.4.5. IR Study of Carbonized Coal

Coal samples have been heat treated at temperatures 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C in a tubular furnace under argon atmosphere. The heat treatment set-up is shown in figure (3.4.4). About 1 gm of powdered coal sample is taken in a porcelain boat. The covered boat is then placed inside a reactor tube. The tube is then placed in the furnace. The reactor tube has been purged with argon for 10 minutes to expel all oxygen from the system before heating. The furnace is then switched on and temperature is increased at a rate of 20 °C per minute upto desired temperature and kept at the final temperature for 15 minutes. The temperature of the

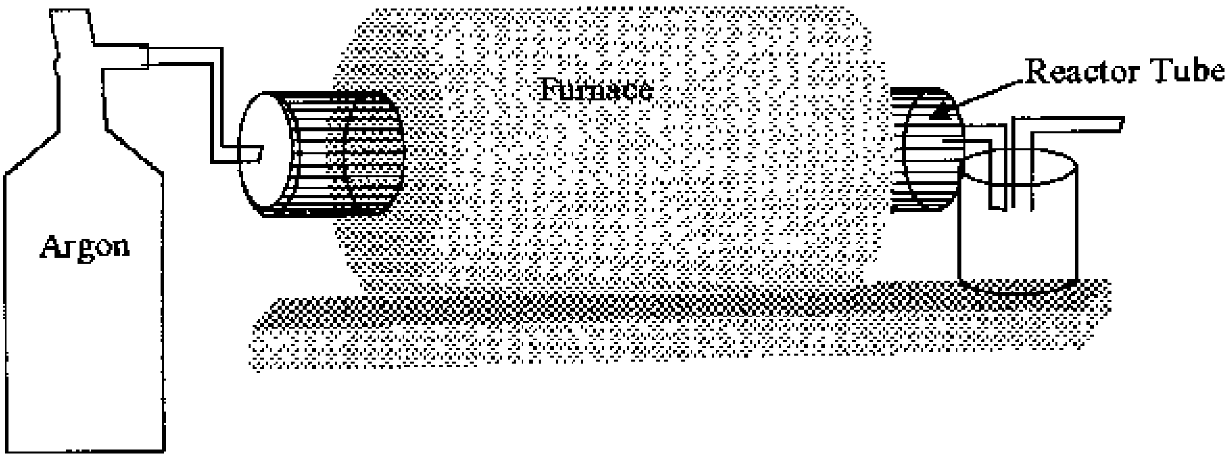


Figure (3.4.4) : Carbonization system

furnace is then lowered to room temperature gradually. A steady flow of argon is maintained through the tube throughout the experiment. The heat treated samples are then stored in a desiccator. Later IR spectrum of these samples are taken using KBr technique.

3.5. X-RAY DIFFRACTION OF COAL

3.5.1. Introduction

X-rays are most direct tools for studying the structural regularities and irregularities of solids. The first X-ray examination of coal was carried out by Mahadevan(7). The examination of coals at large scattering angles ($S = 2\sin\theta/\lambda > 0.4$ Å^{-1}) gives information on the structure and examination at medium scattering angle ($0.15 < S < 0.4$ Å^{-1}) gives information on the packing of molecules. X-ray diffraction has been used to see structural ordering by d- value calculation and crystallite size determination(7-9).

3.5.2. Instrumentation

Diffraction spectra of coals have been carried out using an X-ray Diffractometer (JDX-8D, JEOL Co. Ltd.,Tokyo, Japan) at 30 KV operating voltage and 30 mA current. The incident X-ray radiation is Cu-K_α with $\lambda = 1.542$ Å.

Coal samples are ground to 200 mesh (Tyler) size powder which are pressed on to the rectangular groove of a glass substrate which is then mounted on the frame of X-ray diffractometer.

3.5.3. d - Spacing Calculation

d - spacing for [002] line is calculated using well known Bragg equation

$$2\, d_{hkl} \sin\theta_{hkl} = n\lambda$$

Where, $\lambda = 1.542$ Å is the wave length of Cu-K_α radiation and θ_{hkl} is position of [hkl] band on the diffraction curve and 'n' is the number of order (here n=1).

3.5.4. Crystallite Size Determination

Crystallite dimension is determined using formula used by Blayden$^{(8)}$ which was derived by Warren$^{(9)}$. Layer diameter (L_a) has been calculated using the following equation.

$$\beta = \frac{1.84\lambda}{L_a Cos\theta}$$

where β is the full width at half maximum intensity of the diffraction pattern and θ is the position of the [100] plane. Stack height parameter (L_c) has been calculated using the following formula.

$$\beta = \frac{1.00\lambda}{L_c Cos\theta}$$

where β is the full width at half maximum intensity of the diffraction pattern and θ is the position of the [002] plane.

3.6. PARTICLE INDUCED X-RAY EMISSION SPECTROSCOPY

3.6.1. Introduction

In the present day world, the energy dispersive X-ray spectrometry (EDXS) has emerged as one of the powerful analytical methods for rapid simultaneous multielement analysis, either in trace or minor concentration.

The identification and the quantification of characteristic X-rays has been found as the basis of this method for qualitative and quantitative analysis respectively.

Electrons and photons (X-rays and γ-rays) have long been used to excite characteristic X-rays from target atom. Protons and other heavy ions such as alpha particles with few MeV of kinetic energy are now being widely used for this purpose, in view of the fact that such an excitation process produces relatively lower background and has large X-ray production cross-section. The method of characteristic X-ray excitation where charged particles are used is commonly referred to as Particle Induced X-ray Emission (PIXE) spectroscopy

The development of high resolution X-ray detectors [Si(Li) and HPGE] and the availability of low energy proton accelerator has augmented the scope of PIXE which is now very much known as proton induced X-ray emission spectroscopy.

3.6.2. Basic Principle

In PIXE analysis a specimen is bombarded with charged particle namely proton so that inner shell vacancies are produced in the target with the life time being of the order of 10^{-13} seconds. These vacancies are then filled up by electronic transition from higher shells resulting the emission of X-ray [Figure (3.6.1)] and also of auger electrons. The migration of shell vacancies by Coster-Kronig transition is another pessibility. The X-rays emitted in this process is characteristic of any element present

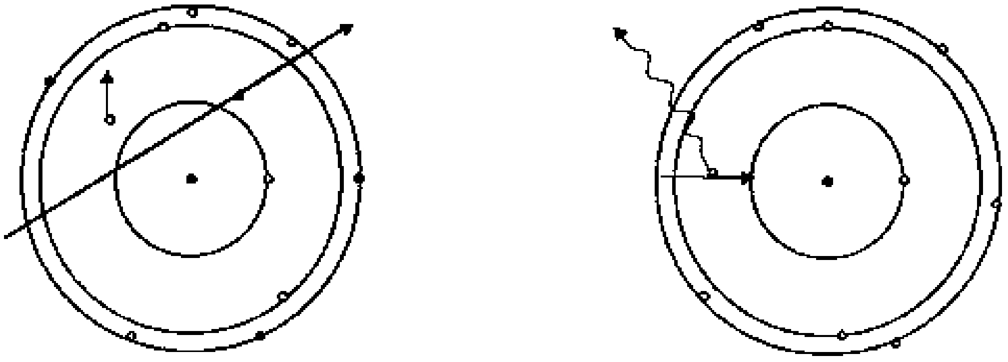

(a) (b)

Figure (3.6.1) : Schematic of inner-shell vacancy creation (a) and subsequent X-ray emission

in the matrix. In case of thin samples the yield of characteristic X-rays due to any element present in the specimen is determined by the X-ray production cross-section at the incident energy E_0. For uniform thin specimen , the yield $Y_0(i)$ of characteristic X-rays from an element '*i*' due to the passing of N_p number of proton is given by

$$Y(i) = N_p \varepsilon_i \frac{\Omega C_i N_a}{4\pi A_i(z)} \sigma(E_0) \quad \text{--- --- --- --- --- --- --- --} (1)$$

where, ε_i = efficiency of the detector at energy of X-ray for element '*i*',
Ω = detector solid angle,
N_i = number. of atoms of element '*i*' per gram of the matrix,
C_i = concentration of element '*i*' in the sample,
N_a = Avogadro's number,
$A_i(z)$ = atomic mass of the element '*i*',
$\sigma_i(E_0)$ = X-ray production cross-section at energy E_0,

In case of a thick specimen the proton energy loss and attenuation of characteristic X-rays have to be taken into account. In such cases, the production of characteristic X-rays by bombardment of proton can be calculated by integrating the X-ray production cross-section between the incident and exit proton energies 'E_0' and '0', taking the self absorption of emitted X-rays into account. Therefore, taking account for detector efficiency, experimental geometry and energy degradation proton beam within the material the X-ray yield for a thick target is given by,

$$Y(i) = N_p \varepsilon_i \frac{\Omega}{4\pi} \int_{E_0}^{0} \frac{C_i N_a}{A_i(z)} \exp(\mu_i x) \sigma_i(E) \frac{dE}{S_m(E)} \quad \text{--- --- --- ---} \quad (2)$$

where, μ_i = mass absorption coefficient of X-ray from the element 'i' in the absorber,

$S_m(E)$ = stopping power of proton within the sample matrix,

E = instantaneous energy of proton in the sample,

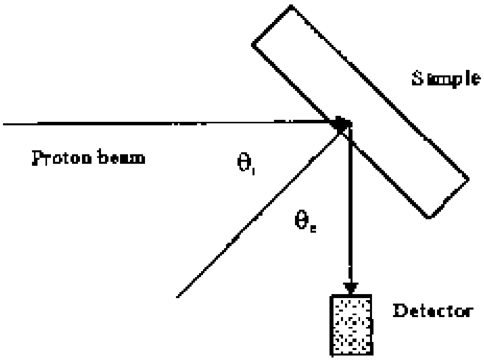
x = depth within the matrix at which the protons have degraded from incident energy E_0 to energy E.

The thickness x is given by

$$x = \int_{E_0}^{E} \frac{dE}{S_m(E)} \frac{Cos\theta_i}{Cos\theta_e}$$

θ_i = angle between the beam and an axis perpendicular to target surface,

θ_e = emergence angle of the X-ray w.r.t. target.



Figure(3.6.2) : Path of P-beam & X-ray

For absolute measurement of concentration numerical solution of equation (2) has to be obtained

3.6.3. Instrumentation

In this investigation the external beam PIXE method has been used. The details of the method has been discussed elsewhere$^{(10,11)}$ and the set-up is shown in figure (3.6.3). The proton beam of 2.5 MeV energy is obtained from the 3 MeV Van de Graaff accelerator at the Atomic Energy Centre Dhaka (AECD). The radial intensity distribution of the beam is roughly Gaussian in both x and y direction, the transport direction being z-axis$^{(12)}$.

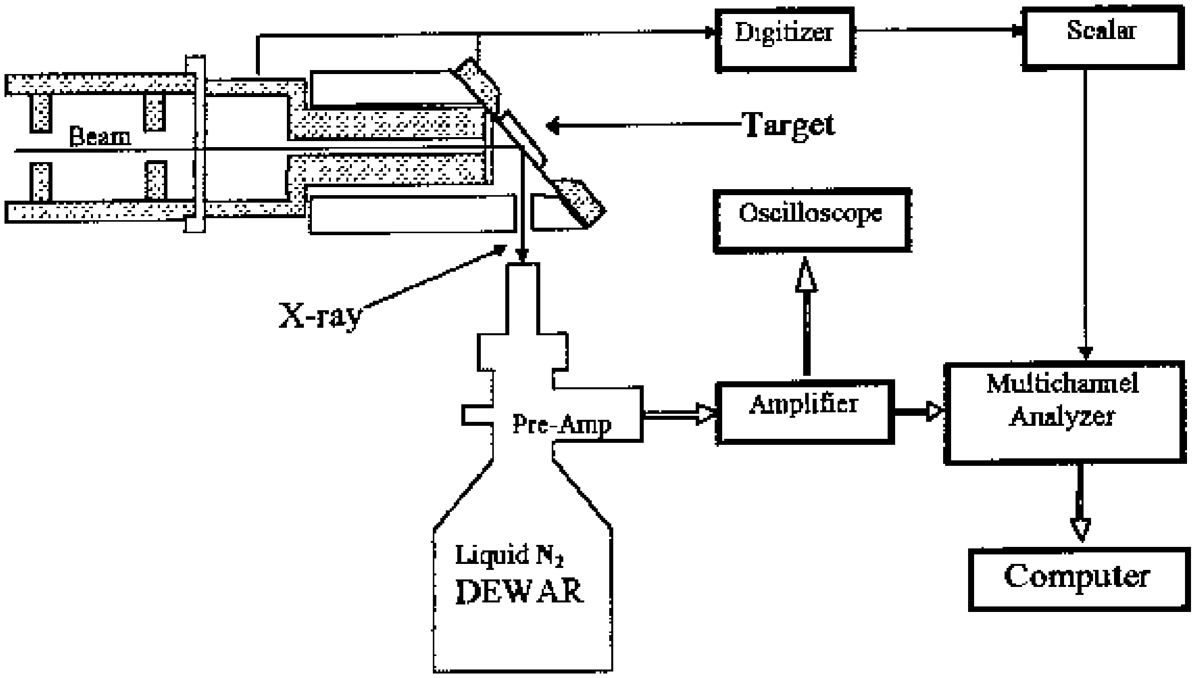


Figure (3.6.3) : Schematic diagram of PIXE setup

The proton beam is extracted through a Kapton window of 1.12 mg/cm^2 thickness. The window frame is insulated from the beam port and the collimator. To integrate the proton charge bombarding the sample, total current on the Kapton window and the target is monitored by measuring the ionization of air caused by proton beam outside the window. The Kapton window acts as diffuser so that proton beam outside is uniform across it cross-sectional area.

