A STUDY OF ELECTRICAL PROPERTIES OF PERMIAN GONDWANA COAL OF BARAPUKURIA OF NORTH WESTERN BANGLADESH.

by

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The thesis titled "A Study of Electrical Properties of Permian Gondwana Cool of Barapukuria of North-Western Bangladesh" submitted by SUNIRMAL MAJUMDER, Roll No. 931420F, Session 1992-93-94 has been accepted as satisfactory in partial fulfillment of the requirements for the degree of ***Master of Philosophy*** *in* ***Physics*** *on 10 April, 2000.*

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Abstract

The coal samples were collected from different depths of bore-holes GDH-38 and GDH 39 of Barapukuria coal mine. For characterization, proximate analysis were done according to ASTM standards. 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 borehole GDH–38 were about 2.72 wt% and 6.26 wt% respectively with an average volatile matter content of 35.5% and fixed Carbon content of 55.28% on dry ash free basis (daf). The average moisture and ash content of the coals of bore hole GDH –39 were about 2.7% wt% and 6.07% respectively with an average volatile matter content of 30% and fixed Carbon content of 58.8% on dry ash free basis. The calorific value of the coals of these two bore holes were about 28750 KJ/Kg and 29000 KJ/Kg.

Structural characterization was accomplished using infrared (IR) spectroscopy, X-ray diffraction (XRD) analysis. KBr pellet 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

D.C. electrical resistivity have been measured of coal samples as functions of voltage, temperature and thickness. For the voltage variation measurements the range was 0-150 V and for the temperature variation the temperature range was 300K to 500K. Both the lump sample and disc sample were used for the voltage variation measurements. For temperature variation only lump samples were used. For the thickness variation measurement disc samples of different thickness were prepared. The resistivity is not highly affected by voltage variation but trends to decrease. From the experimental result it is observed that in the temperature range 300-360K the resistivity decreases and increases upto 440K. Over this temperature the resistivity decreases. Then it can be concluded that the variation of resistivity with temperature have not a definite trend. But at different temperatures all the samples exhibit almost the same nature. the activation energy of the coal samples of GDH-38 and GDH-39 have been quantitatively calculated from $\log_{10} \rho_{dc}$ vs 1/T (K) curve for the sample of 205m and 340m deapth of GDH-38. two activation energy have been calculated for both samples for GDH-38 (205m depth) the activation energies are 0.27eV and 0.50eV. For GDH-38 (340m depth), the activation energy 0.45eV and) 0.20eV. The results of activatuobn energy for all the samples is below 1eV.

Aat lower temperature resistivity decreases. Impurity ions and moisture play an important role in the flow of electric current. The removal of moisture is accompanied by a characteristic change in resistivity. At low temperature, the moisture percentage is high and the change in electrical resistivity increases on evolution of moisture. At low temperature, there is a sharp decreases in the resistivity of coal.

To observe dielectric properties of coal sample dielectric constant, a.c. conductivity and dielectric losses are measured as a function of frequency. The frequency ranges from 10kHz to 12MHz. The general trend is that the conductivity increases as the frequency increases. At high frequency ($6x10^6$Hz), conductivity decreases sharply and again increases upto 10[illegible] Hz. The dielectric loss decreases as the frequency increases upto $8x10^6$Hz and above this frequency it increases, after that it decreases. The dielectric onnstant decreases as the frequency increases and at high frequency it decreases very small and above $7x10^6$Hz, the dielectric constant increases. This behaviour suggests that the probable mechanism of conduction is hopping either by tunneling or by jumping over the barrier.

List of Abbreviations

A	*Ampere*
ASTM	*American Standards for Testing & Materials*
AECD	*Atomic Energy Centre Dhaka*
ac	*Alternating Current*
C.m.	*Coulomb meter*
°C	*Degree centigrade*
Cal	*Calorie*
d.b.	*Dry Basis*
d.a.f.	*Dry Ash Free*
d.c.	*Direct current*
eV	*Electron Volt*
F.C.	*Fixed carbon*
f.c.	*Femto-coulomb*
GDH	*Geological drilling hole*
IR	*Infrared*
LMO	*Local molecular orientation*
μV	*Micro volt*
mV	*Mili volt*
m	*Meter*
nC	*Nano coulomb*
p.f.	*Pawer factor*
r.p.s.	*Revolutions per second*
TEM	*Transmission electron microscopy*
V.M	*Volatile matter*
XRD	*X-ray diffraction*

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Chapter 1

General Introduction

1.1 Introduction to the Coal Research

Coal is the most plentiful resource of conventional energy and it forms the backbone of the modern industrial civilization. In the modern development of coal science including coal mining, a detail study of physical behaviour of coal is essential. The recent discovery of coal mines in the Northern zone of Bangladesh provides a major opportunity in studying the quality of coal and to find their possible diversified uses. At present, it is in the state of extraction from the mines.

Coal is a very important natural resource and much effort has been expended and is still being expended on making the best use of it. This has been paralleled by the intensive investigation of coal structure, which has proved to be a challenging subject for scientific study.

Coal consists of a complex mixture of organic chemical substances containing carbon, hydrogen and oxygen in chemical combination, together with smaller amounts of nitrogen and sulfur. Coal is, in fact, a fossil formed mainly by the action of temperature and pressure on plant debris. The organic part of coal has associated with its various amounts of moisture and minerals[1-3] .

The degree of coalification or rank of the coal increases progressively from lignite through low-rank coal to high rank coal to anthracite. The carbon content increases and the oxygen and hydrogen contents decrease throughout the series, while the reactivity decreases.

The three main types of coal, namely low-rank (non-coking or weakly coking), medium-rank (coking) and high-rank correspond approximately to three types of structure. The first type characteristic of low-rank coals, has small layers more or less randomly orientated and connected as cross-links, so that the structure is highly porous. The second type characteristic of coking coals, shows a greater degree of orientation and consequently a greater tendency towards parallel stacking; there are less cross-links, fewer pores and the structure has some similarities to that of a liquid. The third type, seen in high-rank coals and anthracites, shows a growth of the individual layers a marked increase in the degree of orientation and the development of a new type of pore elongated parallel to the stacks of layers. The progressive changes throughout the coalification process can thus be visualized.

Coal is a physically heterogeneous and chemically complex solid. Coal rank and maceral composition play key roles in the chemical reactions of coal. The effect of coal rank on coal reactivity is obvious because the basis of rank classification, namely per cent carbon, also characterizes the chemical structure of coal. As the coal rank increases, the aromatic lamellae grow in proportion and in size, and their alignment becomes more perfect[4-8] .

Coal is ranked as lignite, sub-bitumious coal, bituminous coal and anthracite. Classification of coal by rank is based on the continuous evolution of the parent material towards a pure carbon structure[9]. Consequently, the percent carbon of a coal is a basic variable in coal classification by rank. Nevertheless, the ASTM rank classification is based upon the percent volatile for high rank coals and the calorific value for low rank coals.

1.2 Review of earlier work

The techno-economic feasibility as well as the precursor states for the graphitization of coal found in Northern zone of Bangladesh has already been studied[10-15]. Coals are classified as higher rank of bituminous type with low sulfur content, mostly medium volatile and partly coking type. Coking coals are used in the metallurgical industry. Higher rank coal behaves as an intrinsic semiconductor because of having higher number of aromatic ring compounds. The dielectric constant of the coal increases with increasing degree of metamorphism, which arises due to the presence of polarizable electrons in the condensed aromatic system. Dielectric constant, dielectric loss and electrical conductivity are the basic electrical parameters of coal. The conductivity of coal is caused by the partial mobility of electrons in the coal structure, which occurs because of unpaired electrons or the free radicals. The rapid rise in electrical conductivity is believed to be increasing graphitoid character of the coal i.e. three-dimensional ordering of the carbon atoms to form a graphitoid lattice.

The structure of graphite consists of extensive parallel layers of carbon atoms arranged in condensed, aromatic arrays, the layers being mutually orientated and separated by a distance of 0.335nm (the carbon-carbon Vander Waals' distance)[16]. The parallel stacking of layers in coal is similar, but lacks mutual orientation between layers, and the average spacing between layers is somewhat larger.

Electrical properties of coal also include electrical phenomena like tribo-electric effect, induced polarization, high voltage polarization and electrical breakdown. The electrical properties are of interest in the electrolinking process for permeability enhancement and as a means to locate regions with different physical properties during in-situ coal gasification. Thermal and electrical properties of Herrin No. 6 Illinois Basin bituminous coal have been measured by Hasan Dindi, Xiao-Hong Bai and William B. K. Krantz[17]. The electrical resistivity has been determined as a function of temperature, applied voltage and moisture content using the ASTM standard method D257-78 and a special guarded-electrode apparatus. The dielectric breakdown strength has been determined as a function of sample moisture, sample thickness, electrode size, voltage rate of rise and temperature using the ASTM standard method D 149-81. They concluded that these coals are electrically anisotropic in nature. After reviewing several studies on bituminous coal, anthracite, Clendenin *et al.* concluded that anthracite and bituminous coal are electrically anisotropic[18]. The electrical properties of coals are functions of moisture, applied voltage, temperature, organic and inorganic impurities, contents of ash etc. Electrical properties of these coals are to be studied to elucidate their graphitizability.

1.3 Objectives of the Research

Several researchers[19-21] have worked on the electrical resistivity of coal in abroad. However, no work has been carried out to date on the electrical properties of Bangladeshi coal. Coals are heterogeneous in character. The formation of coal varies from place to place and that is why no two coals are same. A study of the electrical properties may provide necessary information, which might help in mining of coal from Barapukuria shallow basin. It is from this point of view, the present work on electrical resistivity has been undertaken.

The present study is directed towards an investigation of the electrical properties of coals. The majority of the experiments were made with the bright coals, of relatively uniform elemental composition

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Chapter 2

Physics of Coal and Carbon

2.1 Structure of Coal

Coal is a fossilized plant material. Coal is a sedimentary rock accumulated as peat composed principally of macerals and subordinately of minerals, and containing water and gases in submicroscopic pores. Macerals are organic substances derived from plant tissues cell contents and exudates that are variably subjected to decay incorporated into sedimentary strata, and that altered physically and chemically by natural (geological) processes.

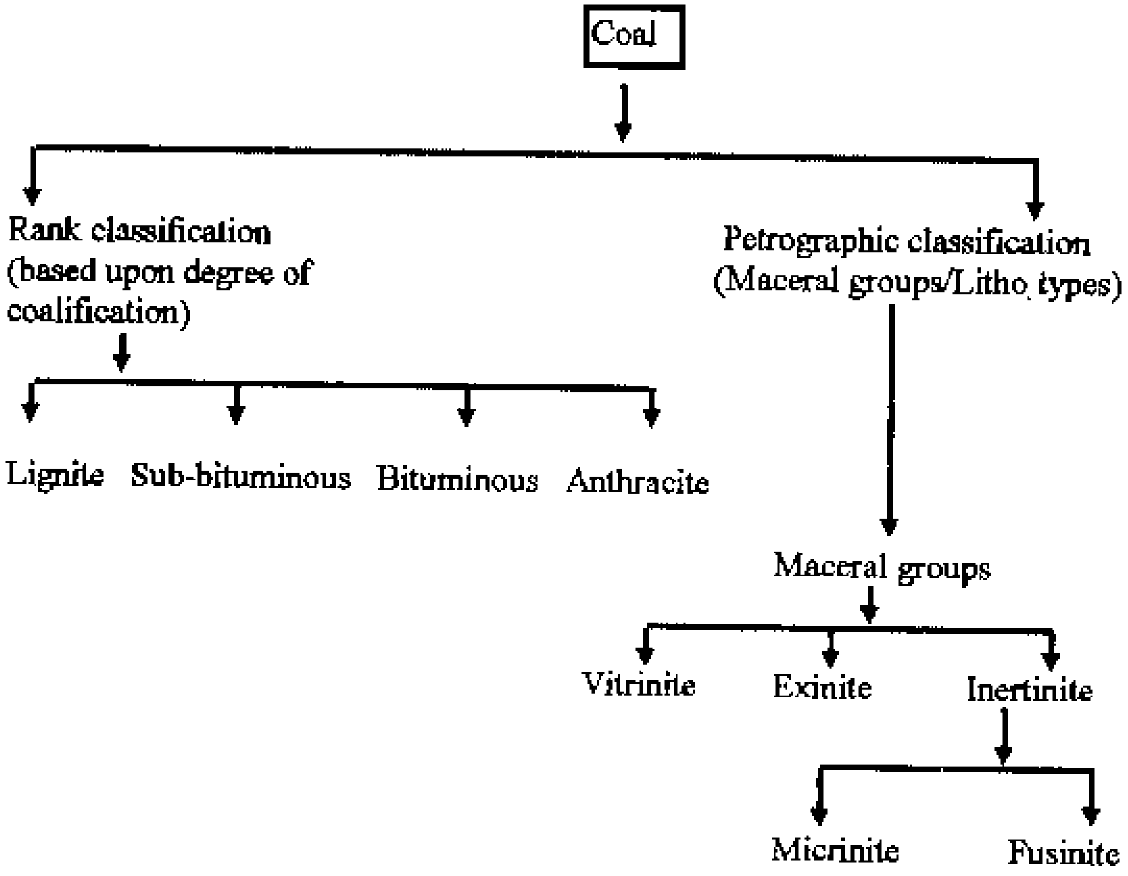
Coal is not a uniform mixture of carbon, hydrogen, oxygen, sulfur and minor proportions of other elements, simply a uniform, polyaromatic, polymeric substance. Thus coal is a complex polymeric solid without repeating monomeric units Specifically the basic structure of coal is a graphite-like aromatic/ hydroaromatic system. The aromatic rings in the aromatic/hydroaromatic structure form lamellae. The corresponding number of condense aromatic rings per lamellae increases with coal rank: one to two rings for low-rank vitrains and three to five for vitrains containing 90% carbon (on an maf basis). These aromatic lamellae, in groups of two or more, are stacked and form larger, imperfect sheets or ring clusters. The sheets or clusters are buckled due to the presence of hydroaromatic or five membered rings. The fraction of aromatic lamellae in the stacked sheets or ring clusters aud thus, the aromaticity increase as the rank increases. Meanwhile, the average separation between lamellae comes smaller and the buckled sheets become flater. As a result, a graphite like structure is reached as the rank reaches anthracite.

Coals of the lowest rank possess a polymeric character i.e. their lamellae are linked by bridges. As coalification advances these bonds gradually disappears while the aromatic lamellae start growing in size with the result that the Vander Waals forces acting between them become stronger. As the resultant of these two effects is weakest in the range 85%-91% carbon, it follows that the aromatic lamellae of coking coal possess the highest degree of mobility. Thus it is clear that as coalification advances the number of bridges decreases and the crystalline formation increases.

2.2 Classification of Coal

Coals are classified by rank and by petrographic composition. Petrographic classification is concerned with coal constituents of different origins while rank classification is based upon the degree of coalification[1,2]. The coalification is a continuous evolution and degradation of the parent plant material toward a pure carbon or graphite structure. The parent material itself originating from different parts of the plant, is rather heterogeneous. The heterogeneity is amplified as a result of mixing with inorganic sediment during coalification. These physically distinctive, chemically different entities form the basis for petrographic classification. Specifically, petrographic classification is based on variations in physical characteristics as derived from degradation of different parts of the parent material. In contrast, rank classification is based on the maturity of the coal as a whole in the coalification process.

Classification of Coal



Rank Classification

Coal is ranked as lignite, sub-bituminous coal, and anthracite. Classification of coal by rank is based on the continuous evolution of the parent material towards a pure carbon structure. Consequently, the percent carbon of a coal is a basic variable in coal classification by rank.

In coal petrography, the rank of coal is measured by the reflectance of vitrinite since vitrinite is the most abundant maceral group. The rank of coal increases as the reflectance of vitrinite increases. The mean reflectance of vitrinite increases from 0.26% to 6.09% and an increament of 1% is called a V-step.

Petrographic Classification

i) Coal maceral groups

Coal is composed of physically distinct entities. These entities are coal macerals, pores, and minerals. Coal macerals are commonly grouped into exinite, vitrinite and inertinite. Inertinite is often further divided into micrinites and fusinites.

Macerals are grouped[3] into vitrinite, exinite (liptinite) and inertinite, as shown in following table

Maceral Group	Maceral
Vitrinite	Collinoid Telinoid
Exinite (Liptinite)	Sporinoid Cutinoid Alginoid Resinoid Waxes
Inertinite	Micronoid Sclerotinoid Semifusinoid Fusinoid

ii) Lithotypes

Coal constituents were classified macroscopically by Stopes into four lithotypes: Vitrain, Clarain, durain and fusain.

The maceral groups of these lithotypes are given below:

Stopes classification of lithotypes.

Macroscopic Lithotypes	Microscopic Maceral groups
Vitrain	Vitrinite
Clarain	Vitrinite dominant Exinite and inertinite less dominant
Durain	Micrinite dominant Vitrinite less dominant
Fusain	Fusinite

2.3 Thermal behaviour of Coal

Coal is predominantly used as a fuel for production of heat and power. Basic steps in the use of coal for power generation consist of

1 Conversion of the chemical energy stored in coal to thermal energy, in the form of high temperature gases, by combustion with air in a furnace (or burner),

2. Transfer of heat from the combustion gases to an intermediate working fluid such as high pressure superheated steam through a boiler unit,

3. Expansion of the working fluid through an engine or turbine to produce mechanical energy and

4. Conversion of the mechanical energy to electrical energy for distribution. Many arrangements are possible in the assembly of components forming the boiler unit.

Combustion of coal involves three stages :

1. Devolatilization
2. Vapor phase oxidation of the volatile matter
3. Burning of the solid residue (or char)

Devolatilization and vapour phase oxidation of the volatiles involve simple reactions affecting the ignition temperature and flame stability only. In contrast the burning of char involves complex reaction mechanisms[4] which have much to do with how fast and efficiently combustion progresses.

The heat of combustion (i.e.) calorific value of an organic compound is associated with the band energies between the atoms and therefore, with the character of the bonds.

When coals are heated under inert atmosphere, five stages of reactions are seen.

i) Endothermic reaction at 100°C to 120°C due to evaporation of water,
ii) Exothermic change with a small amount of volatilization in the temperature range of 200°C -300°C being more pronounced for lignite than for higher rank coals, (possibly due to decarboxylation),
iii) Endothermic reaction with considerable volatilization and development of plasticity at temperature ranges of 350 to 460°C (less in low rank coals),
iv) Exothermic reaction with little volatilization at 480 to 540°C due to resolidification of the plastic mass,
v) Endothermic reaction at 670-720°C with release of hydrogen and shrinkage of the residual mass or coke[5,6].

When bituminous coals are heated up they undergo a series of changes of phase.

1. The coal particles soften (around 400°C) and become fluid like
2. Swelling takes place as soon as the particles are sufficiently fused together to offer appreciable resistance to the flow of the volatile matter which has resulted from decomposition,
3. Swelling ceases at a temperature around 500°C when the coal has lost its plasticity and begins to resolidify into a coherent body with a porous structure called coke. These behaviour of coal between the softening and resolidification temperatures are generally referred to as plastic properties of coal. Softening is a pure physical phenomenon of melting, independent of pyrolytic reactions.

2.4 Electrical behaviour of Coal

2.4.1 Electrical conductivity

Electrical conductivity is a measure of the ability of a material to conduct electric current. The electrical conductivity of coal is generally discussed in terms of specific resistance which is reciprocal of conductivity. Specific resistance is defined as the resistance of a block of coal 1m long and having $1m^2$ cross-section.

Main constituent of coal macerals, is carbon. One of the allotropic form of carbon is diamond which is an insulator in its pure form. Practically all the conductivity in diamond is due to impurities which make it an intrinsic semi-boron which lowers its resistivity. Coal is an organic rock having inorganic

organic materials have centred on resonance structure. The benzene ring is the best example. The six sided ring consists of alternating single and double bonds which are capable of shifting back and forth at tremendously high frequency. This resonance bond, not only increase the stability but also permits the motion of electrons ring. If such resonance structures could be produced in which the resonance path were very long, electronic conductivity could be realised.

Coal being a complex heterogeneous substance, the nature of its electrical conductivity is very complex. Electrical conductivity of coal consists of (i) electronic charge transport as is observed in graphite, but the conduction would depends upon the localized band tails overlapping in the mobility gaps as observed in amorphous material (ii) charge transfer through bulk motions due to presence of polar side chains and aliphatic bridges (iii) ionic conductance in most sample due to dissolved impurities. The conductivity of coal is explained in part by partial mobility of electrons in coal lattice which occurs because of unpaired electrons and free radicals. The conductivity of coal is a function of its physical and petrographic character, the mineral composition and degree of metamorphism. The conductivity also depends on several factors such as temperature, pressure and moisture of coal. Minerals matters also influence the conductivity.

Bituminous coal macerals have liquid like structure. Lamellae show same orientation, forming crystallites comprising two or more units lamellae. This short range ordering of the bituminous coal might be imparting a semi-conducting property to it. In anthracite, degree of ordering of lamellae is greatly aromatic compounds like ovelene show the properties of intrinsic semi-conductivity. This intrinsic semi-conducting behaviour can be easily visualized if we remember the graphitisation of coal in anthracite.

The resistivity (reciprocal of conductivity) of dry sample of clarain and vitrain is more than 3 × 10^6 Ohm-m, while the resistivity of susain is lower, 10 to 10^2 Ohm/m. Weakly metamorphosed low rank coals with less percentage have resistivity as high as 10^8 to 10^{12} Ohm-m, when dry and as low as 10^3 to 10^4 Ohm/m when moist. With increasing metamorphism, the resistivity increases to a maximum. Further metamorphism leads to a reduction of the organic radicals in coal causing the resistivity to be lower. Impurities like kaolinite in a coal with intermediate degree of carbonisation will be marked by decrease in the resistivity.

Transition from subanthracite to anthracite coal cause a sharp decrease in the resistivity. This rapid fall in resistivity of semi-anthracite and anthracite is attributed to graphitization i.e. three dimensional ordering of the carbon atom to form a graphitoid lattice.

The electrical resistivity of coal are quite pronounced at high temperature (especially above 600°C) where coal structure begins to breakdown. Moisture affects the resistivity to a marked extent, resulting in greater decreased resistivity. To avoid the anamolies initial measurement are usualy taken at approximately 200°C and then continued to lower temperature.

On Sandar, Schuyar and Van Krevelen found that resistivity of anthracite decreases exponentially with rising temperature. It can be concluded from their findings and the findings of Inokuchi that anthracite is intrinsic semi-conductor. Upto 94% carbon content coal is isotropic semiconductor and above 94% carbon content coal is anisotropic semi-conductor.

Tiwary and Mukhdeo[6] have observed that resistivity of vitrain decrease with increasing dielectric constant which is just opposite to general trend. The similar result have been reported by Parkhomenko for coal with more than 80% carbon content.

The rapid rise in electrical conductivity with rank in the region of 87% carbon and higher is undoubtedly due to the increasing graphitoid character of the coal in this region; conduction is only possible when the electrons are free to move from one molecule to another, which movement will be hampered the more as the molecule are less well oriented and holes are left between them. Consequently, graphitization i.e. three-dimensional ordering of the carbon atoms to form a graphitoid lattice, necessarily involves an increase in electrical conductance..

In fact, this phenomenon has been observed by many investigators. Some of them even went so far as to suggest that electrical conductivity might be used as a measure of the intricate chemical and physical modifications occuring in coal during coke formation[8] or as an index of the coke quality

An important factor in electrical conduction is the influence of temperature. It is well known that the resistance of metallic conductors is proportional to the absolute temperature. The resistance of semi-conductors, on the other hand, decreases exponentially with a rise in temperature, and obeys the relation.

$$\rho = Be^{\frac{\Delta u}{2kT}}$$

where B is a temperature independent constant and Δu is an energy barrier which the electrons have to surmount in order to participate in the conduction.

The theoretical interpretation of semi-conduction is based on the band theory of solid substances. An electron in a crystal wanders through the periodic field produced by the regular arrangement of the atom nuclei. As a result, the energy levels of the electrons, which in the isolated atoms are discrete, broaden into bands in the crystal. If the valence band is not fully occupied with electrons, the electron may (by the action of an electric field) be excited to a somewhat higher energy level, thus acquiring a greater impulse and making the crystal an electric conductor.

If the valence band is completely filled this can not occur at the absolute zero of temperature. At higher temperatures, however, this possibility exists for those electrons which, owing to their kinetic energy, are capable of traversing the forbidden region between the filled and the unfilled levels.

If now this forbidden region (Δu) between the two levels is wide compared with kT, the material will behave like an insulator. If, on the other band, Δu is comparable to kT, the substance is an intrinsic semi-conductor figure 2.1.

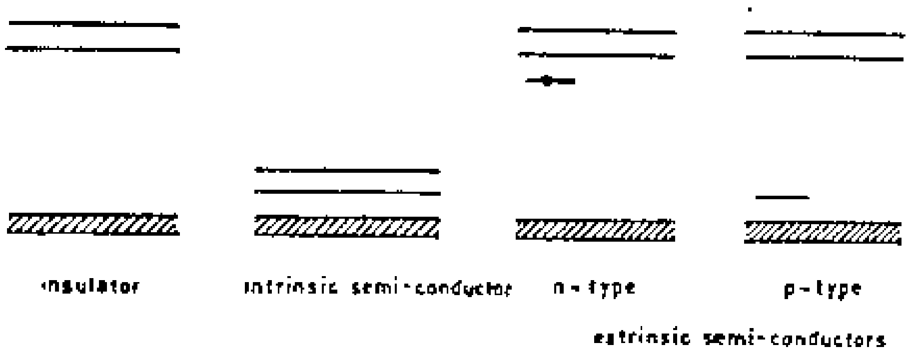


Figure 2.1: Band structure of semiconductors and insulator

If the periodicity is disturbed, as may be the case when the lattice contains a foreign atom, "discrete" levels whose wave functions are localized about the disturbance or foreign atom, will also occur.

If such a perturbation level is located in the forbidden region at a short distance below the conducting band, an electron of the foreign atom may, by its thermal movement, penetrate into the conducting band; then the substance is an extrinsic semi-conductor of the n-type. When the perturbation level lies just over the filled valence band, it may take up electrons from the filled band thus leaving vacancies in it so that conduction by holes may occur. In that case the substance is an extrinisic semi-conductor of the p-type figure 2.1.

2.4.2 Anthracite as intrinsic semi-conductor

It has been stated that polycondensed aromatics may behave like semi-conductors. More specifically, these aromatics must be included among the group of intrinsic semi-conductors. Inokuchi's investigations[9] on compounds of such types as ovalene, violanthrene, violanthrone, etc. have shown that these are intrinsic semi-conductors.

As coal is largely built up of large aromatic ring systems, it might be anticipated that coal will also behave like an intrinsic semi-conductor. As pointed out earlier, this is only possible if the coal has been "graphitized" to some extent. Evidence in support of this supposition has been furnished by Sandor[10], who noted that the resistance of carbonized coal decreases exponentially with rising temperature. It was also found by Schuyer and Van Krevelen[11] from measurements on anthracites (vitrinites with 91%-96% carbon) between room temperature and about 200°C. In view of their own findings and the results obtained by Inokuchi, Schuyer and Van Krevelen concluded that anthracites are intrinsic semi-conductors.

According to Northrop and Simpson[12] there is a finite probability of ionization from the bound excited states due to the perturbing field. From a free electron model Platt[13] derived that the energy levels are inversely proportional to the aromatic surface area. hence, the linear relation between Δu and S^{-1} is plausible.

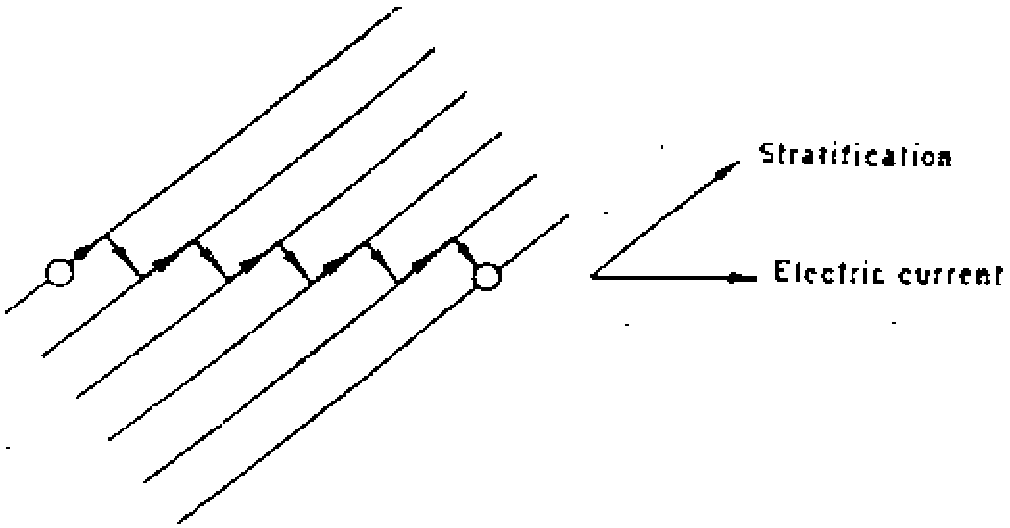


Figure 2.2 Diagram of charge transport through coal.

An important aspect of the semi-conductance of anthracites is that the Δu value of electrically anisotropic coal is practically independent of the direction of the current with respect to the bedding plane. This may be understood by starting from the supposition that charge-transfer between the lamellae occurs exclusively in a direction perpendicular to the aromatic surfaces[14].

The schematic representation of charge-transfer between the lamellae picture in figure 2.2 shows that Δu is independent of the angle between the bedding plane and the direction of the current, provided the electrons in the aromatic lamellae possess a fairly high degree of mobility.

The conclusion therefore, is that the anisotropy of the semi-conductance must be attributed almost exclusively to the temperature independent constant B. It is not until the carbon content has risen to over 94% that this anisotropy becomes strongly marked.

2.5 X-ray Analysis of Coal

When X-ray strike a crystalline substance, the regular arrangement of the atoms gives rise to interference phenomena. Reflection occurs when the x-ray are scattered at such an angle that the path-difference between the rays reflected by two adjacent atoms is a hole multiple of the wavelength. When the angle of reflection is slightly larger or smaller, the rays reflected by neighboring atoms will somewhat differ in phase. For more distant atoms this phase-difference may build up to such a degree as to cause the intensity of the reflected radiation to fall to zero.

The crystalline regions existing in coal (crystallites) are so small that the "more distant" atoms which are necessary to cause zero-intensity, are "absent". This explains why the diffraction pattern reveals wide diffuse bands. Moreover, it should be borne in mind that coal is only partly composed of crystalline material and that the three dimensional arrangement is not regular. As a result the compton (incoherent) scattering is relatively strong and therefore has an appreciable effect upon the x-ray pattern. It has been established that compton dispersion produces the continuous back-ground of the x-ray pattern, which is also dependent on the scattering angle. With crystalline substances no such background is observed.

The first X-ray examinations of coal were carried out by Mahadevan[15] (1929). Of the more recent work done in this field special mention should be made of the

Warren's[17] work on the structure of amorphous carbon and carbon black, introduced their turbostratic lamellae model. They look upon coal molecules as flat polycondensed aromatics (lamellae) whose average dimensions and degree of ordering increase with rank. A number of lamellae showing parallel orientation coalesce to form one crystallite.

Riley explains the softening of coal at higher temperatures by assuming that the small lamellae become mobile on heating and then act as a "lubricating agent" for the bigger ones.

The diameters of the lamellae as determined by Riley and co-workers differ considerably from the micelle dimensions given by Bangham[18]. The former found that in the range of rank between 60% and 90% carbon the diameter of the lamellae increases very slowly from about 19Å to about 21Å and then increases rapidly up to about 30Å at 95% carbon figure 2.3.

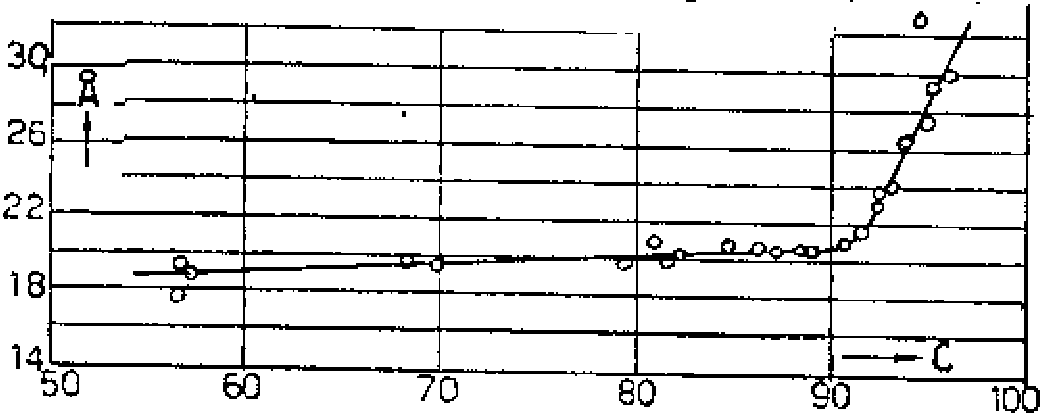


Fig 2.3 Crystallite diameter, determined by X-ray measurements, according to Riley

Hirsch, on the basis of his investigations, developed a model that may be looked upon as a refinement of Riley's model. He distinguishes between three types of structures that may be described as follows figure 2.4.

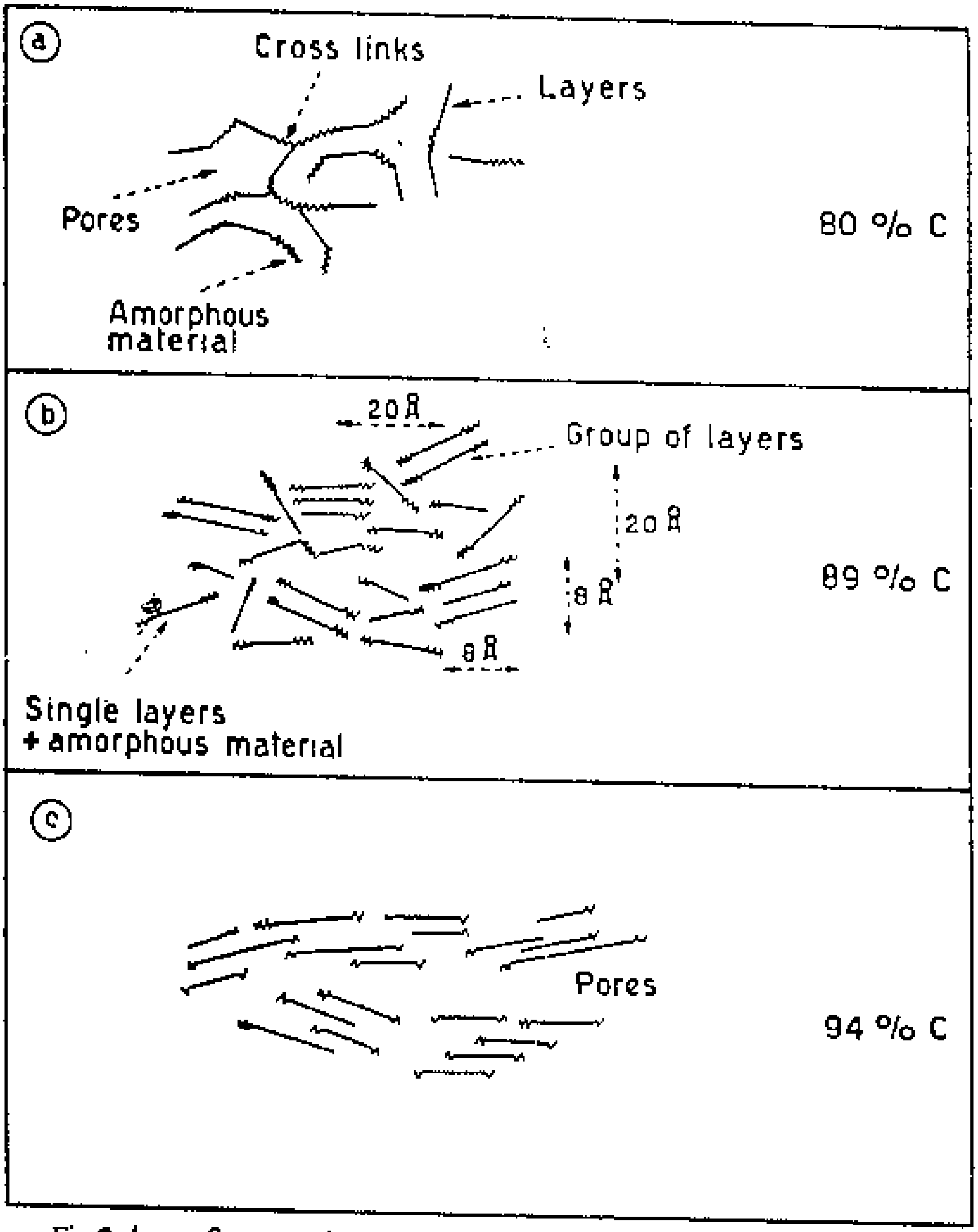


Fig. 2.4 Structural model of coal, according to HIRSCH[30].
a = "Open structure"; *b* = "Liquid structure"; *c* = "Anthracitic structure".

