Heavy Metal Fractionation Studies in the Aquifer Sediments of Ojhapatti area, Bhojpur district, Bihar

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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled **"Heavy Metal Fractionation Studies in the Aquifer Sediments of Ojhapatti area, Bhojpur district, Bihar"** has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any university or institute.

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Dedicated to

My Parents, My Sister
& My Brother

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Chapter 1

Introduction

Groundwater is an important natural resource. Worldwide, more than 2 billion people depend on groundwater for their daily supply (Kemper, 2004). The natural quality of water depends upon the physical environment, and the origin and movement of water as the water moves through the hydrological cycle, various chemical, physical and biological processes change its original quality through reaction with soil, rocks and organic matter. Natural processes and human activities cause changes in ground water quality directly or indirectly. Groundwater is degraded when its quality parameters are change beyond their natural variation, by the introduction or removal of ions/pollutants. The most concern pollutants get into water from both natural and human (agricultural and urban) activities.

Worldwide agriculture is the single biggest drain on water supplies, accounting for about 69 per cent of all use. About 23 per cent of water meets the demands of industry and energy and just 8 per cent goes for the domestic and commercial use. Whether groundwater or surface water is exploited, for water supply, is largely dependent on the location of aquifers relative to the point of demand.

In the developing world, groundwater is extensively used for drinking water supplies, especially in smaller towns and rural areas, where it is the cheapest source. Groundwater schemes consist typically of large numbers of boreholes, often drilled on an uncontrolled basis, providing untreated, unmonitored and often unconnected supplies. Shallower dug wells are also abundant in most places. Pollution sources include unsewered pit latrines to dispose of human wastes, inorganic fertilizers and pesticides used in an effort to secure self-sufficiency in food production, and industrial wastes continue to contaminate the ground water quality in urban areas. With the onset of green revolution in the mid-sixties in some parts of the country, groundwater depletion has emerged as a major problem in both rural and urban India. Agriculture accounts for as much as 93 % of total water withdrawals in comparison with mere 4 % for industrial use (Raju, 2003).

Origin of Groundwater

Most of the groundwater originates as meteoric water via precipitation in the form of rain or snow. If it is not lost by evaporation, transpiration or to stream runoff, water from these sources may infiltrate into the ground. Initial amounts of water from precipitation onto dry soil are held very tightly as a film on the surfaces and in the micro pores of soil particles in a belt of soil mixture. At intermediate levels, films of water cover the solid particles, but air is still present in the voids of the soil. This region is called unsaturated zone or zone of aeration, and the water present is vadose water. At lower depths and in presence of adequate amounts of water, all voids are filled to produce a zone of saturation, the upper level of which is the water table. Water present in a zone of saturation is called groundwater (Hiscock, 2005).

The porosity and structure of the ground determine the type of aquifer and underground circulation. Groundwater may circulate and be stored in the entire geological stratum: this is the case in porous soils such as sand, sandstone and alluvium. It may circulate and be stored in fissures or faults in compact rocks that are not themselves permeable, like most of volcanic and metamorphic rocks. Water trickles through the rocks and circulates because of localized and dispersed fissures. Compact rocks of large fissures or caverns are typical of limestone (Marsily, 1986). These properties are important in the adsorption of water molecules and dissolved ions on mineral surfaces, especially on clay.

Continental weathering and erosion are major components of the exogenic cycles of elements on the earth. Weathering breaks down the rocks and the resulting dissolved particulate materials are transported by rivers into the sea. Chemical weathering of rocks and minerals determines the flux of dissolved materials carried by rivers whereas physical weathering regulates the particulate transport.

Processes controlling groundwater quality

The geochemical properties generally depend on recharge of water from atmospheric precipitation, in land surface water and seawater and surface geochemical processes. Temporal changes in origin and constitution of recharge water, hydrologic and human factors cause periodic chances in ground water quality. The knowledge of geochemical processes, often leads to an understanding of groundwater quality and occasionally aid in making useful predictions. The different geochemical process which influence groundwater greatly is given below (Todd, 1980; Drever, 1982): -

A) Reduction

The important constituents of groundwater to be affected by this process are sulphates and nitrates. The important of sulphate is generally due to microbial activity (Scholler, 1962) and is accompanied by subsequent oxidation of available organic matter (by released oxygen) resulting in production of CO_2, which in turn produces large quantities of HCO_3^-, H^+ and CO_3^{-2} ions.

B) Ion exchange

The replacement of structural and adsorbed ions present in the solution has been termed as ion exchange (Garrel and Christ, 1965; Hem, 1985). The degree to which the ion exchange (both cation and anion exchange) occurs, depend on:

a) Concentration of exchangeable ions in the solution

b) The type of solid material or sediments in contact with solution

c) The state of the ion in the solid structural adsorbed and

d) Degree of saturation of that ions in the solid

The exchangeability of an adsorbed ion is far greater than that of structural ion. The common exchange is, therefore, between the ions adsorbed by the solid, which is commonly seen in clay minerals, Zeolites and organic substances. The adsorption capacity of some mineral is also influenced by other characteristics of adsorbed ions, besides its charge, e.g. ion radius and degree of hydration.

Scholler (1962) has explained two types of Base Exchange:

(i) Positive, when alkaline (Na^+, K^+) in water get exchanged for alkaline earth (Ca^{2+}, Mg^{2+}) in the aquifer material.

(ii) Negative, when alkaline earth in the water get exchanged with alkalis in the rock.

Former is generally the case, when saline water inters the fresh aquifers and later takes place in the areas of inland saline water or in transition cone between the fresh water and saline water.

C) Evaporation and dissolution

The processes of evaporation and dissolution control the concentration of aqueous solution to greater extent, which in turn is influenced by the climatic factors. Scholler (1962) listed main factors influencing the main process of mineralization as dissolution and concluded that the ground water is commonly highly mineralized due to large residence time is sub surface formation under relatively higher temperature gradients (resulting in considerable depths), thus allowing greater rock water interaction.

D) Sediment-Water Interaction

Suspended solid surfaces (particles or colloids) in waters play a prominent role in controlling the concentration of dissolved trace elements. Most of these elements are eliminated by sedimentation after incorporation on to or into particles, generally by complexation with the surface sites. The most common inorganic particles and colloids are: non-clay silicates [quartz, potash feldspar, plagioclase, opaline silica (diatoms)]; clays (illite, smectite); carbonates (calcite, dolomite); Fe–Mn oxides (goethite, magnetite); phosphates (apatite); sulfides (mackinawite). Particles and colloids in a water body may be classified as a function of their origin:

(1) Allogenic compounds (mainly pedogenic, i.e. Originating from soils) are mostly clays and other silicates, and Fe and Mn oxyhydroxides leached out by rain water;

(2) Endogenic compounds (or aquagenic, i.e. formed in the water column) may be subdivided into inorganic compounds formed by chemical precipitation (mostly Fe and Mn oxyhydroxides, Ca and Mg carbonates, Fe sulfides in anoxic waters) and inorganic compounds that are the backbones of certain micro-organisms and are released after their death (SiO_2, $CaCO_3$) (Jones and Bowser, 1978).