3.6.4. Sample Preparation

Coal samples have been collected at depths 673′, 1102′, 1121′, 1149′ of borehole GDH-38 and at depths 574′, 593′, 614′, 630′ of borehole GDH-39, from the top of the surface of Barapukuria Coal mine. The samples of each bore hole are mixed and ground together to 200 mesh size (Tyler..). Pellets of about 100 mg wt, 12mm in diameter and 1 mm thickness, are formed with a graduated stainless steel pellet maker under 15000 psi pressure. The pellets thus formed are found to be sufficiently strong for mechanical handling. For subsequent analysis the pellets are mounted on a 35 mm slide frame with adhesive tape and preserved in a desiccator until irradiation.

3.6.5. Sample Irradiation

Coal pellets mounted on slide frame have been irradiated in the external beam of PIXE set-up of the Van de Graaff accelerator at AECD, placing their smooth surface inclined at 45^0 to the beam direction. The beam current is maintained at 10 nA and each sample is irradiated with a total charge of approximately 10 μC. The energy of proton beam after energy loss at the exit window and the air path is about 2.0 MeV.

3.6.6. Data Collection

A Lithium drifted Silicon crystal [Si(Li)] is used to detect characteristic X-rays produced from the sample. Such a detector of 30 mm^2 area has a resolution of 170 eV at 5.9 KeV energy region. The data acquisition system includes a pre-amplifier, main amplifier, a 1024 channel Multichannel Analyzer (MCA) in pulse height analysis (PHA) mode, and an IBM compatible 486 Computer.

3.6.7. Data Analysis

Analytical information on the presence and concentration of elements in the sample lies in the spectrum of characteristic X-ray peaks superimposed on a background due to various atomic and secondary electron bremstrahlung processes and also due to gamma rays from various nuclear reactions. A typical X-ray spectra is complicated by the interference between X-ray lines of different elements.

A computer code AXIL (Analysis of X-ray spectra by Iterative Least Square fitting) is used for unfolding the spectra. The code is used to deconvolute the spectra and calculate peak areas giving X-ray yield for each element. These X-ray data are then used for determination of concentration of different elements present in the sample. The yield of X-ray per microgram of element per gram of matrix for one micro Coulomb of proton irradiation in a given geometry is calculated from equation(2) using ECPSSR theory(13) of X-ray production cross-section. The energy loss is calculated assuming 90% carbon as matrix and from the knowledge of proton stopping power which are calculated from Anderson and Zeigler(14). The lower limit of the integral is set to 0.5 MeV. The following parameters have to be calculated for deriving the solution of equation (2).

(a) Shell ionisation cross-section, $\sigma(E)$

(b) Stopping power of the matrix at different X-ray energy $S_m(E) = \Sigma W_i S_{mi}(E)$

(c) Energy loss ΔE

(d) Attenuation coefficients μ, for the characteristic X-rays in the sample matrix

and, (e) The efficiency of detector (ε_i) at different X-ray energy.

All the calculation procedure can be found elsewhere(13-16).

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Chapter 4 Results & Discussion

4. RESULTS & DISCUSSION

4.1. INTRODUCTION

Coal samples from bore holes GDH-38 and GDH-39 of Barapukuria are examined in this investigation. Some selected samples having vitrinite sections are characterized physically by proximate analysis and structurally by IR spectroscopy and X-ray diffraction. Trace elemental analysis is performed on coal samples of bore-hole GDH-38 and 39 of Barapukuria coal mine and bore-holes GDH-45 and 46 of Khalashpir coal mine using particle induced X-ray emission (PIXE) spectroscopy . Plate (4.1) and (4.2) shows an over view of some of the coal samples used in this investigation. The prominent vitrinite sections are shown in plates (4.1b), (4.2a) and (4.2b). Results of different analysis are discussed in the following sections.

4.2. RESULTS OF PROXIMATE ANALYSIS

The results of proximate analysis for the coal samples of bore hole GDH-38 and GDH-39 are shown in table (4.2.1) and table (4.2.2) respectively. The data shows that the moisture content of the investigated samples have a low moisture content and below 4 percent for almost all of the samples.

The ash content are minimal and varies from 1 to 16 percent with an average of about 7.0 percent for coals of bore-hole GDH-38 and about 7.5 percent for coals of bore-hole GDH-39. The upper most layer of GDH-38 at depth 673 feet has the maximum ash content and the lower most layer at 1149 feet has the minimum ash content. The GDH-39 bore hole has the highest ash at the 614 feet layer.

The volatile matter content and calorific value of the samples show that the Barapukuria coals are high volatile bituminous type. The volatile matter content of GDH-38 samples varies from 33 to 42 percent and those of GDH-39 samples varies from 32 to 40 percent on dry basis(db). The fixed carbon content of GDH-38 samples varies from 57 to 66 percent and those of GDH-39 samples varies from 60 to 68 percent on dry ash free (daf) basis. This indicates that on the average 65 wt % of carbon in Barapukuria coal are aromatic in nature.

The calorific values of the examined samples are considerably higher in magnitude. The calorific values of the GDH-38 samples varies from 14000 to 15500 Btu/lb. on moisture and ash free basis. The GDH-39 samples also have similar fuel values. These values were found to conform with the theoretically calculated values according to Forrester(1).

The proximate analysis suggests that Barapukuria coals are high volatile A bituminous type. The low moisture content, nominal ash content and high calorific values render its suitability for combustion in heating and power generation. At the same time the high volatile matter content suggests that Barapukuria coals can be used for chemical extraction.

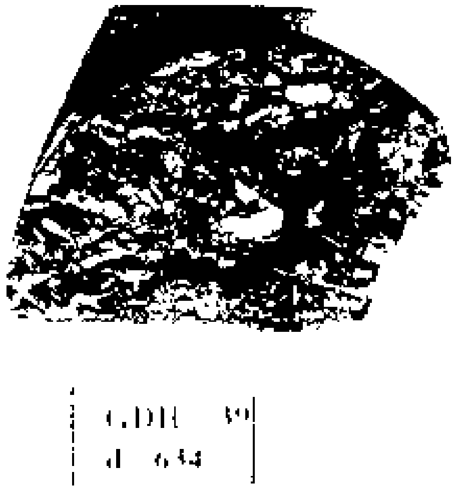


Plate (4.1.a) : Over view of lump coal sample of GDH- 39, Depth 634′ showing glossy vitrinite surface.

Plate (4.1.b) : Cross sections of lump coal sample of GDH-38, Depth 673′ showing banded structure of coal

Plate (4.2a) : Cross sections of lump coal sample of GDH-38, Depth 673' showing banded structure of coal

Plate (4.2) : Cross sections of lump coal sample of GDH-45, Depth-1022' showing banded structure of coal

Table (4.2.1) : Proximate Analysis of Barapukuria coal

Bore hole	Depth (in feet)	Moisture (wt %)	Ash % db	V.M % daf	F.C. % daf	Calorific Value Btu/lb. daf	Bulk density Kg/m^3	ASTM Rank
GDH-38	673	3.19	16.58	40.88	59.12	14296.64	1200	HvAb
	1102	2.46	10.25	42.73	57.27	15064.82	1400	HvAb
	1111	2.77	4.01	34.66	65.34	15205.53	1416	HvAb
	1121	2.43	4.40	41.84	58.16	15176.74	1280	HvAb
	1149	2.08	1.53	39.52	60.48	15136.20	1320	HvAb
	1161	3.24	5.79	33.97	66.03	15376.31	1312	HvAb

db = dry basis ; daf = Dry ash free

Table (4.2.2) : Proximate Analysis of Barapukuria coal

Bore hole	Depth (in feet)	Moisture (wt %)	Ash % db	V.M % daf	F.C. % daf	Calorific Value Btu/lb. daf	Bulk density Kg/m^3	ASTM Rank
GDH-39	563	3.57	4.30	36.66	63.64	14507.10	1316	HvAb
	574	3.59	3.90	40.05	59.95	14749.75	1680	HvAb
	593	3.65	6.40	39.42	60.58	15513.45	1530	HvAb
	614	3.30	14.58	32.15	67.85	15081.98	1280	HvAb
	630	2.97	11.30	35.51	64.49	15841.72	1330	HvAb
	638	3.82	4.43	34.02	65.98	14575.28	1334	HvAb

db = dry basis ; daf = dry ash free

4.3. RESULTS OF INFRARED SPECTROSCOPY

A total number of eight samples are examined by infrared (IR) spectroscopic study using the KBr technique. The IR spectra of different coals samples show similar results and suggest similar carbon skeleton, functional group and mineral matters present in coal. The spectra for GDH-38 coals are shown in figure (4.3.1) and figure (4.3.2) and the results are summarized in table (4.3.1).The spectra for GDH-39 coals are shown in figure (4.3.3) and (4.3.4) and the results are summarized in Table(4.3.2). The scale of ordinate for one sample is different from another and hence no quantitative interpretation is possible.

The common feature of all the spectra is the sloping of the base line toward the higher frequency (above 1000 cm^{-1}). The sloping is due to scattering of transmitted radiation by coal particles in KBr pellets.

All the spectra suggest higher degree of aromaticity of the samples which can be inferred from the band between 3000 and 3100 cm-1 and between 900 and 700 cm^{-1}. The aromatic C-H stretching region at 3050 cm^{-1} might be overlapped by broad –OH absorption band around 3300 cm^{-1} .

The band around at 2920 cm^{-1} is due to anti-symmetric C-H stretching modes of methylene group and the band near 2850 cm^{-1} is due to aliphatic C-H stretching mode. These two bands suggest the presence of aliphatic hydrogen species.

The large absorption band near 1600 cm^{-1} is indicative of condensed polynuclear aromatic ring vibration [2-5]. The intensity of this band is assumed to be enhanced by the presence of hydroxyl group on the ring and nitrogen in the ring[5-7].

The bands at 1400 and 1370 cm^{-1} indicates the presence of methyl CH_2 and aliphatic methylene (CH_3) respectively. The higher absorption in the 1400 cm^{-1} suggests that the GDH-38 and GDH-39 samples are composed of fewer aliphatic methylene group than methyl.

A pronounced band at 1030 cm^{-1} in all of the spectra indicate the presence of Kaolinite in all the samples.

The aromatic wag region is made-up of three primary peaks at 870, 817 and 753 cm^{-1} corresponding to one isolated two adjacent and four adjacent aromatic C-H group(8). The 870 cm^{-1} band due to isolated C-H wagging in condensed aromatic ring is indicative of higher degree of aromatic ring condensation. There are also some other mineral peaks at 540 cm^{-1} and 460 cm^{-1} due to kaolinite and at 435 and 410 cm^{-1} due to pyrites in the spectra of different samples.

IR spectra of carbonized coals are shown in figure (4.3.5), (4.3.6) and (4.3.7) respectively and the results are summarized in table (4.3.3). A little change is observed in spectra of coals heated to 300 ^{0}C. Intensity of band at 3400 cm^{-1} is found to decrease due to loss of water and other hydroxilic matter. The 900 to 700 cm^{-1} region remains unchanged.

At 500 ^{0}C a pronounced decrease in the absorption band at 3400 cm^{-1} due to loss of –OH is observed. Aromatic C=C stretching vibration band is found to shift toward 1580 cm^{-1}. This is due to conjugaton of aromatic rings and removal of aliphatic chains. The mineral band at 1030 cm^{-1} is also found to decrease. An observable phenomena in the 500 ^{0}C spectra is the overall increase of background absorption.

Structureles background absorption extends throughout the 4000 to 400 cm^{-1} region for coal samples carbonized above 500 ^{0}C which means that the chars have become opaque in the infrared. This suggests that above 500 ^{0}C some graphitization has occurred which is supported by XRD data that there is an increase in crystallite size or an increase in ordering of aromatic rings.

Table (4.3.1) : Infrared spectrum of GDH-38 coals

Depth (feet)					Band assignments
673	1102	1121	1149	Standard Coals	
Bands observed in (cm^{-1})					
3410	3410	3410	3410	3300	-OH / -NH Stretching vibration
——	——	——	3030	3030	Aromatic C-H stretching vibration
2910	2900	2910	2910	2925	Aliphatic C-H stretching vibration
2850	2850	2850	2850	2850	-CH stretching vibration
1600	1590	1590	1600	1600	Aromatic ring (C=C) vibration
1430	1440	1430	1430	1460	Aliphatic -CH_2 and -CH_3 groups
——	1370	1370	1370	1370	Aliphatic -CH_3 (methylene),Cyclic CH_2
——	1117	1120	——		
1040 ——	1030 1010	1030 1010	1030 ——	1035 1010	Si - O - Si stretching vibration
----	940	940	----		
——	910	910	910		
870	——	870	870	870	Out of plane vibration of single aromatic C-H group
820	820	810	820	817	Out of plane vibration of 2 adjacent aromatic C-H group
750	750	750	750	750	Out of plane vibration of 4 adjacent aromatic C-H group
——	690	690	——		
540 460	540 460	540 460	540 460	540 460	Kaolnite absorption
430	—— 410	430 410	430	430 415	Pyrite

Table (4.3.2) : Infrared spectrum for GDH-39 coals

Depth (in feet)					Band assignments
574	593	614	630	Standard coals	
Bands observed in (cm^{-1})					
3410	3410	3400	3400	3300	-OH / -NH stretching
2900	2900	2900	2910	2925	Aliphatic -CH stretching vibration
2850	2850	2850	2850	2860	Aliphatic C-H stretching vibration
1600	1595	1590	1600	1600	Aromatic C=C vibration
1440	1440	1440	1440	1450	Aliphatic -CH_2 and -CH_3
	1370		1370	1370	Aliphatic -CH_3 (methylene), Cyclic CH_2
	1120	1120	1100		
	1095	1095	1095		
1030 1010	1030 1010	1030 1010	1030 1010		Si - O - Si stretching vibration
		950	940		
915	915	917	915		
——	870	870	——	870	Out of plane vibration of single aromatic C-H group
——	815	815	——	817	Out of plane vibration of 2 adjacent aromatic C-H group
750	750	750	750	750	Out of plane vibration of 4 adjacent aromatic C-H group
690	690	690	690		
540 465	540 465	540 465	540 465	540 465	Kaolinite absorption
430	—— 410	430 410	430	430 415	Pyrite