Pore Structure

1. The "open structure". This structure is characteristic of the low-rank coals in the range upto about 85% carbon. The lamellae are connected by cross-links and are more or less randomly orientated in all directions, thus constituting a highly porous system.

2. The "liquid structure". This is the typical structure of the bituminous coals in the range from about 85% to 91% carbon. In this structure the lamellae show some orientation, which accounts for the formation of crystallites comprising two or more lamellae. The number of cross-links has decreased considerably. Pores are practically absent.

3. The "anthracitic structure". This type of structure is especially common in high-rank coals with a carbon content of over 91 per cent. The cross-links have disappeared altogether, the degree of orientation of the lamellae with regard to each other has increased greatly. This model suggests that the porous system becomes orientated during the anthracitic structure stage.

Even in the case of low-rank coal, Hirsch succeeded in proving that the aromatic clusters have a slight degree of orientation parallel to the bedding plane.

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Chapter 3

Experimental Study

3.1 Coal sampling

Coal samples were collected systematically from different depths by making bore holes in Barapukuria. The Barapukuria coal deposit is situated in an area of the shallow basement in northwestern zone of Bangladesh. Barapukira is situated under the Parbatipur thana of Dinajpur district. The latitude of this land is 25°31′45″ - 25°33′5″ N and longitude is 88°57′55″ -88°58′55″ E. Total area covered by coal deposit is about 5.25 sq. km in Barapukuria. Depth of coal ranges from 118 to 508 m[1,2]. The total in-situ geological reserves is estimated to be about 300 million metric tones. Twenty samples were collected from each boreholes GDH-38 and GDH–39 at different depths (160-450m depth to top) of Barapukuria The samples were preserved in airtight polythene bags.

3.2 Proximate Analysis

The proximate analysis is essentially an examination of the suitability of coal for combustion or for coking purposes. The proximate analyses involve the determination of the over all composition of coal and is in reality, the determination of moisture content, volatile matter content, ash content, and fixed carbon (by difference) content. Proximate analyses were carried out according to ASTM standard D3172[3].

Sample Preparation

The collected samples were first broken up into small pieces and spread on trays for drying. The dried samples were then ground into fine powder by mortar and pestle and passed through a 250 µm (60 mesh) sieve. Tyler USA standard sieves were used. The powder was stored immediately in air tight container to avoid water absorption. Before each measurement, the samples were again dried in order to ensure absolute drying.

Moisture content

The moisture content of coal was determined as per ASTM standard D3173[1] by measuring the percentage weight loss of a sample. The sample (~19) was maintained under controlled conditions (107 ± 3°C) in an inert atmosphere for 1hr. Moisture content was determined by the following formula:

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

where w = weight of the sample before air drying

w_1 = weight loss in air,

w_2 = weight loss in oven.

Ash content

The ash content is defined as the incombustible material, which remains when a coal sample is burned. The amount of ash was determined by burning (about 1 to 2g) of a coal sample in an adequately ventilated muffle furnace at a temperature 725 ± 25°C as per ASTM D3174 [1].

A porcelain crucible containing 1g of moisture free sample was placed in a cold muffle furnace and was gradually heated to redness at such a rate as to avoid mechanical loss and rapid expulsion of volatile matter. The ignition was continued until a constant weight is reached at a temperature between 700 and 750°C. The crucible was then allowed to cool in a desiccator and the weight was taken as soon as it became cold. Ash content was determined by using the formula:

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

Volatile matter

The volatile matter content was determined by measuring the loss in weight per cent. About 1g of moisture free coal sample was put into the reactor and air was expelled from the tube by passing argon gas for about 10 minutes. The air free reactor tube containing the sample under the flow of argon gas was put inside the tubular furnace which has already been heated to a temperature of ~950°C. After 20 minutes the reactor tube was removed from the furnace and was allowed to cool under argon flow. The difference between the weight of the sample before and after the experiment was considered as the weight loss due to emission of volatile material.

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

where w = weight of the sample before experiment,

W_1 = weight of the sample after experiment.

Fixed carbon

The fixed carbon value was determined as per ASTM D3172[1] by subtracting from 100 the resultant summation of moisture %, volatile matter %, and ash %.

i.e., Fixed carbon % = 100 – (ash% + volatile matter % + moisture%).

Calorific value

The calorific or heat value of a coal is a direct indication of the energy content. It is an important property for determining the usefulness of coal. The calorific value was determined as gross calorific value. For fuel analyses of coal, the calorific value was determined with a bomb calorimeter by isothermal method as per ASTM D3286[3]. In the isothermal method, the calorific values were determined by burning 1gm. weight of the coal sample in Oxygen under controlled conditions at a pressure of about 2500 KN/m^2 and the calorific value was computed from temperature observations made before and after the combustion.

3.3 Infrared (IR) spectroscopy

Introduction

Infrared (IR) spectroscopic study provides valuable information about the rank, variation of the constituent groups with carbon content in coal structure, and as well as the nature of the aromatic systems. The IR spectroscopy was first used by Cannon and Sutherland[4,5] on coal materials in 1945. As coal molecules have complex structure, it becomes more difficult to interpret the spectrum because of the partial or even complete overlapping of characteristic bands.

Principle of IR spectroscopy

Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Infrared radiation in the range of wavelength (1-100 μm) is absorbed and converted by an organic molecule into energy of molecular rotation. In a molecule total energy (Emol) comes from various sources, like translational, rotational, vibration and electronic etc. Thus $E_{mol} = E_{trans} + E_{rot} + E_{electronic}$. Rotational spectra result from the absorption of photons by molecules with the complete conversion of the energy of molecular rotation. Whereas vibrational spectra results due to the absorption of radiant energy by the molecules thereby changing in the energy of molecular vibration. Vibrational spectra appear as bands rather than 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 the atoms, the force constants of the bonds, and the geometry of the atoms.

Band positions in infrared spectra are presented either as wave numbers or wave lengths. The wave number unit (cm^{-1}) is used most often since it is directly proportional to the energy of the vibration.

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

There are two types of molecular vibrations: Stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom. For example, twisting, rocking, and torsional vibrations involve a change in bond angles with reference to a set of coordinate arbitrarily set up within the molecule.

Sample preparation:

Potassium bromide (KBr) pellet technique developed by Schiedt[6] has become the most popular method of obtaining infrared specra of coals over the other technique, because, (KBr) does not produce specific absorption in the region 2.5-15μm.

In the present work, KBr pellets of coal were prepared by mixing ≈1mg of dry finely powdered raw coal with ≈ 300mg of KBr. The mixture was finely milled in a agar crucible for two minute and then pressed into a pellet of 13mm dia under 20,000 IBs. PSI in an evaquable die. The resulting pellet was very thin and transparent. Since KBr is hygroscopic, the pellet was dried overnight in a vacuum oven at 105°C and then kept in a vacuum dessicator to avoid any moisture absorption.

3.4 X-ray Diffraction Study(XRD)

Working procedure for taking XRD pattern

Coal samples were crushed into fine powder using mortar and pestle and then powder was sieved through 200 mesh seive. The coal powder was mixed with silicon vacuum greeze. The paste like materials was taken as thin layer on a glass substrate in an area of 1 ×1.5cm^2. X-ray powder diffraction was carried out using Cu Kα radiation at 30 mA/35KV. X-ray diffraction system made by Seifert and Co. Germany, Siefert XRD 3000 P Cu Kα radiation was used.

Calculation of Interplanar spacing

The Bragg equation for the first order diffraction is written as:

$$2d_{hkl} \sin\theta = n\lambda$$

where, d_{hkl} is the interplanar spacing

θ is the angle of diffraction

λ is the wavelength of the X-ray radiation used for diffraction (i.e. λ =1.5418A)

3.5 D.C. electrical measurements

3.5.1 D.C. Conductivity (theory)

Electrical conduction is the transport of charge carriers through a medium under the influence of an electric field. The rate at which an element of charge dQ is transported over an area A in a time dt is given by the current, $i = dQ/dt = nqV_DA$, where n is the number of charge carriers, q is the charge per carrier, and V_D is the drift velocity of the charge carriers. The conductivity (Ohm^{-1}m^{-1}) is defined by $\sigma = id/VA$, where d is the sample thickness in m, A is area in m^2 and V the applied voltage. Assuming the electric field E to be uniform across the medium, i.e. E=V/d,

$$\sigma = qn\mu$$

If there is more than one type of charge carrier, the conductivity is

$$\sigma = \sum_i q_i n_i \mu_i$$

In any particular system the number and mobility of the charge carriers will depend upon the material and the experimental parameters of voltage, temperature and ambient atmosphere. If the material is crystalline or oriented, the conductivity will depend on the direction with respect to some molecular axis in which the measurement is made. These dependence can be expressed by writing:

$$n = n(T, V);$$
$$\mu = \mu(T, V, Z); \text{ and } \sigma = \sigma(T, V, Z)$$

where T represents temperature, V the applied potential, and Z the direction in which the measurement is being made.

Phenomenologically, the conductivity is obtained by measuring the current flowing through a piece of the material and using the sample dimensions to calculate σ from the equation:

$$\sigma = \frac{d}{AV} i$$

where d(m) is the sample thickness, A its area (m^2), and V the potential across the material in volts.

The usual type of electrical measurement has involved measuring the current as a function of potential, temperature and in some cases ambient atmosphere. The conductivity and its change with voltage, ambient atmosphere and temperature are then related to the physical processes thought to be occurring in the material.

Frequently, it is found that the conductivity varies exponentially with temperature T according to the equation.

$$\sigma = \sigma_0 \exp(-Er/kT)$$

where k is the Boltzman's constant and Er the activation energy,

The resistivity is the reciprocal of conductivity.

Therefore, $$\rho = \frac{1}{\sigma} = \rho_o \exp(Er / kT)$$

The activation energy Er can readily be evaluated from the slope of the linear in ρ vs. 1/T plot, which describes the nature and types of carrier involves in the conduction process.

3.5.2 Apparatus

(a) Polisher: A metallographic specimen polisher type MSP-2 of Shimadzu Scientific Instrument Company Ltd., Japan, is used to polish the samples. CAMBIMENT special silicon carbide grinding paper with grit numbers 320, 400 and 420 are used.

(b) Die : Die is the shaping unit of powder specimen. Die may be of different shape and size depending on the required specimen dimension. To prepare samples of required dimension, a die is designed and fabricated. Two steel bars of same diameter (0.05m) are used for the fabrication of the die. A circular hole (female) of diameter 0.01m and thickness 0.005m is dug on to one of the bars using a lathe machine and the other steel bar is cut to fit the inner dimension of the female which acts as male. Two cylindrical bars of length 0.005 m and diameter 0.01 m are also made between which sample powder is to be place for pressing.

(c) Electroding : Silver paint was pasted at opposite flat faces of the dry polished specimen for a good electrical contact. During parting, a care was taken to avoid the short circuit condition. Then the specimen were kept in precise order for several hours for complete drying of the paint before taking resistivity measurement.

(d) D.C. Power supply : Model: 140a-160 of Metronix corporation, Tokyo, Japan of high voltage d.c. power supply was used for measuring the conductivity of all the specimen. The unit was capable of supplying d.c. voltage from 0-150 volts with current range of 0~3.5A maximum.

(e) Keithley Electrometer : A digital Keithley electrometer (model 614 of Keithley Instrument Inc., Cleveland, Ohio, USA) is used for resistance measurement. The Keithley 614 electrometer is a versatile instrument, which measures a wide range of dc. voltage, current, resistance and electric charge. This electrometer can measure current as low as 10^{-14} amp. Voltage sensitivity is $10\mu V$ to 20V with an input impedance of greater than 5×10^{13} Ohms. Resistance sensitivity of this model is from 1 Ohm to 2×10^{11} Ohms using the constant current technique. Charge sensitivity (nC) is from 10 fC (10^{-14} Coulombs) to 20nC (2×10^{-8} Coulombs).

(f) Specimen chamber with an inbuilt heater : Specimen chamber and the heater are designed and fabricated in the workshop of Bangladesh University of Engineering and Technology, Dhaka. A schematic diagram of the chamber alongwith its accessories is shown in figure. 3.1. This unit is basically consists of three main parts, namely, the iron tube, the sample holder and the electric heater.

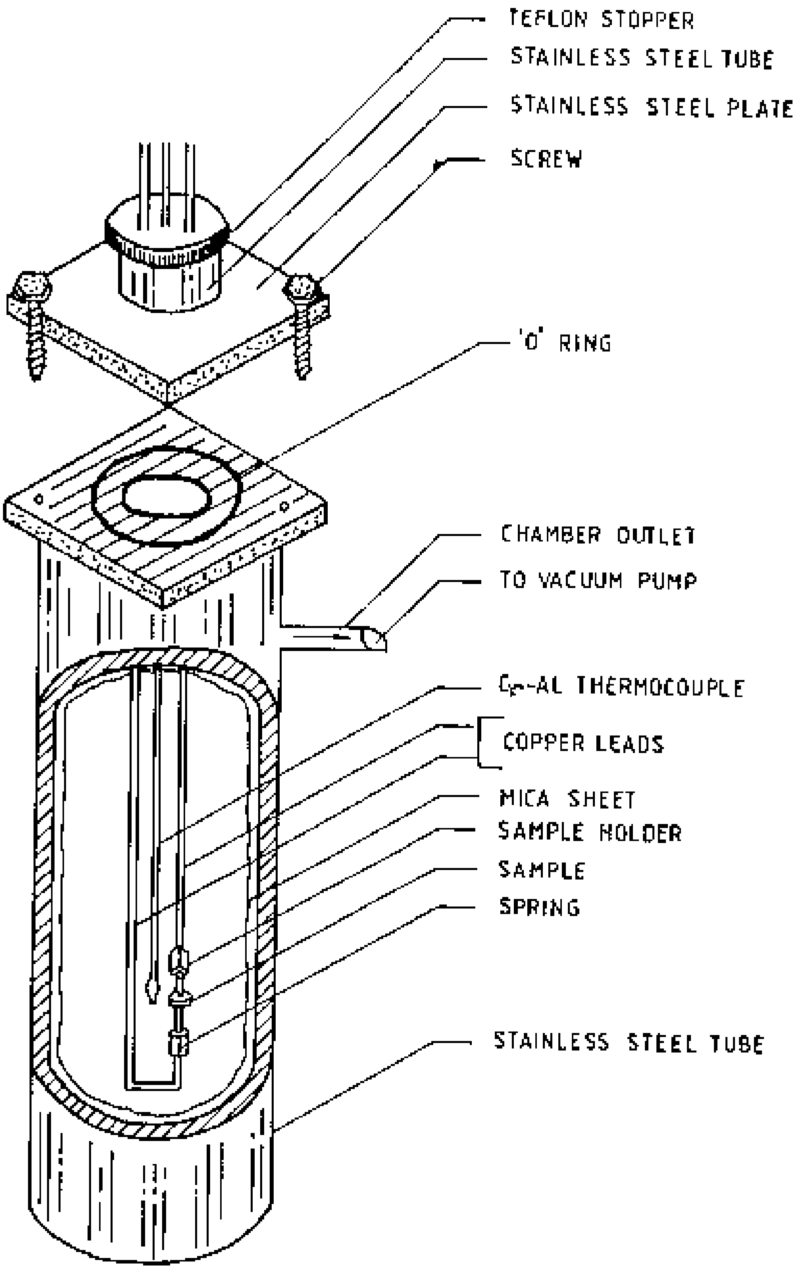

Fig. 3.1: The Schematic diagram of the specimen chamber

An iron tube having inner diameter of 0.06 m and of length 0.3m is used. The lower end of the tube is closed by welding a circular piece of iron sheet. At the upper end of the tube one flat iron sheet (0.1m) with a circular hole (diameter 0.06m) at its centre is welded. Another iron sheet with a hole of the same dimension is welded to an iron tube of diameter 0.06m and of length 0.05m. A rubber gasket is placed in between the two iron sheets. The upper portion can be fixed to the lower portion by screws. The top opening is closed tightly with a perspex stopper. Two copper leads (electrodes) which hold the specimen holder, two leads for heater connection and the thermocouple are passed through the perspex stopper.

A thick layer of mica sheet is placed on to the inside wall and bottom of the iron tube for electrical insulation. A nichrome heating coil is wound around the outer wall of a Pyrex tube of diameter 0.04m and of length 0.1m. The coil is covered with China clay. This heater is placed at the bottom of the specimen chamber and the heater terminals are connected to the leads passing through the stopper. For this experiment a Cromel-Alumel thermocouple is used.

3.5.3 Experimental procedure

(i) Two Probe method

A Keithley 614 electrometer is used for the direct measurement of resistance at different temperatures. For raising temperature, the chamber of the specimen is heated by the inbuilt electric heater within the specimen chamber. Resistance is measured at every 1 millivolt increase of thermocouple reading from room temperature to 500K on different samples. This operation is repeated for different samples. The experimental arrangement is shown in figure 3.2.

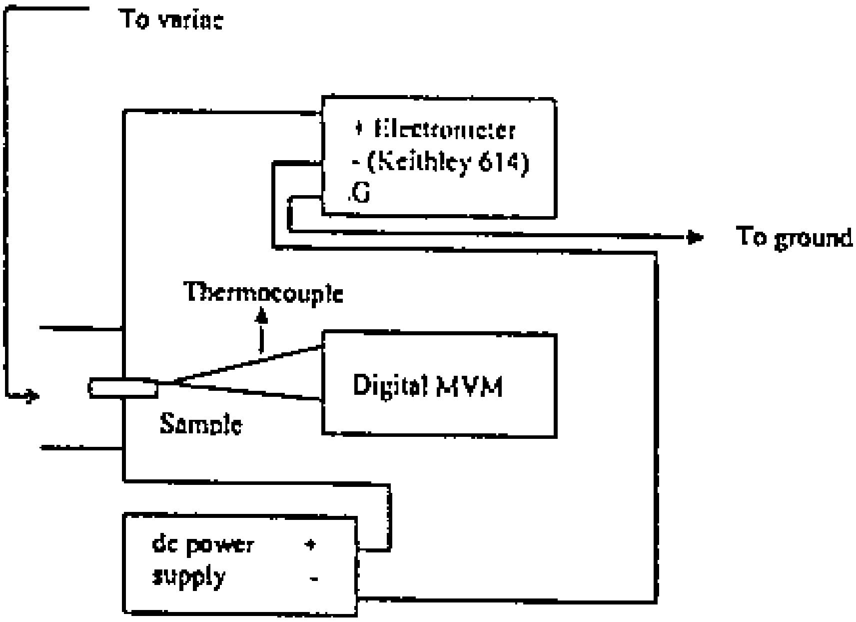

Fig. 3.2: Block diagram of d.c. measurement

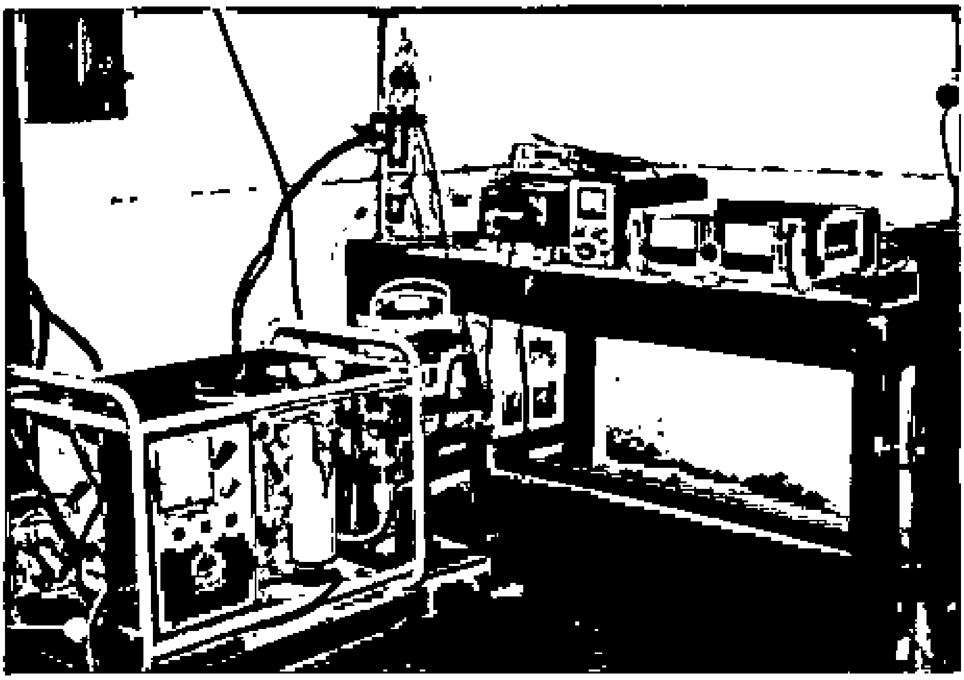

Plate 1: PHOTOGRAPH : D.C. EXPERIMENTAL SET UP

(ii) I-V method

Coal is highly resistive, the direct method of measuring the conductivity is not the best way to choose because in that case the voltage across the specimen is not known. The Keithley electrometer is connected parallel to measure the voltage drop across the resistance R. A constant current d.c. power supply is used to supply desired voltage. Firstly, the voltage drop across the resistance is recorded by varying the total voltage drop across the specimen is then found out by subtracting the voltage across resistance from the total voltage and finally the current across the specimen is calculated by using the following relation:

$$Is = \frac{V_R}{R}$$

where, V_R = voltage across the resistance

R = resistance in series with the specimen

I_s = current through the specimen

From these sets of data the various curves are drawn.

Precautions

Precautionary measures are necessary at every step of any such measurement. First of all it is ensured that the chamber of the specimen holder is dried otherwise error would be introduced in the readings. The sealing is checked from time to time for the confirmation that no moisture from atmosphere entered into the chamber. The measurements have to be done carefully so that the specimen does not touch the body of the chamber. Heating is done carefully for the temperature variation so that the rate does not exceed 0.4 K/min for ensuring that the temperature of the specimen and the thermocouple are approximately the same. The chamber is properly screened to avoid pick ups. Continuous care is taken against any abrupt disconnection of power supply.

Working formula

The resistance of the specimen is obtained from the data of the I-V method by the relation:

$$r_s = \frac{V_s}{I_s}$$

where, $V_s = v$

v_s = voltage drop across the specimen,

I_s = current through the specimen and

r_s = resistance of the specimen.

Resistivity ρ is calculated from the measured resistance of the sample, from the thickness of the specimen and the area of electrodes by using the following relation:

$$\sigma = \frac{1}{r_s} \frac{d}{A}$$

where, r_s = resistance of the specimen,

d = thickness of the specimen and

A = area of the electrodes.

Then the curves $\log_{10} \rho_{dc}$ vs. $1/T(K^{-1})$ drawn.

3.6 Instrument used in a.c. conductivity measurement

The Hewlett-Packard Model 4192A LF impedance Analyzer is used for measurements of dielectric properties and a.c. conductivity of coal samples.

The HP Model 4192 A LF impedance Analyzer is a fully automatic, high performance test instrument. The 4192A improves efficiency and quality on the development and production of many types of complex components semiconductors, and materials. Complete network analysis of devices such as filters, crystals and audio/video equipment plus evaluation of the impedance characteristics of their circuit components can be performed. These tests can be performed using test signals equivalent to those found under actual operating conditions.

The two measurement display section, DISPLAYA and DISPLAY B provide direct readout of the selected measurement parameters with 4½ digit resolution along with the appropriate units. In NORMAL mode operation the 4192A performs approximately five measurements per second. The 4192 A also provides and AVERAGE measurements mode.

Approx. one measurement per second) to obtain measurement data of higher resolution and repeatability than is possible in NORMAL measurement mode to perform approximately ten measurements per second.

The 4192A can provide measuring frequency, OSC level, and d.c. bias voltage (impedance measurement only) equivalent to actual operating conditions. The sweep capability of the built in frequency synthesizer and d.c. bias source permits quick and accurate measurements. The built in frequency synthesizer can be set to measuring frequency within the range from 5.00 Hz to 13 MHz with 1 mHz maximum resolution. OSC level is variable from 5mV to 1.1 V rms with 1mV resolution (5mV for levels higher than 100 mV). The internal d.c. bias voltage source (impedance measurements only) provides ± 35V in 10 mV increments. Measuring frequency or d.c. bias voltage can be automatically or manually swept in either direction.

The 4192A employs certain functions which make the best use of the intelligence capability of its microprocessor. This microprocessor based design of the hardware makes operation of the 4192A simple, yet improves performance to realize the accurate measuring capabilities.

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Chapter 4

Dielectric Measurements

4.1 Introduction:

The materials offer a very high resistance to the passage of electric current under the action of the applied direct current voltage are considered as electrically insulator or dielectrics. In these materials electrostatic field can persist for a long time and sharply differ in their basic electrical properties from conductive materials.

The dielectric is determined as a substance whose basic electrical property is the ability to be polarized and in which an electrostatic field can exist, and the dielectric material as "an electrical engineering material possessing the properties of a dielectric but the electrical insulating material is defined as a dielectric material used to prevent the leakage of electric charges in electrical engineering devices[1]". Thus strictly speaking the term dielectric material is broader than the term "insulating material". The resistively of electrical insulating material has a finite and extremely high value that lies between 10^5 to 10^{12} ohm-m. The higher the resistivity of an electrical insulating material, the better its quality. The active dielectrics acquiring an increasingly wider importance in present day engineering play an active role due to the variability of the properties under the effect of various factors is used in various devices, for instance in many types radio-electronic apparatus. Active dielectrics include ferroelectrics whose permittivity varies appreciably with a change in the intensity of the electric field and temperature. Piezoelectric which generate electric charges under the action of mechanical stresses and conversely, change their dimensions under the action of an electric field, electric's which can be regarded as electrical analogs of permanent magnets because they are capable of preserving an electric charge for a long time etc.

Measurements of dielectric constant, loss factor, dipole moments, relaxation time etc. have been investigated by scientists during the past half-century. The studies of electrical properties of dielectrics have been largely stimulated by many attractive devices like high capacity condenser, radio-electronics, automatics high voltage insulator, piezoelectric devices, and dielectric amplifiers also in the integrated circuits. Recently there have been systematic attempts to explain the macroscopic behaviors of the dielectrics in terms of the atomic and molecular structure of the materials and chemical bonds.

If C is the capacitance of a parallel plate capacitor with a dielectric medium between the plates and C_o is the capacitance of that capacitor with vacuum between the plates, then the dielectric constant of dielectric material is

$$\epsilon' = C/C_0$$

The relative permittivity ϵ is an important property of the dielectric materials, which affects the capacitance of any circuit. The capacitance of the parallel plate geometry is given by.

$$C = \epsilon' \ \epsilon_0 \ A/d, = \epsilon' C_0$$

where $C_0 = \epsilon_0 \, A/d$

'A' being the plate surface area and d is the spacing between the plates. Thus for given dimensions, C is proportional to ϵ', which can be affected by the frequency of the applied field, temperature and pressure.

4.2 Types of dielectrics:

All dielectrics can be subdivided into two classes:

i) Polar (Dipole) dielectrics,

ii) Nonpolar (neutral) dielectrics.

This classification is extremely important when electrical, general physical and chemical properties of matter are considered. A molecule of any matter consists of separate parts (atoms or groups of atoms, ions), each having a definite electric charge–positive or negative. The interaction forces between these charges determine, the mechanical strength of the matter[1]. Since the algebraic sum of all the charges in a molecule of any substance is equal to zero a substance in a sufficiently large volume does not display an electric charge (if only it is not electrified by the action of some outward cause).

The dielectrics in which the polar molecules have permanent electric dipole moments are called polar dielectrics, where as the molecules in the dielectrics have no permanent electric dipole moment, are called non-polar dielectrics.

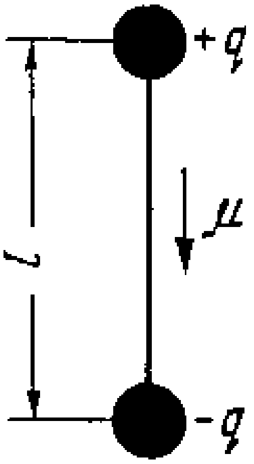


Fig. 4.1: Diagram of a polar molecule

The magnitude of the electric moment of a molecule is

$$\mu = ql$$

where q is the summary positive (or numerically equal negative) electric charge of a molecule, and l is the arm of the dipole. In most cases the electric moment of polar molecules is of the order of 10^{-30} C.m.

It stands to reason that l=0, in the molecules of non-polar matter and therefore $\mu=0$.

Symmetrically arranged molecules (having a center of symmetry) are non-polar since in this case the centers of gravity both of positive and negative charges of a molecule coincide with the center of the symmetry of the molecule and therefore with each other (in this case the sign of the charge of separate atoms and ions from which the molecule is built may even be disregarded). Conversely, asymmetric molecules are always polar.

The electric dipole moments in polar molecules lead to align themselves with an external electric field. The alignment will not be completed but increases with the increased electric field and also as the temperature is decreased, because the molecules are in constant thermal agitation[2-5]. In non-polar molecules they acquire alignment by induction when placed in an electric field. The external electric field tends to separate the negative and positive charges in the atom or molecule.

4.3 Dielectric polarization mechanism:

When external electric field is imposed on a dielectric substance the electrically charged particles with their displacement are ordered in space. These ordering of electrically charged particles with in the substance is called polarization. This cause the formation of an electric moment in the entire volume of the dielectric and in each separate polarizing particle (atom, ion, molecule).

Under the influence of the external electric field different processes of polarization takes place due to the distortion and alignment of the molecules and their average orientation change. Both the distortions of the molecules and their average orientation changes as the field changes. Different types of polarization (i. e. Electronic, molecular and orientational polarization) occurs at different range of frequencies figure 4.2. Electronic polarization occurs in all atoms or ions can be observed in all dielectrics irrespective of whether other types of polarization are displayed in the dielectric. For a very short duration, (of the order of 10^{-15} sec) i. e. the time of the period of oscillations of U-V rays.

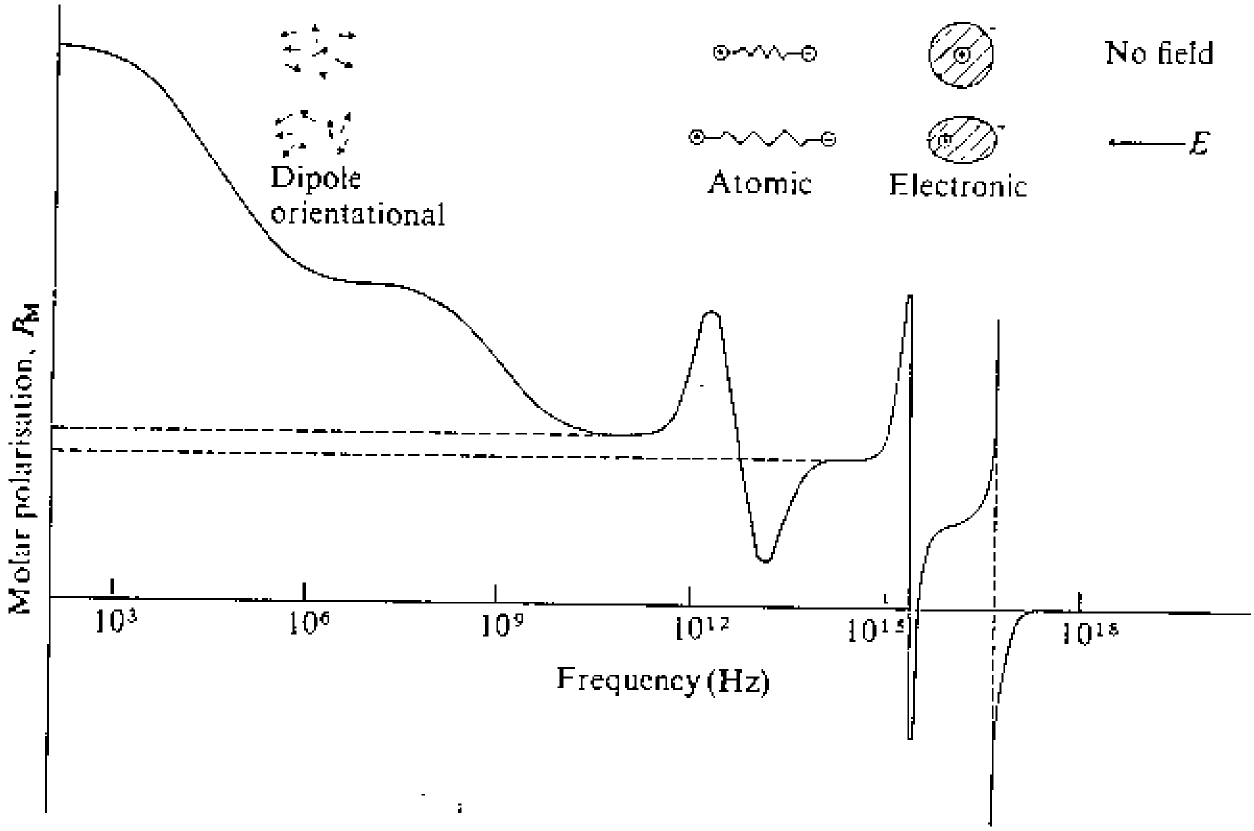


Fig.4.2. Dispersion of molar polarisation in a dielectric (schematic).

Atomic polarization is observed in the infrared region for the polar molecules. Dipolar molecules show orientational polarization, which is directly proportional to the local field strength and inversely proportional to temperature.

Polarizability reflects the properties of an individual particle of matter and not of a certain very large volume of it and is a most important microscopic electrical parameter of a dielectric. Both polarization and electrical conduction are caused by the motion in space of the electrically charged particles of a dielectric and therefore there is a certain affinity between these two phenomena. During polarization (at least during electronic, ionic and dipole polarization) the charges linked with the definite molecules of matter are brought into motion. These charges can't leave the confines of a given molecule. Whereas electrical conduction is caused by the motion (drift) of free charges (carriers) which can move in matter over comparatively large distances.