The tendency of an element to be accumulated by organisms in aquatic systems depends in particular upon the capacity of a sediment to retain this element. This capacity might be weakened in anthropogenically stressed sediment–water systems. Solid components in sediments govern the dissolved levels of these elements via sorption/desorption and dissolution/precipitation reactions coupled to complexation, acidification or redox reactions. Therefore, particulate trace metal species identification tends to be far more instructive than any total elemental concentrations.

Geochemical association of metals in sediments and their mobility

Sediment is an integral and dynamic part of aquifers, river basins, including estuaries and coastal zones. Sediment originates from the weathering of minerals and soils upstream and is susceptible to transport downstream by the river water. Flow rates decline in lowland areas where transported material settles along the river banks (sedimentation) and on the bed of the river. A large number of sediment analyses, which have been performed for the inventory, monitoring and surveillance of pollution in aquatic systems have clearly shown that it is imperative, particularly for river sediments, to base their data on a standardized procedure with regard to particle size (Forstner, 1989). The methods will mostly reduce (not eliminate) the fraction of the sediment that is largely chemically inert (i.e. mostly the coarse-grained, feldspar and carbonate minerals) and increase the substances active in pollutant enrichment (i.e. hydrates, sulfides, amorphous and fine-grained organic materials). In natural systems the fine-grained material commonly occurs as complex aggregates, such as clay particles coated with organic matter and inter-layered or intermixed hydrous oxides of Fe and Mn.

It is now generally accepted that the distribution, mobility, biological availability and toxicity of chemical elements depend not simply on their concentrations but, critically, on their forms. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Some of the more important controlling factors include pH, redox potential and the availability of reactive species such as complexing ligands (both organic and inorganic), particle surfaces for adsorption and colloidal matter.

Species distribution studies have shown that trace element (e.g. metals) concentrations in soils and sediments vary with physical location (e.g. depth below bed surface) and with particle size. Speciation science seeks to characterise at least some of the most important forms of an element in order to understand the transformations between forms that are likely to occur, and to infer from such information the probable environmental consequences.

The concept of chemical leaching is based on the idea that a particular chemical solvent is either phase or mechanism specific (e.g. buffered acetic acid will attack and dissolve only carbonates, neutral magnesium chloride will only displace adsorbates), i.e. it may serve to estimate the speciation of a trace element in sediments or solid waste Bedrock formed from natural geological processes undergoes weathering and ultimately releases inorganic constituents into the soil (Stigliani, 1988; Forstner, 2003). To gain information on the activity of specific elements, it is necessary to establish not only the total content of the element but also to gain an indication of its individual chemical and physical forms (Hong et al., 1994). In cases where elevated inorganic background constituents are present, an understanding of the levels that are present and the effect the constituents have on the surrounding environment, including human health, is vital. Inorganic background soil constituents are of interest for several reasons:

1. they can be used to characterise soil;
2. they are part of the nutritional food chain from soil to plants to animals (including man); and,

3. they are essential to the assessment of anthropogenically contaminated soil (Krantzberg et al., 2000) in order to compare contaminated soil levels to that of background soil constituent levels.

According to the official definition which is currently under discussion at IUPAC; Speciation analysis is the process leading to the identification and determination of the different chemical and physical forms of an element existing in a sample (Templeton et al., 2000). Although this definition tends to restrict the term speciation to the state of distribution of an element among different chemical species in a sample, in practice the use of this term is much wider, specifying the transformation and /or the distribution of species, or the analytical activity, to identify chemical species and measure their distribution.

Speciation can broadly be defined as the identification and quantification of the different, defined species, forms or phases in which an element occurs (Ure et al., 1990). The term "fractionation" is frequently used interchangeably with speciation but emphasizes the concept of subdividing a "total content". Also, the analytical preparations for separating metal species are referred to as "fractionation".

Operationally and functionally defined species characterization

Operationally and functionally defined species characterization must be distinguished from chemical speciation analysis (Quevauviller et al., 1996; Ure et al., 1993; Kersten and Forstner, 1989). The Operationally defined species characterization leads to a characterization of molecule groups (not single species) according to their similar behavior during an analytical procedure, such as extraction. Functionally defined species characterization provides information about the function of species groups in biochemical pathways and their impact on organisms (Quevauviller et al., 1996; Caroli, 1996; Ure et al., 1993; Mota and Simaes Goncalves, 1996; Irgolic, 1989).

Speciation of metals using sequential extraction

Sequential extraction methods for heavy metals in soils and sediments have been developed and employed in an effort to provide detailed information on metal origin, biological and physicochemical availability, mobilization, and transport (Tessier et al., 1989; Boughriet et al., 1992, Ure et al., 1993). Sequential extraction procedures also provide information about the differentiation of the reactive bounding strength of metals on various solid phases and about their reactivity under different physio-chemical environmental conditions. Partitioning studies on materials from core profiles are particularly useful, since they provide information on relative variations of elemental phases, irrespective of the method applied, and thereby provide an insight into diagenetic processes taking place after deposition of the sediment components.

Environmental Importance of Studied Metals

The effects of metals in water, sediments and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essentials to plant and animal growth while others may adversely affect water consumers, wastewater treatment systems, and receiving waters. The benefits versus toxicity of some metals depend on their concentration in waters and sediments. The most likely metals to cause growth problems in crops are copper, zinc, and nickel, partly because they can occur at high concentrations. Certain metals are particularly toxic to animals and humans are lead, cadmium, mercury, arsenic, selenium and molybdenum.