Table (4.3.3) : Infrared spectrum of carbonized coals

Carbonization temperature							Band assignments
300 ^{0}C	400 ^{0}C	500 ^{0}C	600 ^{0}C	700 ^{0}C	800 ^{0}C	900 ^{0}C	
Bands observed							
3400	3420	——	3410	——	——	——	-OH / -NH stretching
2910	2900	2910	2920	——	——	——	Aliphatic -CH stretching vibraton
2850	——	2850	——	——	——	——	Aliphatic C-H stretching vibration
2300	2300	2300	2350	——	——	——	
1600	1600 - 1580	1600 - 1580	1580	——	——	——	Aromatic C=C vibration
1440	1420	1440	1450	——	——	——	Aliphatic -CH$_2$ and -CH$_3$
1040 1010	1030 1010	1040 1010	1030	——	——	——	Si - O - Si stretching vibration
860	870	——	870	——	——	——	Out of plane vibration of single aromatic C-H group
800	815	800	800	——	——	——	Out of plane vibration of 2 adjacent aromatic C-H group
750	750	750	750	——	——	——	Out of plane vibration of 4 adjacent aromatic C-H group
690	690	690	690	——	——	——	
540 465	540 465	540 465	540 465	——	——	——	Kaolinite
430	—— 410	430 410	430	——	——	——	Pyrite

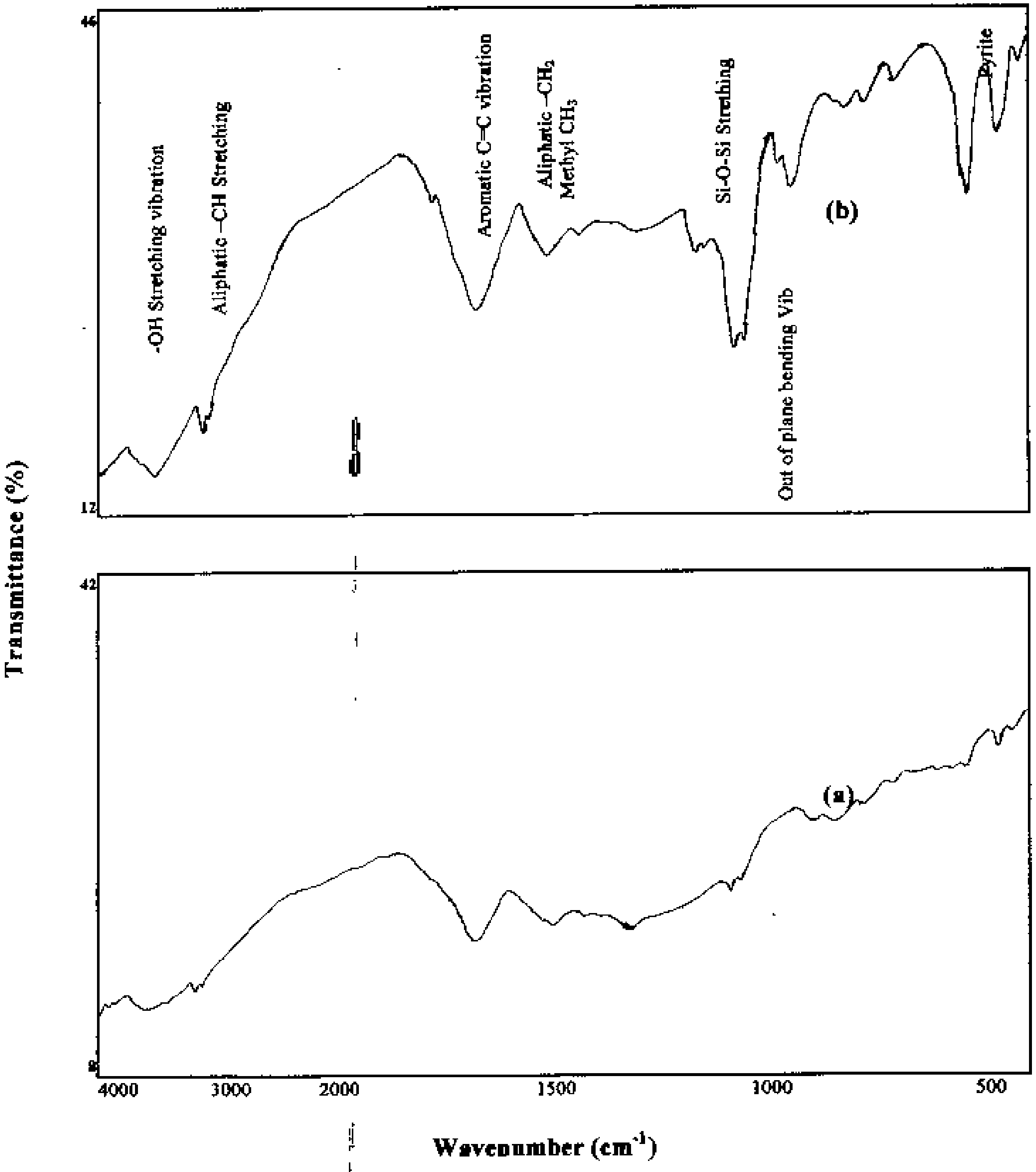


Figure (4.3.1) : Infrared spectrum of Barapukuria coals of bore-hole GDH-38 (a) d-673′ (b) d- 1102′.

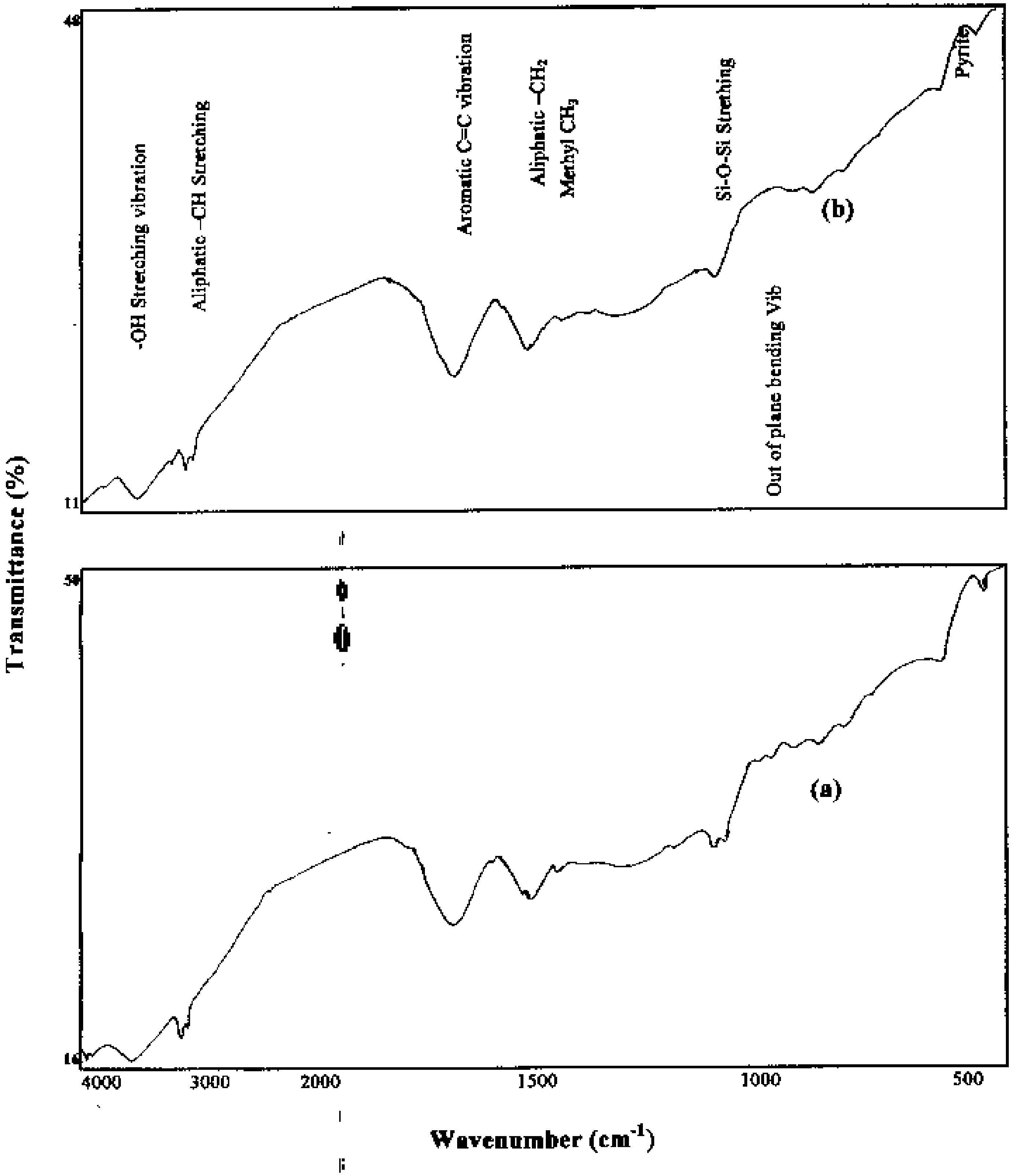


Figure (4.3.2) : Infrared spectrum of Barapukuria coals of bore-hole GDH-38 (a) d-1121′ (b) d-1149′.

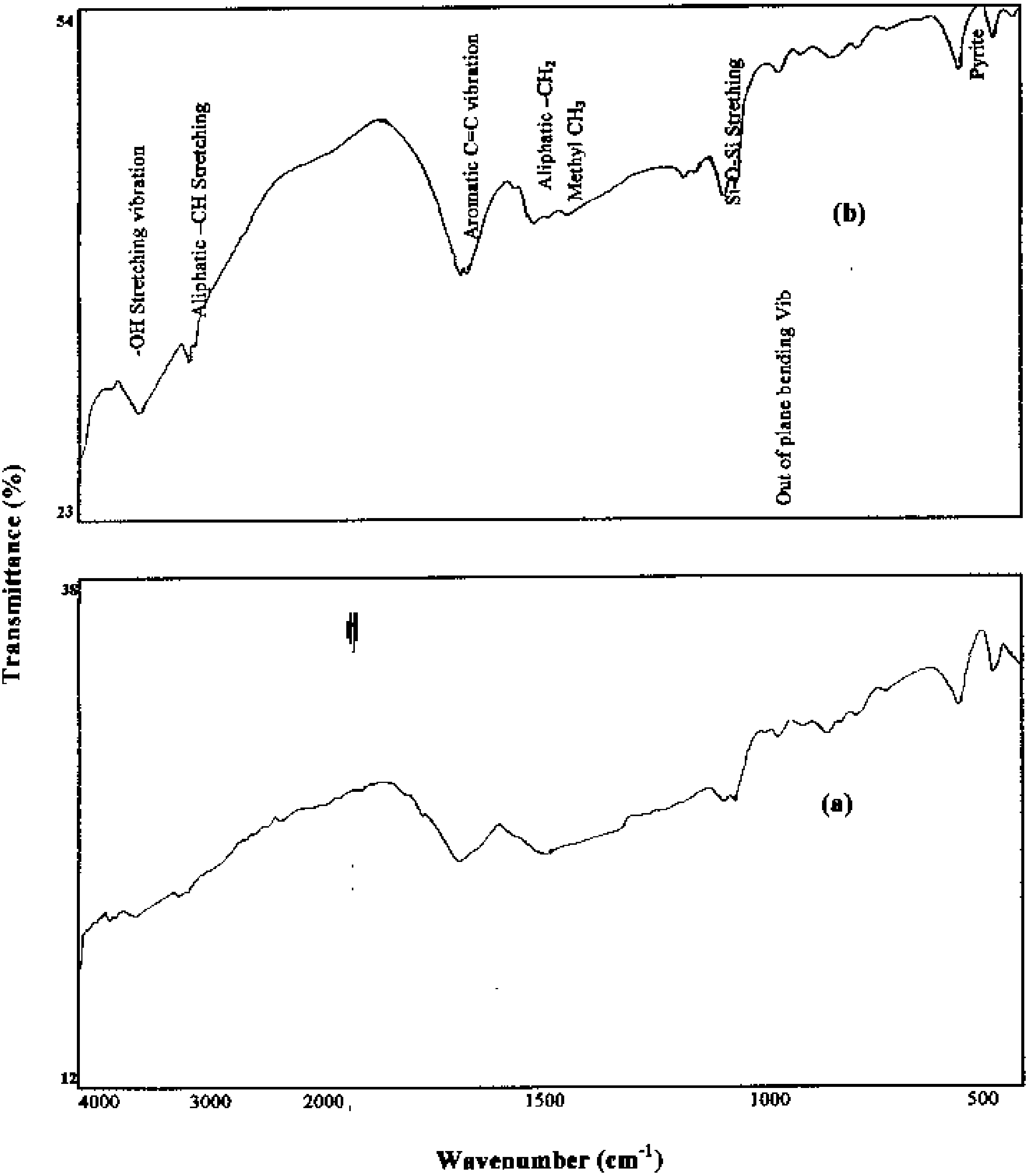


Figure (4.3.3) : Infrared spectrum of Barapukuria coals of bore-hole GDH-39 (a) d-574′ (b) d-593′.