Polarization takes place in all the molecules of a dielectric and it is its 'bulk' property. The physical picture of polarization of a dielectric may be represented as a negligibly small displacement in space of a very large number of charged particles of matter.

When a dielectric is placed in an electric field. the charges of a non-polar molecule suffer a small displacement. Under the influence of an external field, dielectrics both polar and non-polar, behave in the same way. It can be imagined that these dipoles in the applied electric field can have excess negative charges on the surface and positive charges on the opposite surface as shown in the figure 4.3.

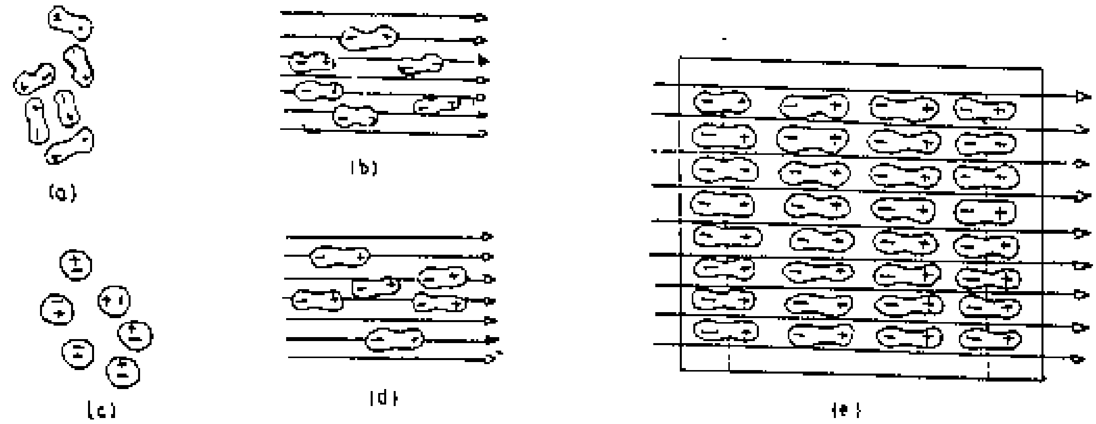


Fig. 43 (a) and (b) Behaviour of a polar molecule in the absence and in the presence of electric field.

(c) and (d) Behaviour of non-polar molecules in the absence and in the presence of electric field.

(c) Polarization of a dielectric in an electric field.

If the surface area A of a parallel plate capacitor is much greater than the square of the distance between plates, d^2 then we can say that the electric field between the plates is uniform and perpendicular to the surfaces.

Suppose a vacuum exists between the plates and the surfaces are electrically charges with density 's' then from the theory of electro-magnetism in C.G.S. units the intensity of the electrostatic field between the plate is $E_o = 4\pi S$ and the potential difference is given by $\varphi o = E_o d$. Let us insert a dielectric substance between the plates and maintain the surface electrical charge density S, then the electric field intensity between plates is $E = 4\pi S/\epsilon$, where ϵ is the dielectric constant

Thus $\epsilon = E/E_0$.

In actual practice the dielectric constant is defined by the use of the electrical capacity C. Since the capacity of the parallel plate electrical capacitor is given by, C= SA/ϕ - A/4πd, if we denote the capacity of a standard substance with known dielectric constant, ϵ_1 by and the capacity of the substance to be measured with dielectric constant ϵ_2 then the unknown quantity ϵ_2 may be measured from

$$C_1 / C_2 = \epsilon_1 / \epsilon_2.$$

Linear dielectrics show a direct proportionality between the electric moment P (induced moment) acquired by the particle during the process of polarization and the intensity E of the electric field acting on the particle

$$P = \alpha E$$

The coefficient of proportionality α in the above expression is called the Polarizability of a given particle. Since α is defined in terms of dipole moment, its magnitude will be a measure of the extent to which electric dipoles are formed by the atoms and molecules. These may arise through a variety of mechanism, any or all of which contribute to the value of α. Thus the total Polarizability can be written as the sum of the individual polarizabilities arising from one particular mechanism i. e.

$$\alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_i$$

where the terms on the right hand side stand for electronic, atomic, orientational and interfacial Polarizability respectively. We like to focus our attention to the electronic, atomic and orientational polarization.

4.3.1 Electronic Polarizability:

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, to the more precise form -- the displacement under the action of an external electric field of the orbits in Which negatively charged electrons more around a positively charged atomic nucleus. In an atom there is a positively charged inner shell surrounded by electron clouds having symmetries determined by their quantum states[6-8]. The electron clouds are displaced slightly w.r.t. the positive cores when a field is applied.

The electrons have natural frequencies equal to, or higher than those of visible light. The strength of the induced moment μ_e for an atom is proportional to the local field in the region of the atom and is given by

$$\mu_e = \alpha_e E.$$

Where α_e is called the optical Polarizability, it is sometimes also referred to as the electronic Polarizability.

Homopolar neutral dielectrics (i. e. without ionic structure) possessing only one type of polarization, namely electronic polarization satisfy the equation

$$v = \sqrt{\epsilon} \text{ or } \epsilon = v^2$$

which is the corollary of Maxwell's theory. Where v^2 is the refractive index of light rays and ϵ is permittivity.

In general, atoms with many electrons tend to have a larger Polarizability than those with few electrons. As the outer electron shells are not so strongly bound to the nucleus, the outer electronic shells will contribute more to α_e than to electrons in the inner shells. Therefore, positive ions will have relatively small polarizabilities compared to the corresponding neutral atoms. Reverse is free for negative ions.

4.3.2 Atomic Polarizability:

An electric field can also distort the arrangement of atomic nuclei in a molecule or lattice. The movement of heavy nuclei is more sluggish than electrons so that atomic polarization can not occur at such high frequencies as electronic polarization and it is not observed above infrared frequencies. In the molecular solids it is observed from vibrational spectroscopy that the force constants for bending or twisting of molecules, are generally much lower than those for bond stretching, so one may expect bending modes to make the major contribution to atomic polarization. The magnitude of atomic polarization is usually quite small, often only one-tenth of that of electronic polarization, although some exceptions. In ionic compounds the effect can sometimes be very large. For instance there is a special contribution in the case of crystalline sodium chloride from a relative shift of all the positive ions w.r.t. negative ions.

4.3.3 Interfacial Polarizability:

In practice a material have regions of non-uniformity and impurities may be present as a second phase. Due to the transport of charge carriers interfacial or space charge polarization occurs which causes a pile up charge, either of the dielectric metal interface or against inhomogeneties within the bulk of the dielectrics. This produces distribution of the electric field. The image charge induced by the accumulation of charge at the barrier produces an effective dipole. In a real crystal there exists a large number of defects such as lattice vacancies, impurity centres, dislocations and so on. Free charge carriers, migrating through the crystal, under the influence of an applied field, may be trapped by or pile up against a defect[12]. The effect of this will be the creation of a localized accumulation of charge, which will induce its image charge on an electrode and give rise to a dipole moment. This mechanism causes interfacial Polarizability (α_i)

In heterogeneous materials, there is usually an interfacial polarization arising from the accumulation of charge at structural interfaces. The non-polar materials generally show variation of permittivity in the infrared as well as in the optical region. In addition, dipolar materials show orientational polarization. The three atomic or molecular polarizabilities α_e, α_a, and α_d lead to a general classification of dielectric materials. All dielectrics will fall into one of three groups:

a. Non-polar materials which show variations of permittivity at frequencies in the optical range.
b. Polar materials having variation of permittivity in the infrared as well as the optical region.
c. Dipolar materials which in addition, show orientational polarization.

4.4 Dielectric loss Mechanism:

Orientation of molecular dipoles is a relatively slow process in comparison to electronic transitions or molecular vibrations which have frequencies generally above 10^{12} Hz. Furthermore, it does not consists of uniform switch in the arrangement of all molecules; it is more in the nature of slight adjustment of their average orientations in the face of continued thermal agitation. If sufficient time is allowed after the application of an electric field for the orientation to attain equilibrium will the maximum polarization. corresponding to the highest observable dielectric constant. If ample time is allowed, then the observed dielectric constant is called the static dielectric constant ϵ_s. On the other hand, if the polarization is measured immediately after the field is applied allowing no time for dipole orientation to take place, then the observed instantaneous dielectric constant denoted ϵ_∞, will be low and due to deformational effects alone. Somewhere in between these extremes of time scale there must be a dispersion from a high to a low dielectric constant.

When electric field is applied across a dielectric substance the power is lost by some amount is generally known as dielectric loss. This is the general term determining the power loss in an electrical insulation both at a direct and an alternating voltage. The dissipation factor (tan δ) in a dielectric is a useful indication of the energy lost as heat. In reference to the energy loss dielectric materials are divided into high loss materials and low loss materials. Ceramic materials are high loss materials. Polar organic materials are typical high loss materials.

For mathematical interpretation suppose we are applying an alternating electric field E, of amplitude E_o and angular frequency ω,

therefore $E = E_o \cos \omega t$. (1)

This will produce polarization, which alternates in direction. If the frequency is high enough the orientation of any dipoles which are present will lag behind the applied field. This can be expressed as a phase lag δ in the electric displacement.

$$D = D_0 \cos(\omega t - \delta) \qquad (2)$$
$$= D_0 \cos\omega t . \cos\delta + Do \sin\omega t . \sin\delta$$
$$= D_1 \cos\omega t + D_2 \sin\omega t.$$

where $D_1 = D_0 \cos\delta, \qquad (3)$

$$D_2 = D_0 \sin\delta \qquad (4)$$

It is observed experimentally that D is directly proportional to E_0 for many substances, so we can write

$$D_1 = \epsilon' E_0 \qquad (5)$$

and $D_2 = \epsilon'' E_0 \qquad (6)$

Therefore $D = \epsilon' E_0 \cos\omega t + \epsilon'' E_0 \sin\omega t \qquad (7)$

$$\therefore D_1 = \epsilon' E_0 = D_0 \cos\delta$$
$$D_2 = \epsilon'' E_0 = D_0 \sin\delta$$
$$\therefore \tan\delta = \epsilon''/\epsilon'$$

It is convenient to combine these two quantities into a complex dielectric constant or relative permittivity $\epsilon^* = \epsilon' - i\epsilon''$

The meaning of the real and imaginary parts may be readily appreciated by considering the material in a capacitor (capacitance Co when empty) as shown figure 4.4.

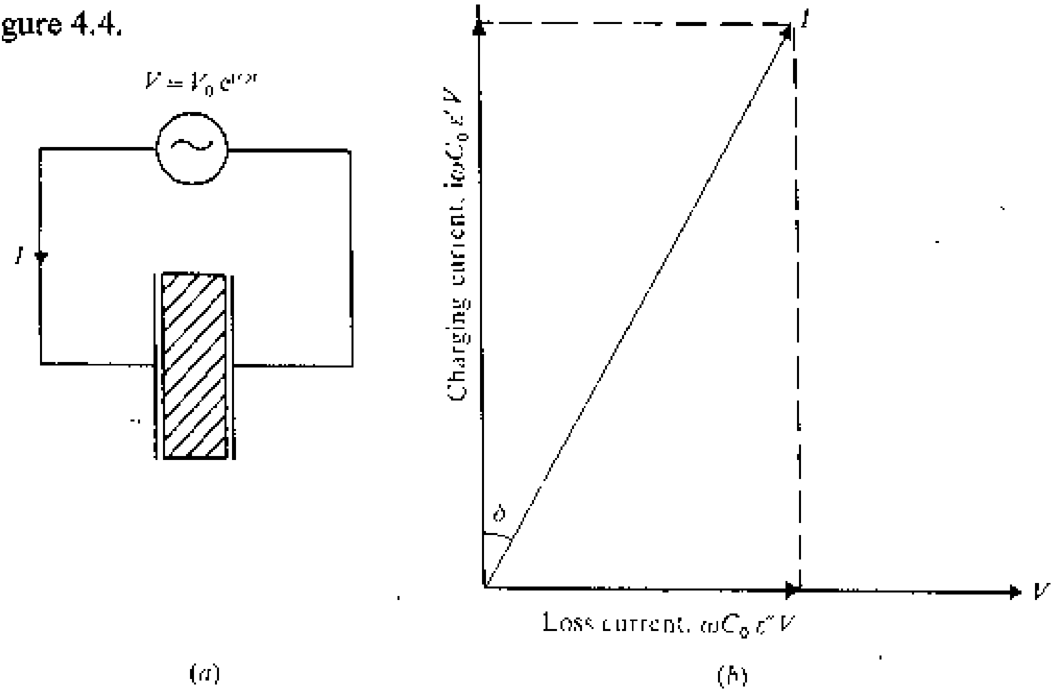


Fig. 4·4 AC losses in a dielectric: (a) circuit diagram (b) Argand diagram of complex current–voltage relationship

The current I which flows in the external circuit after application of an alternating voltage given by the real part of $V = V_o e^{i\omega t}$ may be calculated as follows;

$$\begin{aligned} I &= \epsilon^* C_0\, dv/dt \\ &= i\omega\, \epsilon^* C_0 V \\ &= \omega C_o\, (\epsilon'' + i\epsilon')V \end{aligned}$$

This implies that we have a capacitive component of the current,

$$I_c = i\omega\, C_0 \epsilon' V$$

which leads the voltage by 90°, and a resistive component

$$I_R = \omega C_0 \epsilon'' V$$

which is in phase with the voltage. Work can only be done by the latter component and the physical meaning of the useful quantity $\tan\delta$ previously defined becomes apparent:

$$\tan\delta = \epsilon''/\epsilon' = \text{Energy dissipated per cycle/Energy stored per cycle.}$$

ϵ'' is called the dielectric loss factor and $\tan\delta$ is usually called the dielectric loss tangent or dissipation factor. ϵ' and ϵ'' are experimentally observable quantities, which may be used to characterize the dielectric dispersion over a range of frequencies.

The change of the electric field with time brings a new terms $\epsilon'' E_0 \sin\omega t$ into D. This ϵ'' is proportional to the energy loss in a dielectric, normally the loss caused by the scattering of electric energy as ion heat[12]. If the frequency ω is very small, the second term of equation (7) can be neglected and D approaches $D = \epsilon' E_0$. When molecules with dipoles are present in an oscillating electric field, they absorb from or give energy to the electromagnetic field, their own energy being in the form of oscillation or rotational energy.

When molecules try to turn to the direction of the electric field and thereby move about molecules, oscillation energy and rotation energy are induced in the surroundings when a molecules system is constantly moving[9-12] in an oscillating electric field towards the direction of lower potential energy, the energy absorbed from the electromagnetic field becomes higher than that given to the field, the energy difference being lost as heat energy.

4.5 Dependence of Permittivity:

Dielectric constant, dielectric loss and electrical conductivity are the basic electrical parameters of coal. Dielectric constant and dielectric loss characterize the electrical behaviors of insulators, the electrical conductivity is the characteristic of a conductor. Coal is considered to be a semi conductor since the sp. resistance of bituminous coal ranges from 1×10^{8} to 1×10^{12} ohm – m and the anthracite has a values ranging from 10^{-2} to 10^{2} ohm–m. The dielectric loss is combination of dielectric constant and conductivity. The permittivity ϵ depends on the changeable external factors, such as the frequency of applied voltage, temperature, pressure, humidity, particle size etc.

4.5.1 Dependence of $\in$ on frequency:

The time required for electronic or ionic polarization to set in is very small as compared with the time of voltage sign change (i. e. with the half period of alternating voltage) even for the highest frequencies. For this reason the polarization of dielectrics distinguished only by a deformational mechanism of polarization whose duration is for very short period as compared with the voltage half period. We have no right to expect that any practically essential dependence of ϵ on the frequency should appear in such dielectrics. The permittivity of non-polar dielectrics does not depend on frequency when it changes within very broad limits. But it is different for dipole polarization. When the frequency of alternating voltage increases the value of ϵ of a polar dielectric at first remains invariable but beginning with a certain critical frequency when polarization fails to settle itself completely during one half period, ϵ begins to drop approaching at very high frequencies the values typical of non-polar dielectrics.

4.5.2 Dependence of ϵ on temperature:

Temperature does not affect the process of electronic polarization in non-polar dielectrics, and the electronic Polarizability of molecules does not depend on temperature. However, due to a thermal expansion of matter, the ratio of the number of molecules to the effective length of the dielectric diminishes when temperature increases, for which reason ϵ should also diminish in this case.

The nature of dependence of permittivity on temperature may be different in solid ionic (linear, i. e. not ferroelectric) dielectrics. In most cases an ionic mechanism of polarization increases ϵ when the temperature grows. In some cases, the value of ϵ may diminish when the temperature rises, particularly in those substances in which ionic displacement intensifies the internal field and thereby the electronic polarization (for example T_iO_2 and $Ca\,T_iO_3$)

In most of the cases in polar dielectrics in the low-temperature region the molecules can't orient themselves. With the increase of temperature the origination of dipoles is facilitated and this increases permittivity. As the temperature grows the chaotic thermal oscillations of molecules are intensified and the degree of orderliness of there orientation is diminished.

In the case of chemically individual polar matter having a distinct melting point there can be observed a jump like change in ∈ during melting. Sometimes the dependence of permittivity ∈ of dielectrics and also the capacitance C of capacitors on temperature are estimated by means of the temperature co-efficient of permittivity

$$TC_{\epsilon} = \frac{1}{\epsilon}\frac{d\epsilon}{dT}$$

and the temperature co-efficient of capacitance

$$TCC = \frac{1}{C}\frac{dC}{dT}$$

4.5.3 Dependence of ∈ on humidity:

In hygroscopic dielectrics with ∈ smaller than ∈ of water, the permittivity is noticeably increased with moistening. Of course it is difficult to utilize as a positive factor an increase in the capacitance of a dielectric under moistening. For example in capacitors since moistening appreciably deteriorates the important parameters of a dielectric, i. e. decrease resistivity increases a dielectric loss angle and reduces electric strength.

4.6 Electrical conduction mechanism in solids

Electrical conduction in insulating solids may occur through the movement of either electrons or ions. There may be contribution to the conductivity from several different types of carriers, notably electrons and holes in electronic conductions and cation and anion pairs in ion conduction. In most of the insulating materials, it is very diffcult to observe any electronic conductivity and whatever conductivity there is, it usually depends on the movement of adventitious ions. Therefore (a) ionic conductivity and (b) electronic conductivity are all important in there own way in insulating solids. Again, the electronic conducitivity may be of (i) band conduction and (ii) hopping (tunnelling) conduction within localized levels in the forbidden gap.

(a) Ionic conduction

In bulk material ionic conduction occurs due to the drift of defect under the influence of an applied electric field. The degrees of ionic impurities, which may be totally ignored in the context of other properties, may have a significant effect on conductivity. A theoretical expression may be derived, for the current density, flowing through a sample, on the basis of a simple model and is given by

$$j \alpha \, Sinh(eaE/2KT)$$

where E is the electric field and "a" is the distance between neighbouring potential wells.

(b) Electronic conduction

(i) **Band conduction** : Electronic conduction in insulating solids may differ in several important ways from the more familiar kind in metals and inorganic semiconductors. That is not to say that they are separate subjects and indeed, the well-known band theory of atomic lattice has provided the essential basis of concepts for the discussion of conduction in solids, as in polymers.

In crystalline solid like silicon, where many atoms strongly interact, splitting of energy levels occur. Sets of energy levels for two continuous energy bands, called the valence band and the conduction band.

(ii) **Hopping conduction** : Disorder in a lattice affects both the energetic and spatial distribution of electronic states. For a random distribution of atoms the density of electronic energy states tails into what is normally the forbidden zone and the electrons in these tails are localized. When the electrons are excited to higher energy, conduction via localized electron implies discrete jumps across an energy barrier from one site to the next as shown in figure 4.5.

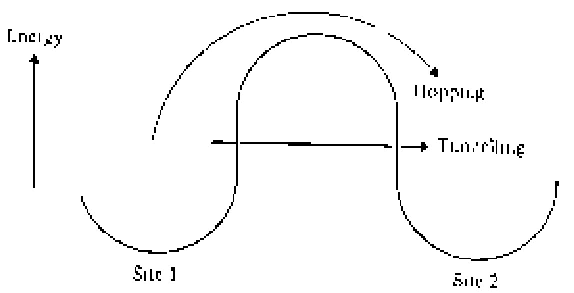
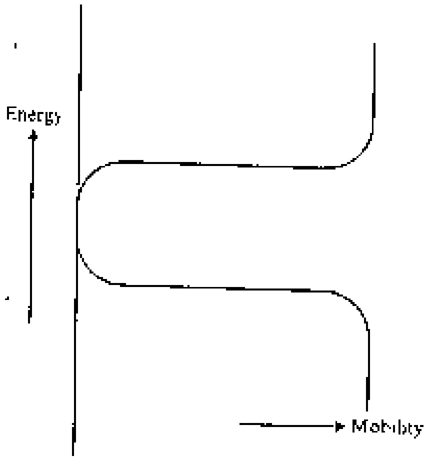


Fig 4.5 Diagram of electron-transfer mechanisms between adjacent sites separated by a potential-energy barrier



A mobility gap

An electron may either "hop" over or "tunnel" through the top of the barrier, the relative importance of these two mechanisms depending on the shape of the barrier and the availability of thermal energy.

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Chapter 5

Results and Discussions

5.1. Introduction

GDH–38 and GDH-39 are the two boreholes of Barapukuria coal mine from where coal samples were collected to investigate physical, structural and electrical properties. For all sorts of investigations some high quality coal samples were selected. To investigate the physical characteristics of the coal samples, proximate analysis and for structural characteristics, IR spectroscopy and X-ray diffraction studies were performed. In order to observe the d.c. electrical behaviour, some selected coal samples of GDH–38 and GDH–39 were analyzed as the function of voltage, temperature, thickness by 2 probe method.

Results of different analysis are discussed in the following sections:

5.2. 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 (5.1) and table (5.2) respectively.

Moisture

Moisture content generally varies from 1%-35%. Generally low moisture levels are desirable. As higher the moisture content, the lower the energy value of a coal. Moisture plays an important role in the reactions of combustion. The results show that the moisture content of the investigated samples are low and below 3.75 wt% for almost all of the samples

Table 5.1: Physical Properties of GDH-38 of Barapukuria Coal

GDH-38	Depth (m)	Moisture wt%	Ash %db.	Volatile matter %daf.	Fixed carbon %daf.	Calorific Value KJ/kg
	200	3.57	12.15	36.08	48.20	26757
	202	3.20	11.76	35.56	49.48	27567
	205	3.33	9.57	35.55	51.55	28332
	339	2.95	4.45	36.45	56.15	29256
	340	2.60	4.20	36.75	56.45	30814
	345	2.25	3.30	37.25	57.20	28948
	348	2.95	3.67	36.50	56.88	29201
	354	2.15	3.26	33.62	60.97	28995
	365	2.10	2.95	35.26	59.69	29650
	366	2.17	7.25	34.33	56.25	29727

Table 5.2: Physical Properties of GDH-39 of Barapukuria Coal

GDH-39	Depth (m)	Moisture wt%	Ash %db	Volatile matter %daf.	Fixed Carbon %daf.	Calorific Value KJ/kg
	172	3.25	6.75	32.85	57.15	29131
	176	3.40	7.86	30.95	57.79	29115
	179	3.45	8.75	29.75	58.05	28556
	182	2.95	9.25	27.56	60.24	28325
	183	3.10	7.36	30.36	59.18	29230
	186	3.33	5.76	30.77	60.14	28193
	189	2.76	7.28	30.76	59.20	29989
	192	2.85	6.87	28.67	61.61	29387
	193	3.20	9.67	29.45	57.68	28596
	195	3.28	10.25	29.48	56.99	28978

Ash content

The ash content of coals can vary from 5% - 25% and is composed mostly of silica, alumina, calcium and iron oxides. The ash content is minimal and varies from 1 to 12 percent with an average value of 6.26% for coals of borehole GDH–38 and about 7.98% for coals of borehole GDH–39. The upper most layer of GDH–38 at depth 200m has maximum ash content and decreases as the height increases but at 366m the ash content is also high and drastically lowered to 7.25%. The GDH-39 borehole has the highest percent at the depth 195m. Ash content is found to be in the range of 2% to 12% on received basis in boreholes of GDH–38 and GDH–39.

Volatile Matter

Volatile matter generally varies from 2%–40%. These volatile include lighter aromatic hydrocarbons, complex oils, tars, phenols and other chemicals. The amount of volatile matter in coal is important because they directly affect the quality of gas produced and need to be removed before using as a fuel. The volatile matter content of coal sample of GDH–38 varies from 33% to 38% and those of GDH–39, samples varies from 27%- 33% on dry basis (db). The volatile matter content of the samples show that the Barapukuria coals are high volatile bituminous type.

Fixed Carbon

The fixed carbon content of coals of GDH–38 varies from 48% - 61% and those of GDH–39 sample varies from 57% - 62% on dry ash free (daf) basis. This indicates that on the average 65% of carbon in Barapukuria coal are aromatic in nature.

Calorific Values

The calorific values of the examined samples are considerably higher in magnitude. The calorific values of the GDH–38 samples varies from 26500 kJ/kg to 31000 KJ/kg on moisture and ash free basis. The calorific value of the GDH–39 samples varies from 28000 KJ/kg - 30000 KJ/kg. As the rank of the coal increases the calorific values also increases. These values were found to confirm with the theoretically calculated values according to Forrester[1]. The Calorific values were found to be in the range of 26000KJ/kg – 31000KJ/kg. The calorific values of the samples show that the Barapukuria coals are high bituminous type.

The proximate analysis reveals that Barapukuria coals are classified as the higher rank of bituminous coal and can be used in heating and for power generation. At the same time Barapukuria coal can be used for chemical extraction.

5.3 Results of X-ray diffraction

To study X-ray diffraction, coal samples of GDH-38 and GDH-39 are considered and are shown in the figures 5.1-5.3. By studying X-ray diffraction pattern it is possible to comment whether the coal samples are crystalline or amorphous in nature. As the carbon content increases, the coal tends to form crystalline structure and for crystalline solid sharp peak is found. If broadened peaks are found then it indicates to the formation of small crystallites[2]. From the investigated coal samples no sharp peak is found, rather all the

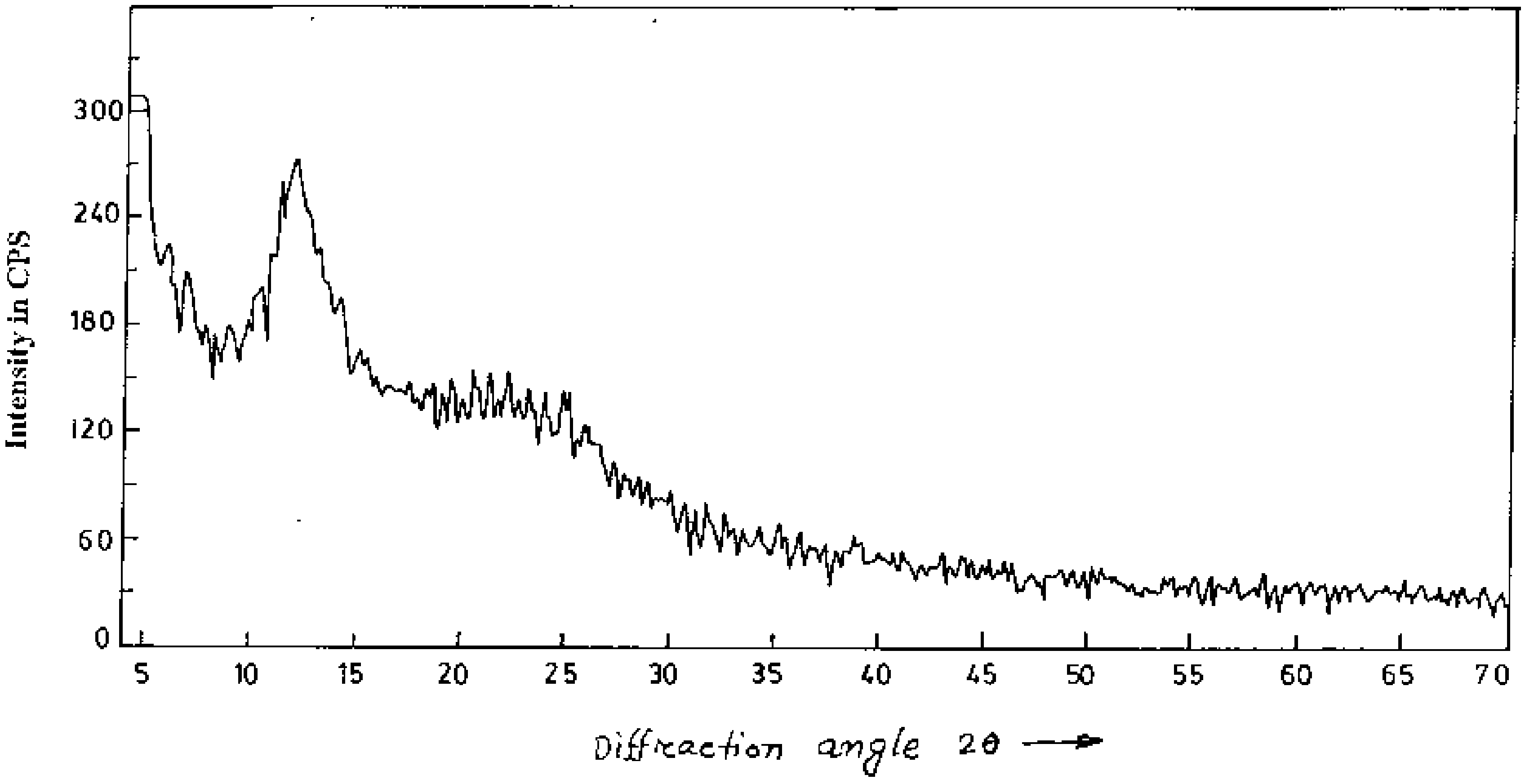

Fig. 5.1: X-ray diffractograms of coal sample of borehole GDH-38 (348m)

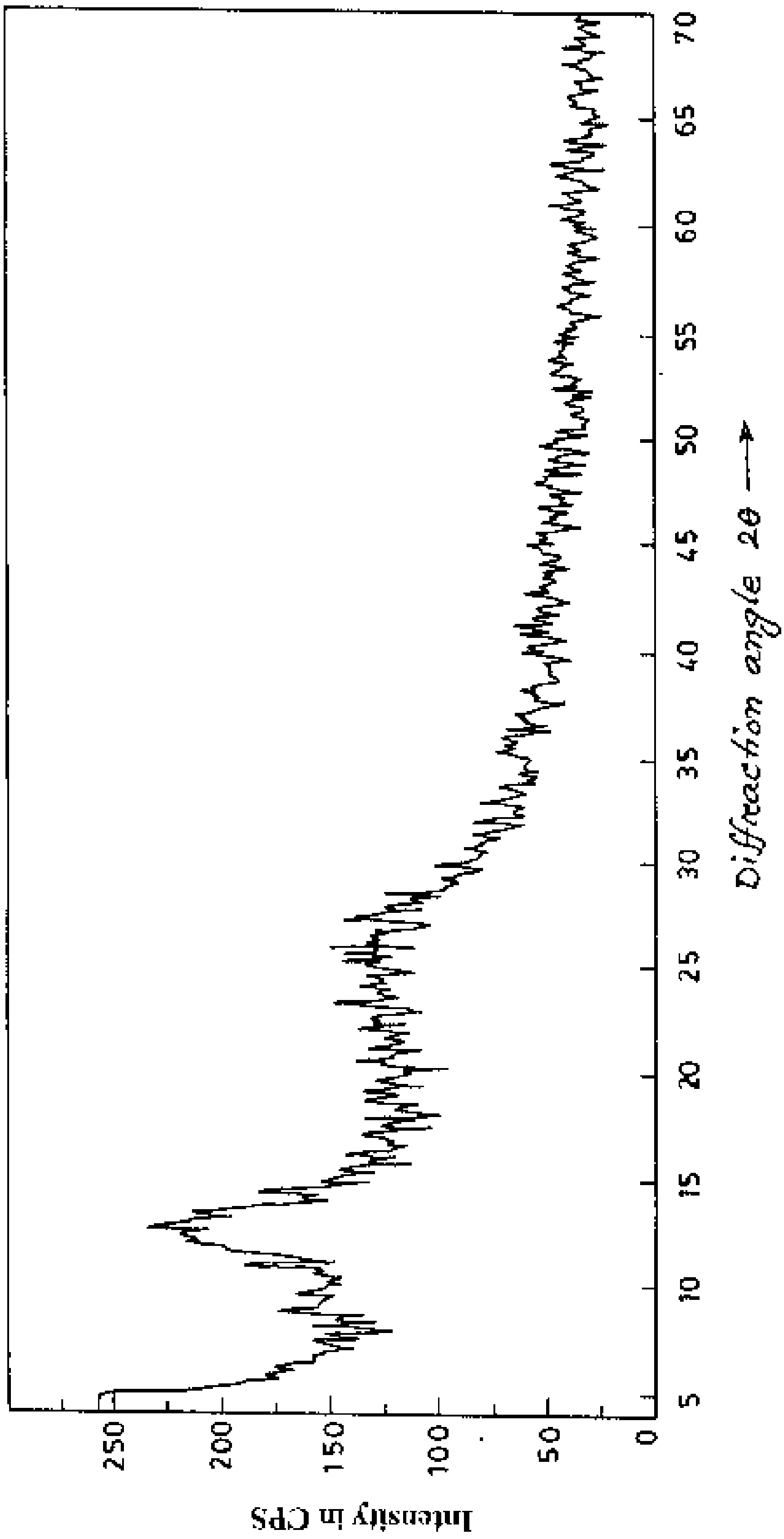

Fig. 5.2: X-ray diffractograms of coal sample of borehole GDH-39 (195m)

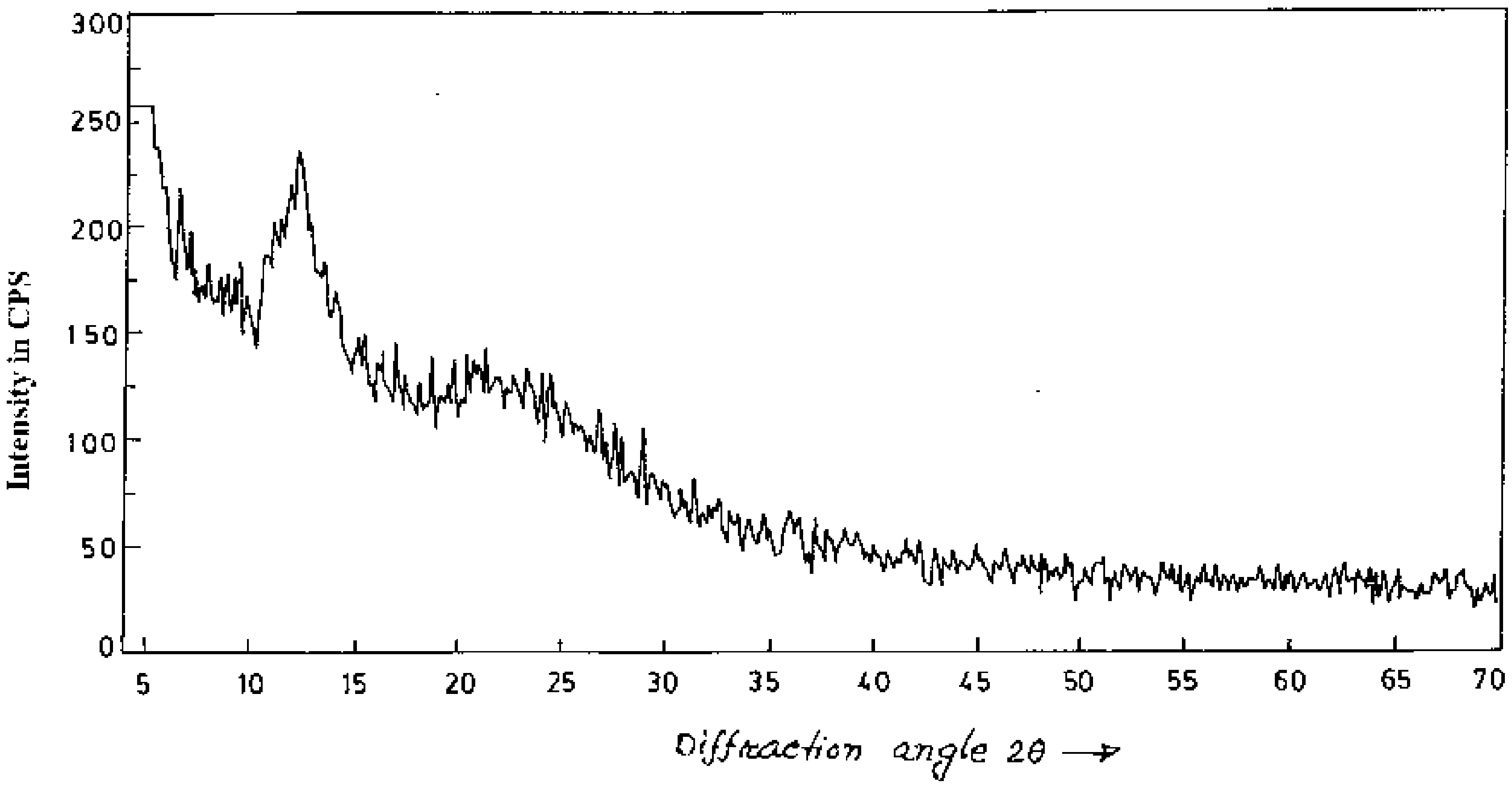

Fig. 5.3: X-ray diffractograms of coal sample of borehole GDH-38, (366m)

diffractograms are continuous curves with initial broad peak between 4° and 20° (2θ) on which more or less diffused peaks are superimposed indicating the largely amorphous nature of coal.