Prologue to the present study

Arsenical skin lesions in villagers were reported in the Semria Ojha Patti village in the Middle Ganga Plain, Bihar, where tube wells replaced dug wells about 20 years ago. Analyses of the arsenic content of 206 tube wells (95% of the total) showed that 56.8% exceeded arsenic concentrations of 50 µg/L, with 19.9% > 300 µg/L, the concentration predicting overt arsenical skin lesions (Chakraborti et al., 2003). British Geological Survey (BGS) has estimated that > 35 million people are drinking water containing concentrations of arsenic ≥ 50 µg/L (BGS and DPHE, 2001). Arsenic-rich sediments derived from the Himalayan mountains and the foothills of the Shillong Plateau are deposited in the Gangetic Plain, Padma–Meghna–Bramhaputra delta of Bangladesh, Terai region of Nepal, Chandigarh area, and now Bihar. Most of the arsenic contaminated tube wells are in the depth range of 20–55 m, similar to that of West Bengal and Bangladesh tube wells. The deposition is expected to be in the Holocene-type deposits. The meandering pattern of the river is responsible for the localized depositions of arsenic rich sediment in selected areas along the course of the river Ganga. Whether the huge groundwater withdrawal, pivotal to the green revolution, allows oxygen to enter into the aquifer, initiating microbial activities, or has any relation to localized increases in arsenic mobilization is yet to be understood.

The processes controlling the transfer of arsenic between aquifer sediments and groundwater are not completely understood (Acharya et al., 1999; 2000; Bhattacharya et al., 1997; Chakraborti et al., 2001; Chowdhury et al., 1999; Das et al., 1996; Nickson et al., 1998; 2000). According to Nickson et al. (1998), the primary source of arsenic is in association with iron oxyhydroxide in aquifer sediment, and the key process of arsenic mobilization is desorption and dissolution of iron oxides due to the reducing conditions of the aquifer and low hydraulic gradients. This theory does not explain the increasing arsenic concentration in existing tube wells, previously safe but now progressively contaminated (Chakraborti et al., 2001). Das et al. (1996), Chowdhury et al. (1999), and Chakraborti et al. (2001) proposed, on the basis of sediment analysis, that oxygen entering the aquifer due to heavy groundwater withdrawal for irrigation favors the oxidation of arsenic-rich iron sulfide and mobilization of arsenic to the aquifer.

Till now, the works which have been undertaken has focussed on hydrogeochemistry; the role of sediments for Arsenic enrichment and mobilty in the Mid Gangetic Plain has not been given importance. Hence the fractionation studies has been undertaken to understand the geochemical fractionation of metals, their mobility potential in the aquifer sediments and its relation to As if any in the Middle Gangetic Plain.

Aim of Study

The objective of the current study is to contribute to the knowledge of inorganic background sediment constituent levels, particularly in aquifer sediments of Semriya Ojhapatti, Bhojpur district, Bihar. Using the database generated the significance of different metals as a background sediment constituent will be probed, along with its bioavailability and speciation.

In particular, this study aims to:

1. Investigate both qualitatively and quantitatively, the speciation of heavy metals in aquifer sediment.
2. Investigate different types of heavy metals found along with the operationally defined species in sediments & to assess their association and bioavailability.
3. Investigate the metal association with sediment components , relationship between metal accumulation pattern and sediment characteristics

Chapter 2

Review of Literature

The rapid increase in the levels of environmental pollution over recent decades has resulted in increasing concern for people's well-being and for global ecosystems. The need to determine different species of trace elements in environmental and biological materials is beyond question since the effects or toxicity of an element and its behaviour depend to a great extent on its chemical form and concentration. These determine the physical and chemical associations that they undergo in natural systems. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Until recently, analytical methods allowed analysts to determine total contents only, but it was soon realised that this analytical information was insufficient. Some of the more important controlling factors include pH, redox potential and the availability of reactive species such as complexing ligands (both organic and inorganic), particle surfaces for adsorption and colloidal matter (Ure et al., 1987; Cornelis et al., 1999). Biochemical and toxicological investigation has shown that, for living organisms, the chemical form of a specific element, or the oxidation state in which that element is introduced into the environment, is crucial, as well as the quantities.

Heavy Metals and Sediments

Heavy metal inputs may be in particulate form or dissolved form. Because most of the heavy metals tend to accumulate in sediments, their presence in water column is usually the result of recent inputs. Both sorption and desorption are controlled by the nature of the total heavy metal loading to sediment type and the surface water characteristics (Todorovic et al., 2001). Sediments conserve important environmental information and are increasingly recognized as both carriers and possible sources of contaminants in aquatic system (Tessier et al., 1994). Heavy metals are not permanently fixed on sediments and can be released back to the water column by changes in environmental conditions, such as pH, redox potential, and the presence of organic chelators (Forstner, 1987). The control of heavy metal partitioning by soil colloids is key to determining their influence on contaminant bioavailability, toxicity, and persistence in the soil-water-sediment system (Di Toro et al., 1992). Sorption and release, i.e., interactions, of heavy metals in the soil and sediment environment depend on their chemical forms and properties and their relative distribution in solution and solid phases (Forstner, 1991). Often, a large percentage of heavy metals are associated with soil solids (Hesterberg et al., 1993; Han et al., 2000). The elemental concentration of sediments not only depends on anthropogenic and lithogenic sources, but also upon the textural characteristic, organic matter content, mineralogical composition and depositional environment of sediments (Presley et al., 1980).

Variation of metals with grain size

The specific surface area of sediments is dependent on granulometric parameters and mineral composition (Juracic et al., 1980; 1982). The ability of sediments to adsorb organic and inorganic contaminants is dependent largely on the grain-size distribution of sediments; fine-grained sediment adsorbs contaminants more readily than coarse-grained sediment (Horowitz, 1991). Increased concentrations of metals in coarse fractions are also observed and it is believed that the coarser particles may better document anthropogenic inputs because of their limited transport and longer residence time at any particular site (Tessier et al., 1982; Salomons and Forstner, 1984; Moore et al., 1989).

It is generally believed that metals are associated with smaller grain-size particles. The specific surface area of sediments is dependent on granulometric parameters and mineral composition (Juracic et al., 1980; 1982). Increased concentrations of metals in coarse fractions are also observed and it is believed that the coarser particles may better document anthropogenic inputs because of their limited transport and longer residence time at any particular site (Tessier et al., 1982; Salomons and Forstner, 1984; Moore et al., 1989). This trend is predominantly attributed to sorption, co-precipitation and complexing of metals on particle surfaces and coatings. Smaller particles have a larger surface area: volume ratio and therefore contain higher concentration of metals (Whitney, 1975; Gibbs, 1977; Filipek and Owen, 1979; Ackermann, 1980; Salomons and Forstner, 1984; Martincic et al., 1990; Biksham et al., 1991). Clay-sized material (<2 lm) represents the fraction with the greatest adsorbing capacity, owing to a larger surface area and greater cation exchange capacity, and because clay material can serve as a host for contaminant 'scavengers', such as Mn/Fe oxides, organic matter, etc. (Horowitz, 1991).