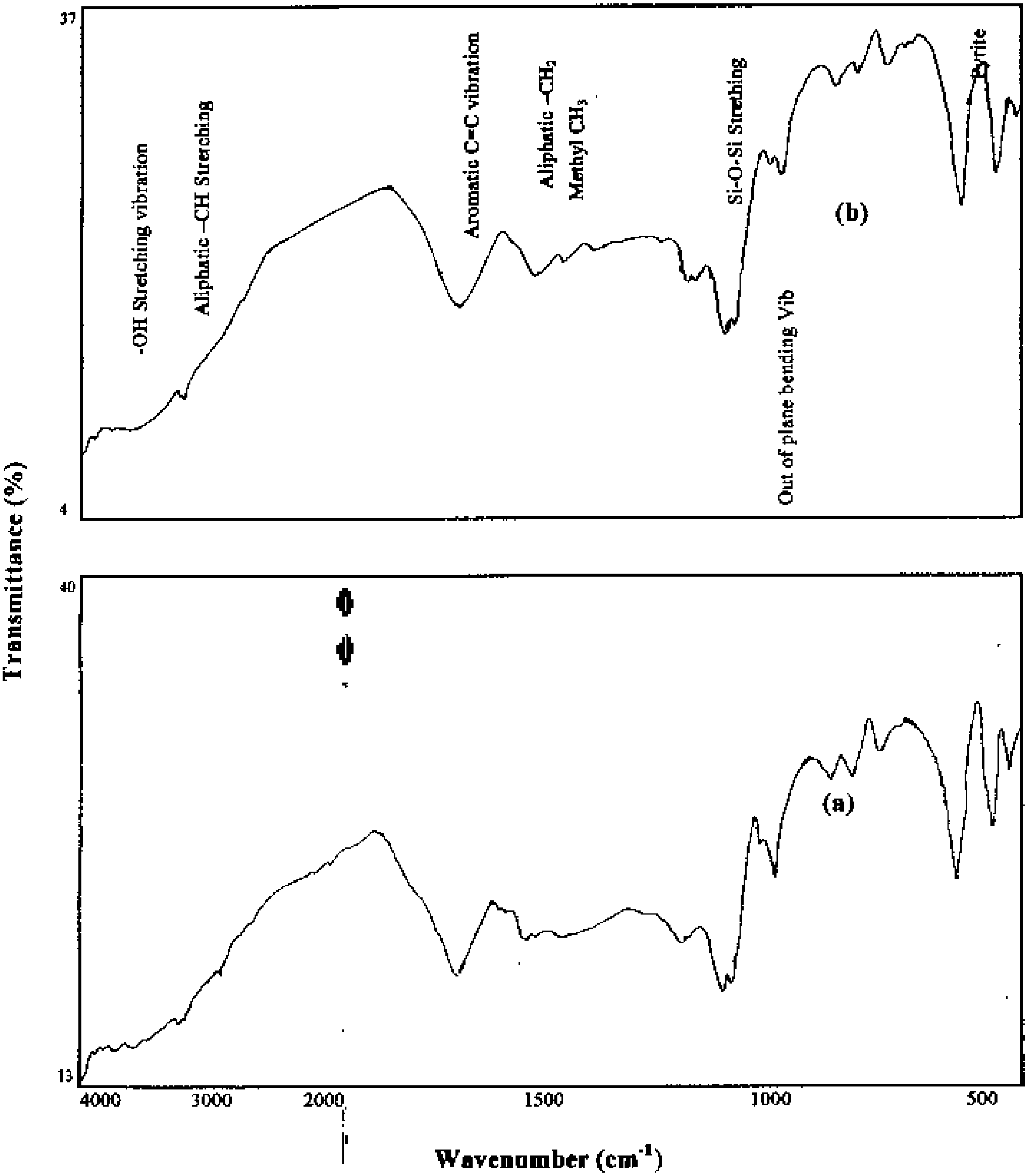


Figure (4.3.4) : Infrared spectrum of Barapukuria coals of bore-hole GDH-39 (a) d-614′ (b) d-630′.

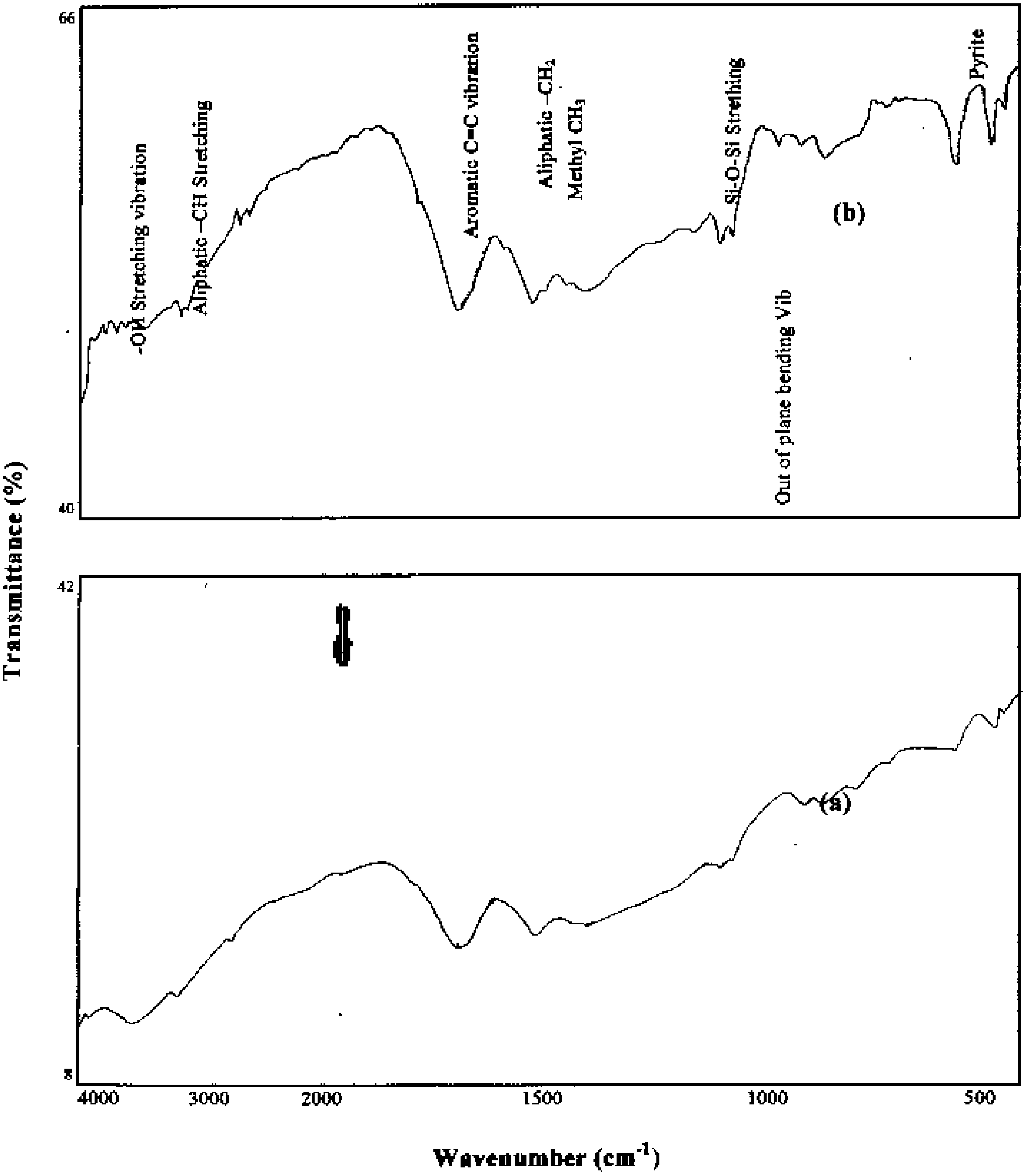


Figure (4.3.5) : Infrared spectrum of Carbonized coals of bore-hole GDH-38 (a) raw sample d-673′ (b) carbonized at 300°C/15 min.

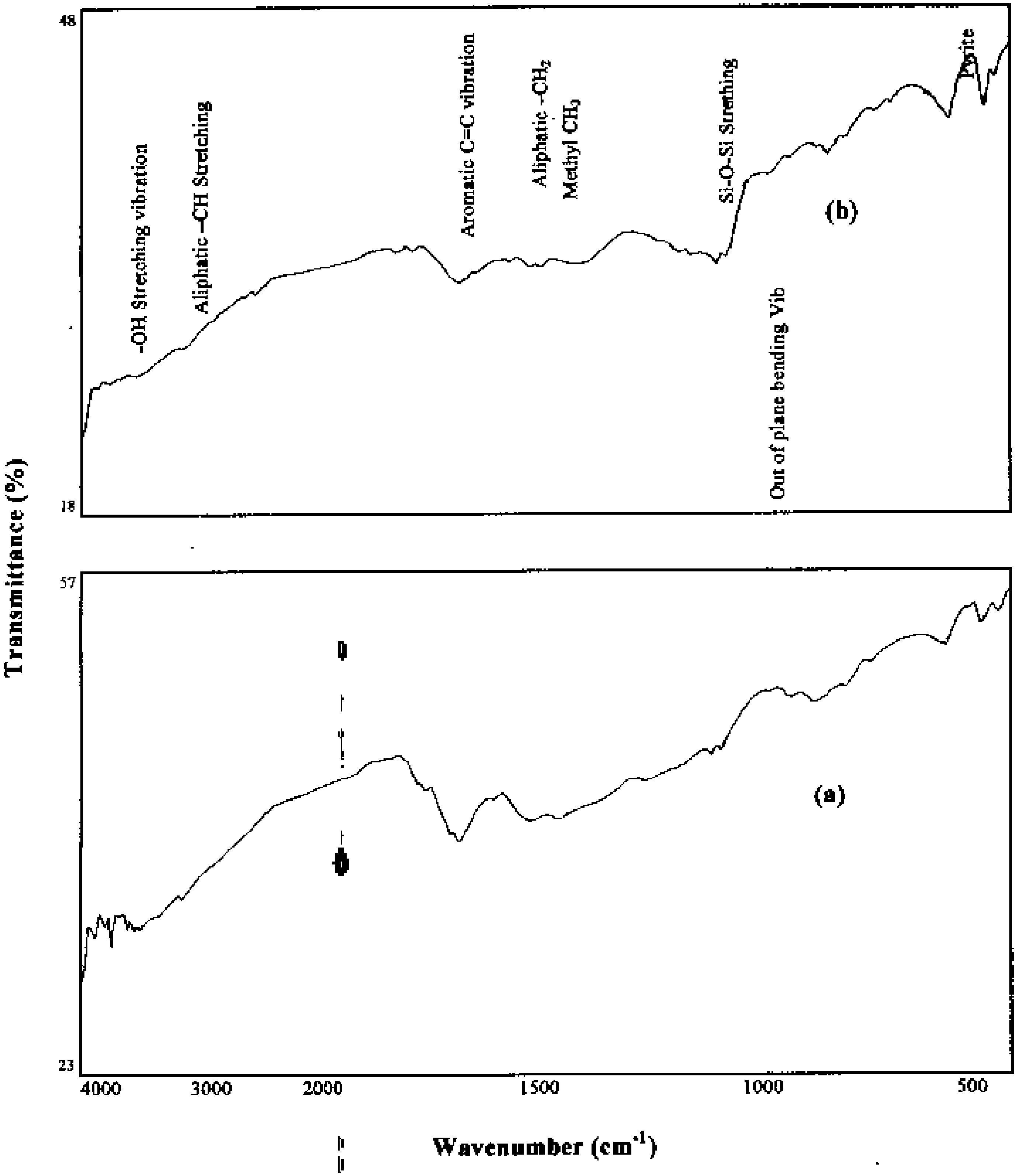


Figure (4.3.6) : Infrared spectrum of Carbonized coals of bore-hole GDH-38 (a) carbonized at 400 ^{0}C (b) carbonized at 500 ^{0}C/ 15 min

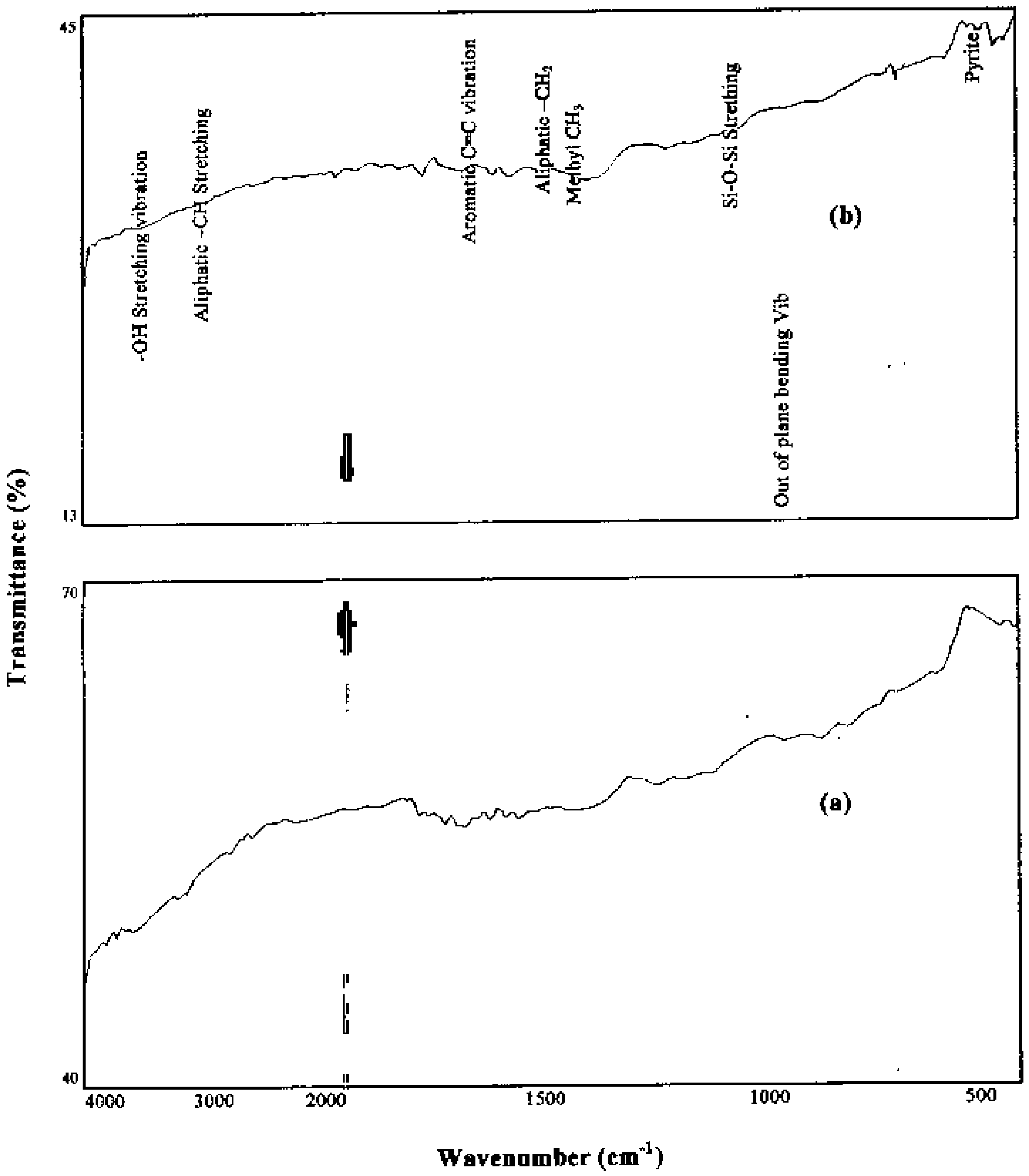


Figure (4.3.7) : Infrared spectrum of Carbonized coals of bore-hole GDH-38 (a) carbonized at 600 °C (b) carbonized at 700 °C/15 min.