The structural arrangement of coal increases upto the formation of organic macromolecules of flat shape with the increase of coal rank as well as with the increase of carbon content. The carbon hexagons are considered to be embryos of the graphite arrangement. Every macromolecule has several carbon hexagons, which make a planar pattern. At the higher stages of coalification, the carbon embryos arrange themselves into parallel positions and come closer, leading ultimately to a regular periodicity in the vertical direction. So with increasing coalification, the interplanar spacing of carbon hexagonal planes decreases and approaches a regular crystalline structure to that of graphite.

5.4 Results of IR Spectroscopy

Coal is a highly variable and complex mixture of organic and inorganic species. The inorganic fraction is primarily composed of mineral species. The greater proportion of the coal is made up of relatively low molecular weight structural units, which are connected by various types of bonds such as covalent (alkyl or ether, oxygen and sulfur bridges) and non-covalent bonds; hydrogen bonds and Vander Waals' forces[3]. The standard bands and the observed bands are shown in table 5.3.

Table 5.3 : The standard bands and the observed bands.

GDH-38 Depth-340m	GDH-39 Depth-186m	Standard coals Band Position	Assignments
3475	3365	3300	-OH (Stretching), -NH (Stretching)
		3030	aromatic C-H (Stretching)
		2940	aliphatic C-H (Stretching)
2915	2915	2925	$-CH_3$ (Stretching), $-CH_2$ (Stretching)
		2860	aliphatic C-H (Stretching)
		1700	C = 0
1591	1595	1600	aromatic C = C (Stretching)
		1575	Condensed aromatic ring C = C, ether aromatic C = C (Stretching)
1443	1443	1450	aromatic C = C (Stretching) $-CH_3$ (assymetric deformation), $-CH_2$ (scissor deformation)
		1380	$-CH_3$ (symetric deformation), cyclic $-CH_2$
1117, 1134	1028	1300-1000	Phenolic and alcoholic C-O (Stretching)
			C_{ar}-O-C_{al} C_{al}-O-C_{al}
			C_{ar}-O-C_{ar}
	911	900-700	aromatic bands
866, 807, 800		860	aromatic HCC (rocking) in single
748	747	750	Benzene rings, condensed system
540	530		
466	465		

Two samples, one from GDH-38 and other from GDH-39 were studied by infrared (IR) spectroscopy using the KBr pellet technique. The IR spectra of these coal samples show similar results and suggest the similar carbon skeleton having same functional group and mineral matter present in coal. The spectra of the coal sample of GDH-38 at depth 340 m and that of GDH-39 at depth 186 m are shown in the figures(5.4) and (5.5) respectively. The scale of ordinate for both the samples is same (i.e. 4000 – 400 cm^{-1} wave number). Comparing with the standard band positions it is observed that both the sample of GDH-38 and GDH-39 exhibit the same nature. The sample of GDH-38 (340m) and GDH-39(186m) show a band at 3475 cm^{-1} and 3365cm^{-1}. This reveals that this band is due to the presence of –OH (stretching), --NH (stretching). Both the samples show a band at 2915cm^{-1}, which is nearly the standard band at 2925cm^{-1}. This may be due to the stretching of $-CH_3$ and $-CH_2$. Band are observed at 1591cm^{-1} and 1595cm^{-1} of GDH-38 and GDH-39 samples, and which is close to the standard wave number 1600cm^{-1}, due to the effect of stretching of aromatic C=C ring. For the both samples, bands are observed at 1443cm^{-1} and where as the standard band is found at 1450cm^{-1}. This may be due to the stretching of aromatic C=C ring, or asymmetric deformation of $-CH_3$ group or scissors deformation of $-CH_2$ group. For the coal sample of GDH-38 two bands are observed at 1117cm^{-1} and 1134cm^{-1} and for the sample of GDH-39 a band is observed at 1028cm^{-1} ,which are found in a wide range of (1000-1300)cm^{-1}. This band may be due to the stretching of phenolic and alcoholic C-O structure or C_{ar}-O-C_{ar} or C_{al}-O-C_{al} structure. For the sample of GDH-38, three bands are observed at 866cm^{-1}, 807cm^{-1} and 800cm^{-1} and these may be due to rocking aromatic HCC in single.

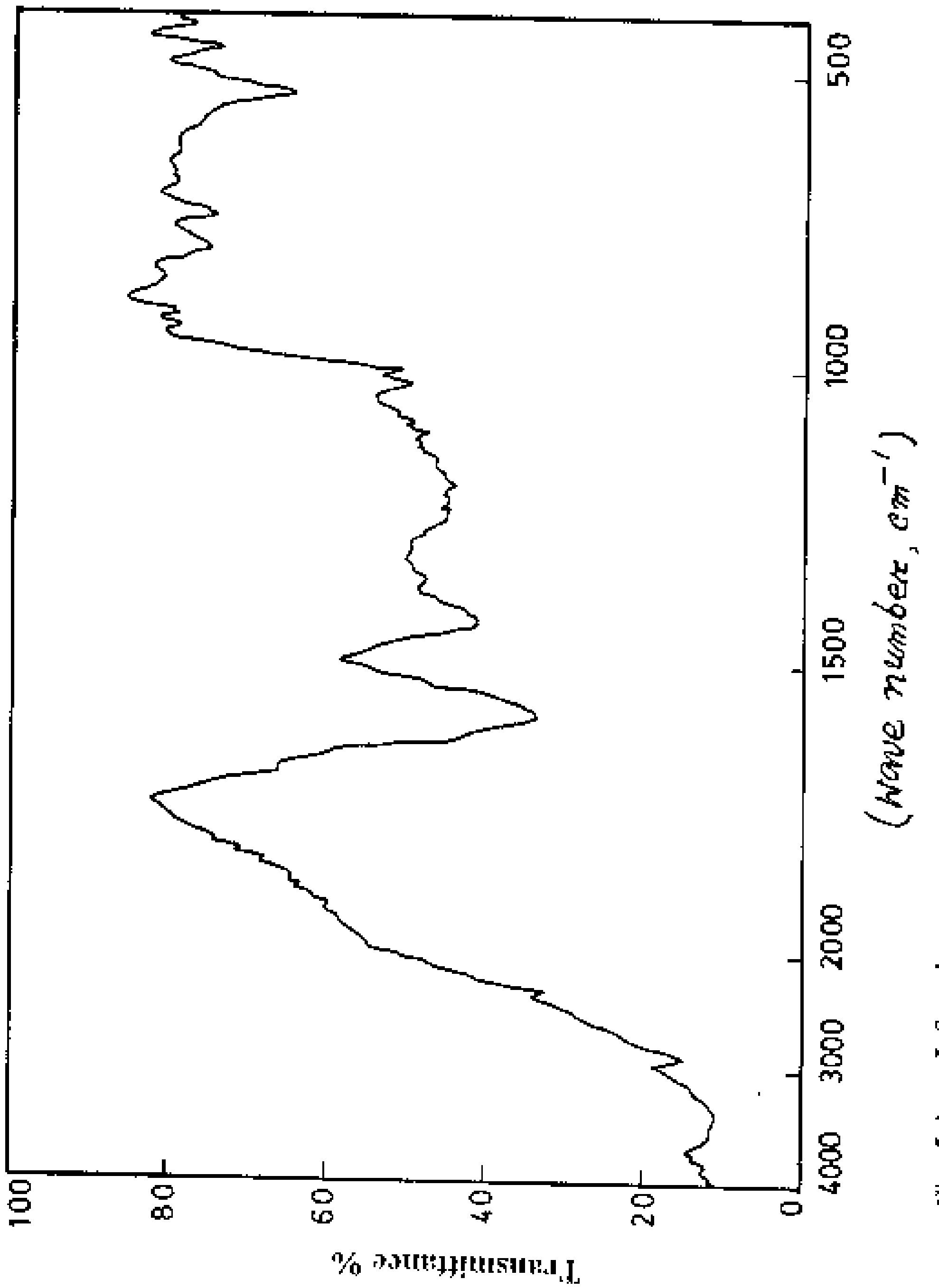

Fig. 5.4: Infrared spectrum of Barapukuria coals of borehole GDH-38, depth - 340m.

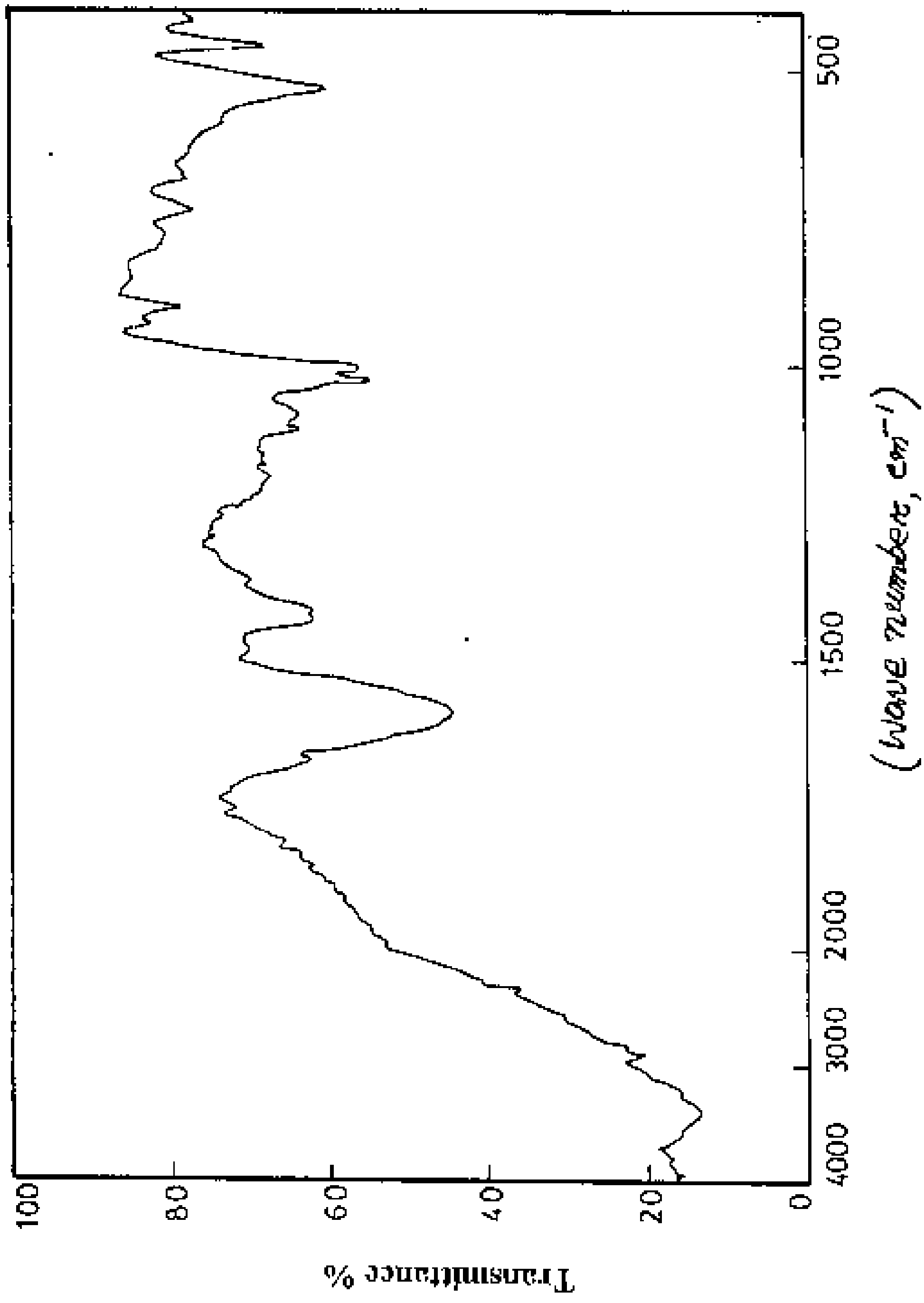

Fig. 5.5: Infrared spectrum of Barapukuria coals of borehole GDH-39, depth -186m

For the coal sample of GDH-39, a band is observed at 911cm^{-1} and this may be considered for aromatic bands. For the sample of GDH-38 and GDH-39, bands are observed at 748cm^{-1} respectively which is similar to standard band at 750cm^{-1} and this may be due to the Benzene rings or condensed system.

5.5 Results of Electrical Measurements

5.5.1 I-V Characteristics

An important role of contacts is observed on the results of electrical measurement on any material. Due to this role it is important to perform current voltage (I-V) measurement to explore the behaviour of the contact before any further study.

To study the I-V characteristics, both lump and disc samples were selected from the boreholes of GDH–38 and GDH–39. The I-V plots for disc samples are shown in the figures 5.6-5.8. All the data are recorded at room temperature. These I-V characteristic curves can be fitted to a relation of the form $I = V^n$ where n is the power factor. By analyzing the curve it can be concluded that the relation is not linear and the value of n is not exactly equal to unity. This means that the contacts are not exactly of ohmic nature.

From the I-V curve it is observed that out of 6 disc samples of GDH-38 and GDH-39, three samples of GDH-38 at depths 199, 206 and 179 m are not linear. For that reason I-V characteristics curves have been fitted to a relation of the form $I=V^n$. The value of n have been calculated from the curve for different samples and it is found to be 1.20, 1.20 and 1.15 (Fig. 5.9-5.11). This indicates that the samples are not linear in nature

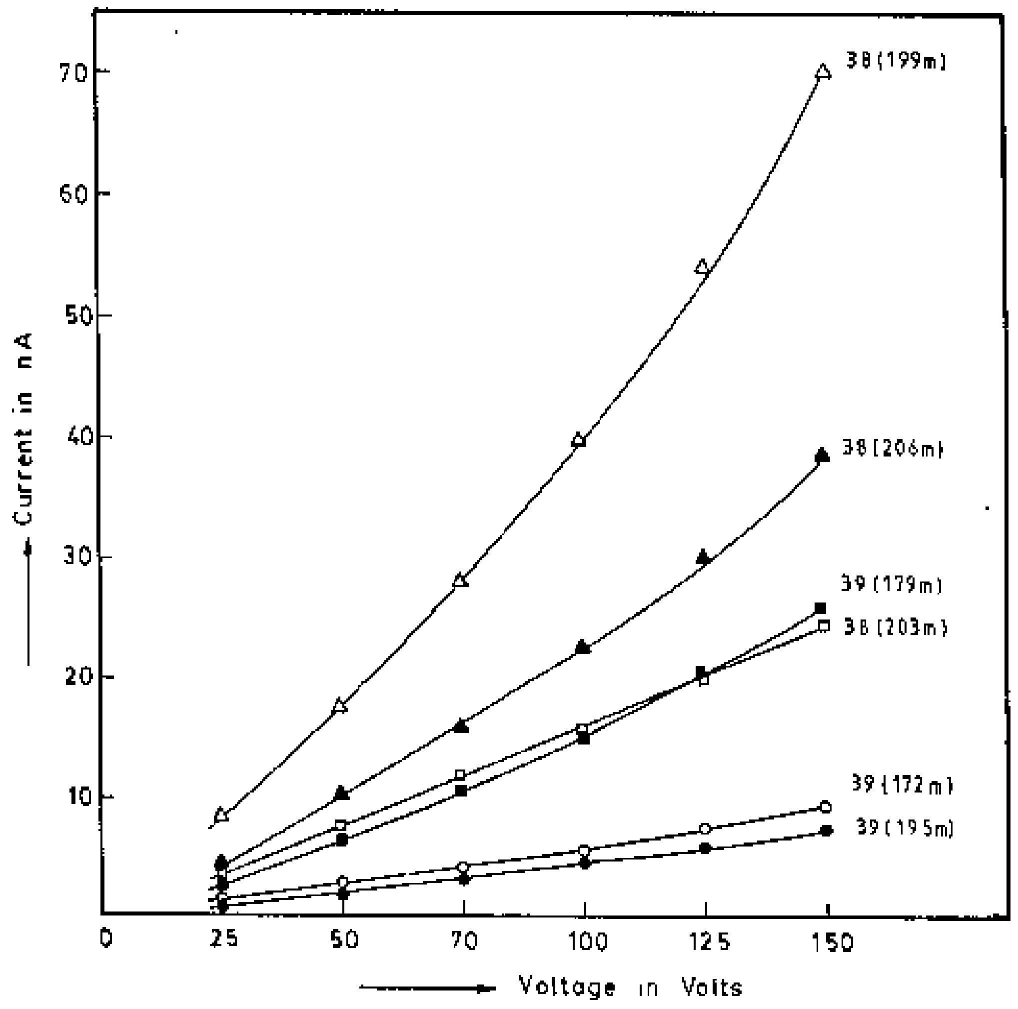

Fig. 5.6: I-V Characteristics curve for disc sample of GDH-38 at different depth.

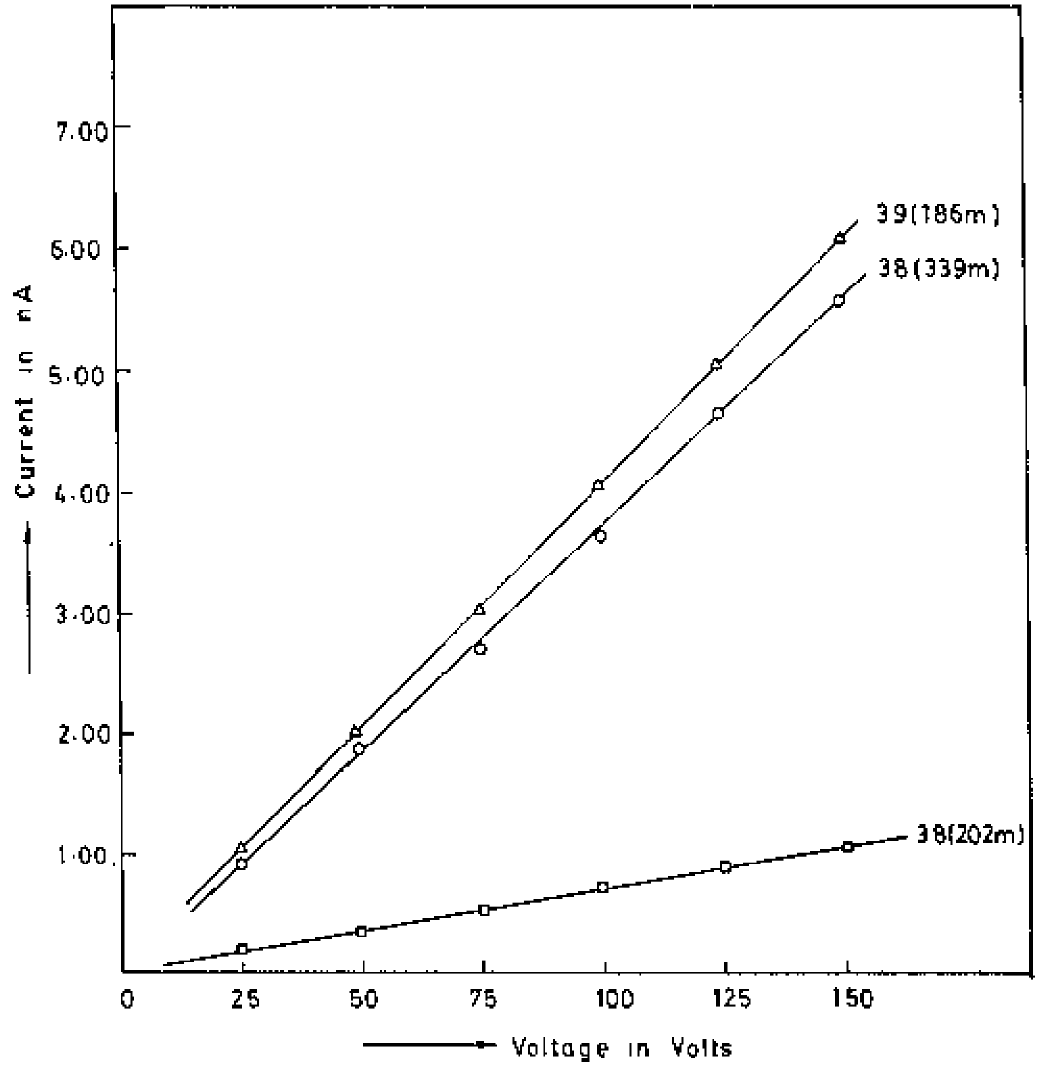

Fig. 5.7: I-V Characteristics curve for lump samples of GDH_38 GDH-39.

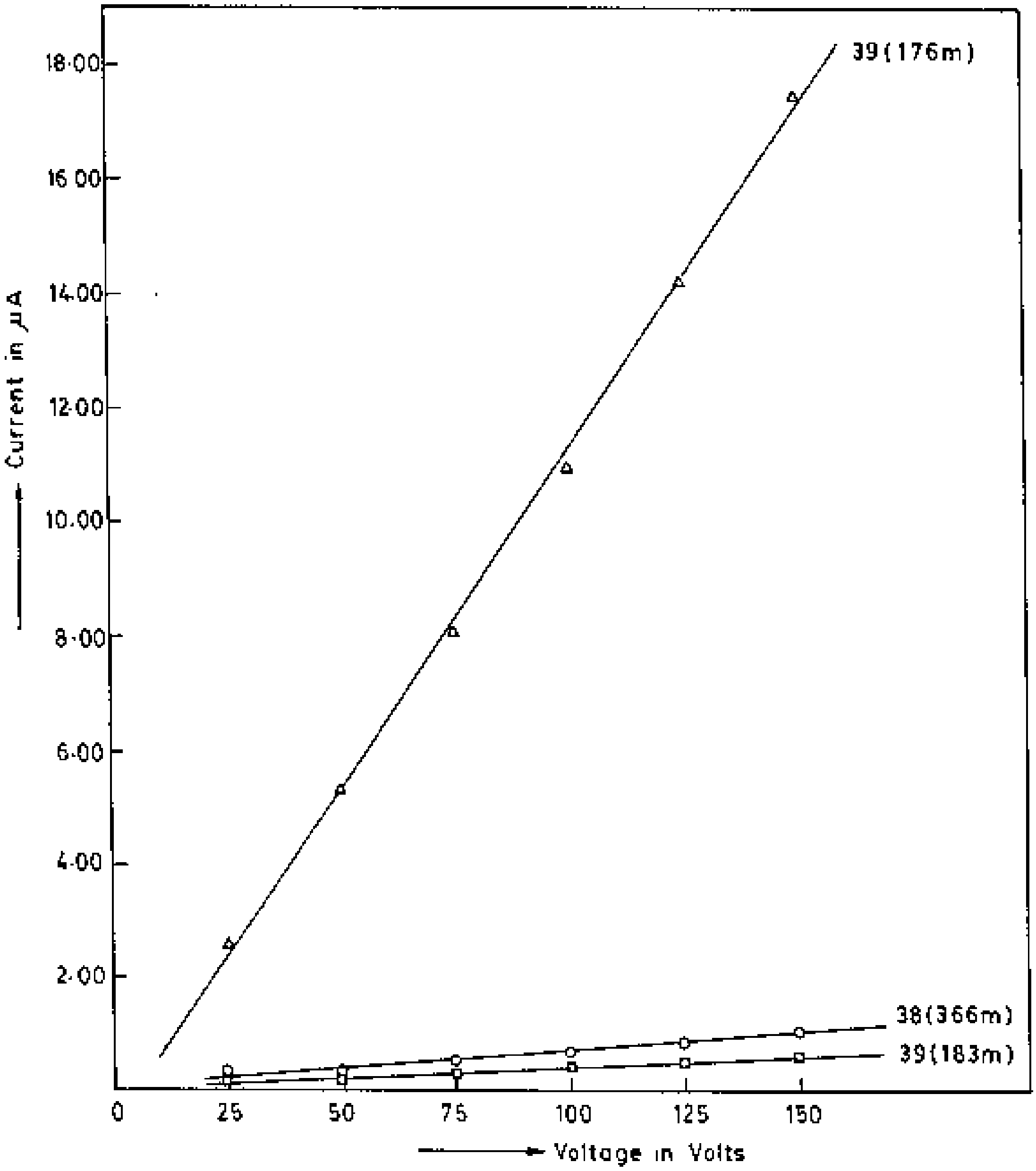

Fig. 5.8: I-V Characteristics curve for lump samples of GDH-39, GDH-38.

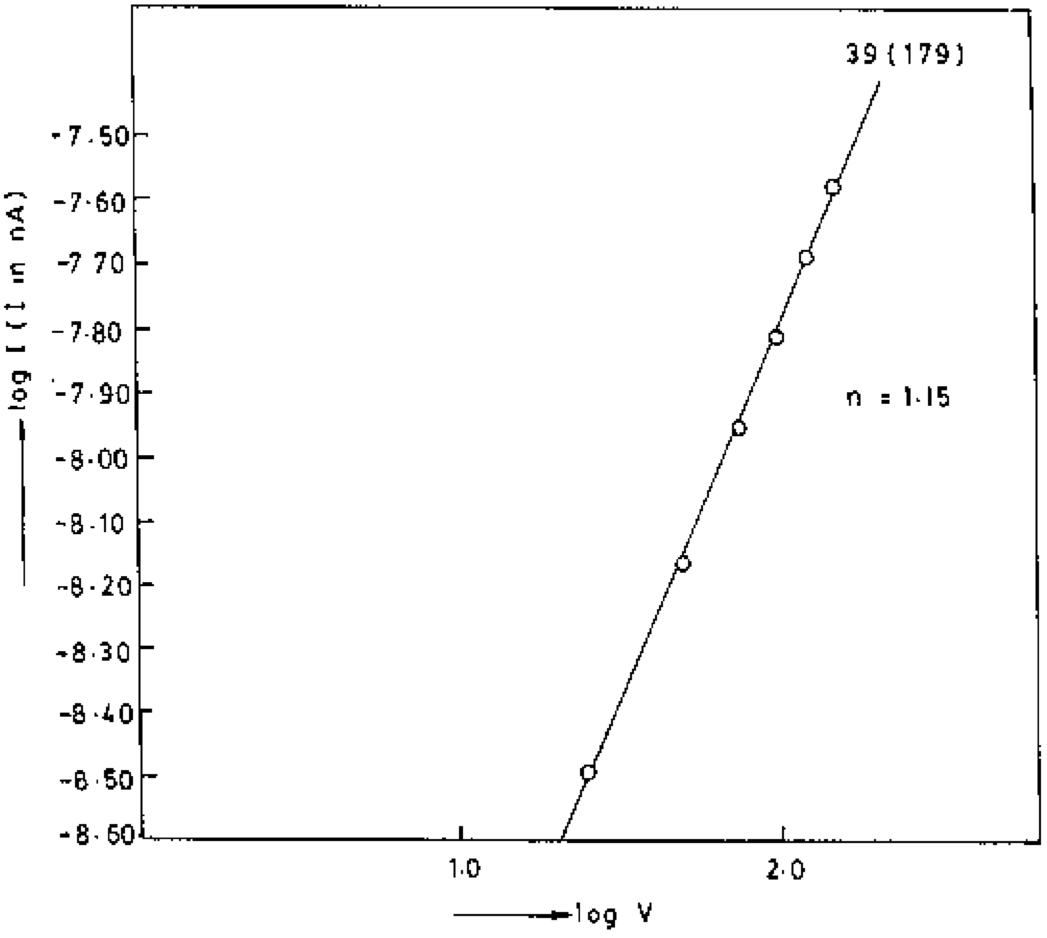

Fig. 5.9: Determination of power factor for the sample of GDH-39, depth-179m

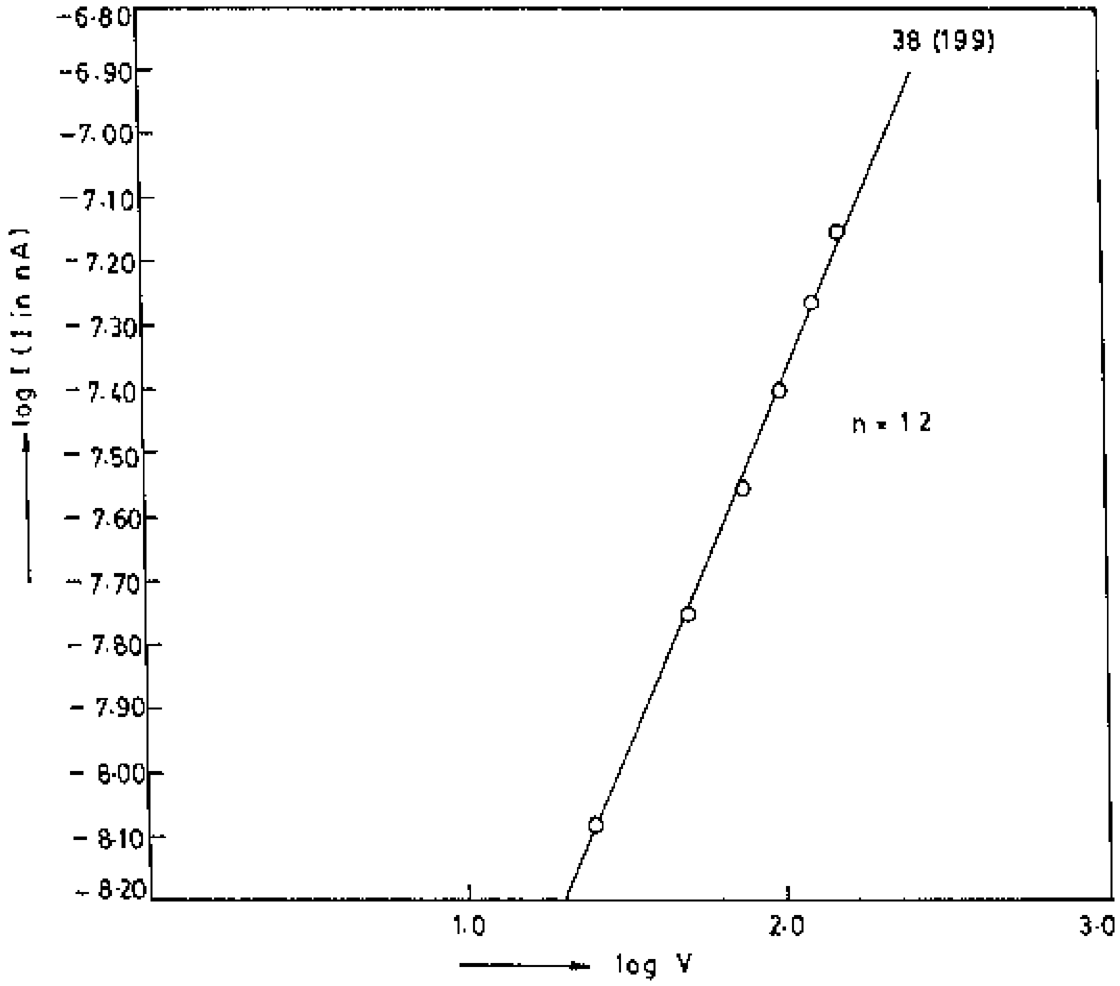

Fig. 5.10: Determination of power factor for the sample of GDH-38, depth 199m.

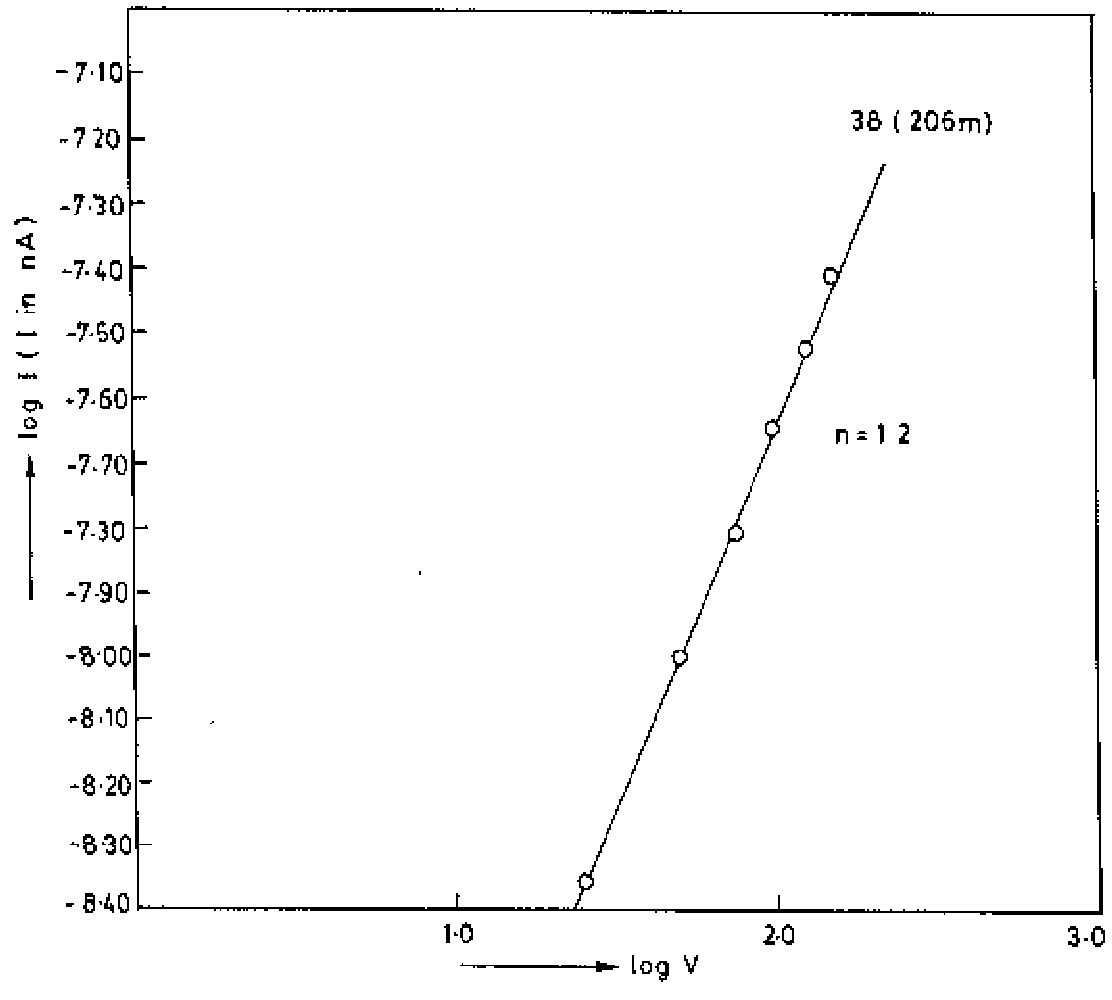

Fig. 5.11: Determination of power factor for the sample of GDH-38, depth 206m.