An evaluation of total metal concentration levels after a strong acid digestion of the sediments may be useful for global budget calculation, but it provides little information on the potential availability of metals to biota under various environmental conditions. Since the mobility of trace metals, as well as their bioavailability and related ecotoxicity to plants, critically depends upon the chemical forms in which metals are present in the sediments, considerable interest exists in trace element speciation (Davidson et al., 1994).

Geochemical fractionation of metal in sediments

The behaviour and fate of metals are governed by a range of different physio-chemical processes, which dictate their availability and mobility in the soil or sediment system. In the water phase, the chemical form of a metal determines the biological availability and chemical reactivity (sorption/desorption, precipitation/dissolution) towards other components of the system (McBride, 1989). Knowledge of total metal concentration in the sediments does not help in understanding their bioavailability and mobilisation in aquatic environment. The binding form in the solid phase is related to the kinetics and equilibrium of metal release to the liquid phase and hence the likelihood of remobilization and bioavailability (Bryan and Langston, 1992). So as to appreciate the potential effects of heavy metals and their complexity in mobilisation, one must understand the various forms of the elements present in the sediments (Presley et al., 1972). This has led to a shift of attention in recent years from the determination of total heavy metals in sediments to other techniques which include the quantitative distribution of metals among various chemical phases such as adsorptive or exchangeable, carbonate, reducible – i.e. Fe-Mn oxide, organic and residual phase.

In soils and sediments, elements of interest exist in several different forms and are associated with a range of components (Cottenie et al., 1979; 1984; Pickering., 1981). It is generally recognized that information about the physicochemical forms of the elements is required for understanding their environmental behaviour (mobility, pathways, and bioavailability) (Bernhard et al., 1986; Lund, 1990).

Several researchers have undertaken studies on quantitative distribution of metals among various chemical phases of sediments under natural conditions to assess the ecotoxic potential (Gibbs, 1977; Rapin et al., 1986; Rosental et al., 1986; Ridgway and Price, 1987; Pardo et al., 1990). Several chemical speciation and fractionation methods for heavy metal analysis in soils and sediments have been and are still being developed and applied. They primarily are intended to understand the particular environmental behaviour of metals, present in a variety of forms and in a variety of matrices (Tack and Verloo, 1995).

Speciation techniques are useful in studies of metal partitioning, distribution, accumulation, and mobility in water and sediment systems (Tessier et al., 1989; Boughriet et al., 1992) and soil (Japenga et al., 1992) to gain a better understanding on the different processes and mechanisms responsible. The complexity of possible reactions and often unknown reaction kinetics in natural soil and sediment systems restricts studies of metal species distribution in solid phases mainly to operationally defined analytical procedures (Brümmer, 1986).

Operationally defined species characterization

Operationally defined species characterizations cannot be considered as real chemical speciation analysis, predominantly because no single species is identified. Characterization of the molecule groups is strongly dependent on the selected analytical procedure, for example the choice of extractant. The original species information (identity) is lost. The functionally defined species characterization characterizes molecule groups by studying their impact on organisms. The determination of heavy metals on operationally defined procedure can be a good compromise to give information on environmentally contamination such as the evaluation of risk of contamination of groundwater (Agata and Namiesnik, 2000).

Speciation of metals using sequential extraction

After many studies and refinements, the chemical extractions steps are designed to selectively extract physically and chemically sorbed metal ions, as well as metals occluded in carbonates, Mn (hydr)oxides, crystalline and amorphous Fe (hydr)oxides, and metal sulfides. The resulting extract is operationally defined based on the proposed chemical association between the extracted species and solid phases in which it is associated. Given that the extraction is operationally defined, the extracted metal may or may not truly represent the defined chemical species (Gleyzes et al., 2002).

The quality and quantity of the respective element species in a matrix are highly responsible for the mobility, bioavailability, and finally the eco-toxicological or toxicological impact of the element rather than the total element concentration

(Templeton et al., 2000; Mota and Simaes Goncalves, 1996; Florence, 1983; Turner, 1984). Therefore, only knowledge of the species present can allow any assessment of toxic, (known) impact at a specific concentration, or essential. Thus, speciation analysis is integral to determining speciation of an element in a specific matrix.

In order to study metal speciation in sediments, leaching/extraction tests are widely used for the assessment of heavy metals mobilisation. These extraction procedures also make it possible to evaluate the mobility of metals in soil environment. In order to assess the reactivity of the species or binding form of the metals in solid phase, sequential extraction has been developed which partitions elements into a number of phase operationally defined geochemical fractions (Quevauvillier et al., 1996; Gleyzes et al., 2002).

To study trace metal partitioning, different schemes have been proposed based on application of sequential procedures, yielding the so-called operational speciation (Tessier et al., 1979; Kersten and Forstner, 1989; 1995; Krishnamurti et al., 1995; Ure et al., 1993; Lylister and Probst, 1999; Gleyzes et al., 2002).

BCR three step Sequential Extraction Scheme

Environmental studies on soil and sediment analysis are often based on the use of leaching or extraction procedures (e.g., single or sequential extraction procedures) which enable broader forms or phases to be measured (e.g., `bioavailable' forms of elements) and which are, in most cases, sufficient for the purpose of environmental policy (Quevauviller et al., 1993). The development and use of these types of extraction schemes started in the early 1980s and aimed to evaluate the metal fractions available to plants (for estimating the related phytotoxic effects and/or nutritional properties of elements) and the environmentally accessible trace metals (evaluation of the mobility of metals) (Tessier et al., 1979; Thomas et al., 1980).

The lack of uniformity in the procedures used did not allow the results to be compared world-wide or the methods to be validated since the results obtained are `operationally defined', *i.e.*, the `forms' of metals are defined by the determination of extractable elements and, therefore, the significance of the analytical results is highly dependent on the extraction procedures used.

There are three major processes leading to the incorporation of a particular metal organic species onto sediment (Saxby, 1973):

1. Reaction between a metal ion and an organic ligand in solution leading to a species which can either precipitate directly or be adsorbed on sedimentary material.
2. Incorporation in a sedimentary pile of all or part of an organism containing biological coordination compounds.
3. Adsorption on sediment, of molecules resulting from the solubilisation of minerals by natural waters containing organic ligands.

In order to improve this situation, the European Commission through the BCR Programme and its successor (Standards, Measurements and Testing Programme) (Rauret et al., 1999) launched a collaborative project which aimed to

(1) design a three-step sequential extraction scheme,

(2) test the selected scheme in inter-laboratory studies involving expert European laboratories and

(3) certify the extractable trace element contents of a sediment reference material.