4.4. RESULTS OF X-RAY DIFFRACTION

X-ray diffractograms for coals of bore-hole GDH-38 and GDH-39 are shown in figures (4.4.1) and (4.4.2) and figures (4.4.3) and (4.4.4) respectively. The results are summarized in table (4.4.1).

All the diffractograms are continuous curves with initial broad peak between 4 and 14^0 (2θ) on which more or less diffused peaks are superimposed indicating the largely amorphous nature of coal. There are some small peaks throughout wide angle region ($S = 2 \sin\theta / \lambda \geq 0.15$ Å^{-1}) which are due to micro-crystallites of ordered aromatic lamellae and due to different mineral phases.

A peak at 12^0 (2θ) superimposed on the left side of initial broad peak is identified as reflection from kaolinite which is accompanied by a peak at 25^0 (2θ). There are some other diffused peaks throughout the wide angle region which might be reflections from different minerals such as quartz, pyrite etc.

A diffused peak between 24 and 26^0 (2θ) can be observed in all of the diffractograms which is identified as c-peak (10,11) and is caused by reflections from planes stacked nearly parallel to each other. These weak peaks indicate poorly ordered regions within the coal matrix. The ordered region are formed by stacking of planer sheets formed by substitution of aromatic rings. The stack height calculation following Blayden et al.(10) formula shows L_c parameter to lie between 11 to 15 Å. Thus there can be 3 to 4 layers stacked parallel to each other. Another peak around 20^0 (2θ) with d-values around 4.44 Å is identified as γ-peak(9,10). The γ-peak is thought to be caused by reflections from buckled aromatic sheets or aliphatic materials.

A small peak around 33^0 with d-values 2.73 Å is due to reflections from crystallites of pyrites or marcasites(13).

Another peak around 35^0 is identified as cross lattice line that is a-peak. This peak is caused by reflections from individual hexagonal (aromatic) planes acting as two dimensional gratings. The layer diameter determined from these peaks are about 20 Å. The layer diameter and stack height parameter determined from broadening of a-peak and c-peak respectively are not true dimension of crystallite region, rather they are related to the degree of coherence of planar layer.

X-ray diffractograms of carbonized coals are shown in figure (4.4.4) and (4.4.5) and the results of analysis are summarized in table (4.4.2). The diffractograms show a clear and sharp appearance of 002 line for the coal samples carbonized at 300 °C. This is a clear indication of increase of ordering between planar aromatic layers. The sharpness and peak height of the line is found to increase with temperature. From calculation it is found that the stack eight parameter increases from 11 Å to 22 Å and the layer diameter increases from 19 Å to 28 Å.

Table (4.4.1) : X-ray analysis of Barapukuria Coal

Sample = Bore-hole	Depth	002 line (2θ) deg	d_{002} Å	100 line (2θ) deg	d_{100} Å	γ-line (2θ) deg	d_γ Å	β_{002} deg	$L_c = \frac{1.00\lambda}{\beta \cos\theta_c}$ Å	β_{100} deg	$La = \frac{1.84\lambda}{\beta \cos\theta}$ Å
GDH-38	673′	26.1	3.41	38.0	2.37	20.6	4.31	8	11.30	9	19.21
	1102′	24.7	3.60	38.2	2.38	18.4	4.82	8	11.30	8	21.50
	1121′	24.4	3.64	35.4	2.58	20.5	4.33	6	15.06	8	21.33
	1149′	24.4	3.64	37.8	2.38	20.2	4.40	6	15.06	9	19.09
GDH-39	574′	24.5	3.63	38.2	2.36	19.1	4.42	6	15.06	8	21.50
	593′	24.4	3.64	38.6	2.33	20.0	4.44	6	15.06	8	21.53
	614′	26.6	3.35	38.2	2.36	20.6	4.31	6	15.13	8	21.50
	630′	24.4	3.64	35.4	2.58	20.2	4.40	6	15.06	----	----

Table(4.4.2) : X-ray analysis of Carbonized samples

Sample	HTT °C	002 line (2θ) deg	d_{002} Å	100 line (2θ) deg	d_{100} Å	γ-line (2θ) deg	d_{γ} Å	β_{002} deg	$Lc = \frac{1.00\lambda}{\beta\cos\theta}$ Å	β_{100} deg	$La = \frac{1.84\lambda}{\beta\cos\theta}$ Å
GDH-38 depth-673'	Raw	26.1	3.41	38.0	2.37	20.6	4.31	8	11.30	9	19.21
	300	26.3	3.39	38.4	2.34	19.2	4.62	6	15.12	8	21.51
	500	26.1	3.41	37.8	2.38	20.5	4.33	4	22.67	8	21.47
	700	26.3	3.39	35.0	2.56	18.5	4.79	5	18.14	7	24.35
	900	26.2	3.41	35.0	2.56	20.6	4.32	4	22.67	6	28.40

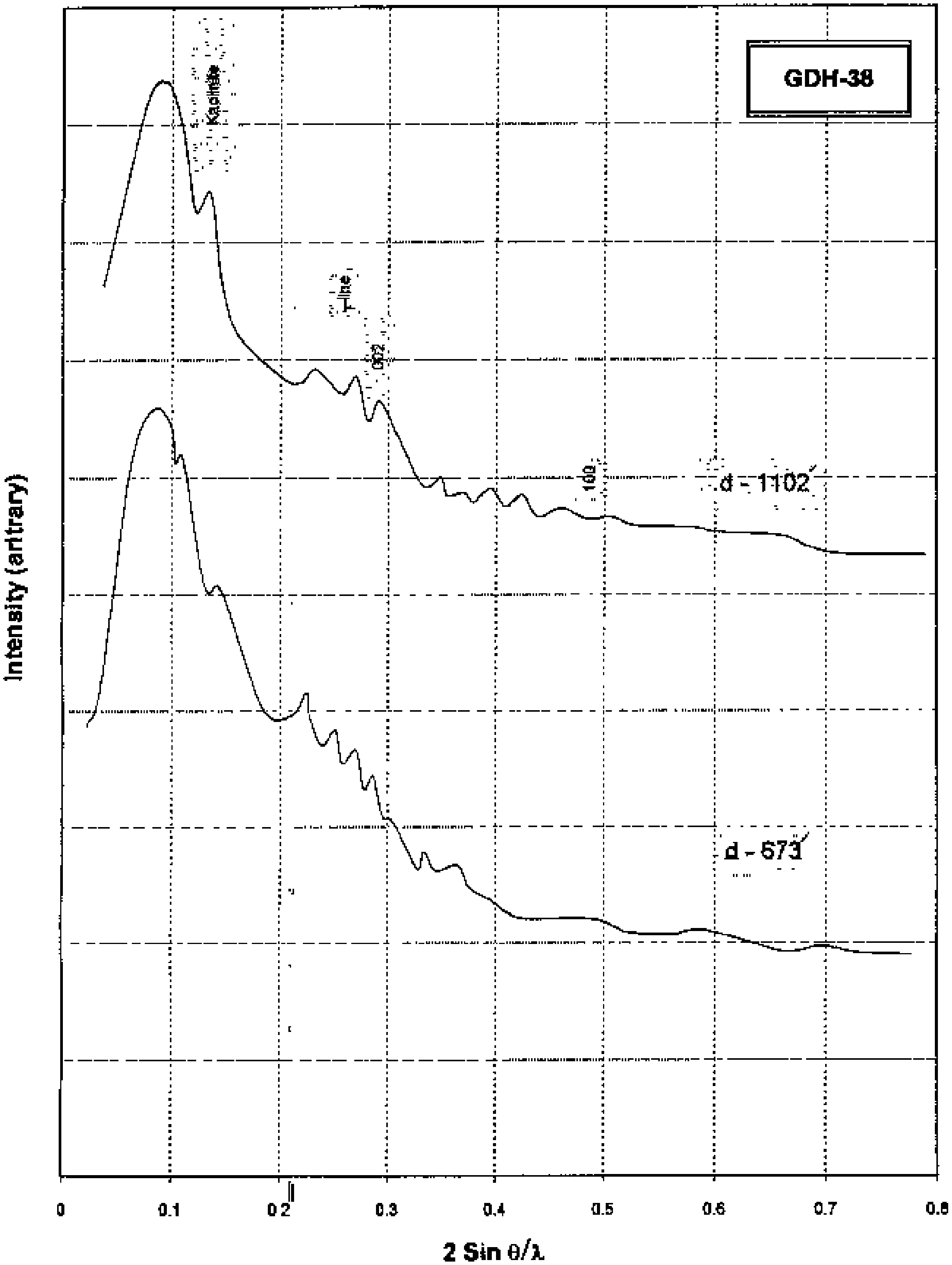


Figure (4.4.1) : X-ray diffractograms of coal samples

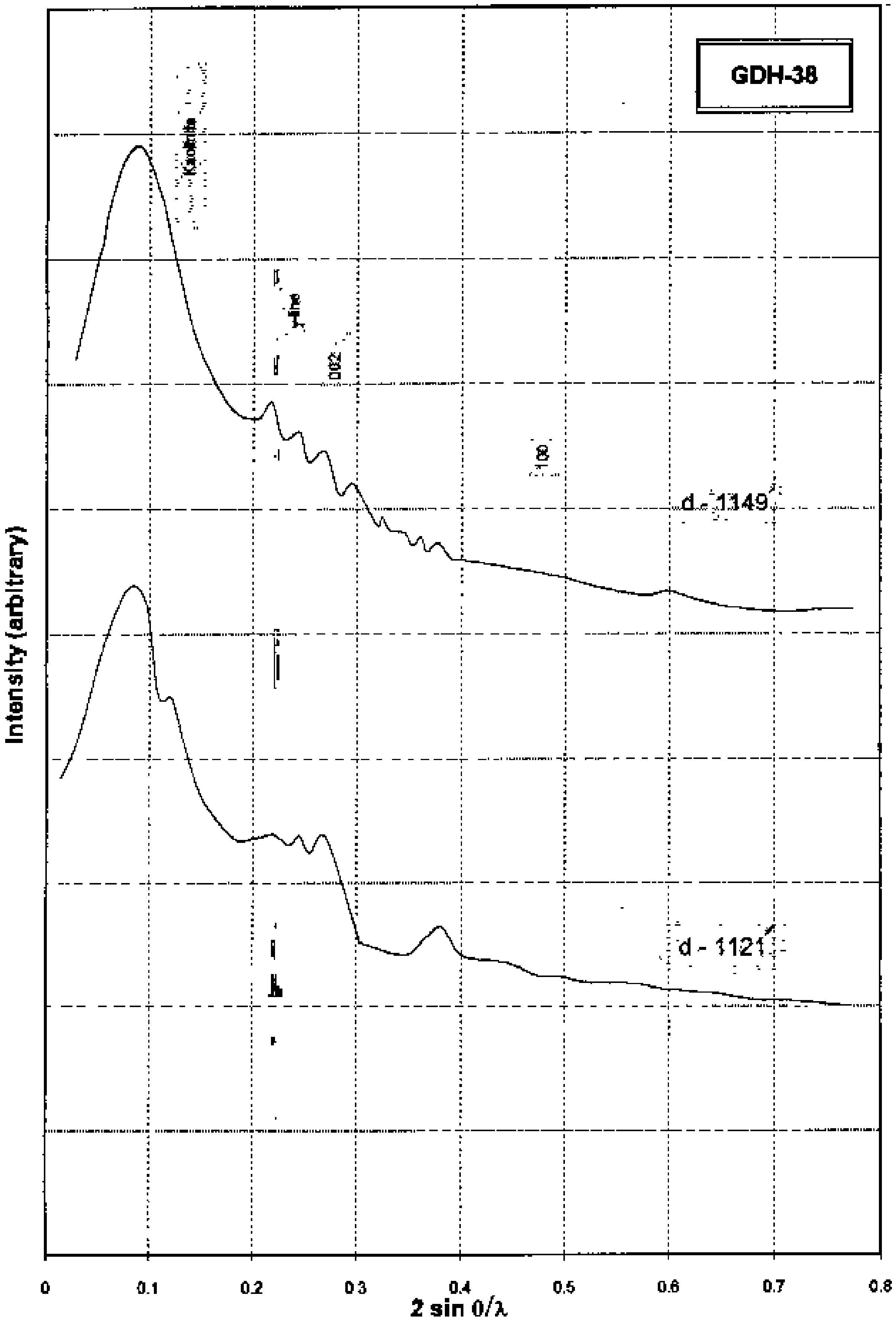
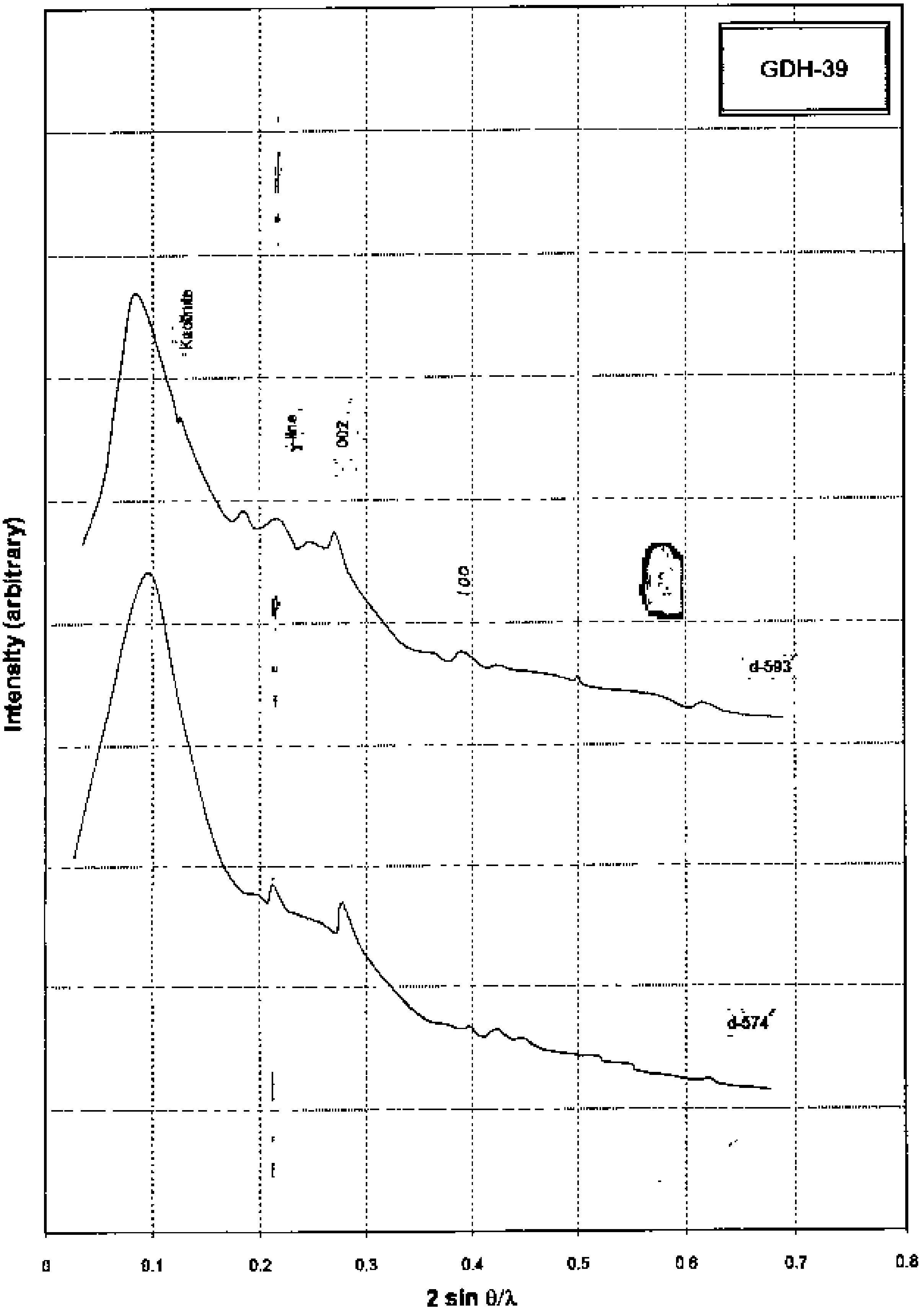