5.5.2 Results of d. c. resistivity as a function of Voltage

The resistivity of 6 lump samples were analyzed as the function of voltage. Out of them 3 samples were selected from GDH–38 and another 3 lump samples from GDH-39. The voltage range was 0-150 Volts and the instrument was the model of 140a–160 of Metronix Corp., Tokyo, Japan, high voltage D.C. power supply, with current range of 0–3.5 A maximum. By measuring the current using keithly 614 electrometer, resistance of the sample and thus the resistivity of the samples were calculated. Voltage versus resistivity (in log scale) is plotted in figures 5.12.-5.23 and it is observed that the variation of resistivity is not highly affected by voltage variation but the trend to decrease. For the measurement of voltage variation, 6 disc samples were selected from GDH-38 and GDH–39. Out of that 3 samples were from GDH–38 and 3 samples from GDH–39. All the samples showed the same nature for voltage variation.

5.5.3 Results of d. c. resistivity as a function of temperature

To observe the resistivity as a function of temperature, 4 samples of GDH–38 and 4 samples of GDH–39 were selected. From the experimental curve it is observed that an increase in temperature from 30°-60°C causes the resistivity to decrease and after that increases upto 180°C. Over this temperature, the resistivity again start to decrease. It can be stated that the variation of resistivity with temperature have not a definite trend. At different temperature it exhibits almost the same nature and the Barapukuria coal is found to have similar properties to that some Russian and Indian coals[4].fig-5.24-5.31

At lower temperature resistivity decreases, the reason is that the impurity ions and moisture can play an important role in the flow of electric current. The removal of moisture is accompanied by a characteristic change in resistivity. At low temperature the moisture percentage is high and the change in electrical resistivity increases on evolution of moisture. At low temperature there is sharp decrease in the resistivity of coal. The relationship between the electrical resistivity and temperature above 100°C for coals may be described by the following formula depending on whether the sample is a semiconductor or a dielectric.

$$\rho_t = \rho_o\, e^{E/2KT} \tag{1}$$

$$\rho_t = \rho_o\, e^{E/KT} \tag{2}$$

where ρ_t = resistivity at given absolute temperature T

E = activation energy,

K = Boltzmann's constant

and ρ_o is a constant.

when there is a change in the slope of the curve between temperature and resistivity, the result may be explained by the sum of two terms as below.

$$\rho_t = \rho_{01}\, e^{-E/2KT} + \rho_t = \rho_0\, e^{E/KT}$$

$$\rho_t = \rho_{01} e^{E_1/KT_1} + \rho_{02} e^{-E_2/KT_2}$$

The first term of this combined equation will correspond to the mechanism of conduction in the low temperature region, while the second term will correspond to that at high temperature[5].

The activation energy of coal samples of GDH-38 and GDH-39 has been quantitatively calculated from $\log_{10}\rho_{dc}$ Vs 1/T (K) curve.[5.32-5.39] The curves show different knee at different temperature and obviously different activation energy[6-8]. The activation energy for various samples has been shown in the table 5.4.

5.5.4 Results of D.C. resistivity as function of thickness

Practically both the lump sample and disc samples were studied to observe the variation of resistivity with thickness. It is observed from the graphical representation that the resistivity increases as the thickness increases figure 5.40-5.42 and resistivity is greater for samples oriented perpendicular to the bedding plane than that of samples oriented parallel to the bedding plane. On the lump sample of equal thickness it is observed that the resistivity of all the samples were greater when the sample oriented perpendicular to the bedding plane than the resistivity of the sample oriented parallel to the bedding plane.

5.5.5 Results of ac measurements

To understand the polarization mechanisms in solid, the study of dielectric constant and dielectric losses as a function of frequency is most essential. Measurements of dielectric properties help to determine the real part of conductivity, Re $\sigma(\omega)$ of the materials. To study a.c. properties, 6 samples were selected and over a large frequency range (10KHz - 12 MHz) at room temperature, the variation of dielectric constant $\epsilon'(\omega)$, loss factor $\epsilon''(\omega)$ and real part of the conductivity Re $\sigma(\omega)$ is measured. From the experimental data and curve it is observed that the dielectric constant gradually decreases as the frequency increases figure 5.43-548 and shows a very simple variation at the frequency 7×10^6 Hz and increases upto 10^7Hz. The general trend of decreasing is observed for all the samples but the magnitude of dielectric constant is different for the different samples It varies from 2.1 to 24.25. It is clear that at low frequencies, the dielectric constant $\epsilon'(\omega)$ is higher and decreases as the frequency increases.

At lower frequency (f → 0) the conductivity tends to zero and gradually increase as the frequency increases up to 6 × 10^6Hz. Above this frequency, the conductivity decreases and above 8 × 10^6Hz, the conductivity again increases upto 12MHz. All the samples have shown the same nature and also reveals that the effect of D.C. conduction becomes increasingly prominent at lower frequencies[9] figure 5.49-5.53.

As the frequency increases, the magnitude of the dielectric loss tangent decreases and thus decreases the dielectric loss factor. At low frequency range upto 10^5Hz the value of tanδ is not observed and thus $\epsilon^{//} = \epsilon^{/}$ tanδ are not calculated. From the experimental curve it is observed, that $\epsilon^{//}(\omega)$ decreases as the frequency increases. At 6 × 10^6Hz to 10^7Hz $\epsilon^{//}(\omega)$ increases figure 5.55-5.59.

The dielectric constant of a material usually composed of four contributions : (i) ionic (ii) electronic (iii) orientational and (iv) space charge polarization's. All of these may be operative at low frequencies. The large values of dielectric constant at low frequencies exhibited at room temperature may be attributed to space charge polarization. The space charge contribution will usually depend on the purity and perfection of the sample. Its influence is noticeable at low frequency range.

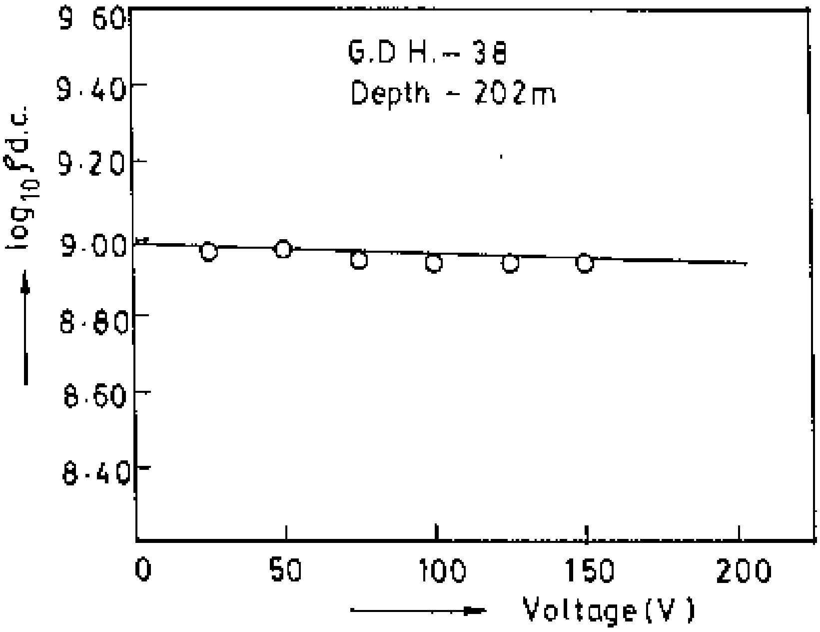

Fig. 5.12: Variation of d.c. resistivity of lump sample with applied voltage sample oriented parallel to the bedding plane.

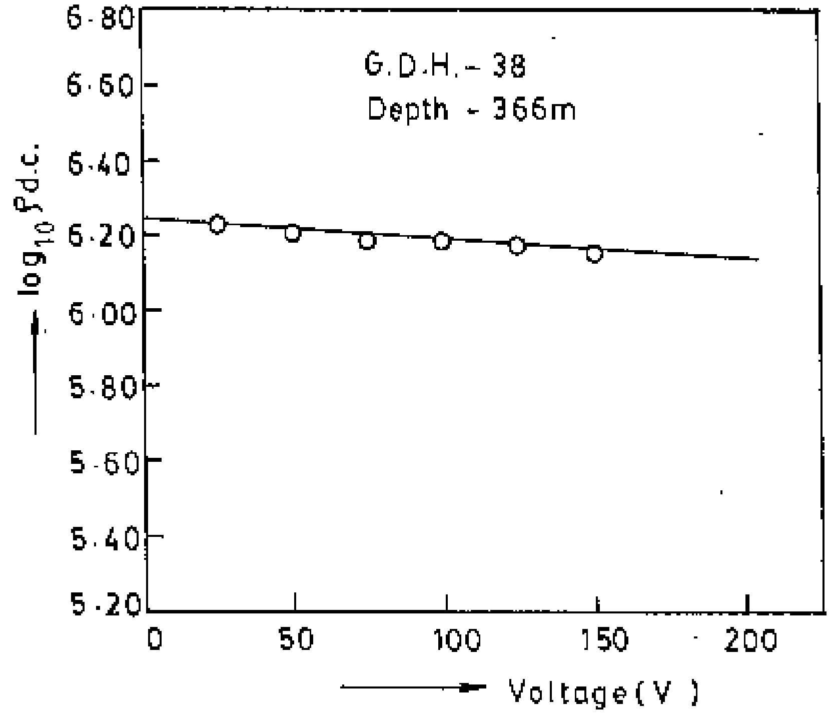

Fig. 5.13: Variation of d.c. resistivity of lump sample with applied voltage sample oriented parallel to the dedding plane.

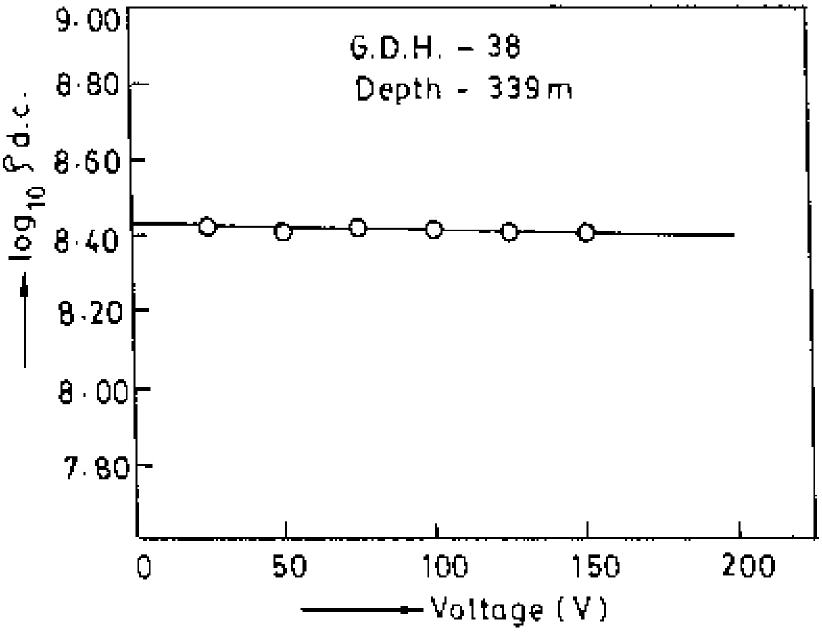

Fig. 5.14: Variation of d.c. resistivity of lump sample with applied voltage samples oriented perpendicular to the badding plane.

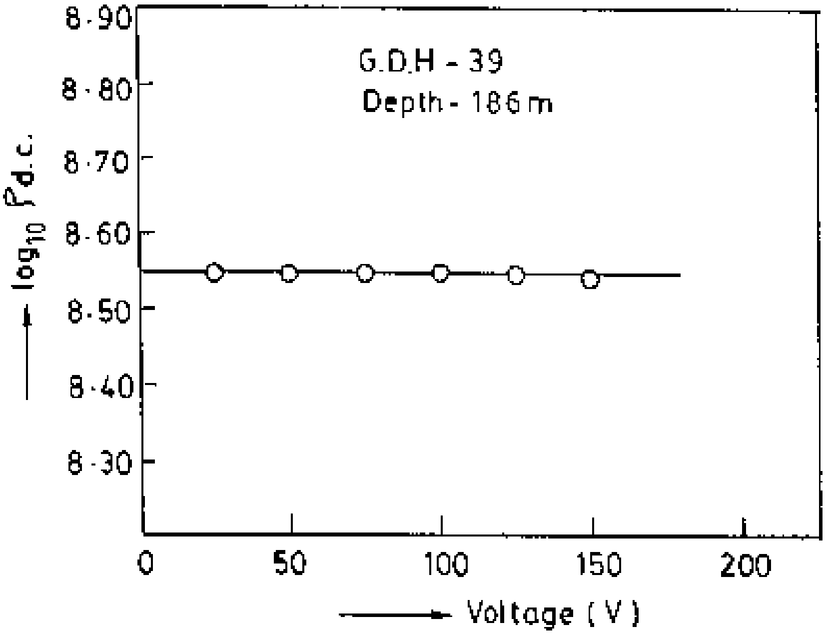

Fig. 5.17. Variation of d.c. resistivity of lump sample with applied voltage sample oriented perpendicular to the badding plane

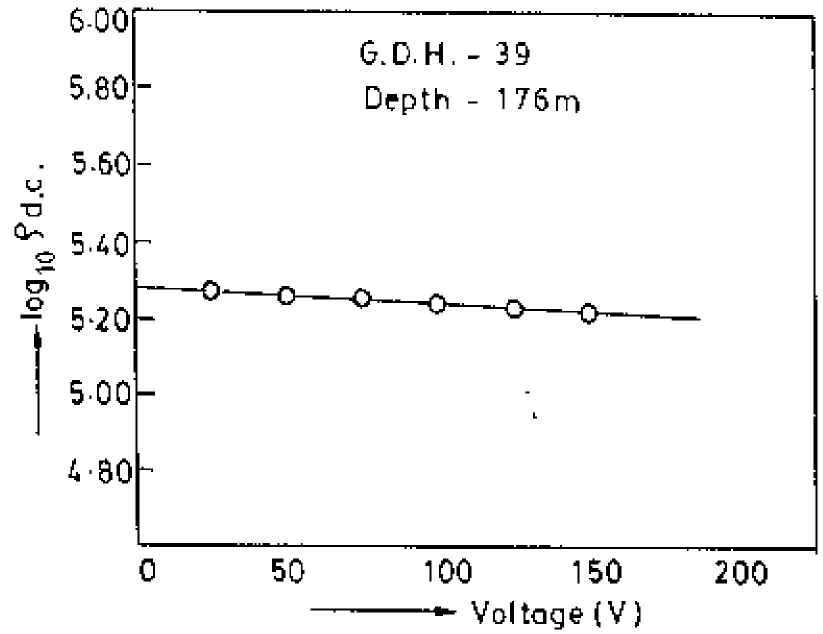

Fig. 5.15: Variation of d.c. resistivity of lump sample with applied voltage sample oriented perpendicular to the badding plane.

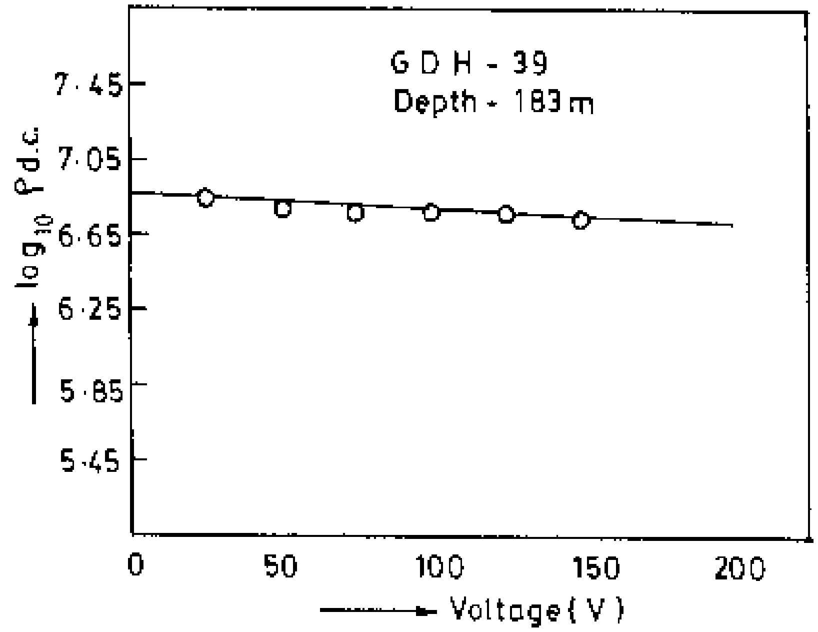

Fig. 5.16: Variation of d.c. resistivity of lump sample with applied voltage samples oriented perpendicular to the bedding plane.

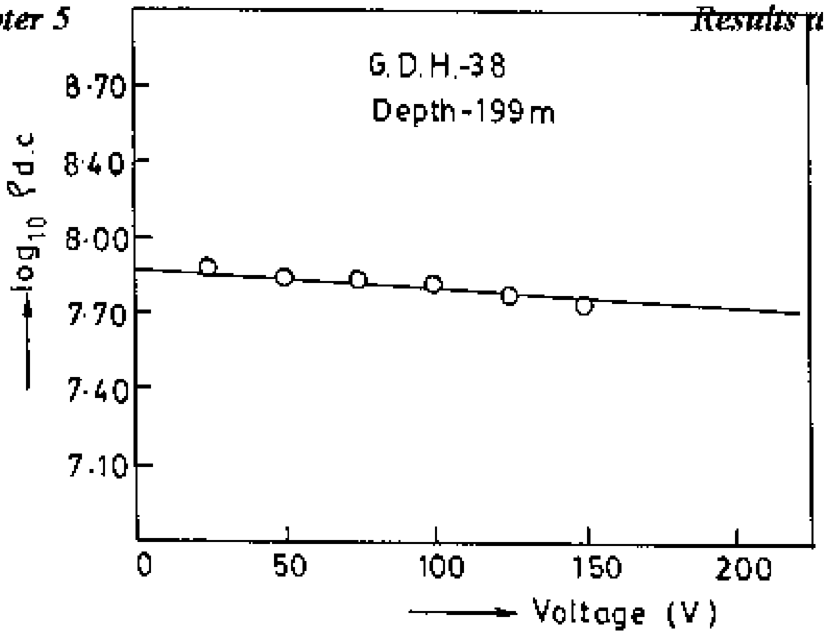

Fig. 5.18: Variation of d.c. resistivity of disc sample with applied voltage.

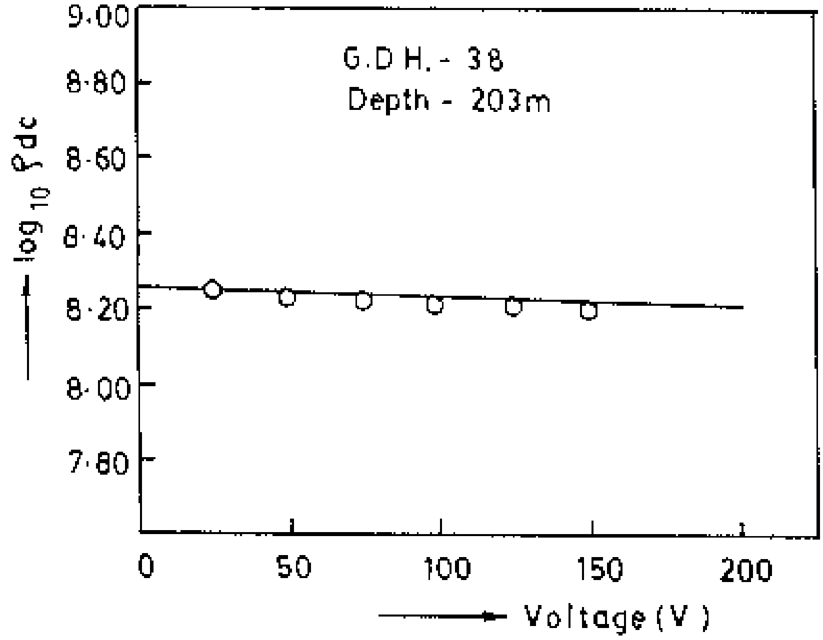

Fig. 5.19: Variation of d.c. resistivity of disc sample with applied voltage.

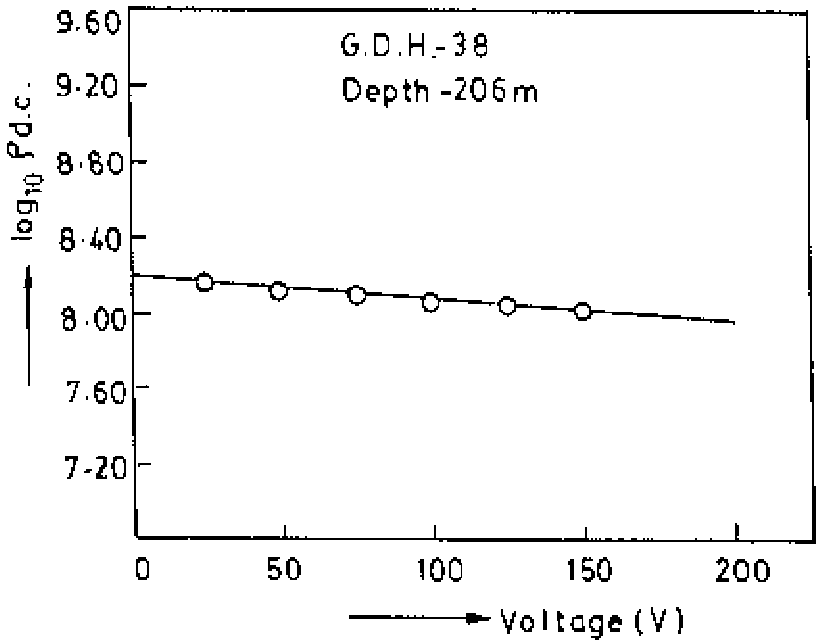

Fig. 5.20: Variation of d.c. resistivity of dies sample with applied voltage.

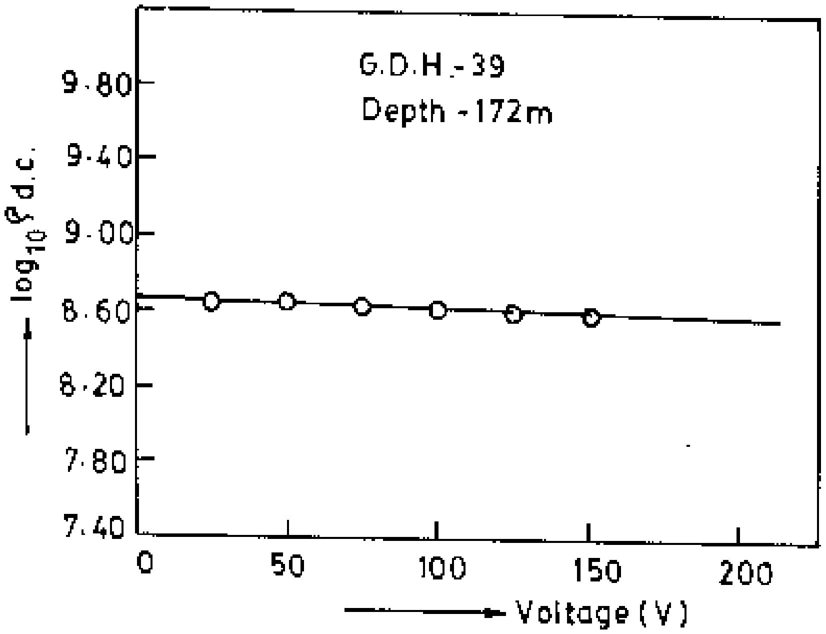

Fig. 5.21: Variation of d.c. resistivity of disc sample with applied voltage.

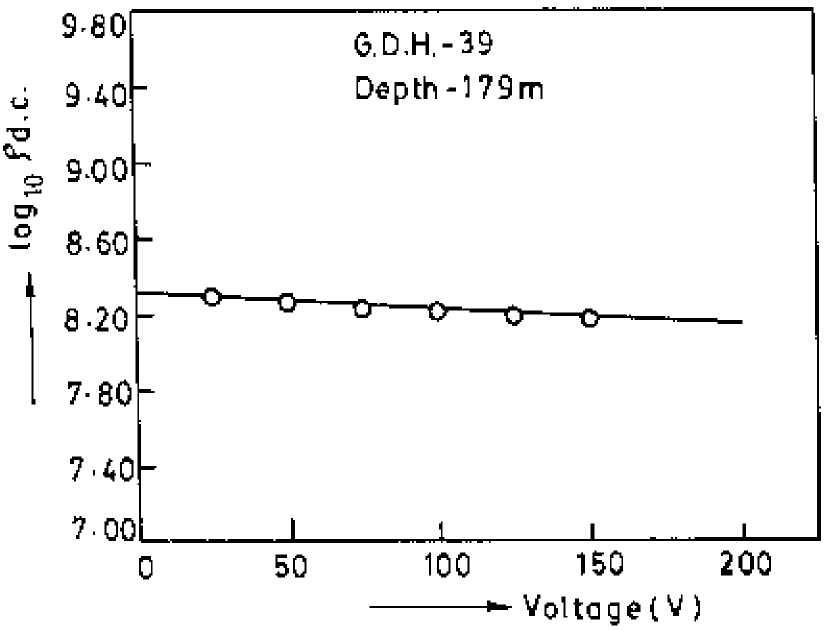

Fig. 5.22: Variation of d.c. resistivity of disc sample with applied voltage.

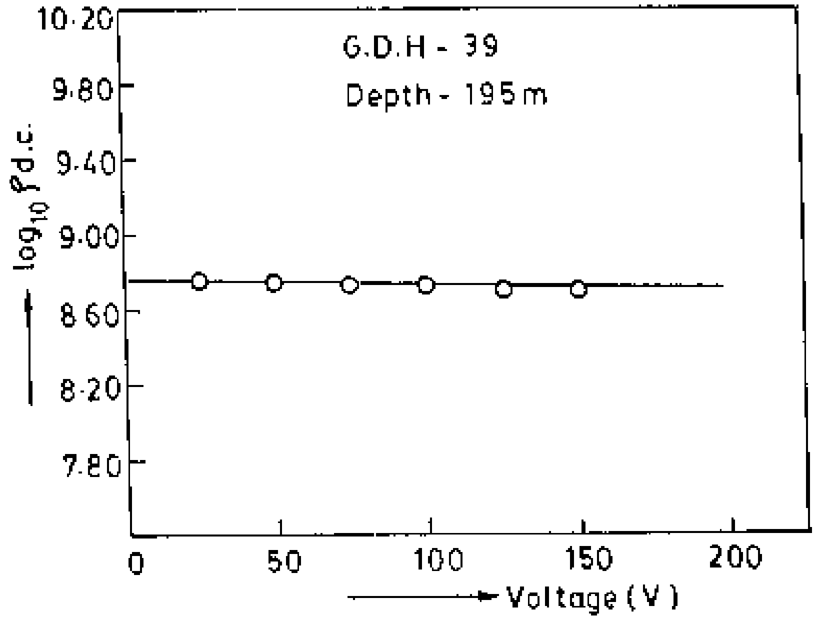

Fig. 5.23: Variation of d.c. resistivity of disc sample with applied voltage.

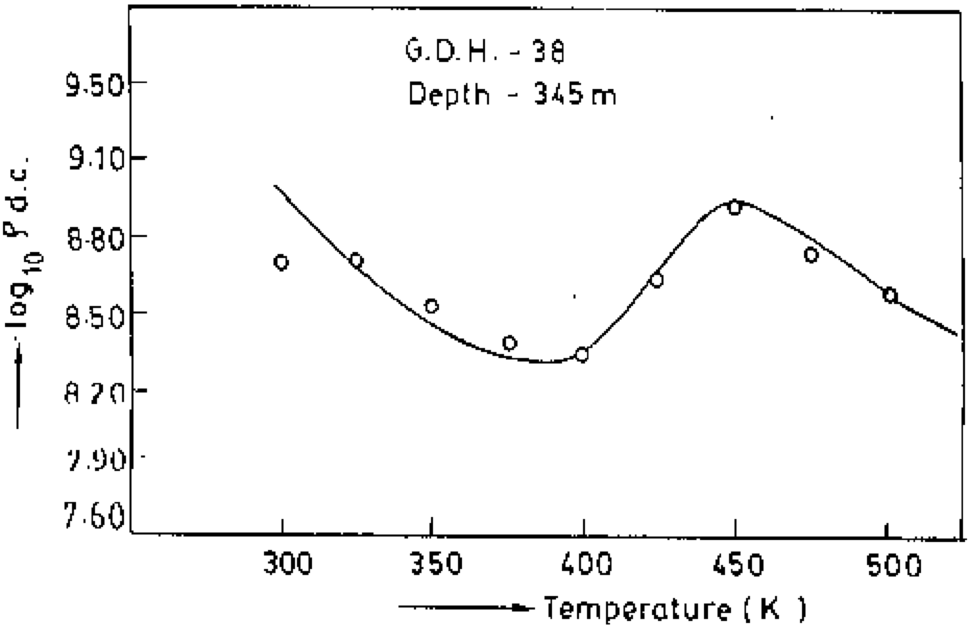

Fig. 5.24: Variation of d.c. resistivity of lump sample with temperature samples oriented perpendicular to the bedding plane.

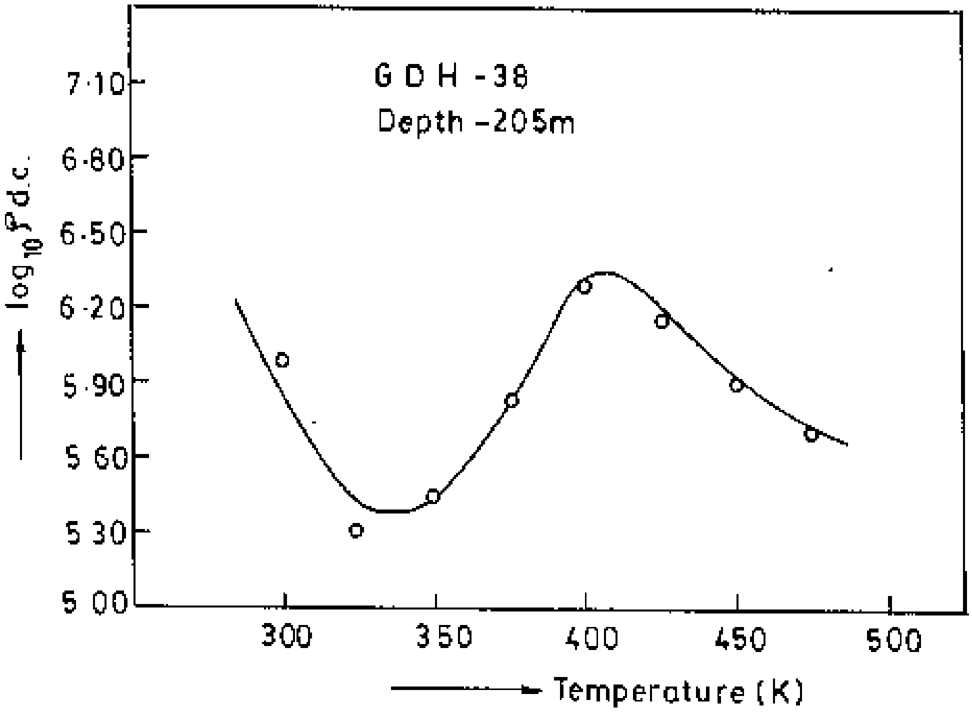

Fig. 5.25: Variation of d.c. resistivity with temperature of lump sample oriented parallel to the badding plane.

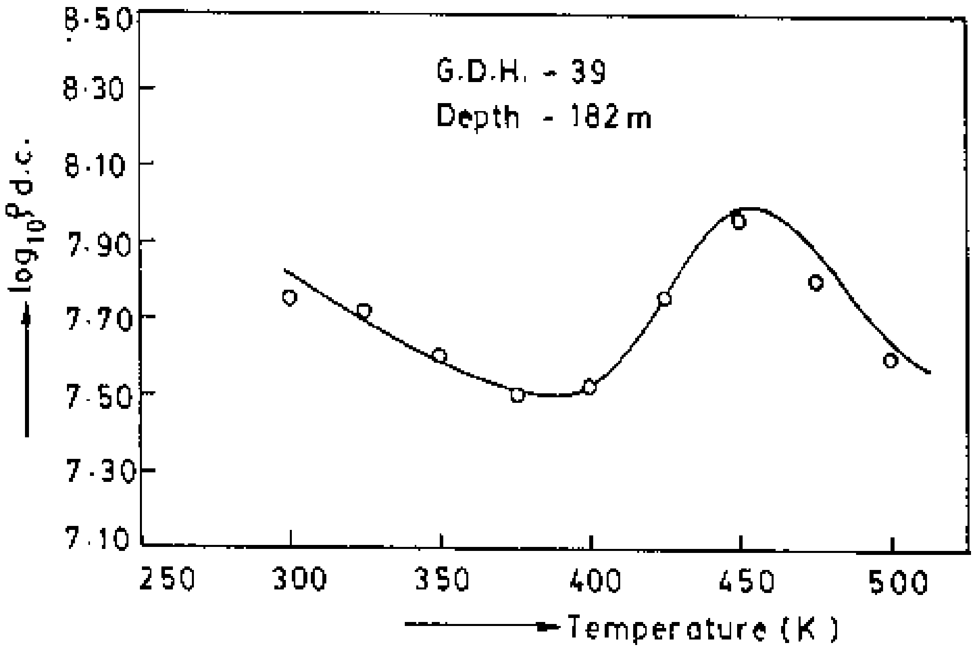

Fig. 5.26: Variation of d.c. resistivity of lump sample with temperature sample oriented perpendicular to the bedding plane.