The BCR scheme produces three geochemical fractions, which include:

1. **Acid soluble phase** (Exchangeable and Carbonate bound):

   The metals present in the exchangeable and carbonate fractions are considered to be weakly bound and may equilibrate with the aqueous phase, thus becoming more bioavailable (Baruah et al., 1996). Metals in this fraction are the most mobile and readily available for biological uptake in the environment.

2. **Reducible phase** (Bound to Fe-Mn hydroxides):

   The Fe and Mn hydroxide constitutes a significant sink for heavy metals in the aquatic system. This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation (Bordas and Bourg, 2001).

3. **Oxidizable phase** (Bound to organics and sulfides):

   The metals that are associated with sulfides and organic matter show very less abundance. The affinity of heavy metals for organic substances and their decomposition products are of great importance for the release of the metals into water. Organic matter, with high molecular weight acids, plays an important role in the distribution and dispersion of heavy metals, by mechanisms of chelation and cation exchange processes (Purushothaman and Chakrapani, 2007).

4. **Residual phase** (Bound to silicates and detrital materials):

   The residual fractions represent samples, which have been leached off of other metals to various other fractions. The residual or lithogenic fraction is a major carrier of transition metals in most aquatic systems. The concentration of heavy metals in the crystalline fraction is largely controlled by the mineralogy and the extent of weathering. Heavy metals in this form are not soluble under experimental conditions and hence may be considered to be held within the mineral matrix. Hence, under normal sediment–water interaction, there is not much possibility for the release of these metals (Ure, 1990; Forstner, 1990; Purushothaman and Chakrapani, 2007).

Metals in river sediments can be bound to various compartments: adsorbed on clay surfaces or iron and manganese oxyhydroxides; present in lattice of secondary minerals like carbonates, sulphates or oxides; occluded in amorphous materials such as iron and manganese oxyhydroxides; complexed with organic matter or lattice of primary minerals such as silicates (Tessier et al., 1979; Schramel et al., 2000). The possibility of metal re-mobilisation from sediment materials will depend on the type of metal linkage to the sediment material and the possibilities of transformation in more labile species (Kersten and Forstner., 1989).

The Fe–Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals. The release of the metals from the matrix is most likely to be affected by the redox potential and pH (Calmano and Forstner, 1993). Zn associated with the Fe-Mn (hydr) oxide bound fraction is caused by the adsorption of these metals by the Fe–Mn colloids (Jenne, 1968). As release to solution could be a result of reductive dissolution of Fe oxides/ oxyhydroxides with absorbed or co-precipitated arsenic (Cummings et al., 1999; Nickson et al., 2000; McArthur et al., 2001; Swartz et al., 2004; Reith and McPhail, 2007; Xie et al., 2008).

Organic matter plays an important role in the distribution and dispersion of heavy metals in the secondary environment, by mechanisms of chelation and cation exchange (Filipek et al., 1982; Forstner and Wittmann, 1983; Guo et al., 2003) suggested that alkaline and reducing geochemical conditions are favourable for the mobilization of arsenic from the aquifer sediments to groundwater. The metal present in the inert fraction, being of detrital and lattice origin, can be taken as a measure of contribution by natural sources (Salomons and Forstner, 1980).

Some case studies in Riverine flood plain

A. Mahanadi River basin (Chakrapani and Subramanian, 1993)

Heavy metals distribution in core sediments, different size fractions of bed sediments (> 212 µm, 90-212 µm, 63-90 µm, 53-63 µm, < 53 µm), and suspended sediments (>30 µm, 20-30 µm, 10-20 µm, 2-10 µm, < 2 µm) have been discussed in the river sediments of Mahanadi basin. Chemical fractionation studies on suspended and bed sediments show Fe, Zn, Cu, and Pb are associated with the residual fraction and Mn with the exchangeable fraction Heavy metals distribution in core sediments shows no systematic variation with depth. Surface sediments show lower concentration due to weathering, leaching, and uptake by vegetation. Metals distribution in the sediments is controlled to a greater extent by the lithology in the basin. Finer sediments show higher concentration of metals. Considering that heavy metals in the Mahanadi River are mostly associated with the residual phase, thus, sediments in the Mahanadi River are less polluted.

B. Damodar River basin (Singh et al., 1998)

As studied by Singh et al (1998) the concentrations of heavy metals (Fe, Mn, Zn, Cr, Cu and Ni) tend to increase as the size fractions get finer (< 63 µm). The exchangeable fraction of the Damodar sediments contains very low amounts of heavy metals suggesting poor bioavailability of metals. The chemical fractionation study of the Damodar River bed sediments reveals that the lithogenic (residual) phase is the major sink for heavy metals. Fe and Mn are the major elements of the lithogenic lattice and Zn is the major element of the non-lithogenic fractions. Fe-Mn oxides and organic matter bound fractions are the significant phases in the non-lithogenic fraction. The organic phase is an efficient scavenger of heavy metals, especially for Cu and Zn, in the Damodar sediments.

C. Taihu lake China (Enfeng et al., 2005)

The sediments are composed of organic-poor clayey-fine silts. The chemical speciations of Cu, Fe, Mn, Ni, Pb, and Zn were analyzed using the BCR sequential extraction procedure. Cu, Fe, Ni, and Zn are mainly associated with the residue fraction; Mn is concentrated mainly in exchangeable/carbonate fraction and residue fraction; and Pb mainly in Fe/Mn oxide fraction and organic/sulphide fraction. The fractions of Ni, Pb and Zn bound to the Fe/Mn oxide have significant correlations with reducible Mn; the organic/sulphide fractions of Cu, Mn, Ni, Pb, and Zn have significant correlations with TOC. The Fe/Mn oxide fraction and organic/sulphide fraction can make a considerable contribution to the potential pollution of lake water with changing redox conditions in the sediments.

D. Ganga River sediment (Chakrapani and Purushothaman, 2007)

The study helped in understanding the GAI (Geo- Accumulation Index) and MEF (Metal Enrichment Factor) for the Ganga river sediments. Since, the river flows through differing geologic, topographic, hydrological and industrial regions the sediments reflect the influence of the natural and anthropogenic additions. The metals show high concentration in the residual fraction except Cu, Cr and Zn which mostly occur in the oxidisable fraction. A good correlation is observed between GAI and MEF in most of the locations for most of the metals, showing the appropriateness of such comparisons in sediment quality studies.

Environmental Importance of Studied Metals

The effects of metals in water, sediments and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essentials to plant and animal growth while others may adversely affect water consumers, wastewater treatment systems, and receiving waters. The benefits versus toxicity of some metals depend on their concentration in waters and sediments. The most likely metals to cause growth problems in crops are copper, zinc, and nickel, partly because they can occur at high concentrations (APHA, 2005). Certain metals are particularly toxic to animals and humans are lead, cadmium, mercury, arsenic, selenium and molybdenum.