Figure (4.4.2) : Xray diffractograms of coal samples



Figur (4.4.3) : X-ray diffractograms of coal samples

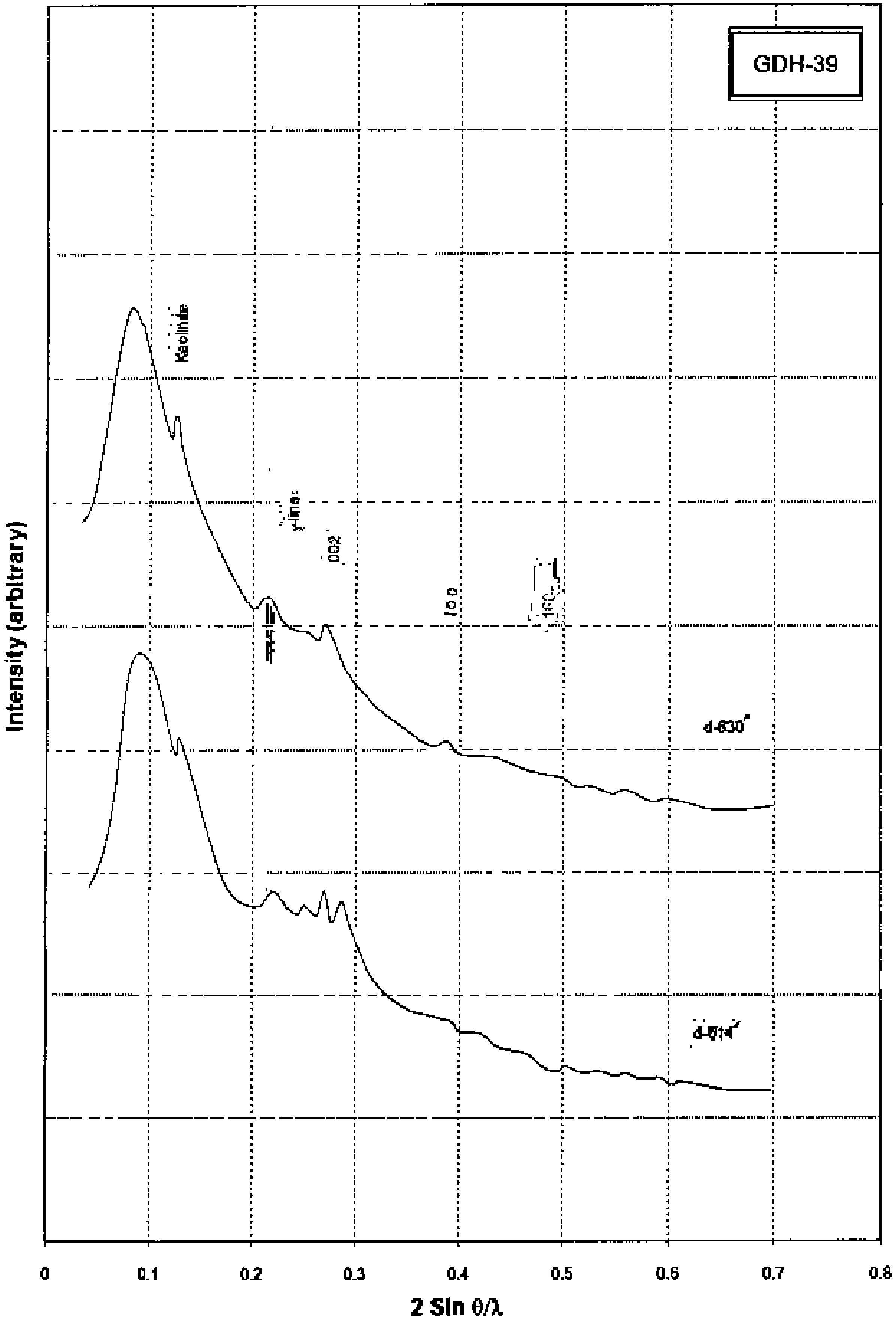


Figure (4.4.4) : X-ray diffractograms of coal samples

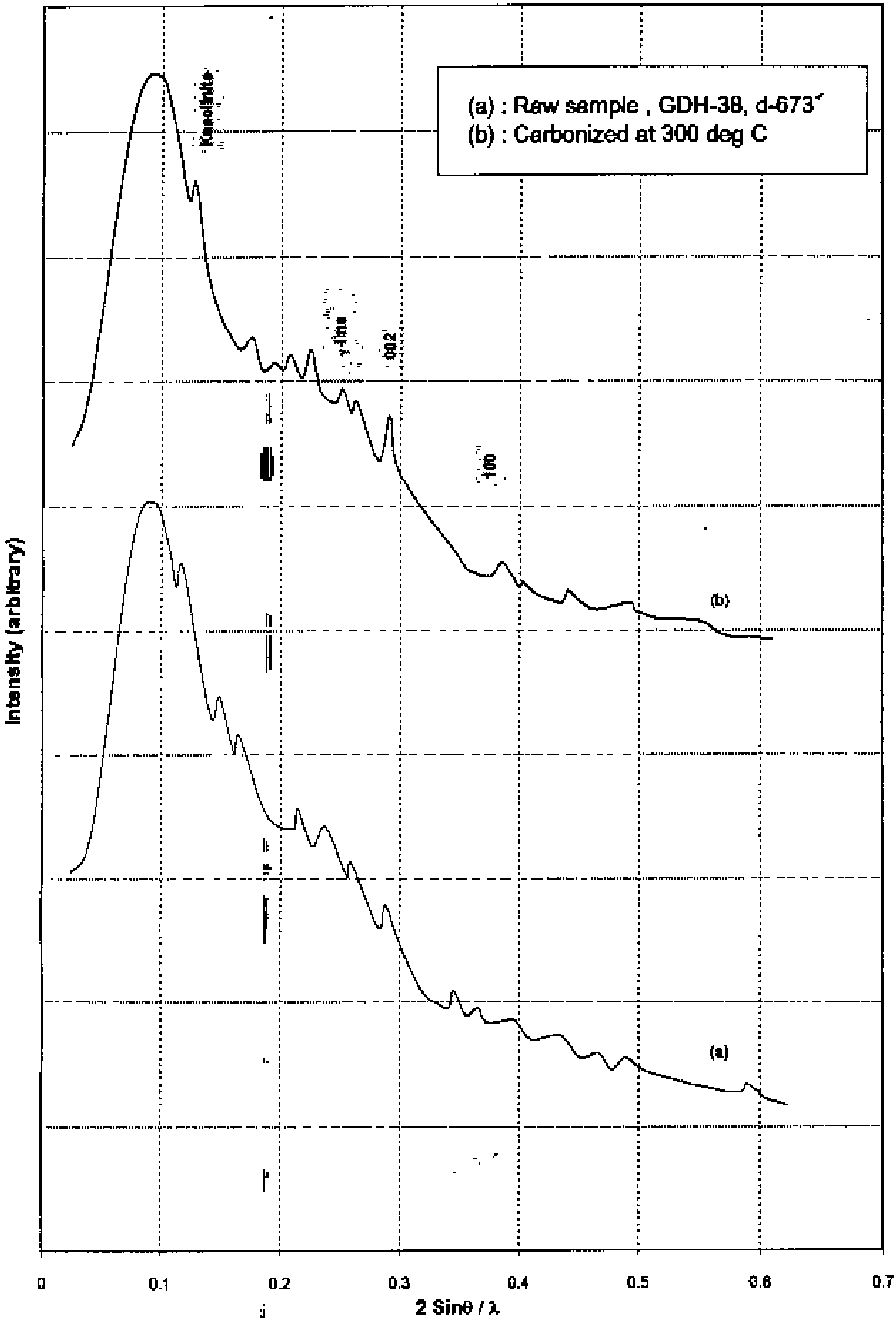


Figure (4.4.5) : X-ray diffractograms of carbonized coals

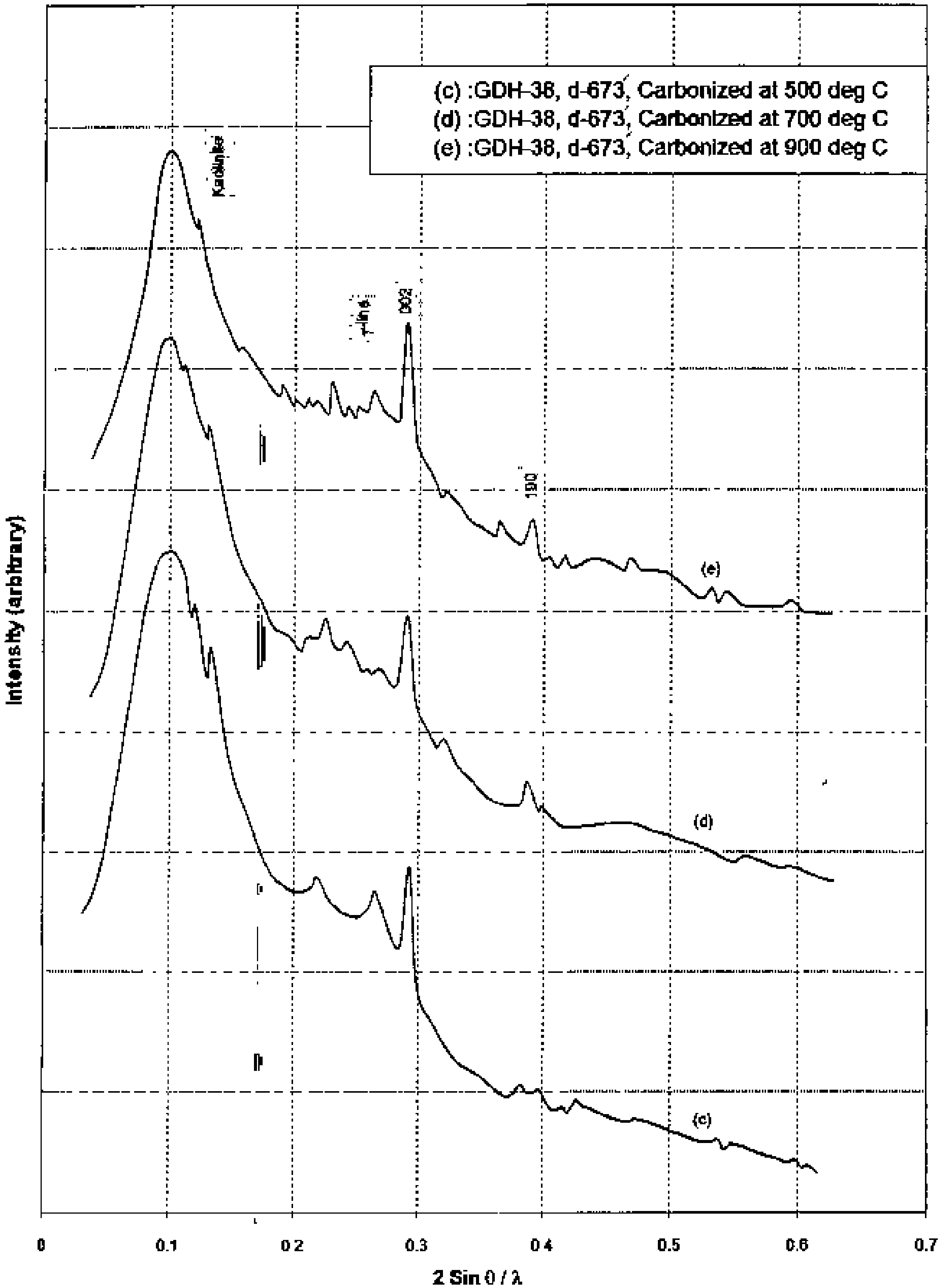


Figure (4.4.6) : X-ray diffractograms of carbonized coals

4.5. RESULTS OF PIXE SPECTROSCOPY

The results of trace element analysis using proton induced X-ray emission spectroscopy are summarized in table (4.5.1) and table (4.5.2). The characteristic spectrum of different coals of the respective bore-holes are given in figures (4.5.1) and (4.5.2) respectively. The analysis shows that arsenic contents are minimum in the coals and is detected only in coal of bore hole GDH-39 in 1.39 ppm, whereas it is not detected in coals of bore-hole GDH-38 of Barapukuria and GDH-45 and 46 of Khalashpir coal mine

Bromine content in coal of bore-hole GDH-38 is found to be excessively high as compared to its content in earth's crust of 2.5 ppm and in Canadian coals (1-13ppm). It's content is minimum in coal of bore-hole GDH-39. Maximum Co is found in GDH-39 coal (73 ppm) and minimum in GDH-38 (7.22 ppm). Cr content in all of the samples is about 20 ppm. The copper content varies from 17 ppm to 31 ppm in the coals investigated.