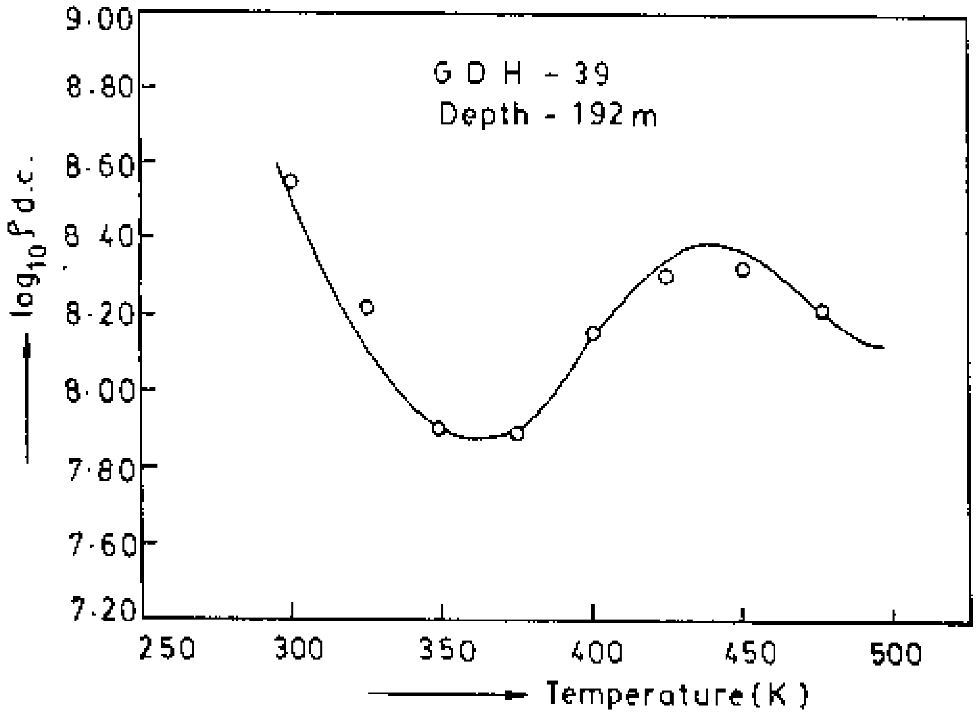

Fig. 5.27. Variation of d.c. resistivity of lump sample with temperature sample oriented perpendicular to the bedding plane

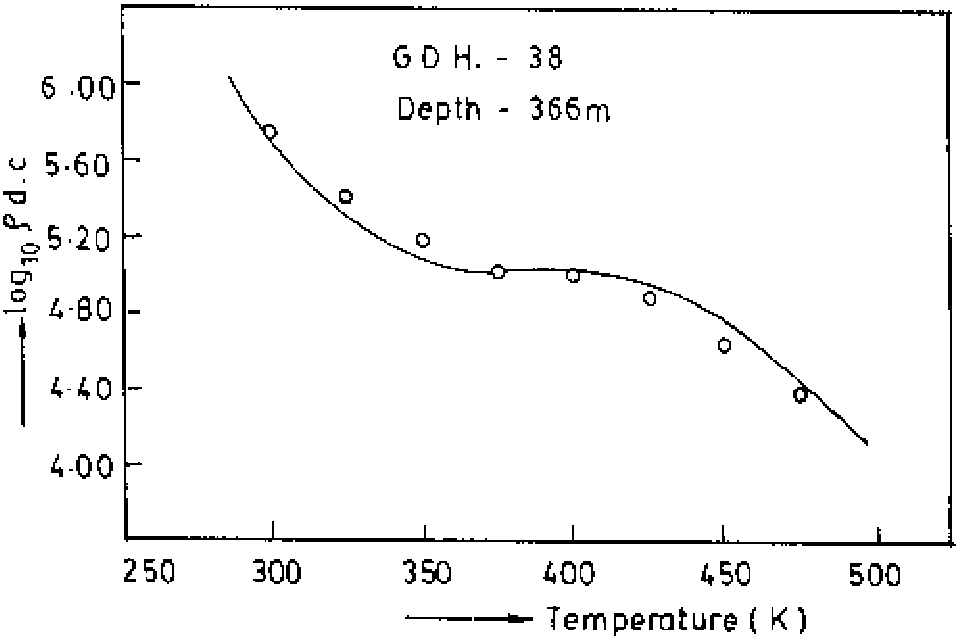

Fig. 5.28: Variation of d.c. resistivity of lump sample with temperature samples oriented parallel to the bedding plane.

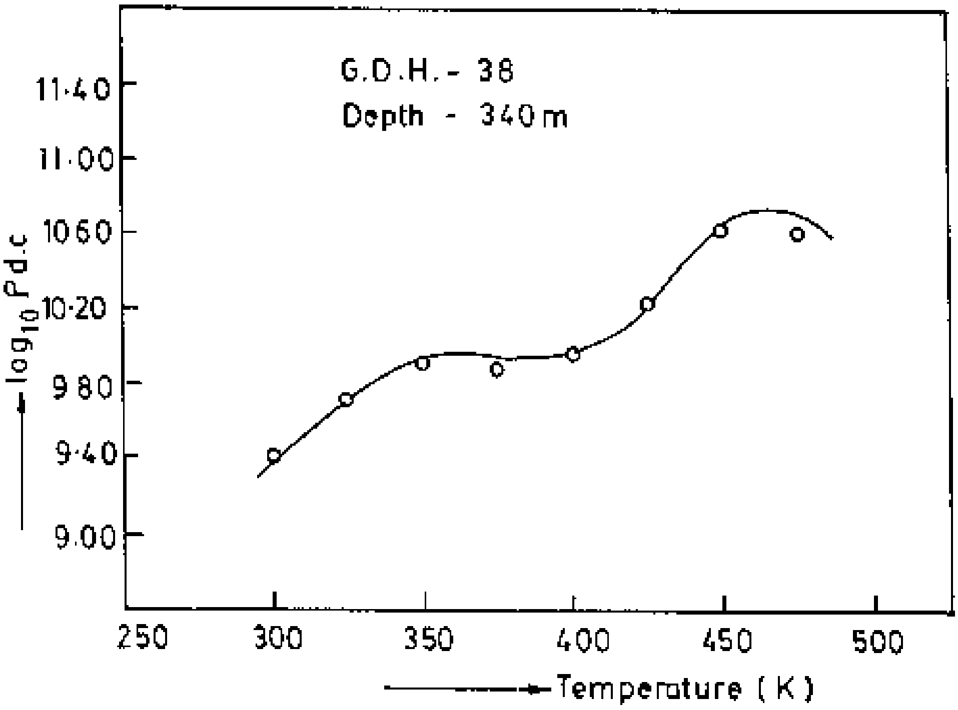

Fig. 5.29: Variation of d.c. resistivity of lump sample with temperature samples oriented perpendicular to the bedding plane.

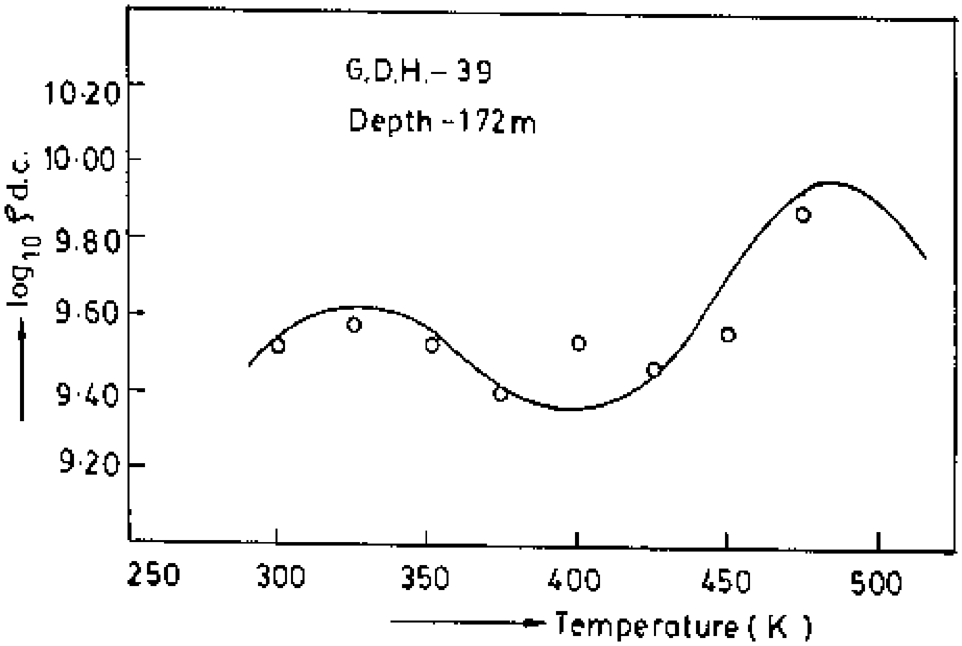

Fig. 5.30: Variation of d.c. resistivity of lump sample with temperature sample oriented perpendicular to the bedding plane.

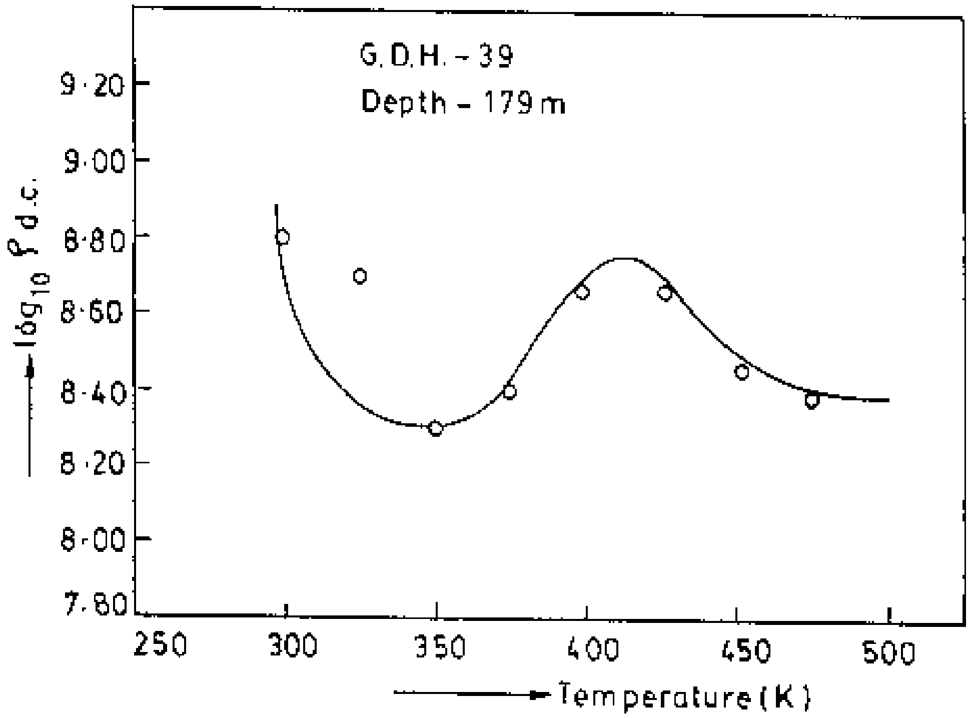

Fig 5.31: Variation of d.c. resistivity of lump sample with temperature sample oriented perpendicular to the bedding plane.

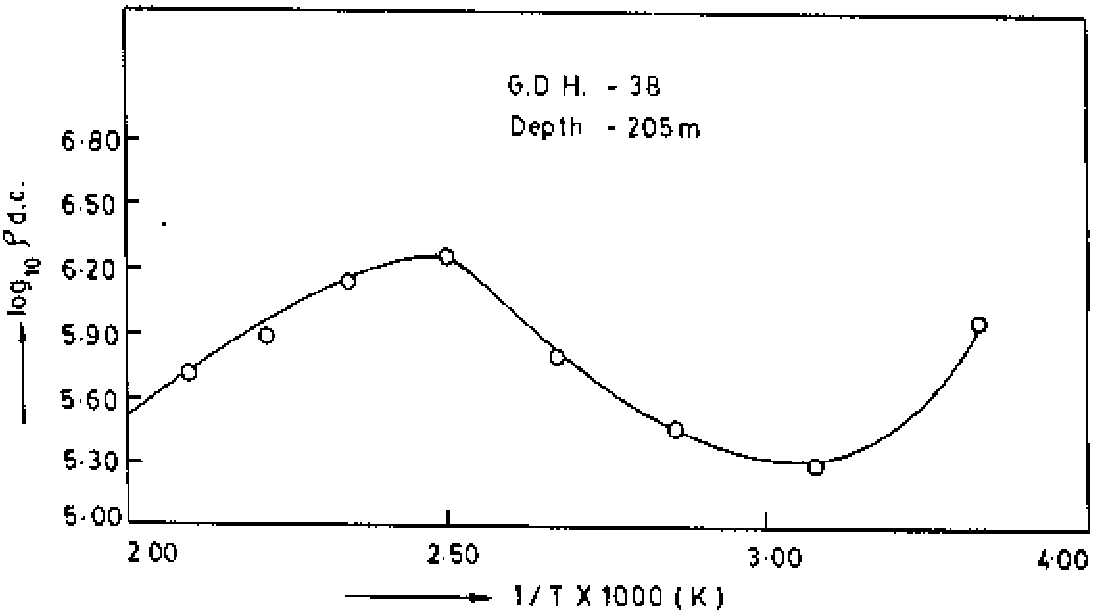

Fig. 5.32: Variation of d.c. resistivity of lump sample with 1/T (K)(1/temperature)

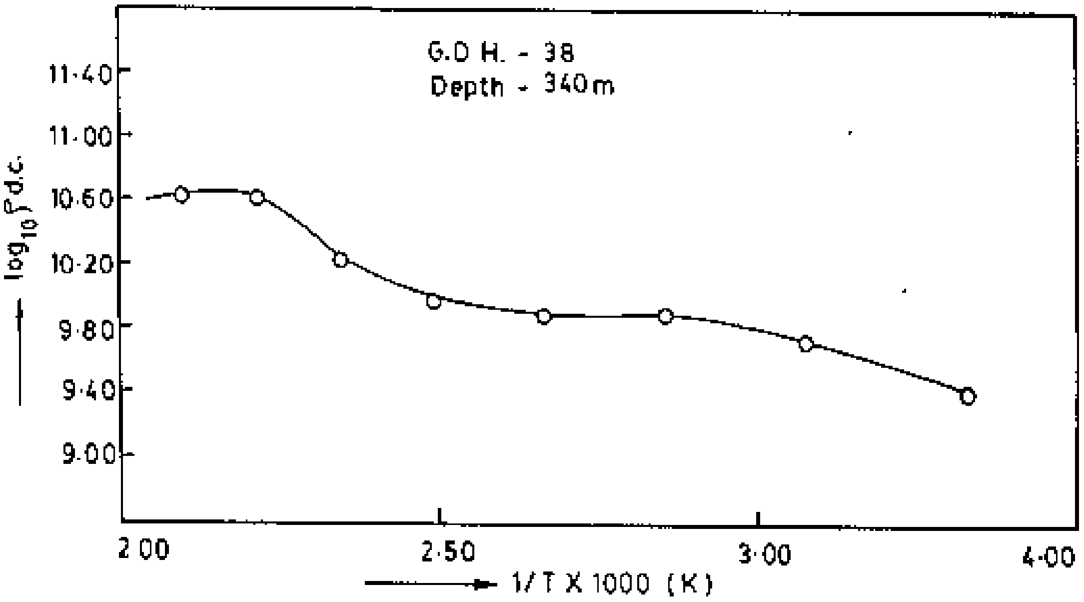

Fig. 5.33: Variation of d.c. resistivity of lump sample with 1/T (K) (1/temperature)

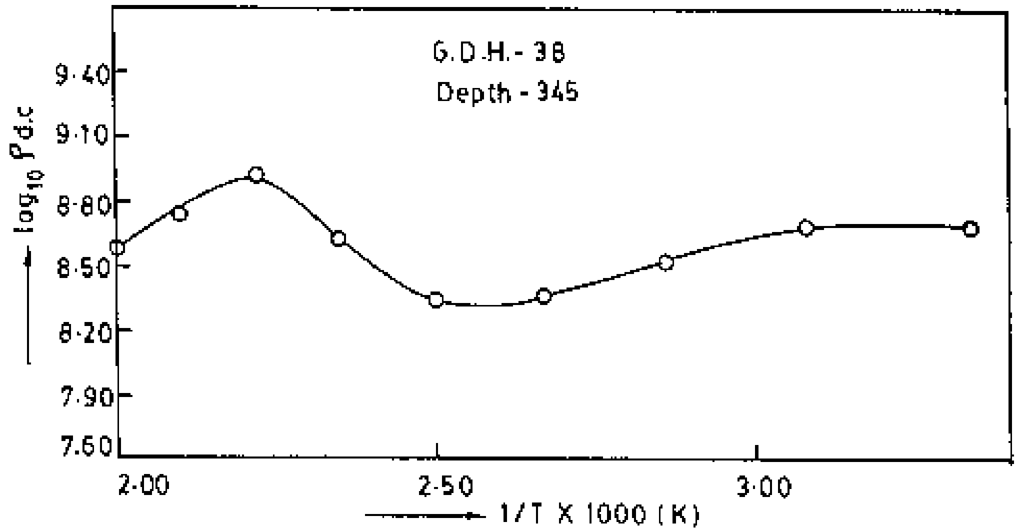

Fig. 5.34: Variation of d.c. resistivity of lump sample with 1/T (K) (1/temperature)

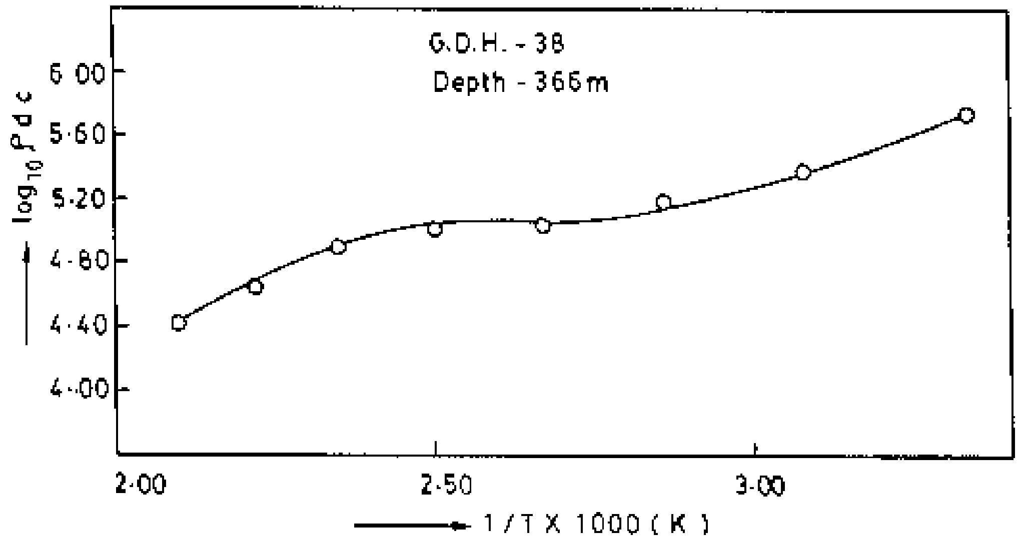

Fig. 5.35: Variation of d.c. resistivity of lump sample with 1/T (K) (1/temperature)

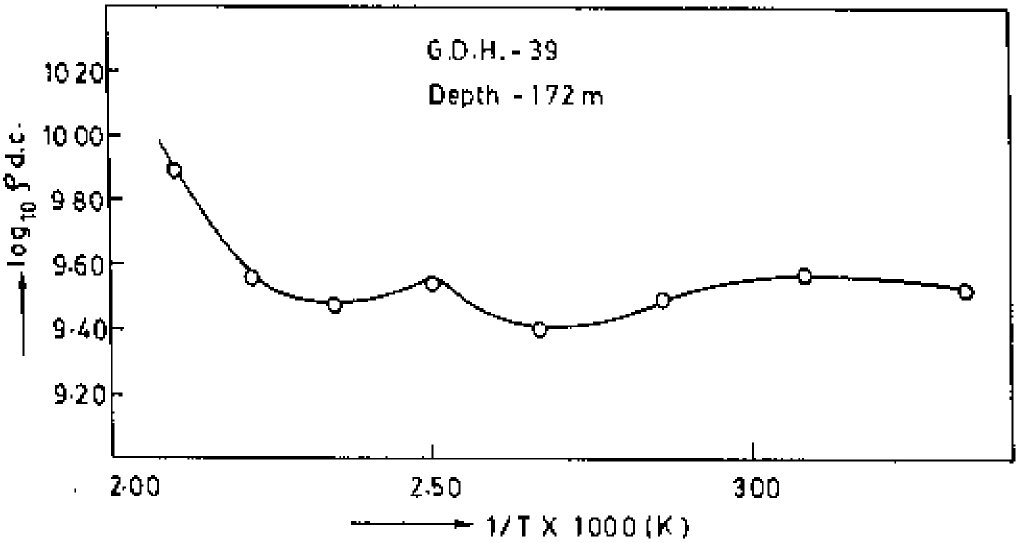

Fig. 5.36: Variation of d.c. resistivity of lump sample with 1/T(K) (1/temperature)

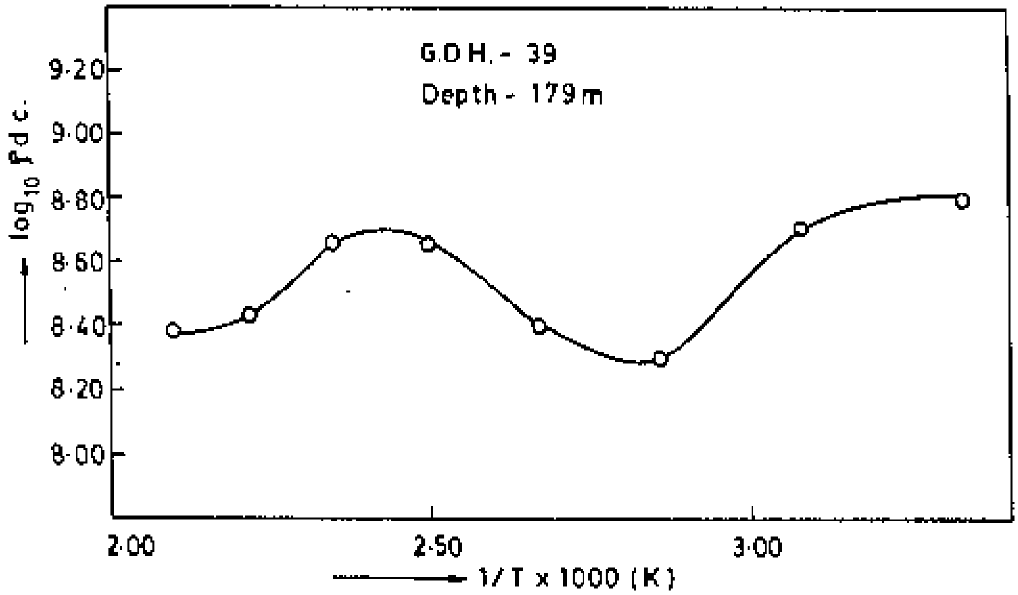

Fig. 5.37: Variation of d.c. resistivity of lump sample with 1/T (K) (1/temperature)

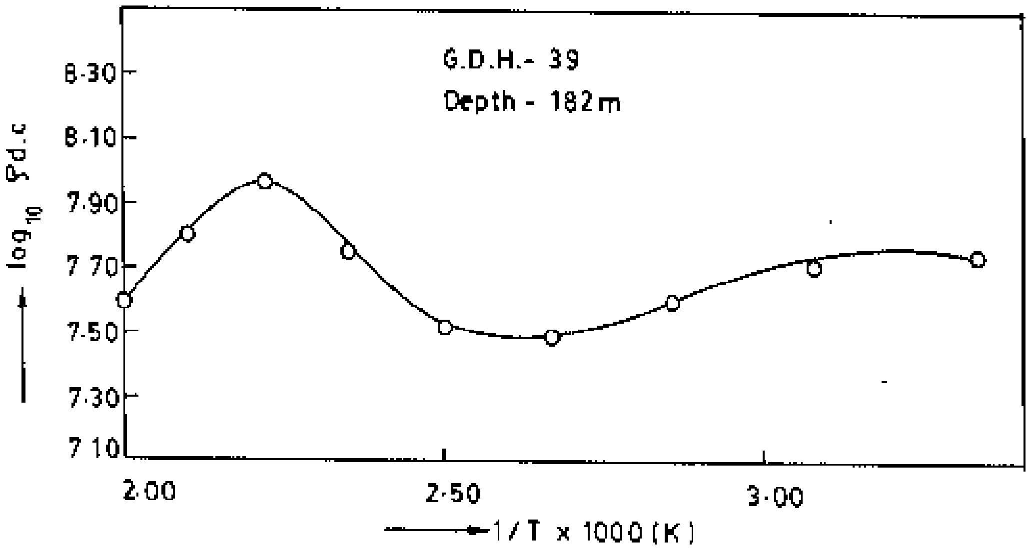

Fig. 5.38: Variation of d.c. resistivity of lump sample with 1/T(K) (1/temperature)

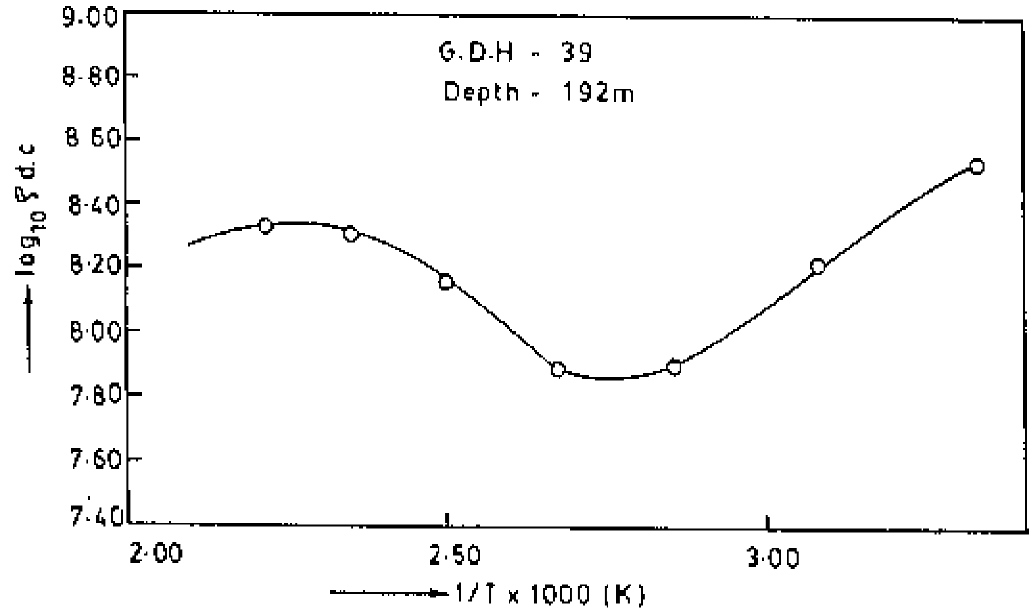

Fig. 5.39: Variation of d.c. resistivity of lump sample with 1/T(K) (1/temperature)

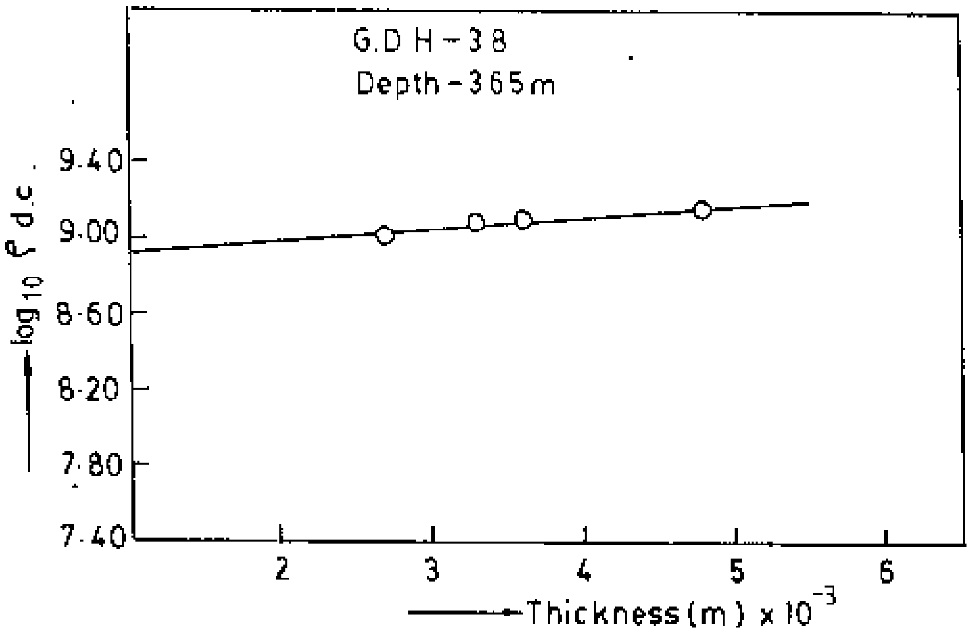

Fig. 5.40: Variation of d.c. resistivity with sample thickness

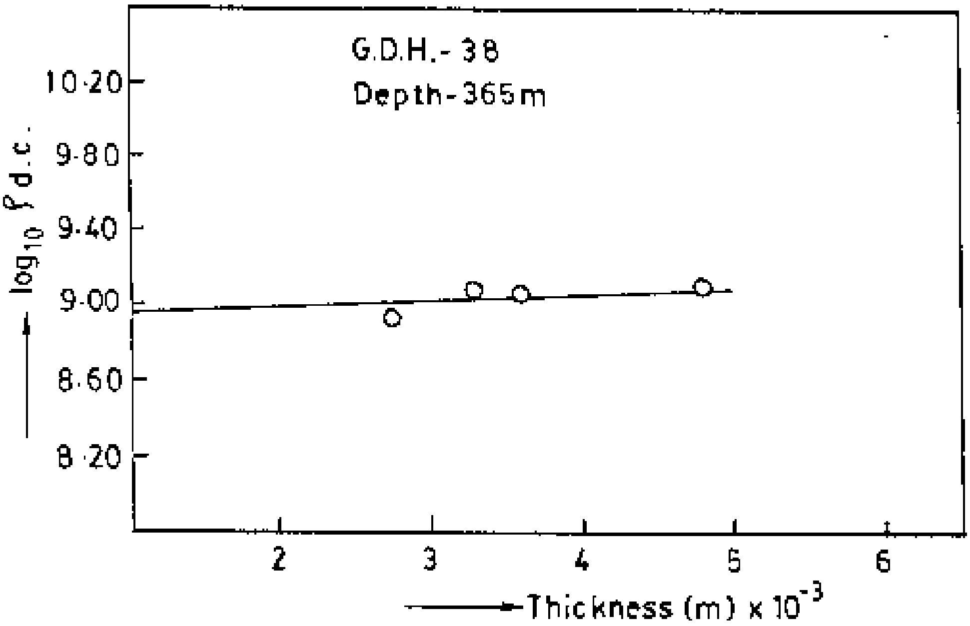

Fig. 5.41: Variation of d.c. resistivity with sample thickness

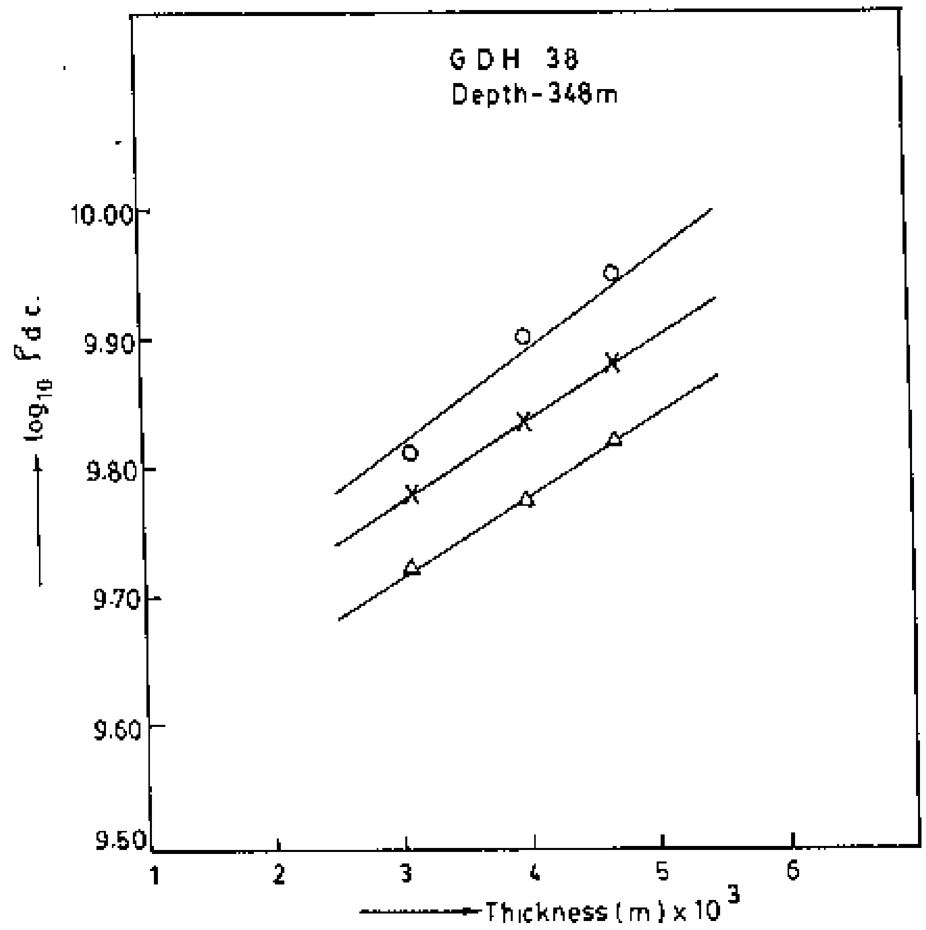

Fig. 5.42: Variation of d.c. resistivity with sample thickness to compare at different voltages (0.50v ‹100v Φ150V)