A brief account of studied metals is described below:

Arsenic

The speciation of arsenic in environmental materials is of interest because of the differing levels of toxicity exhibited by the various species. The average abundance of As in the earth's crust is 1.8 ppm, in soils it is 5.5 to 13 ppm, in streams it is < 2µg/L and in groundwater it is generally less than 100 µg/L. It naturally occurs in sulfide minerals such as pyrite. The predominant form between pH 3 and pH 7 is $H_2AsO_4^-$, between pH 7 and pH 11 it is $HAsO_4^-$ and under reducing conditions it is $HAsO_2$ (aq) or (H_3AsO_3). Aqueous arsenic in the form of arsenite, arsenate, and organic arsenicals may result from mineral dissolution, industrial discharges, or the application of pesticides. The chemical form of arsenic depends on its source (inorganic arsenic from minerals, industrial discharges, and pesticides; organic arsenic from industrial discharges, pesticides and biological action on inorganic arsenic).The toxicity of arsenic depends on its chemical form. Arsenite is many times more toxic than arsenate. The UNFAO recommended maximum level for irrigation waters is 100µg/L.

Copper

The average abundance of Cu in the earth's crust is 68 ppm; in soils it is 9 to 33 ppm; and in groundwaters it is < 0.1 mg/L. Copper occurs in native state, but is also found in many minerals, the most important of which are those containing Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes & to catalyze the oxidation of manganese. Copper forms a number of complexes in natural waters with inorganic and organic ligands. Among the common aqueous species are Cu^{2+}, $Cu(OH)_2$ and $CuHCO_3^+$.Copper is considered an essential trace element for plants and animals. Some compounds are toxic by ingestion or inhalation. The mean levels of copper vary from 6 to 60 ppm, being highest for the ferralitic soil group and lowest for sandy soils and organic soils. The UNFAO recommended maximum level for irrigation waters is 200µg/L.

Iron

The average abundance of Fe in the earth's crust is 6.22%; in soils it ranges from 0.5 to 4.3% and in groundwater it is 0. to 10 mg/L. Iron occurs in minerals hematite, magnetite, taconite, and pyrite. The solubility of ferrous ion (Fe^{2+}) is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron in groundwater is usually in the ferrous state. On exposure to air or addition of oxidants, ferrous iron is oxidized to ferric state (Fe^{3+}) and may hydrolyze to form red, insoluble hydrated ferric oxide. In the absence of complex forming ions, ferric iron is not significantly soluble unless the pH is very low. The UNFAO recommended level for irrigation waters is 5 mg/L. The US EPA secondary drinking water standard MCL is 0.3 mg/L.

Manganese

The average abundance of Mn in the earth's crust is 1060 ppm; in soils it ranges from 61 to1010 ppm and in groundwater it is <0.1 mg/L. Manganese is associated with iron minerals, and occurs in nodules in ocean, fresh waters and soils. The common ores are pyrolusite (MnO_2) and psilomelane. The common aqueous species are the reduced Mn^{2+} and the oxidized Mn^{4+}. The aqueous chemistry of Mn is similar to that of Iron. Since groundwater is often anoxic, any soluble manganese in groundwater is usually in the reduced state (Mn^{2+}). Upon exposure to air or other oxidants, groundwater containing manganese usually will precipitate black MnO_2. It is considered an essential trace element for plants and animals. The US EPA secondary drinking water standard MCL is 50μg/L.

Zinc

The average abundance of Zn in the earth's crust is 76ppm; in soils it is 25 to 68 ppm and in groundwater it is <0.1 mg/L. The solubility of zinc is controlled in natural waters by adsorption on mineral surfaces, carbonate equilibrium, and organic complexes. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life. The UNFAO recommended level for zinc in irrigated waters is 2mg/L. The US EPA secondary drinking water standard MCL is 5mg/L. Concentrations above 5mg/L can cause a bitter astringent taste and opalescence in alkaline waters.

Chapter 3

Study Area

With more than 5,000 inhabitants residing in 4 km^2 in area; Semria Ojha Patti is a small remote village along the bank of River Ganga located in the Ara sub division of Bhojpur. The area studied was the Semria Ojha Patti village in the Ara sub division of Bhojpur District of Bihar. Ara town is the headquarters of Bhojpur district at a Longitude of 83°-45' to 84°-45' East and the latitude is 25°-10' to 25°-40' North. The district is bounded in the north by the district of Saran (Bihar) and Balia district of Uttar Pradesh; in the south by the district Rohtas; in the West by the district Buxar and in the East by the district Patna, Jahanabad and Arwal. Bhojpur occupies a total of 2474 km^2.

The district is drained by two perennial rivers namely Ganges and Sone and their tributaries. The Ganges forms the northern boundary of the district. The low-lying rich alluvial plains in the north-eastern and owe their fertility to the river Ganges. The tributaries Chher and Banas fall into the Ganges. The Sone runs along the southern and eastern boundaries of the district of Bhojpur until it merges in the river Ganges near Maner in Patna district.

Agriculture is the primary activity. About 20 years ago, the large-diameter dug wells (~3 m) were abandoned and replaced by hand tube wells (in which subsurface water is withdrawn by a hand pump) as the primary water source.

Hydrogeology of the study area

Hydrogeologically, the various litho-units of the State can be grouped as unconsolidated/alluvial formation, semi-consolidated formations and consolidated/ fissured formations. The main alluvial tract covers entire north Bihar and a sizeable area south of the Ganga River. These alluvial formations constitute prolific aquifers with a tubewell yield between 120-247 m^3/hr. The Central Alluvial Plain extends from the Piedmont Plain to the exposed basement rocks of peninsular India across the axial river (cf. Singh, 2001). The Ganga alluvium is conventionally subdivided into the Older Alluvium (Pleistocene) and the Newer Alluvium (Holocene). The major parts of the Central Alluvial Plain consist of inter-fluve upland terrace surface (T,) mainly exposing the Varanasi Alluvium (Singh, 2001; Kumar et al., 1996; Kumar, 2003), which represents the upper unit of the Older Alluvium. The Newer Alluvium (Holocene), as distinct from the older unit, is characteristically unoxidised and consists of sand and silt-clay, which were mainly deposited in a fluvial and fluvio-lacustrine setting. The topmost few meters of the Newer Alluvium sediments cover all surfaces.

Soil Characterstics

The mid Gangetic plane consists of a thick alluvial mantle of drift origin (both new as well as old) overlying in most part. The soil is mainly young loam rejuvenated every year by constant deposition of silt, clay and sand brought by different streams. This soil is deficient in phosphoric acid, nitrogen and humus, but potash and lime are usually present.