Ca is one of the major elements present in coal. Its content varies from 300 ppm to 1200 ppm in the coal samples investigated. Iron is another major element in coal whose content generally increases with ash content of coal. Fe content in GDH-38 coal is considerably higher (12774 ppm) than the others. GDH-45 and 46 coals contain only around 4500 ppm of Fe on the average. which indicates their lower ash content.

Cobalt content in the coals are nominal, 7.3 ppm in coal of bore hole GDH-38 and 73 ppm in coal of bore hole GDH-39. Co content of the two other bore holes are similar.

Ga, a semiconducting material, is found in all of the coal samples. Its content varies from 5 to 12 ppm in the samples examined as compared to its concentration of 15 ppm in earth crusts. Germanium, an other important semiconducting material Ge has been found in all the samples. The concentration of Ge in GDH-38 and GDH-39 coals are about 7 ppm. GDH-45 coal contains the largest concentration of Ge (13 ppm) while GDH-46 coal contains the lowest concentration (1.3 ppm). Concentration of Mn is higher in GHD-38 and 46 coal (about 200 ppm) while the other two bore holes GDH-39 and 45 contain much lower amount of it. Overall Mn content of coals are lower than its concentration in earth's crust(14) (950 ppm).

The concentration of Pb, an important trace element in fossil fuel, is found to vary form 25 to 35 ppm in coal of bore bole GDH-38 and in coal of bore-hole GDH-39. Pb concentrations in GDH-45 and GDH-46 bore-hole coals have been found to be 15 and 9 ppm respectively.

The concentration of nickel varies from 5 to 40 ppm in the investigated samples. Rubidium concentration in the samples is found to lie between 5 to 25 ppm and Strontium content varies from 17 to 91 ppm.

Selenium, which is known to be a carcinogenic substance, has been detected only in GHD-39 coal in 1.87 ppm.

The results of PIXE analysis has been evaluated by comparing with Atomic Absorption analysis (AAS) for three elements Mn, Cu and Pb. 0.5g sample is ashed at 488 ^{0}C and then digested in HNO_3 and then dissolved in deionized water and filtrated. The final volume of filtrated sample is 10 ml which is examined in Perkin – Elmer Model-3100 flame atomic absorption spectrophotometer. The results are compared as shown in table (4.5.3).

The results of trace element analysis are compared with their respective values in some Canadian coals(14). Major elements like K, Ca, Fe, Mn,etc and minor elements like Ni, Cu, As, Se, Sr, etc. have concentrations that fall within the range of their respective values in the Canadian coals.

The concentration of Co, Ga, Br, Rb etc. are found to be greater than their values in Canadian coals. The coals are found to be enriched with Se, Br and Pb since their values are greater than their respective values in earth's crust

Table(4.5.1) : Concentration of some trace elements in Barapukuria coals

Z - number	Elements	GDH-38		GDH-39	
		conc. (ppm)	error	conc. (ppm)	error
19	K	315.94	14.24	302.40	4.14
20	Ca	630.14	8.91	396.03	2.07
22	Ti	1161.49	5.40	1362.78	1.60
24	Cr	23.10	1.09	20.88	0.26
25	Mn	211.63	1.92	0.47	0.20
26	Fe	12774.80	12.52	2128.05	1.68
27	Co	7.22	2.53	73.00	0.53
28	Ni	8.03	0.85	5.03	0.20
29	Cu	29.74	1.20	17.15	0.26
30	Zn	23.51	1.76	13.29	0.25
31	Ga	12.59	1.50	5.62	0.25
32	Ge	6.88	2.07	7.08	0.28
33	As	----	----	1.39	0.35
34	Se	----	----	1.87	0.29
35	Br	173.71	5.99	12.74	0.45
37	Rb	24.92	6.61	5.37	0.56
38	Sr	27.19	3.69	91.78	1.58
82	Pb	25.31	2.36	34.30	0.84

Table (4.5.2) : Concentration of trace elements in Khalaspir coals

Z - Number	Elements	GDH - 45		GDH – 46	
		conc (ppm)	error	conc (ppm)	error
19	K	520.82	16.71	593.79	17.2
20	Ca	1813.72	13.64	509.65	8.92
22	Ti	791.48	4.44	125.21	5.11
24	Cr	18.93	0.89	23.78	1.01
25	Mn	14.42	0.80	183.11	1.79
26	Fe	4646.64	7.56	5391.60	8.17
27	Co	15.82	1.77	7.85	1.85
28	Ni	40.24	1.04	22.72	0.90
29	Cu	22.41	1.06	31.34	1.08
30	Zn	45.45	1.57	26.49	1.21
31	Ga	8.10	1.09	8.70	1.16
32	Ge	13.49	1.54	1.92	1.36
35	Br	12.31	2.46	--------	--------
37	Rb	17.01	3.74	23.77	3.93
38	Sr	17.57	2.97	53.47	4.34
82	Pb	15.93	1.91	9.15	0.85

Table (4.5.3) : Comparison between PIXE and AAS analysis

Concentration (C) μg/g				
Element		PIXE (C_p)	AAS (C_A)	Deviation,% $D=\frac{C_P-C_A}{C_P}\times 100$
Mn	GDH-38	211.63	263.5	-24.5098
	GDH-45	14.42	17.60	-22.0527
Cu	GDH-38	29.74	27.41	7.8346
	GDH-45	22.41	21.16	5.5779
Pb	GDH-38	25.31	17.39	31.292
	GDH-45	15.93	13.04	18.1419