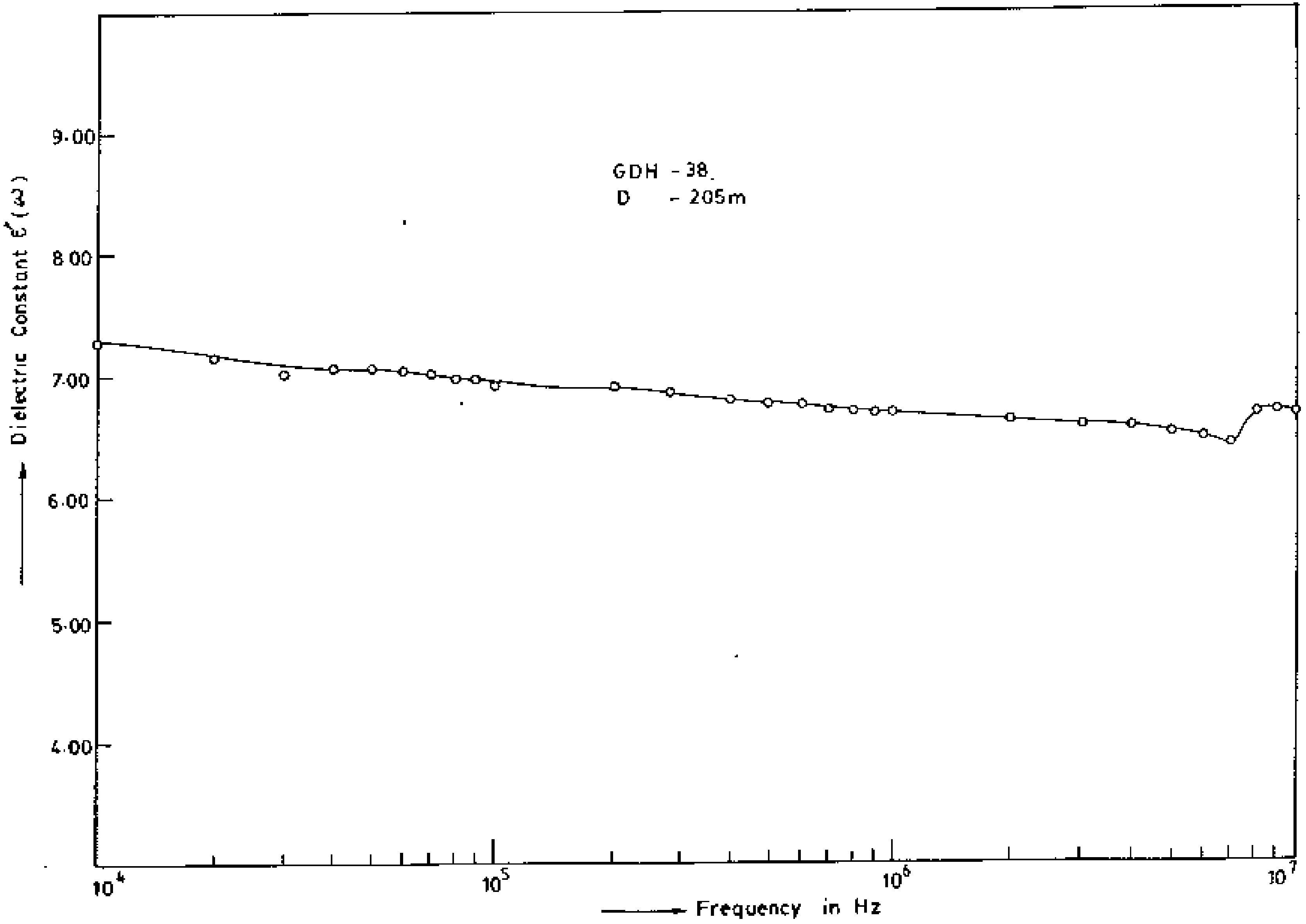

Fig. 5.43: The frequency dependence of dielectric constant of coal

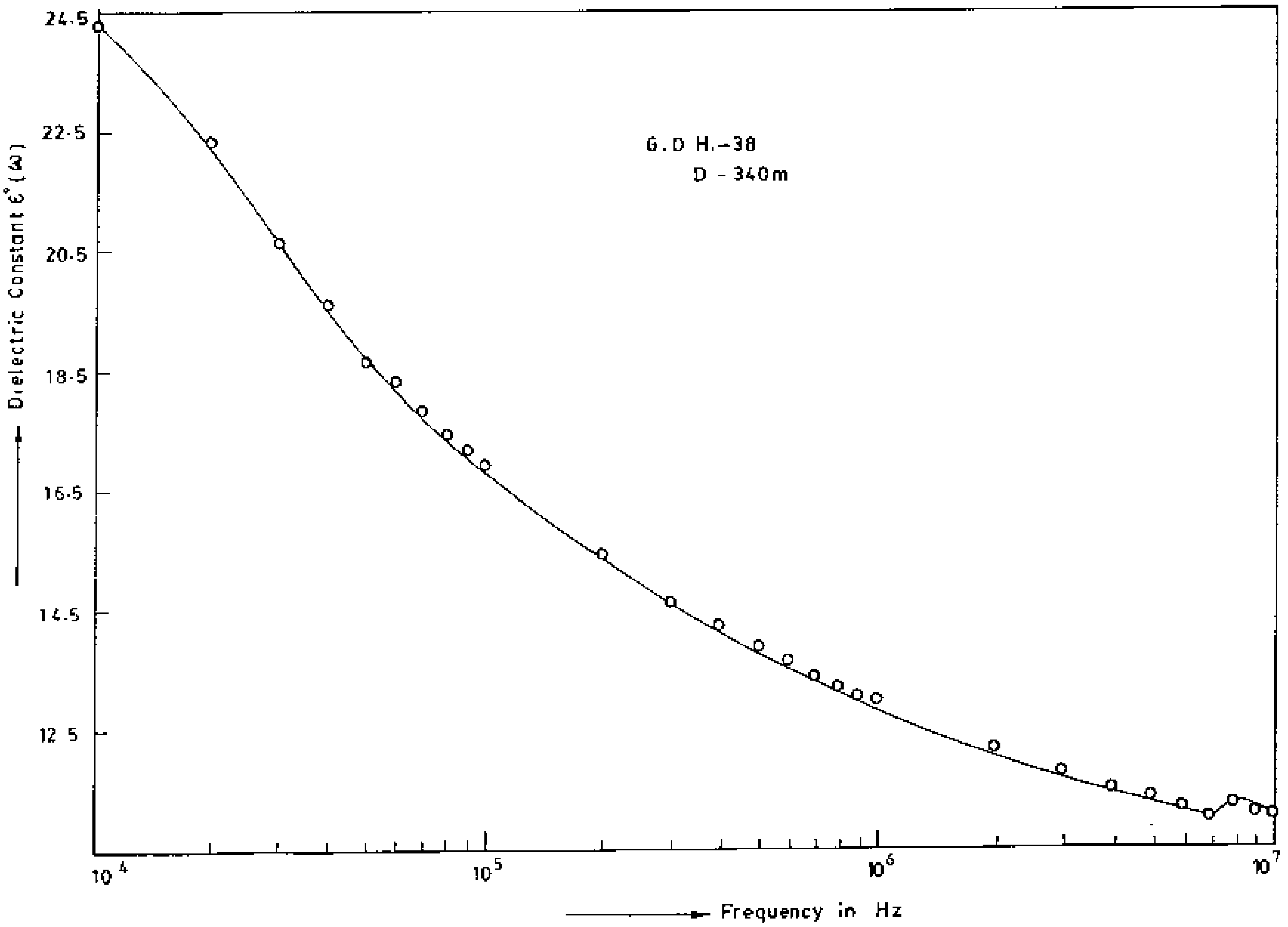

Fig. 5.44: The frequency dependence of dielectric constant of coal sample

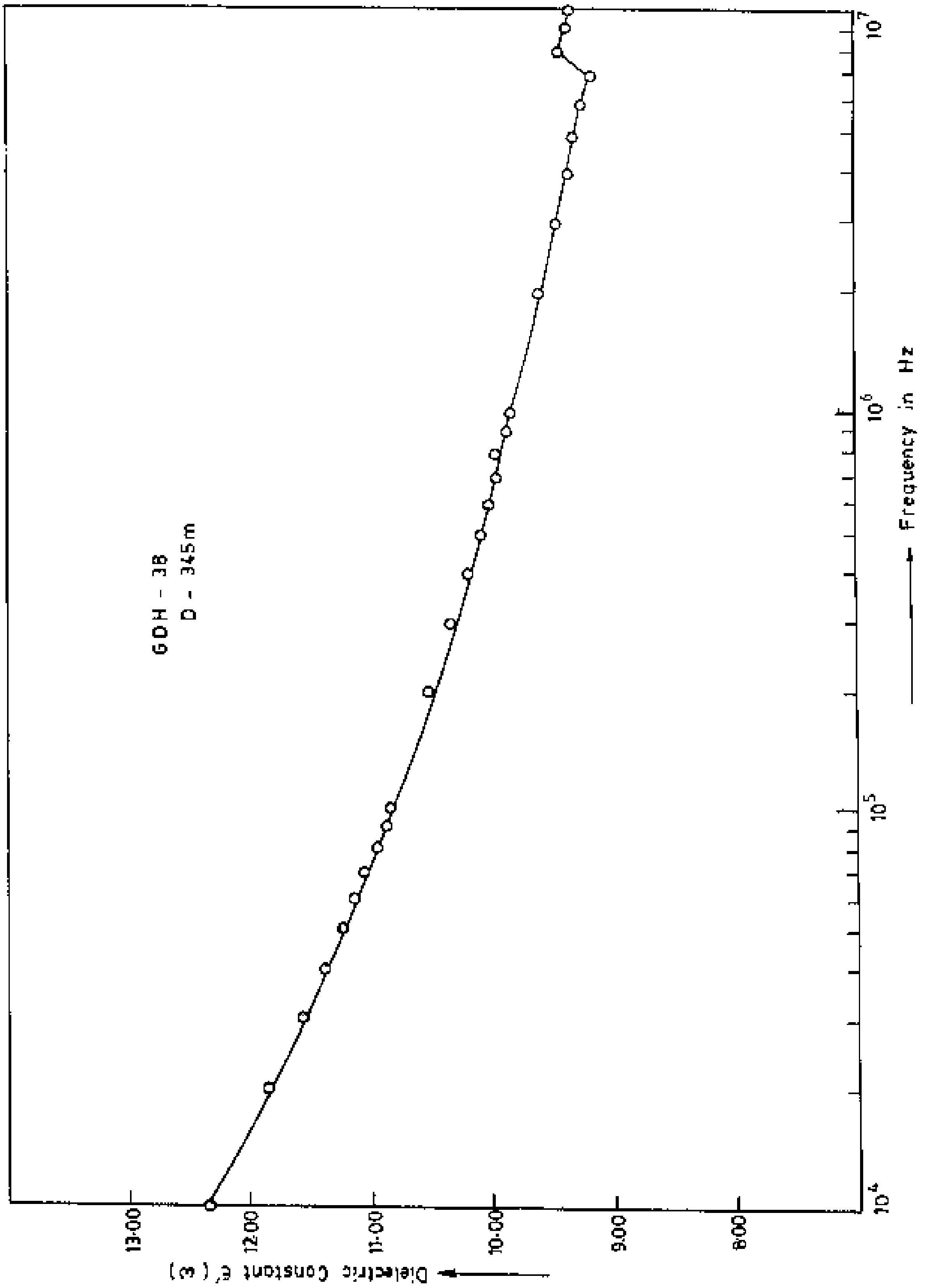

Fig. 5.45: The frequency dependence of dielectric constant of coal

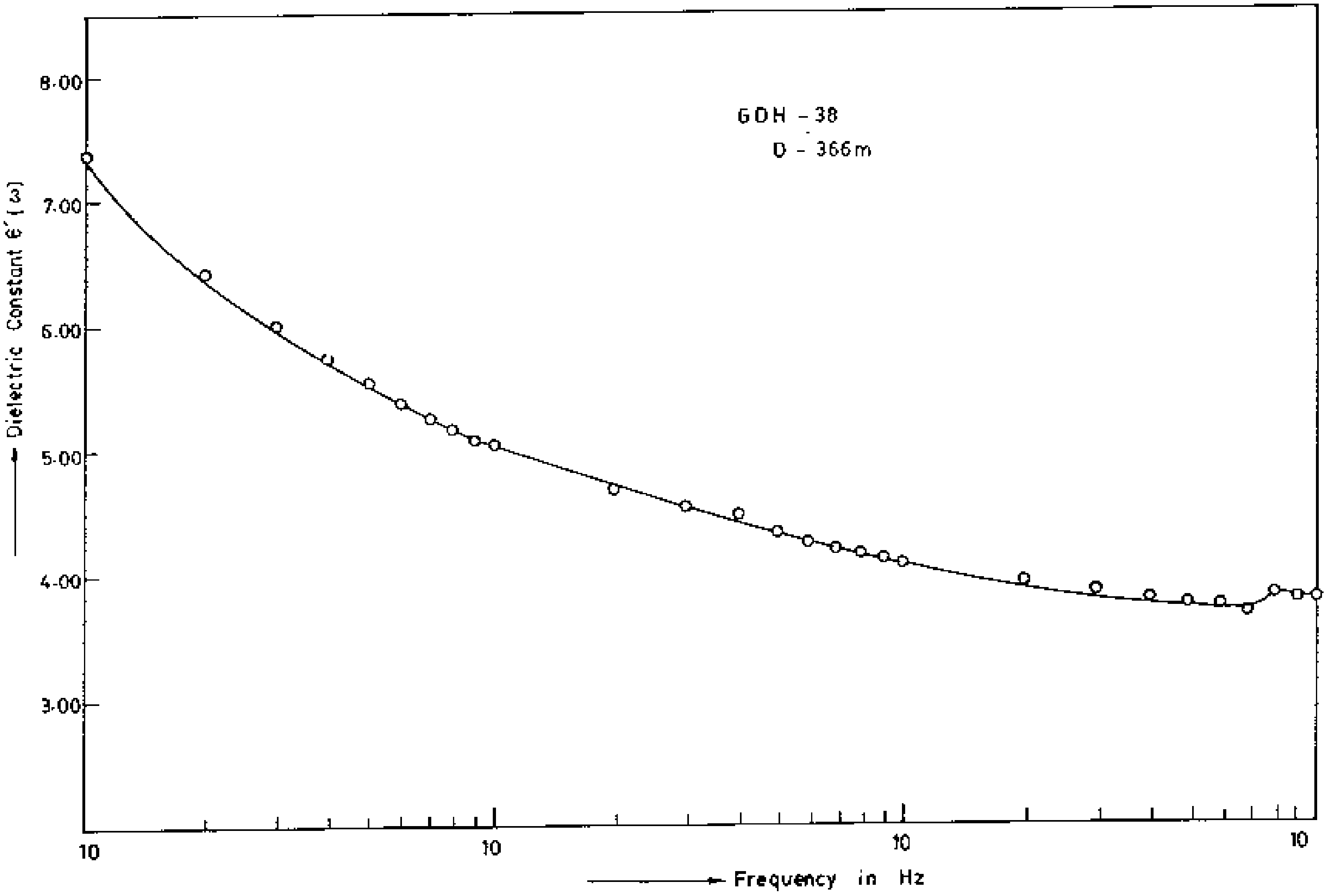

Fig. 5.46: The frequency dependence of dielectric constant of coal

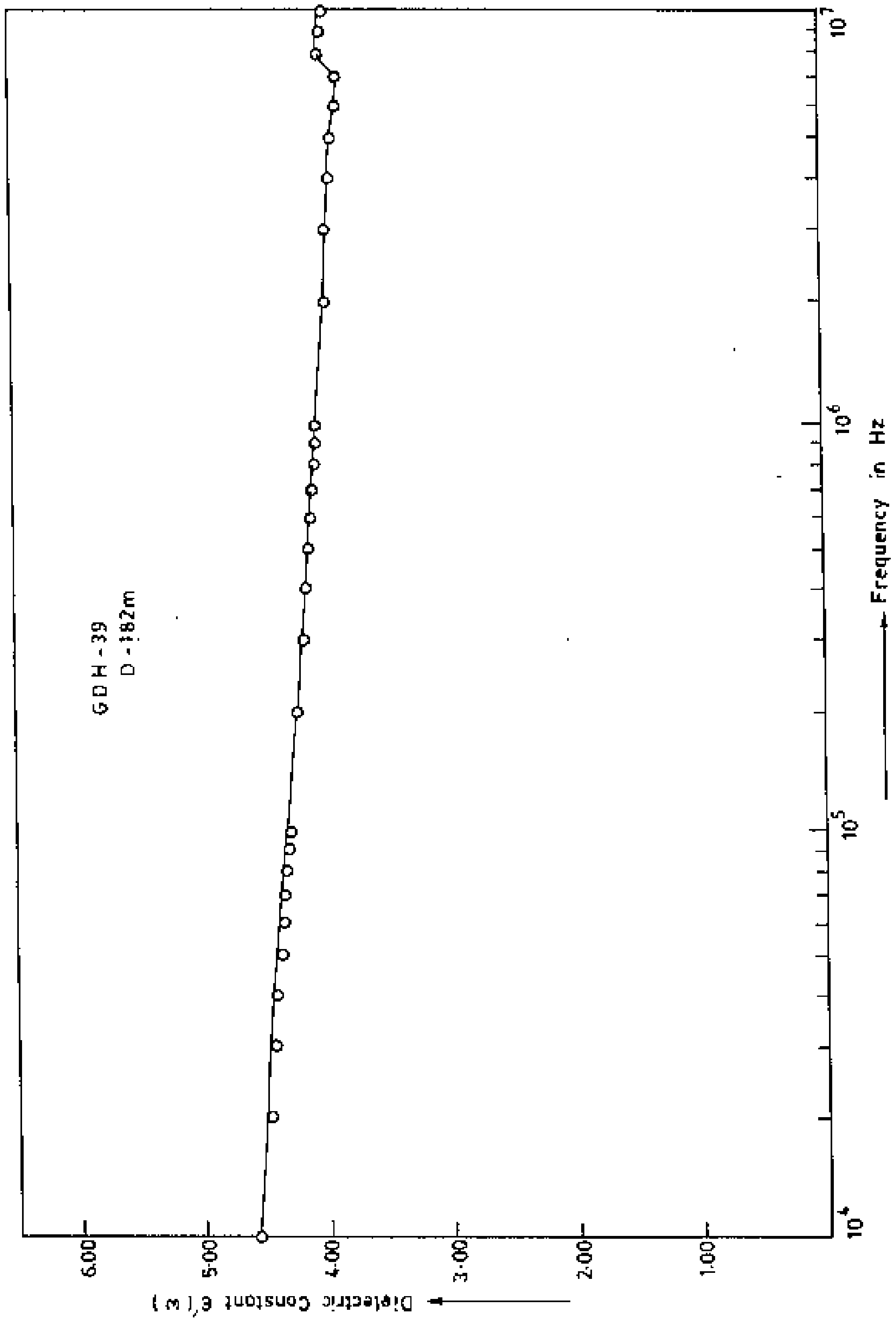

Fig. 5.47: The frequency dependence of dielectric constant of coal

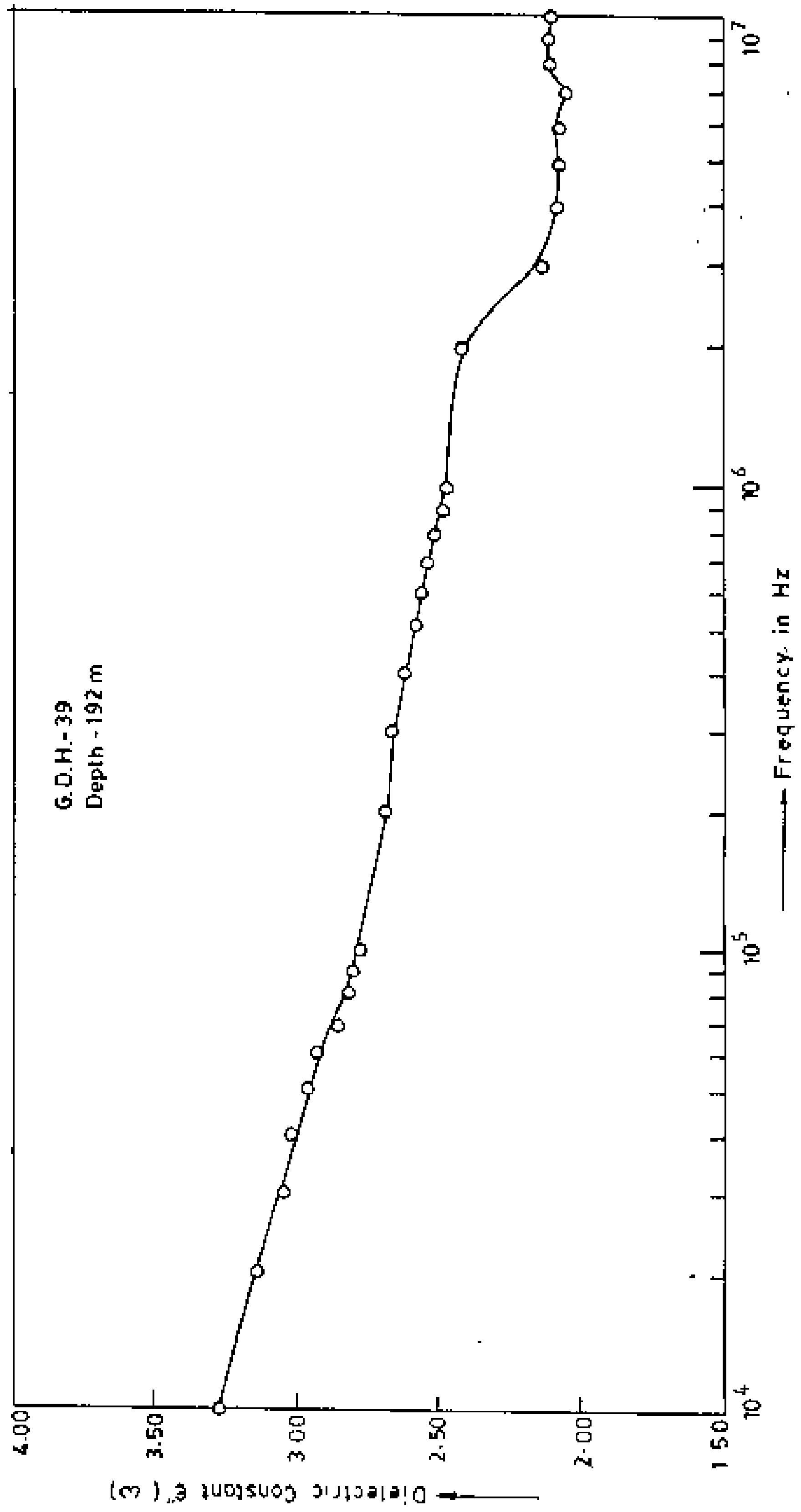

Fig. 5.48: The frequency dependence of dielectric constant of coal

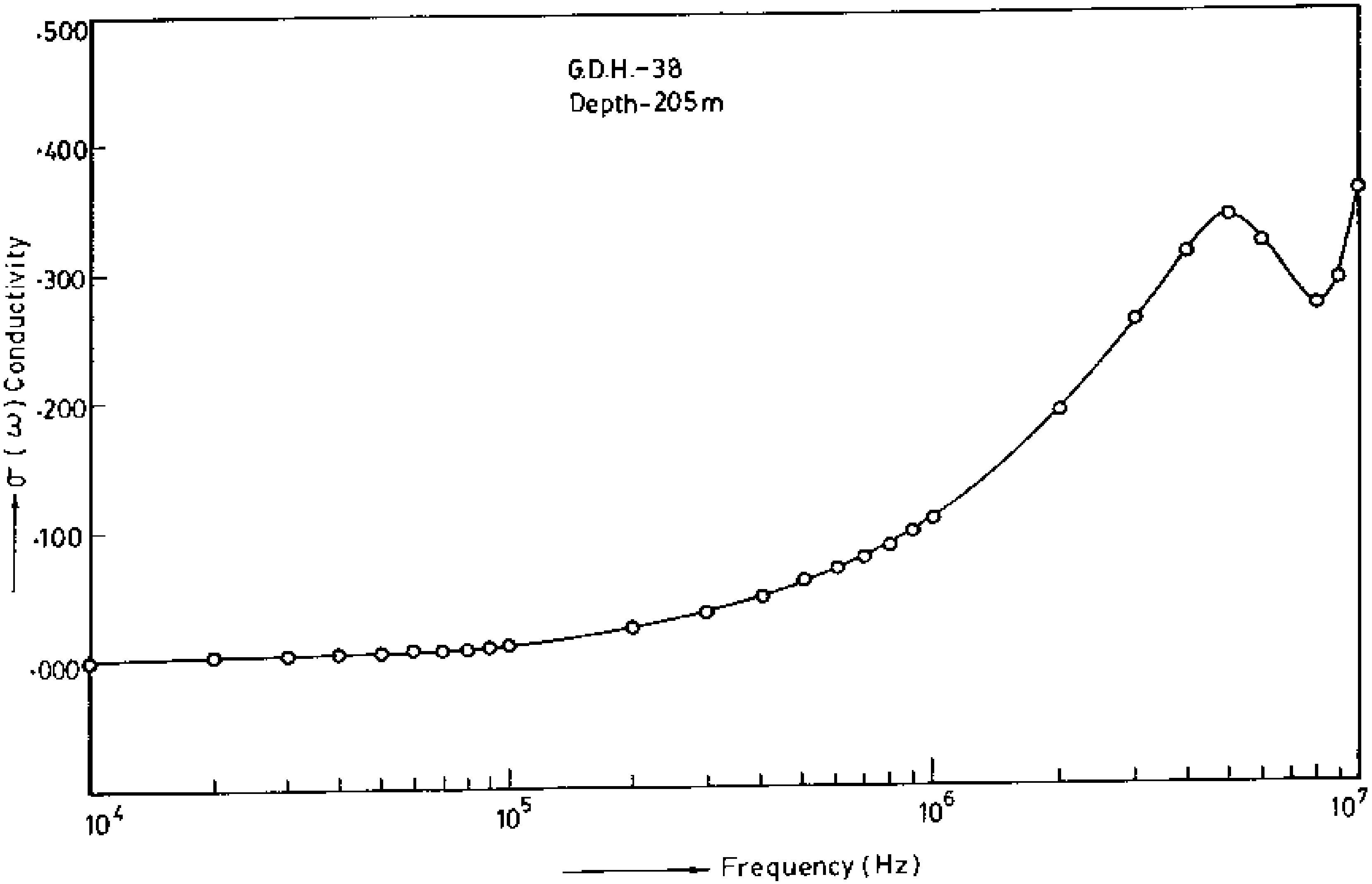

Fig. 5.49: The frequency dependence of the conductivity of coal sample

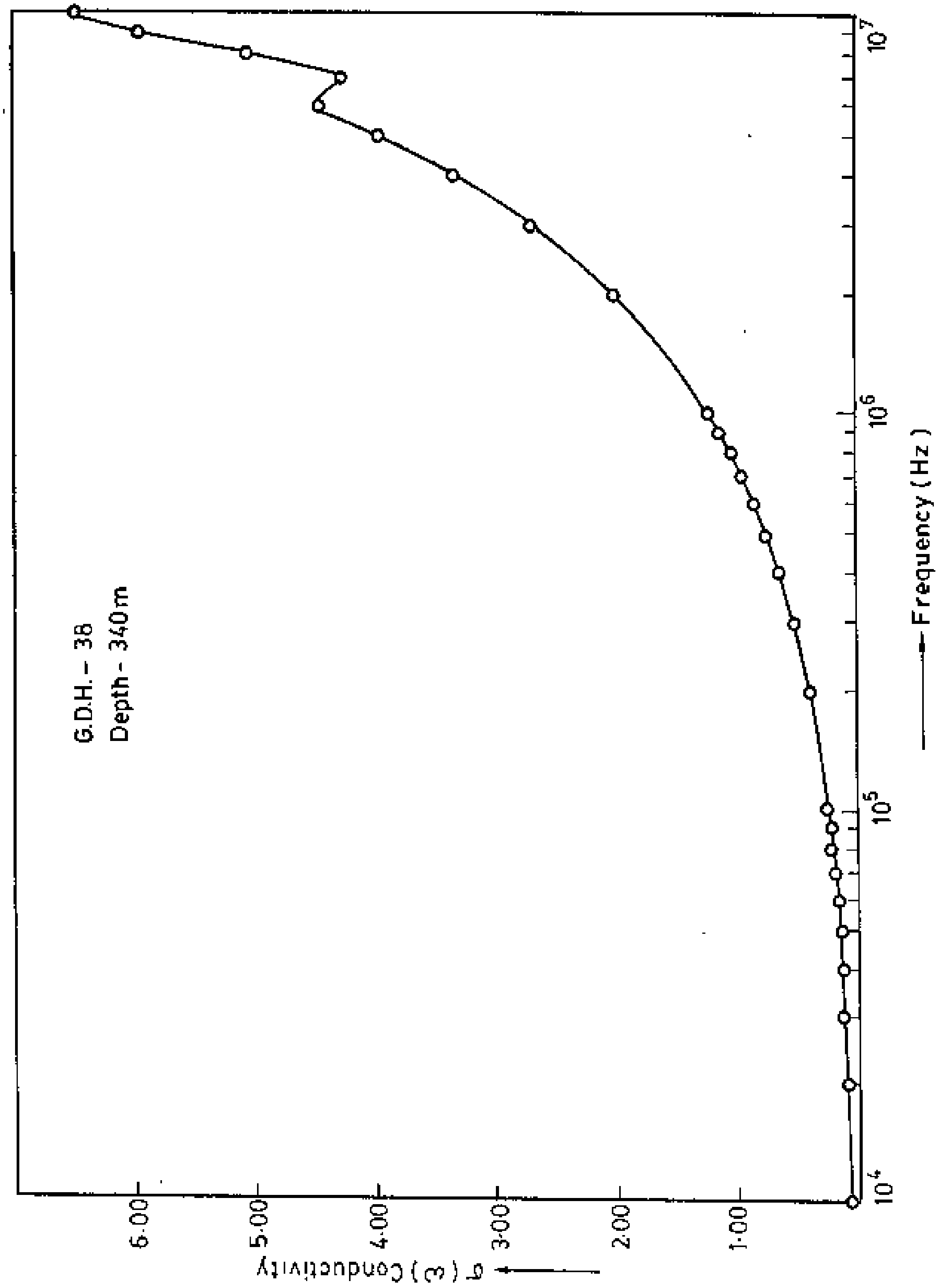

Fig. 5.50: The frequency dependence of the conductivity of coal sample

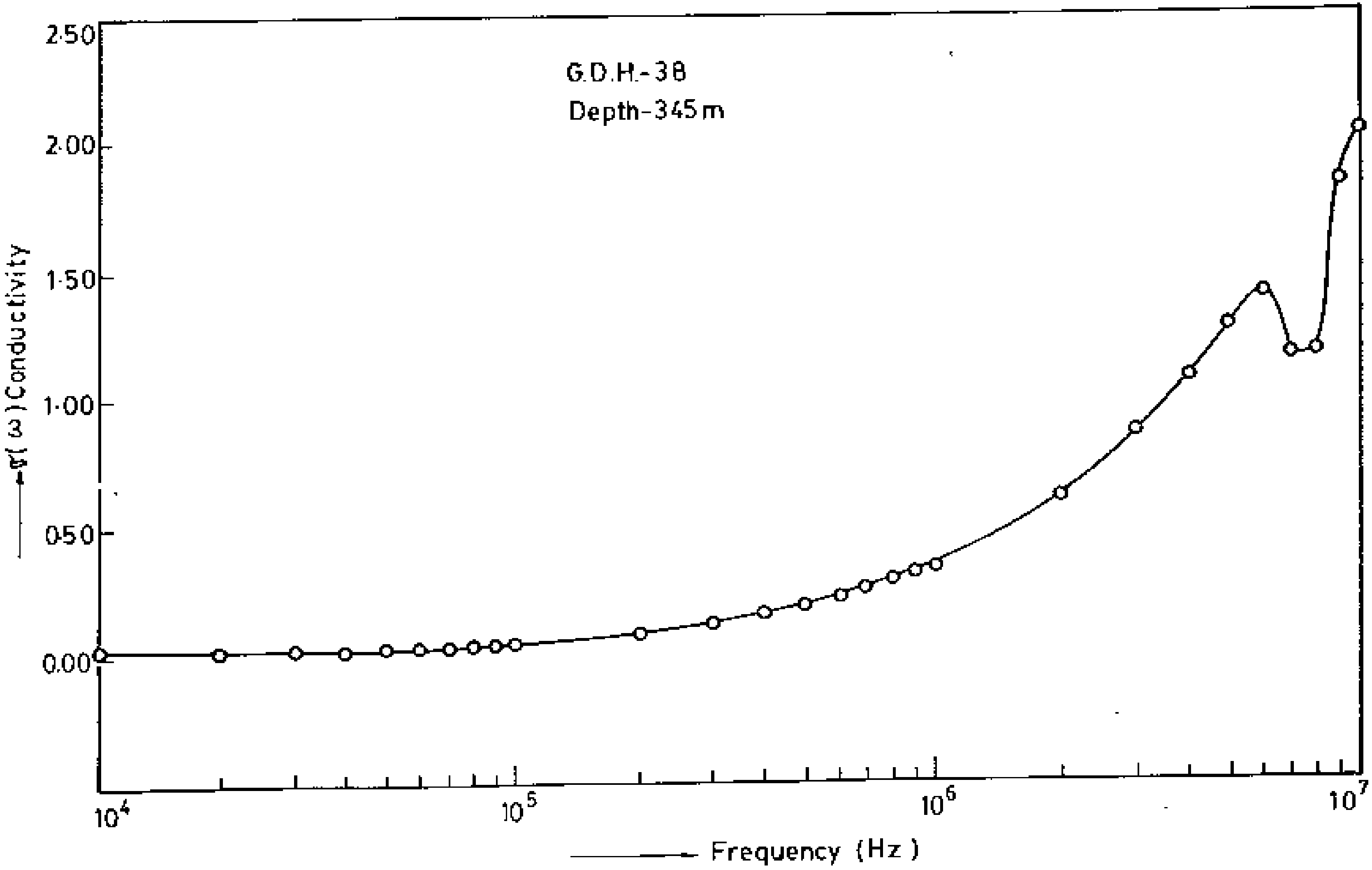

Fig. 5.51: The frequency dependence of the conductivity of coal sample-

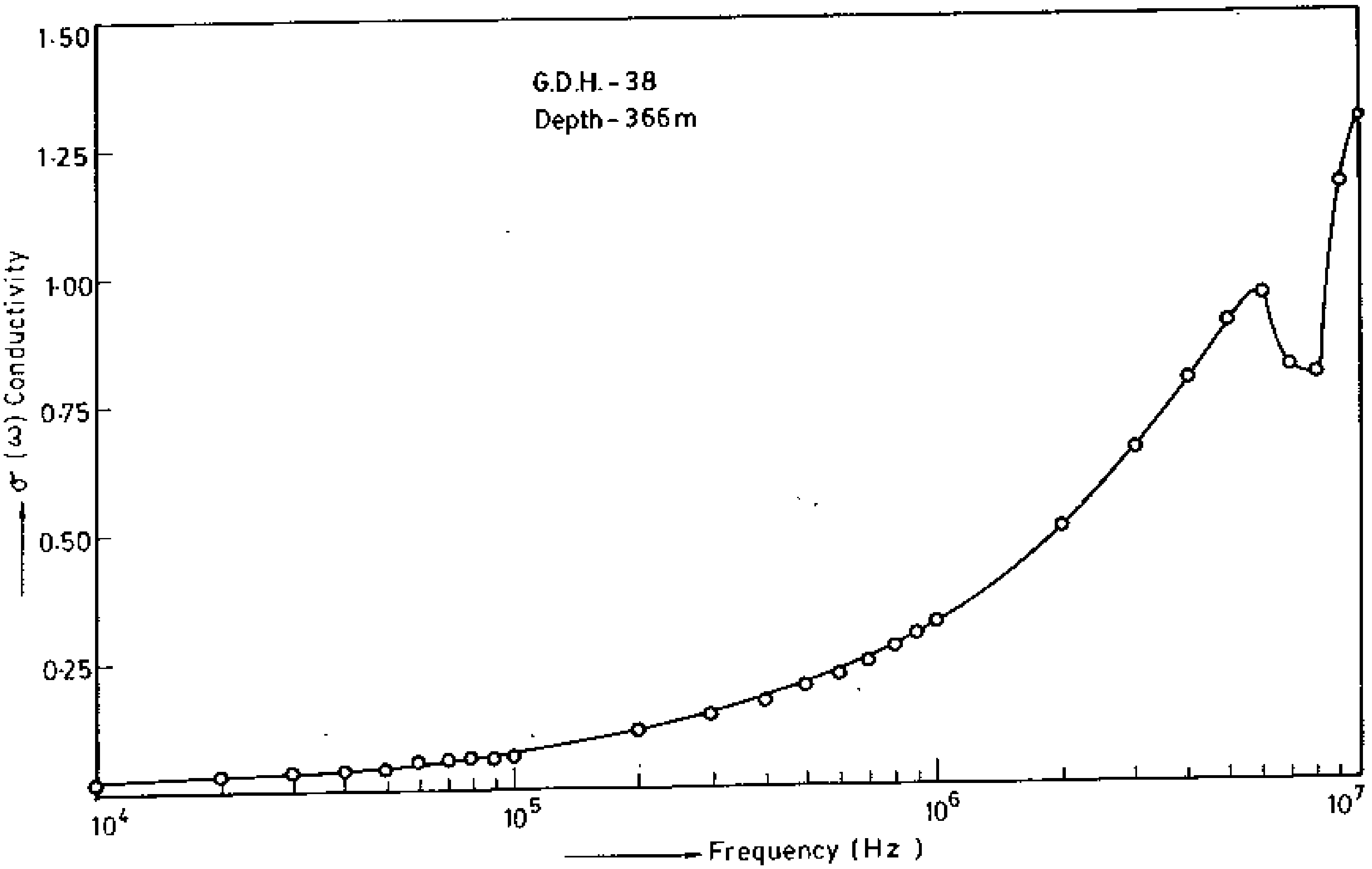

Fig. 5.52: The frequency dependence of the conductivity of coal sample

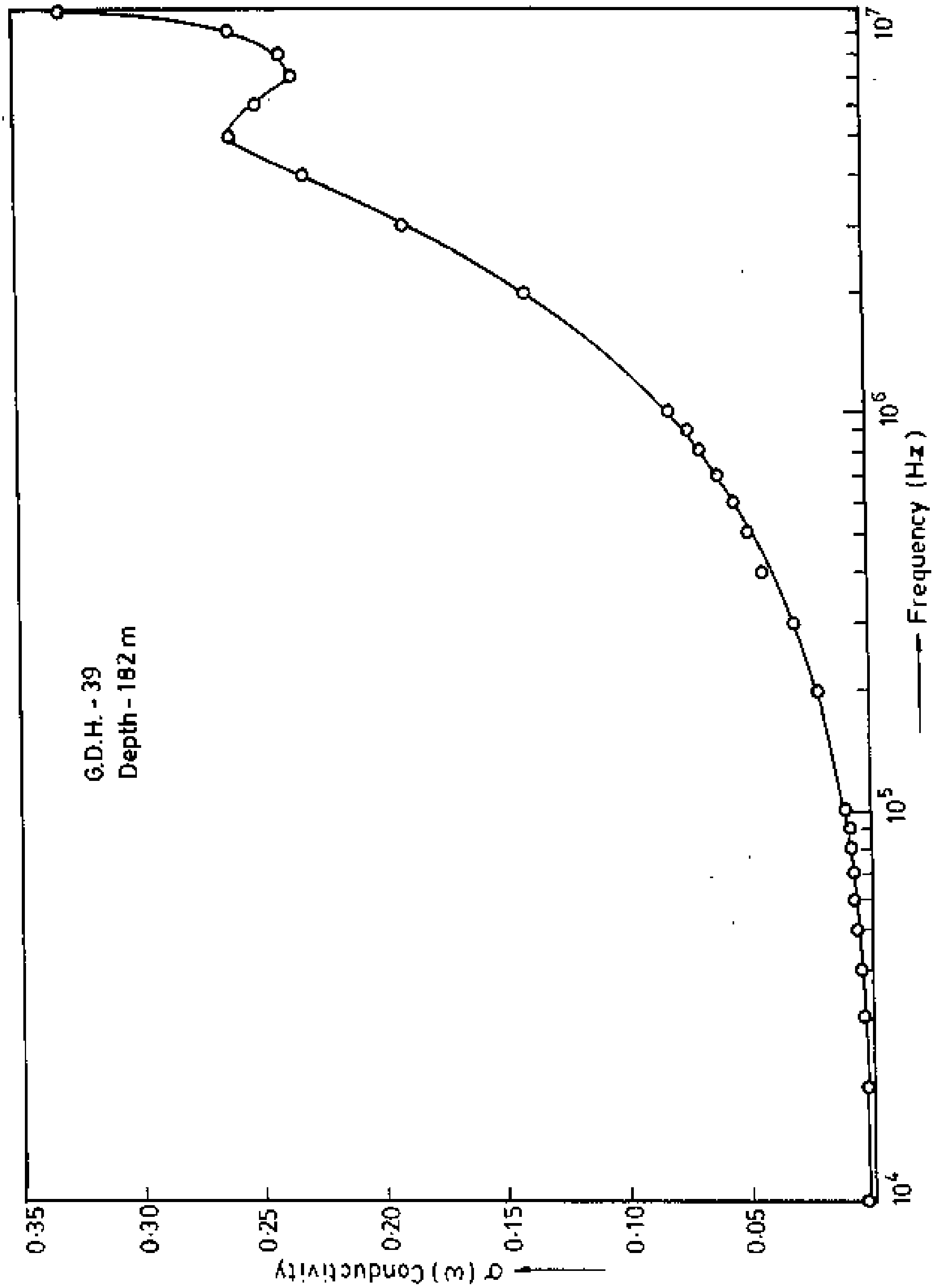

Fig. 5.53: The frequency dependence of the conductivity of coal sample

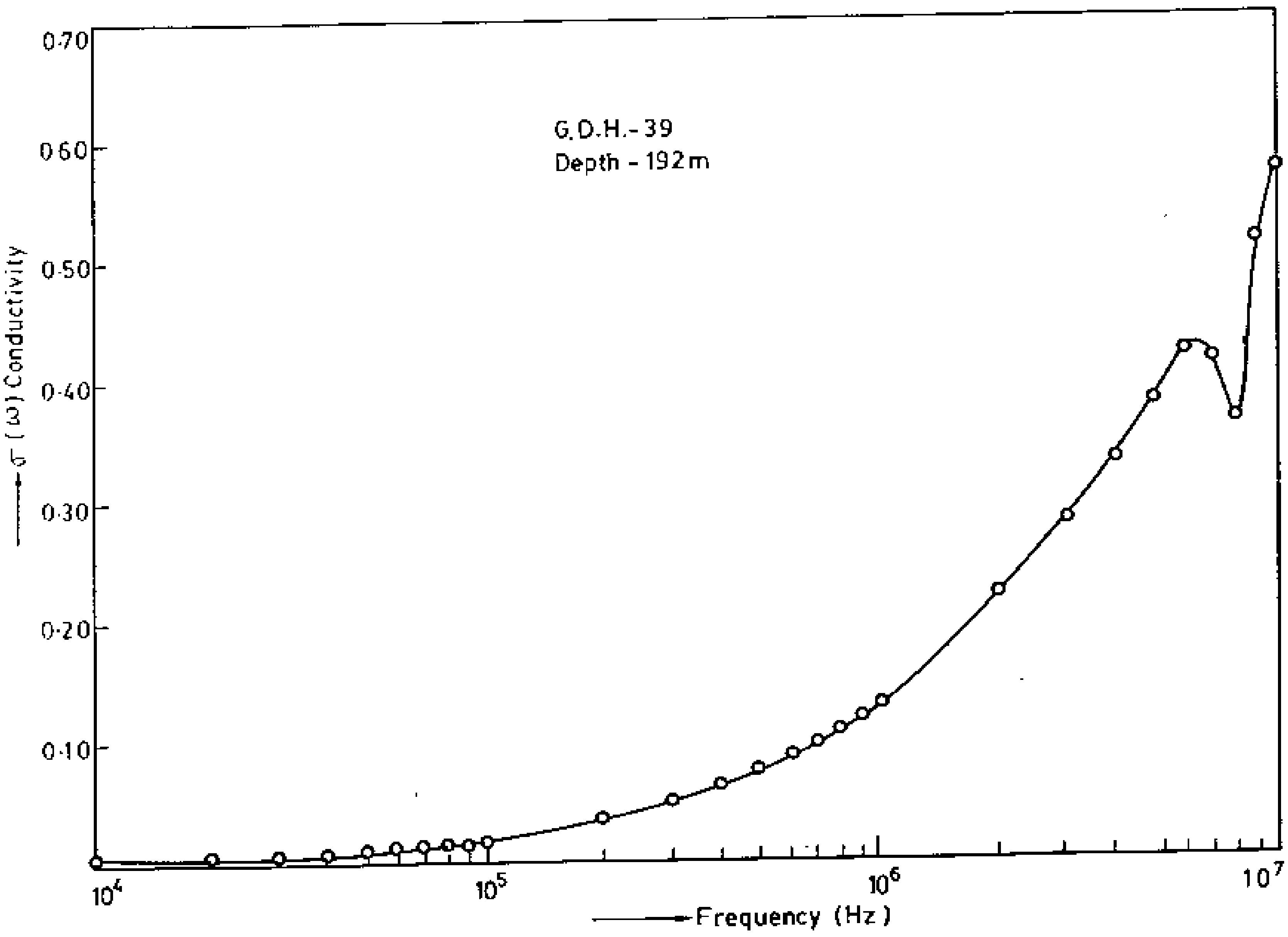

Fig. 5.54: The frequency dependence of the conductivity of coal sample

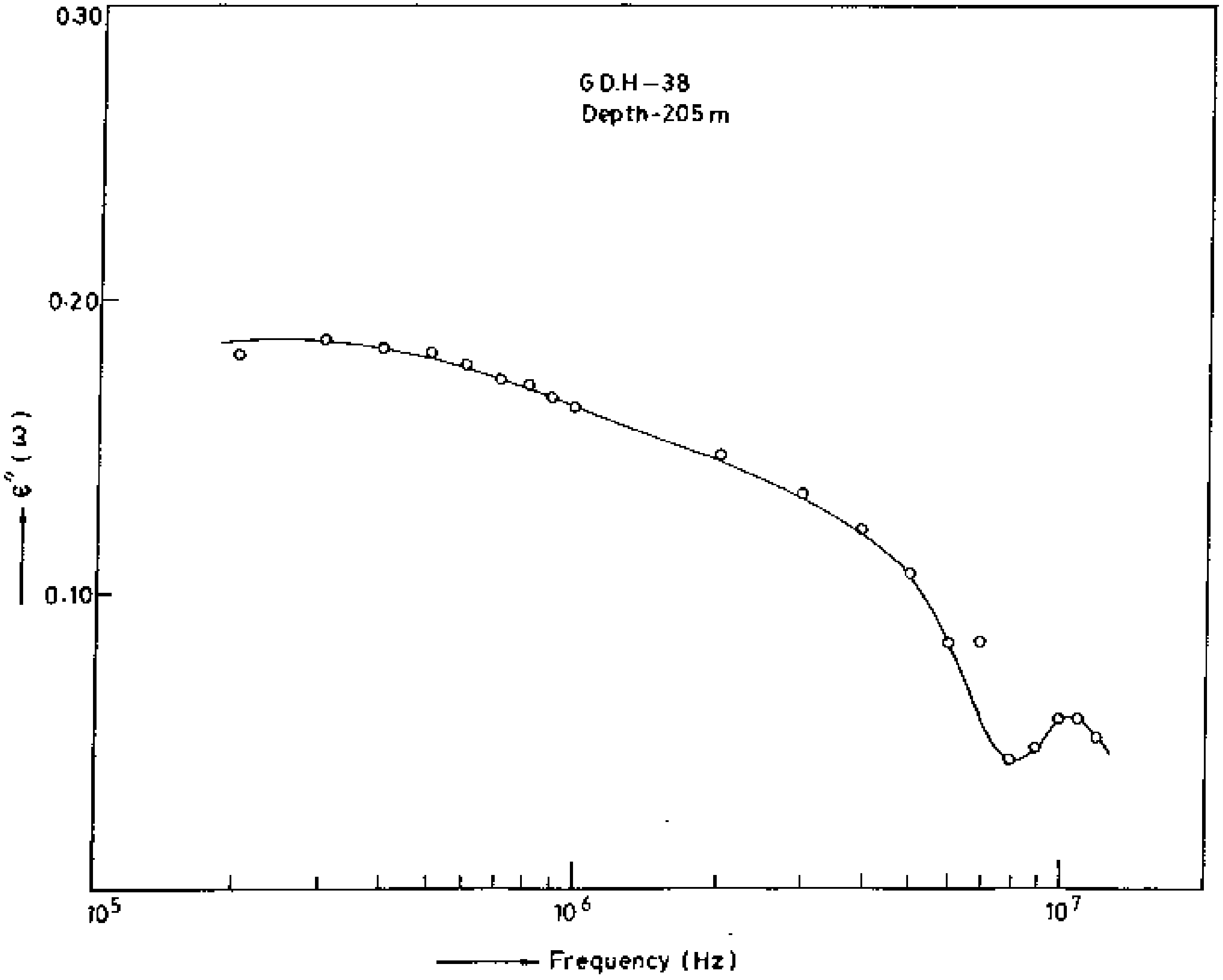

Fig. 5.55: The frequency dependence of loss factor $\varepsilon''(\omega)$ for coal

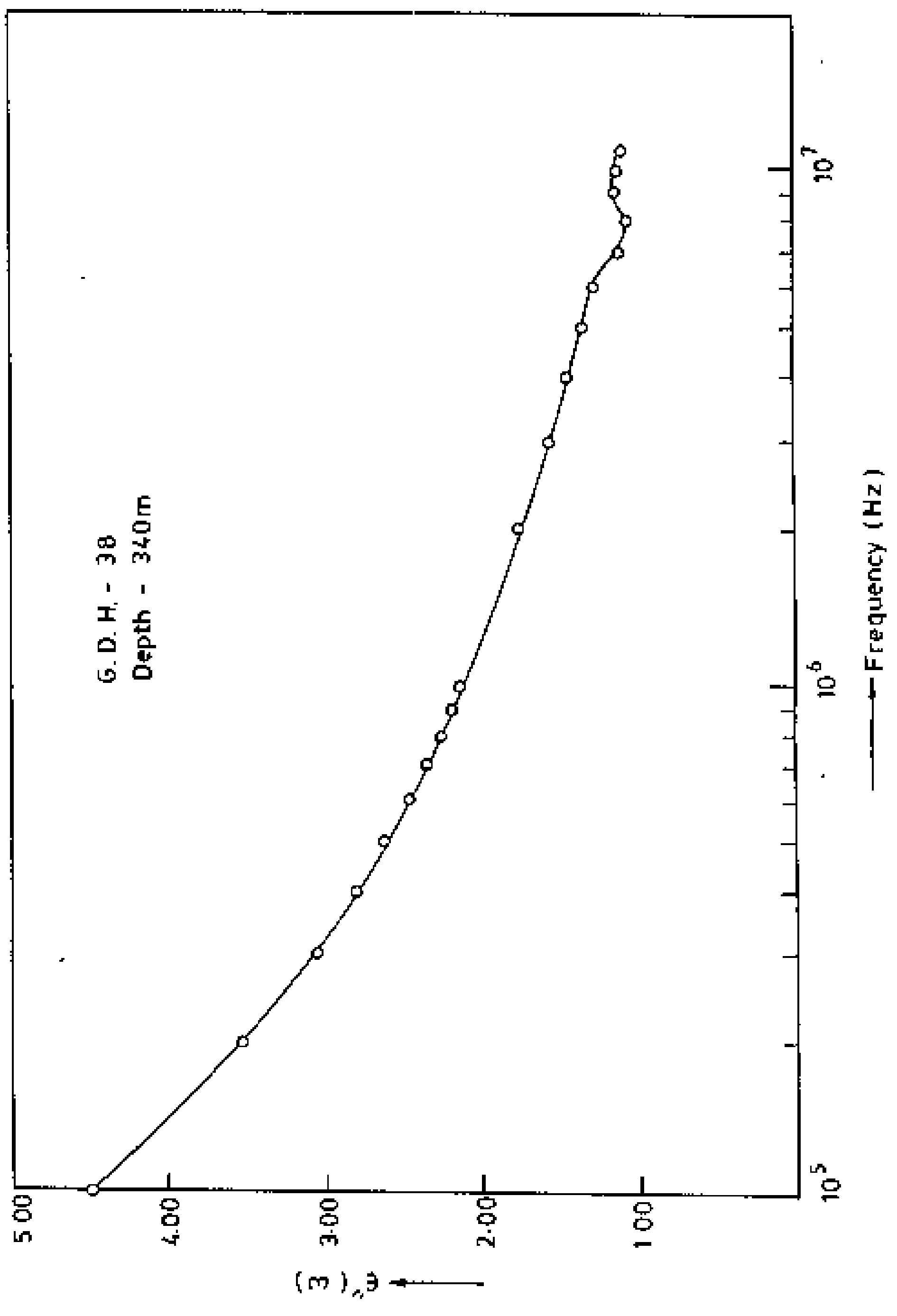

Fig. 5.56: The frequency dependence of loss factor $\in''(\omega)$ for coal

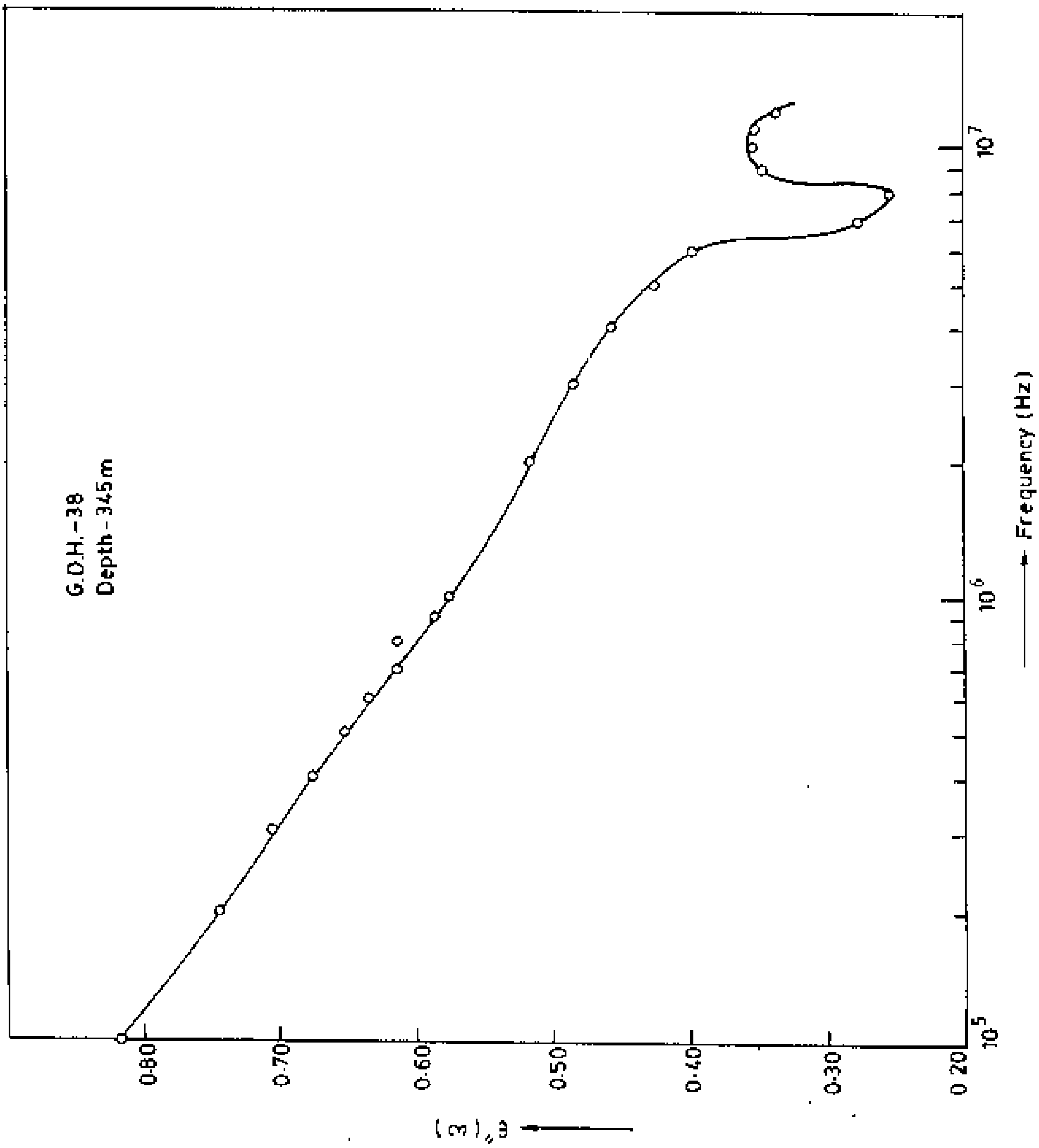

Fig. 5.57: The frequency dependence of loss factor $\varepsilon''(\omega)$ for coal

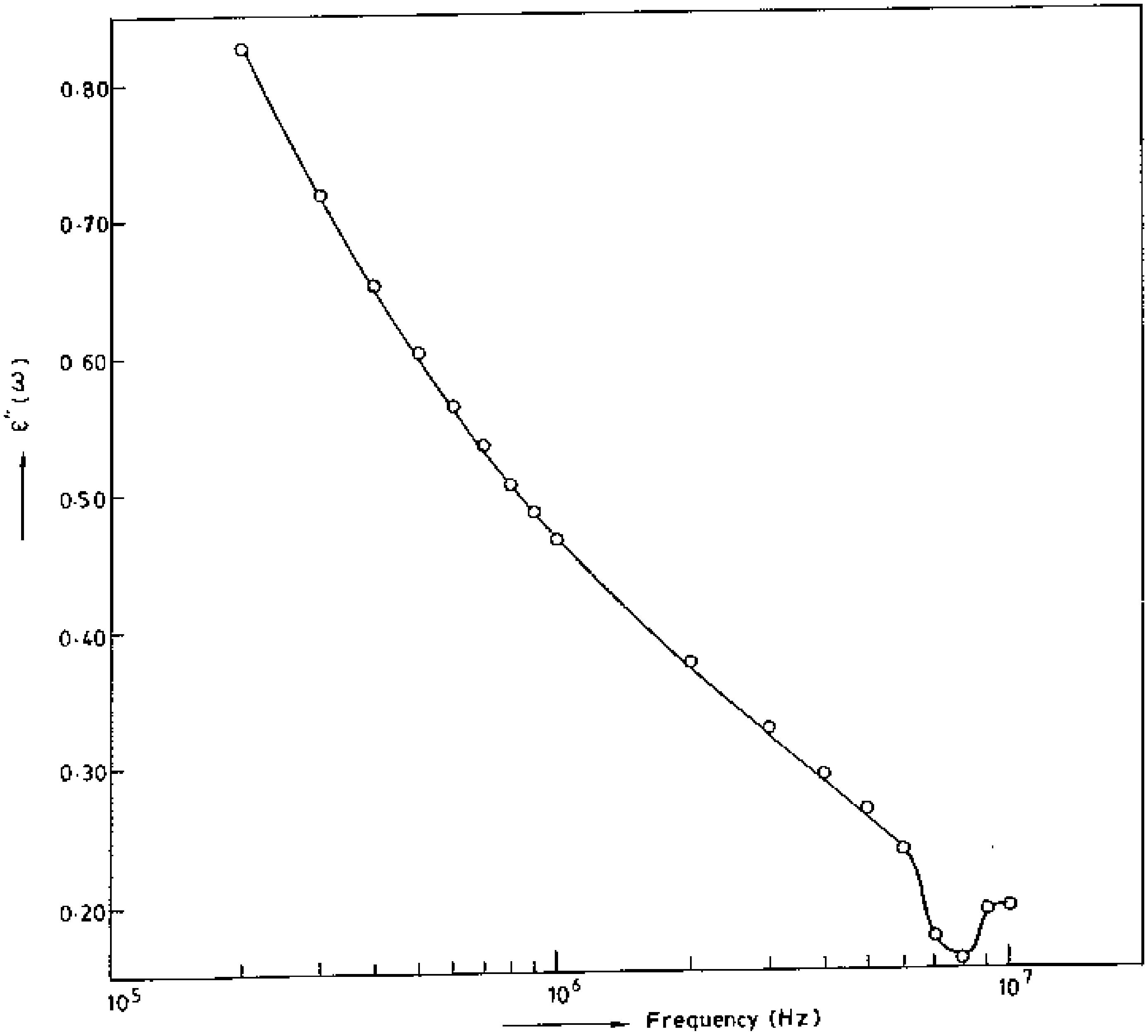

Fig. 5.58: The frequency dependence of loss factor $\in''(\omega)$ for coal

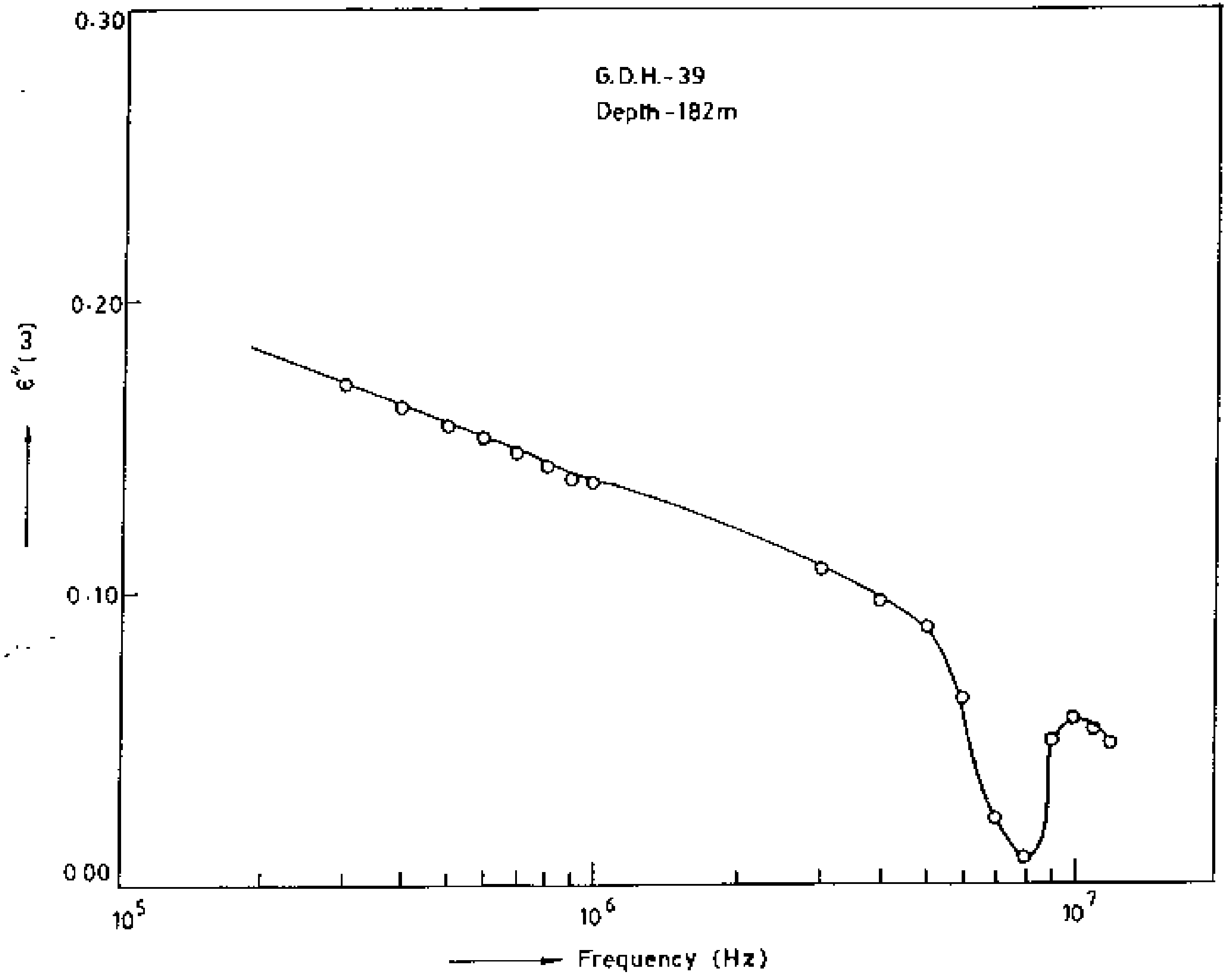

Fig. 5 59: The frequency dependence of loss factor $\epsilon''(\omega)$ for coal

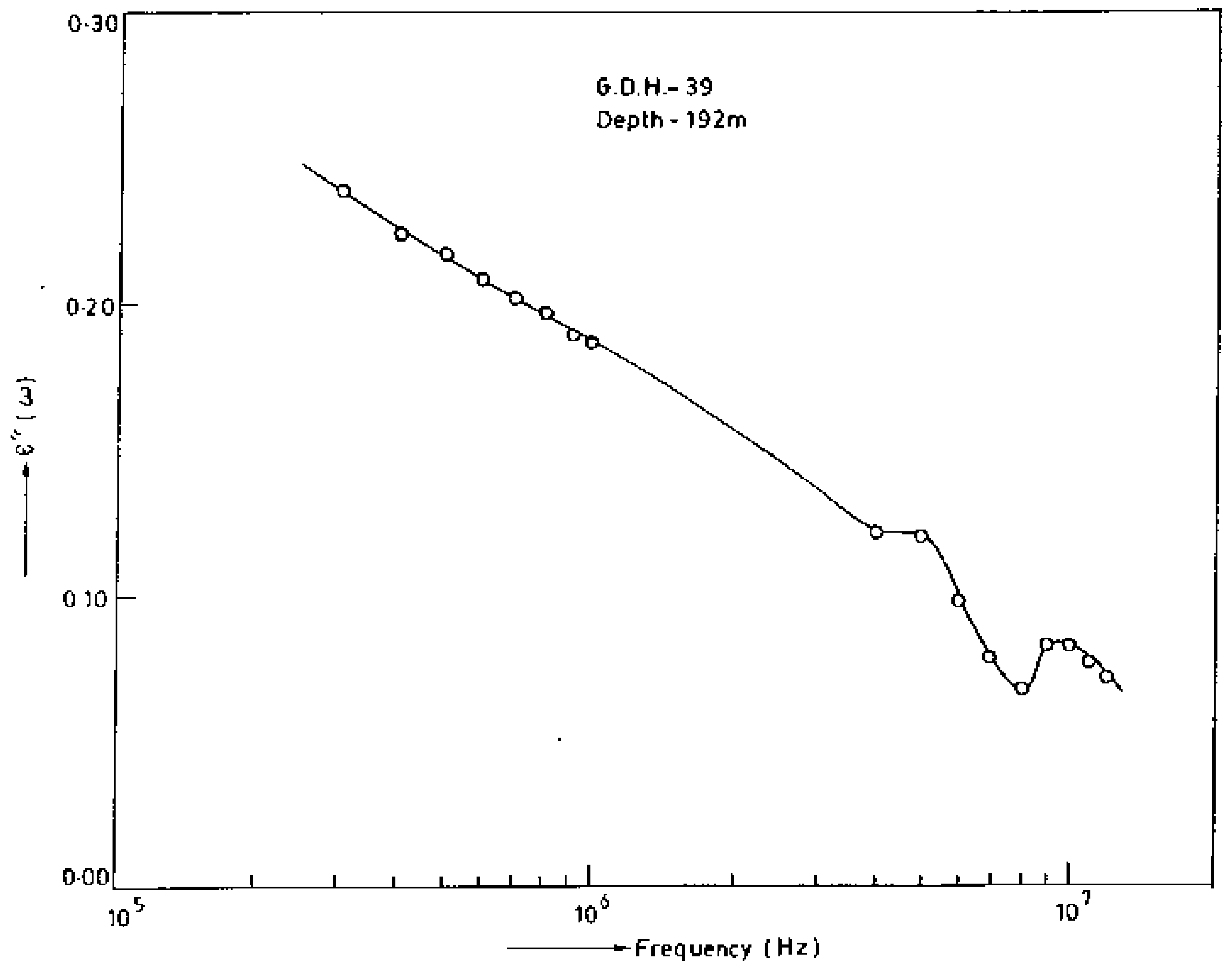

Fig 5.60: The frequency dependence of loss factor $\in''(\omega)$ for coal

Table 5.4 : The activation energy for various samples

Index No.	GDH	Depth (meter)	Activation Energy ΔE (eV)
1	38	205	0.27, 0.50
2	38	340	0.45, 0.20
3	38	345	0.43
4	39	172	0.55
5	39	179	0.24
6	39	182	0.31
7	39	192	0.25

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Chapter 6

Conclusions

Conclusion

The following conclusions can be drawn from the present study.

The Barapukuria coal mine is situated in an area of the shallow basement in the northwestern zone of Bangladesh under the Parbatipur Thana of Dinajpur district. The total area of coal deposit is about 5.25 sq. km. Depth of coal ranges from 118 to 508m. The total reserves is estimated to be about 300 million metric tones. Twenty samples were collected from each boreholes GDH-38 and GDH-39 at different depths (160-450m depth to top) of Barapukuria to investigate the electrical behaviour of this coal.

Proximate analyses were carried out according to ASTM standard. Proximate analyses determines moisture, ash, volatile content and calorific value. From the proximate analysis Barapukuria coals are classified as the higher rank of bituminous coal and can be used in heating and for power generation. At the same time Barapukuria coals can be used for chemical extraction.