Climatic Conditions

The climate of the district is of moderately extreme type. Summer begins about the middle of March, when hot westerly winds begin to blow during the day. The months of April and May are extremely hot. In a normal year, the monsoon sets in by the third week of June and the rains continue with intermissions till about the end of September or the early part of October. Winter begins from the month of November and lasts till the beginning of March. January is the coldest month when temperature comes down as low as 10 degree centigrade.

Rain Fall

Rains set in June accompanied by a fall in temperature and increase in humidity. The district experiences maximum rains during the months of July and August. The average rain-fall, in the normal conditions, recorded in these months is in the proximity of 300 mm. The district gets easterly winds from June to September, which brings rains, From October the direction of the winds is reversed and westerly winds blow till May. There is slight rainfall in October, but November and December are quite dry months. Some winter rain occurs in January and February.

Irrigational Facilities

The river Sone and Ganges are the perennial sources of surface water. They can provide irrigation to major portion of agricultural lands. In the "Pre-Zamindari Abolition" days the Zamindars used to maintain "Ahars" and Pynes" which served the purposes of both irrigation and drainage in certain pockets of the district. Ordinary wells also used to be a good source of irrigation.

The District Statistical Report published by the District Administration in the 2001, 15,493 hectors, and land is irrigated by big Sone canals, 14,940 hector, land is irrigated by middle Sone canals and 18,379 hectors, and land is irrigated by small canals. 2,582 hectors, land is irrigated by Govt. Electronic Tube wells and 2,099

Plate 1. Snapshots from study area

1. Drilling in progress

2. Person suffering from Arsenocosis

3. Core Sediments at sampling location

4. Person suffering from Keratosis

hectors, of land is irrigated by Govt. Tub wells operated by diesel. The area of land irrigated by private Electric Tube wells is 8,263 hectors. And 16999 hectors of land is irrigated by diesel operated private Tube wells 58,586 hectors of land irrigated by other sources or irrigation like Ahars, wells and ponds etc. Thus this statistics shows that 1, 77,341 hectors of land out of 2,37,526 hectors of land (75% of total area) is irrigated . It means 74.66 % land of the district is irrigated.

Land Use Pattern

In this district both the irrigated and un-irrigated areas except the small hills are being exploited for cultivation. Even some of the large ponds and "Jhils" which were duck-shooting areas have been de-watered and put to crop and grows "Boro crops". Intensive agriculture is also being attempted by what is popularly known as "Package Program". The remodeled Sone Canal System has the objective of bringing in more land under cultivation. Horticulture is spreading and orchards are springing up of all parts.

The District Statistical Report published by the District Administration of Bhojpur in the year of 2001 shows the area of different crops production i.e. Paddy-1,05,155 hectors, Wheat-67,259 hectors, Maize- 2,779 hectors, Barley-1,154 hectors Gram-5,017 hectors Peas-2,016 hectors, Arhar-919 hectors Masur-8,115 hectors Khesari-8,989 hectors Oil seeds (Sarso) 2,866 hectors Spices 31 hectors Vegetables 5,119 hectors, Fruits 2,651 hectors and Sugar cane 209 hectors.

Mines and Minerals

Mines and minerals resources in new Bhojpur district are very little. The only mineral product in this district is the sand from Sone river. About 40 kms length of Sone river forms the part of southern and eastern and eastern boundary of the district of Bhojpur. Out of 40 km, only managed sand collecting centre is Koilwar, which is only 5 Kms long.

Industrialization

After bifurcation of the old Shahabad district in the new district of Bhojpur and Rohtas the large scale industries generally fell in Rohtas district. There are, however, different types of small & cottage industries other than some agro-based industries located in the district of Bhojpur.

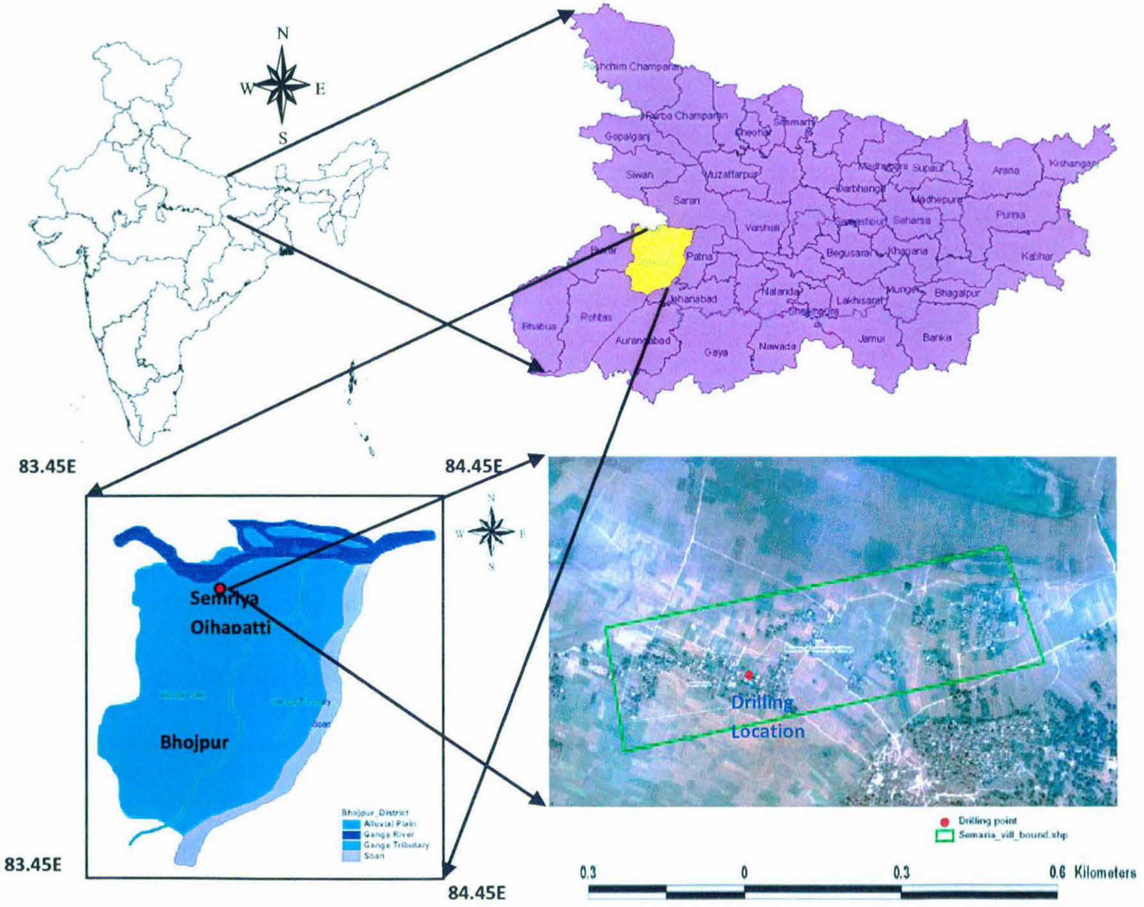


Figure 3.1 Map of study area Semria Ojha patti Village, Bhojpur District, Bihar

Chapter 4

Materials & Methods

It is an old axiom that the result of any testing method can be no better than the sample on which it is performed, therefore, the objective of the sampling is to collect minimum material yet large enough for analytical purposes to give accurate results. The most important approach should be to handle the materials sampled in such a way that no significant changes in the composition occur before the tests occur.