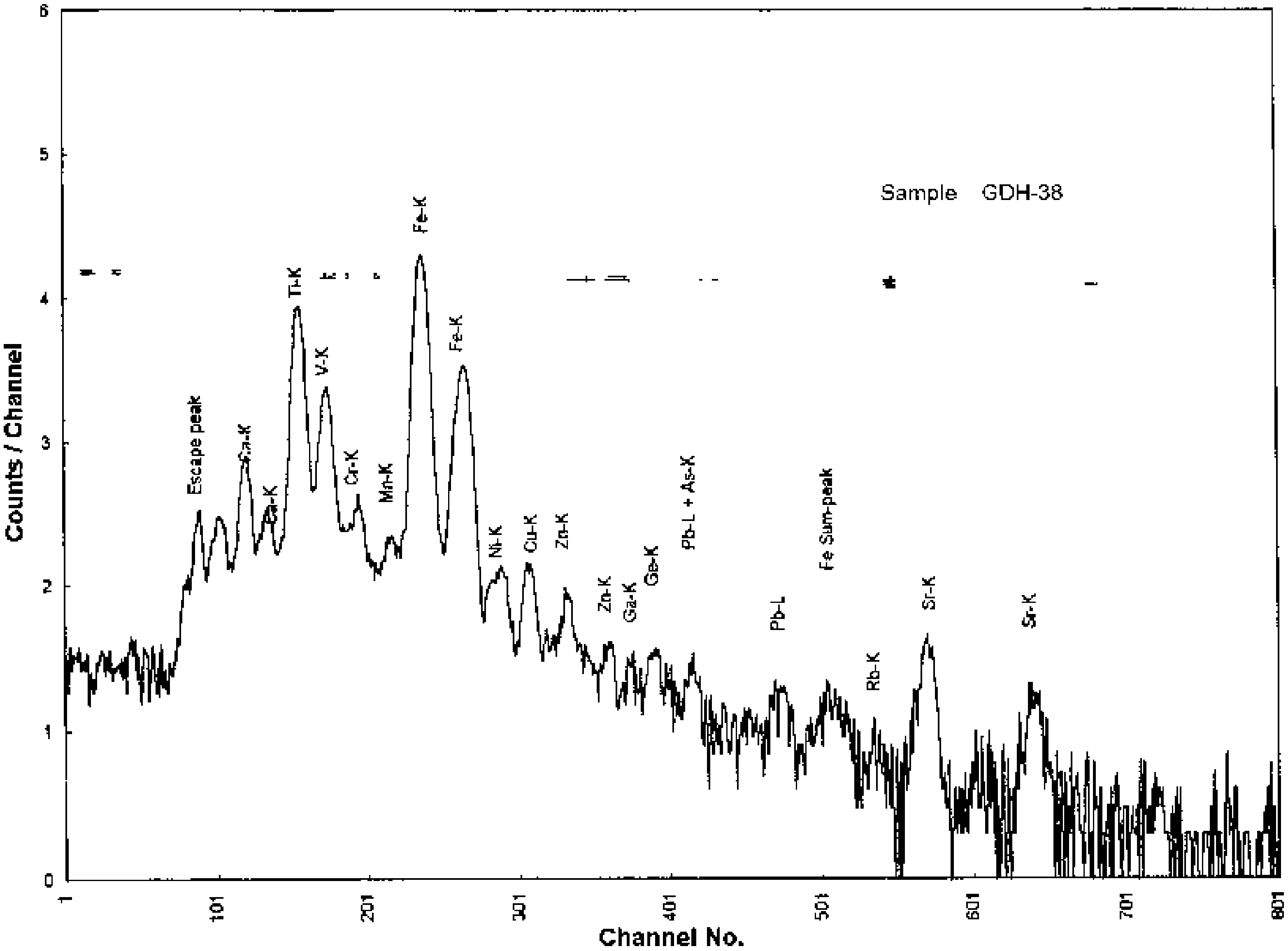


Figure (4.5.1a) : Characteristic X-ray spectrum of Barapukuria coal

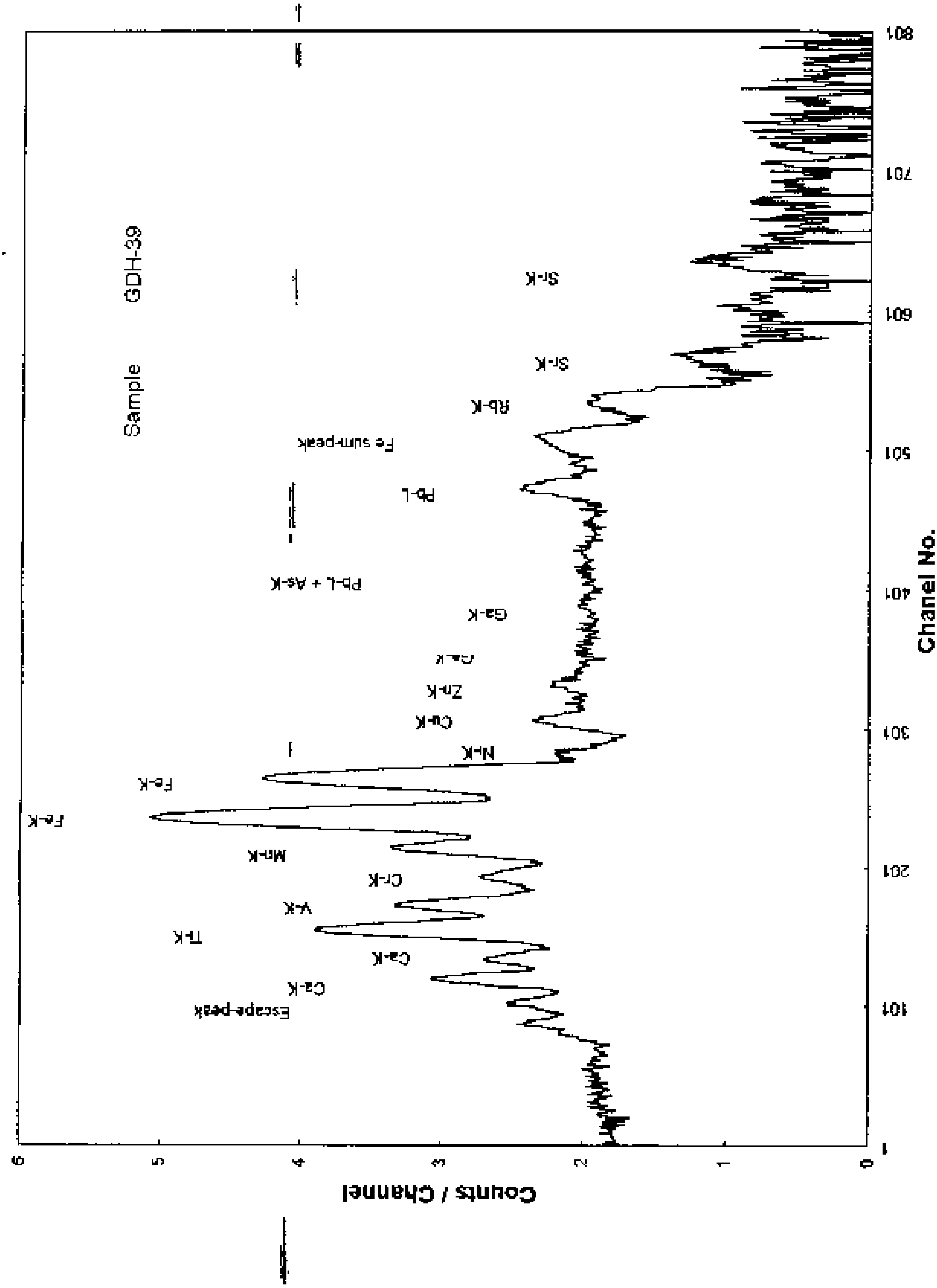


Figure (4.5.1b) : Characteristic X-ray spectrum of Barapukuria coal

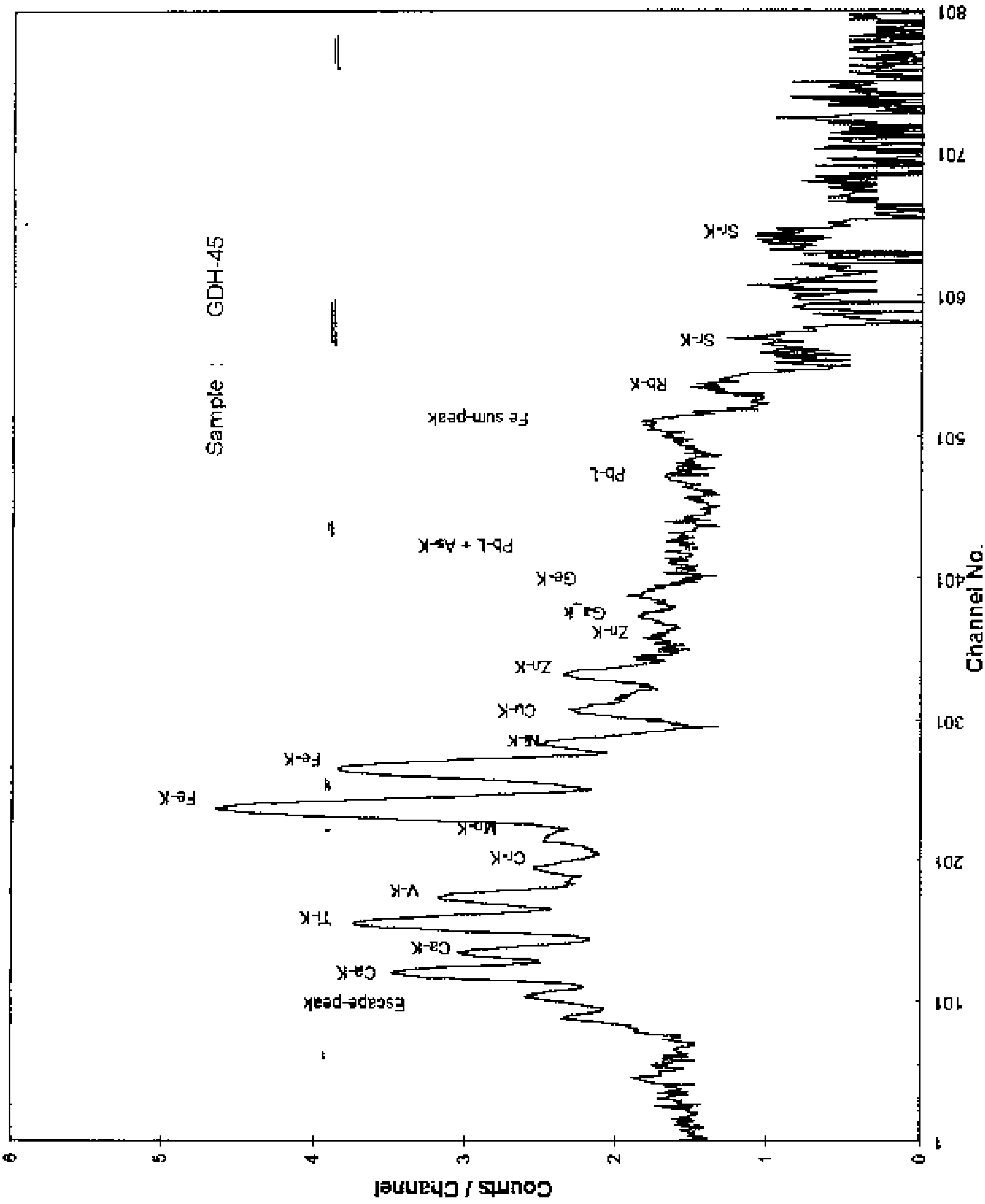


Figure (4.5.2a) : Characteristic X-ray spectrum of Khalaspir coal

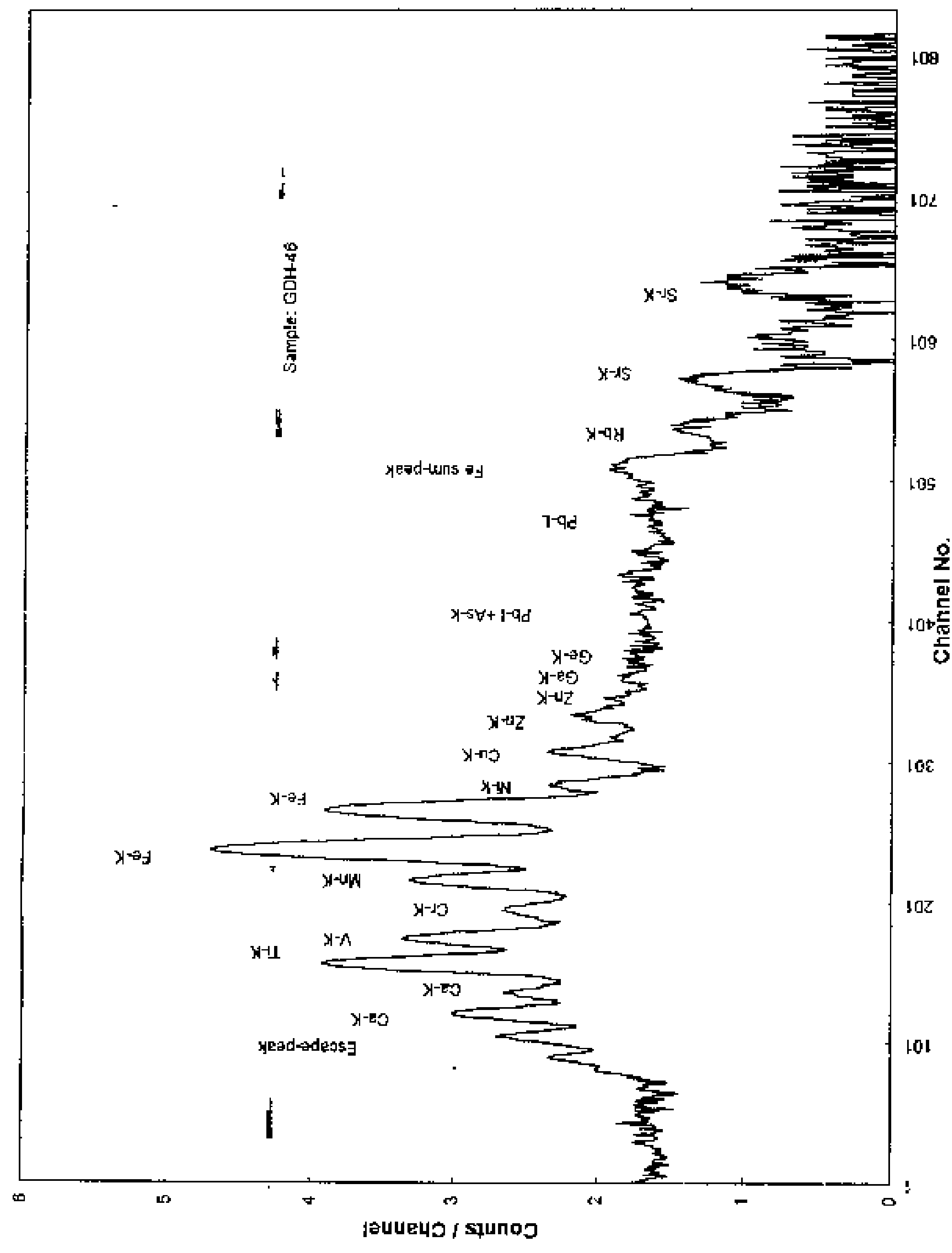


Figure (4.5. b) : Characteristic X-ray spectrum of Khalaspir coal

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Chapter 5 Conclusions

5.1. Conclusions

The following conclusions may be drawn from the present study. The Barapukuria coals under study are ranked mainly as high volatile bituminous type with high calorific value and low ash. The calorific values of the coals are about 14500 Btu/lb on dry ash free basis. Their volatile matter contents varies from 32 to 42% on dry ash free basis. These coals will be suitable for combustion in power generation because of their high calorific values and in chemical industry for chemical extraction.

These coals studied contain about 7 % ash. The ash is nothing but mineral matters associated with the coal. Coal ash has various uses such as in building material production, in cement production etc. Coal ash is seen as potential source of some economically important materials such as, Cr, Mo, V, Mn, Co, etc. which are used in steel industries for steel alloy production. Again coal ash is expected to be enriched with valuable semiconducting elements like Ge, Ga, In etc. So utilization of these coals should be accomplished by an effort to extract the economically feasible elements.

IR spectrnscopic study show that the considerable portion of coal structure is aromatic in nature formed by planar graphitic sheet arranged nearly parallel to each other. X-ray diffraction of these coal samples determined the size of crystallite region from calculation of stack-height parameter and layer diameter. Mineral phases of kaolinite, pyrites, etc. are also identified. A greater degree of orientation among and within the planar sheets obtained from carbonized coals is analyzed by IR spectroscopy and X-ray diffraction.

Trace elemental analysis using PIXE spectroscopy determines about 19 elements in Barapukuria and Khalaspir coals whose concentration are determined and compared with those of some Canadian coals. The concentrations of some major elements like K, Ca, Mn, Fe, and some trace elements like As, Cu, Ni, Se, etc. in the Barapukuria coals are found to lie within their respective range in the Canadian coals. The concentrations of Br, Co, Ga, Rb, etc. are higher than their respective values in the Canadian coals. The coals investigated are found to be enriched in Se, Br, and Pb since the concentrations of these elements are greater than their respective values in earth's crust.

5.2. Suggestions for future work

Extensive quantitative analysis for determination of aliphatic and aromatic hydrocarbons using C^{13} NMR should be carried out for structural analysis of these coals.

Mineral matter composition of coal is important for its use in coke production From this point of view it is useful to study the mineral matter composition of Barapukuria coal. Further analysis on trace elements should be carried out on a large scale involving more coal samples with a view to build a profile of coals of different areas and different depths. In this respect Neutron activation analysis can be employed, which is capable of determining more elements present in coal.

It is expected that recent discovery and extraction of Barapukuria coal will lead to its commercial exploitation for power generation. In view of its proper utilization as a fuel in thermal power plant, the primary and secondary gasification study should be carried out.

Chapter 6 Appendix

6. APPENDIX

Table (6.1) : Proximate Analysis of Barapukuria coal (as received basis)

Bore hole	Depth	Moisture (wt %)	Ash %	V.M. %	F.C. %	Calorific Value Btu/lb.	Bulk density Kg/m^3
GDH-38	673′	3.19	16.05	26.25	54.51	12002.03	1200
	1102′	2.46	6.25	32.48	58.81	14123.27	1400
	1111′	2.77	3.90	32.36	60.98	14612.51	1416
	1121′	2.43	4.30	39.02	54.25	14524.14	1280
	1149′	2.08	1.50	38.11	58.31	14909.16	1320
	1161′	3.24	5.60	30.97	60.19	14515.24	1312

Table (6.2) : Proximate Analysis of Barapukuria coal (as received basis)

Bore hole	Depth	Moisture (wt %)	Ash %	V.M. %	F.C. %	Calorific Value Btu/lb.	Bulk density Kg/m^3
GDH-39	563′	3.97	4.15	33.55	58.93	13905.06	1316
	574′	3.59	3.76	35.31	57.34	14195.16	1680
	593′	3.65	6.17	35.55	54.63	14556.27	1530
	614′	3.30	10.45	29.78	56.47	13505.91	1280
	630′	2.97	10.96	35.56	55.51	14105.47	1330
	638′	3.82	4.26	31.27	60.65	13954.37	1334

Table (6.3) Trace elements in different coals and earth's crust

Element	GDH-38	GDH-39	GDH-45	GDH-46	Canadian coals*	Earth's crust*
K	315.94	302.40	16.71	593.79	79-1.9 K	25.9 K
Ca	630.14	396.03	13.64	509.65	20-19K	36.3K
Ti	1161.49	1362.78	4.44	125.21	120-5.5K	4 K
Cr	23.10	20.88	0.89	23.78	5.79-28.8	100
Mn	211.63	0.47	0.80	183.11	12-213	950
Fe	12774.80	2128.05	7.56	5391.6	1K-11.6K	50 K
Co	7.22	73.00	1.77	7.85	0.93-3.14	25
Ni	8.03	5.03	1.04	22.72	18-23	75
Cu	29.74	17.15	1.06	31.34	11-56	55
Zn	23.51	13.29	1.57	26.49		70
Ga	12.59	5.62	1.09	8.70	2-6	15
Ge	6.88	7.08	1.54	1.92		
As	----	1.39			0.2-3.4	1.8
Se	----	1.87			0.09-1.76	0.05
Br	173.71	12.74	12.31	--	0.96-12.2	2.5
Rb	24.92	5.37	17.01	23.77	1.5-14.5	90
Sr	27.19	91.78	17.57	53.47	32-456	375
Pb	25.31	34.30	15.93	9.15		13

K = ppm × 1000

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* Fariborz Goodarzi, Anthony E. Foscolos and Alexander R. Cameron, Fuel, 1985, 64, 1599