Infrared spectroscopic studies were performed for identifying the presence of functional groups and associated minerals matter in the Barapukuria coals. From IR study it is assumed that the coals samples are composed of higher aromatics.

From the X-ray diffraction pattern no sharp peak is found rather all diffractograms are continuous curves with initial broad peak between 4^{0}-20^{0} on which more or less diffused peaks are to be superimposed indicating the largely amorphous nature of coal on the formation of small crystallities.

Electrical behaviour of the Barapukuria coal samples are studied by d.c. and a.c. electrical measurements. D.C. resistivity of the coal samples have been measured as function of voltage, temperature and thickness by two probe method.

From I-V characteristics curve it is observed that all the samples are not exactly of ohmic nature since the curve is not a straight line. Also the value of n (power factor) is not equal to unity. For three samples the value of n is calculated and it is found to be 1.20, 1.20 and 1.15. To study resistivity as function of temperature and voltage, the temperature range was from 300K - 500K and the voltage range was from 0-150V respectively. Though the variation of voltage has not a marked affect on the resistivity but the temperature has a serious affect on the variation of resistivity. The variation of resistivity has no basic trend. It is difficult to explain this anomalous behaviour of the resistivity with respect to temperature.

The dielectric constant of the coal increases with increasing degree of metamorphism or the maturity of the coal. The dielectric constant of the coal may arise due to the presence of polarizable electrons in the condensed aromatic systems. The dielectric constant increases as the aromaticity in the coal structure increases with the rank of coal. The a.c. electrical measurement has been carried out on frequency variation at room temperature.

Suggestions for future works

To give a general comment on the electrical behaviour of Barapukuria coal, a large number of coal samples are to be studied. Higher rank coal is expected to be the form of graphitic in nature. Higher rank coal behaves as an intrinsic semiconductor.

The temperature dependent a.c. conductivity can be studied in details to interpret the polarization mechanism. Also low frequency dielectric measurements may be performed with temperature variations.

The temperature has been raised upto 200°C above the room temperature. The variation of resistivity with temperature variation has no definite trend, due to this reason it is difficult to interpret the electricial behaviour within the short range of temperature. As the result shows some anomolies, so the resistivity behaviour can be observed in the high temperature range upto 900K.

For the thickness variation only disc samples were used in the present study. A large number of lump samples from different depths are to be studied.