Sample collection and preservation

Sediment:

With the help of local drillers, one borehole was drilled to assess different lithological units and its relationship with different metals. The samples were collected every 1.5 m; and in total 22 samples were collected from single core sediment of upto 34 m. Only washed and disturbed sediments could be sampled as a result of the hand percussion technique. During drilling, the sediment colour and texture was noted. Washed sediments were collected in a bucket and allowed to settle before being transferred. At least, 250g of sediments were collected at each sampling depth.

Collected samples were preserved in ice chest till transfer to the laboratory where they were stored at 4°C until analysis.

Analysis of Sediments

Grain size analysis:

The mechanical analysis normally begins with sieve procedures, the separation of sediment samples into different size classes i.e.> 600μm, 300-600μm, 250-300μm, 125-250 μm, 63-125μm, 37-63μm, 25-37μm and < 25μm from homogenized sediment samples. After sediments separation via mechanical analysis Gradistat software was used to collect the relevant data regarding texture analysis.

The basic LOI method:

Determination of weight percent organic matter and carbonate content in sediments by means of LOI is based on sequential heating of the samples in a muffle furnace (Dean, 1974; Bengtsson and Enell, 1986) in the equations for calculation of LOI the weight loss is related to the wet weight of the sediment instead of the dry weight). After oven-drying of the sediment to constant weight (usually 12–24 h at ca.105°C) organic matter is combusted in a first step to ash at 550 °C. The LOI is then calculated using the following equation:

$$\mathbf{LOI_{550}= ((DW_{105}-DW_{550})/DW_{105})*100}$$

Where, LOI_{550} represents LOI at 550 °C (as percentage), DW_{105} represents the dry weight of the sample before combustion and DW_{550} the dry weight of the sample after heating to 550 °C (both in g). The weight loss should then be proportional to the amount of organic carbon contained in the sample and Dean (1974) showed a strong correlation between LOI at 550 °C and organic carbon content determined chromatographically in lake sediments.

In a second step, carbon dioxide is evolved from carbonate, leaving oxide and LOI is calculated as:

$$\mathbf{LOI_{950} = (DW_{550}-DW_{950})/DW_{105})*100}$$

Where, LOI_{950} is the LOI at 950 °C (as a percentage), DW_{550} is the dry weight of the sample after combustion of organic matter at 550 °C, DW_{950} represents the dry weight of the sample after heating to 950 °C, and DW_{105} is again the initial dry weight of the organic carbon combustion (all in g). Assuming weight of 44 g mol^{-1} for carbon dioxide and 60 g mol^{-1} for carbonate (CO_3^{2-}), the weight loss by LOI at 950 °C multiplied by 1.36 should then theoretically equal the weight of the carbonate in the original sample (Bengtsson and Enell, 1986). Again, LOI shows a good correlation with other methods of determining carbonate content of lake sediments (Dean, 1974).

Analysis of major and minor elements:

Analyses of Major and Minor elements were carried out by the two solution methods (Shapiro, 1975). Solution "A" was used for silica, Alumina and Phosphorus analysis and solution "B" was used for metal analysis.

Preparation of Solution 'A':

0.025 g of finely powdered sediment was taken in 50 ml Nickel crucible and 3-4 pellets of NaOH were added to it. The crucible was gently heated on a furnace in order to mix sediment melt pellets, and then the crucible was constantly heated to dull redness for

30 minutes. Then the crucible was allowed to cool down to room temperature. 10 ml of distilled water was added in the crucible and kept overnight. The solution was transferred to 250 ml volumetric flasks. 5ml of (1:1) HCl and 25ml of water was added. This solution was boiled till it was clear and the total volume was made up to 250 ml by adding distilled water.

0.1gm of finely ground sample was transferred to the Teflon crucible and 2ml of Aqua- regia (HNO_3 and HCl ratio 1:3) and 5ml HF were added to each crucible, these were then sealed in metallic cases. The crucible was heated for 1.5 hrs at 100°C and then allowed to cool down to room temperature. 5.6 g of Boric acid crystal (H_3BO_3) was dissolved in 20 ml distilled water and then added to the bomb content that was made up to 100ml. The solution was transferred to polypropylene bottles for storage. The sample was left undisturbed overnight to allow the formation and setting of borosilicate from the solution. The gelatinous precipitate is separated by centrifugation followed by filtration using Whattman 0.45μ cellulose nitrate filter paper.

Alumina Analysis:

15 ml of solution 'A' (Sample, Standard and Blank) was taken in 100 ml volumetric flasks. 2 ml calcium chloride solution (prepared by dissolving 7 gm $CaCO_3$, 100ml of water, and 15ml of conc. HCl and diluted to 500ml) was added. 1 ml of hydroxylamine hydrochloride solution (prepared by dissolving 5gm of hydroxylamine hydrochloride in 50 ml) was added by swirling the flask. 1 ml of potassium ferricyanide (0.75%) was added to each flask and mixed. 2 ml of Thioglycolic acid solution (4%) was added and kept for 5 minutes. 10ml of Buffer solution (prepared by dissolving 100gm of sodium acetate in water and adding 30gm glacial acetic acid and diluted to 500ml) was added and kept 10 minutes. 10ml of Alizarin Red-Solution (0.05%) was added to each flask and the volume was diluted to 100ml by adding distilled water. The samples were properly stirred and kept for 50 minutes. The absorbance was measured at 470 nm.

Phosphorus Analysis:

Total phosphorus in sediment was determined by Ascorbic acid method (APHA, 1998). Phosphate Standard solution ranging from 0.1 to 3 ppm was prepared using KH_2PO_4. 40 ml of each sample and standards solution was pipetted out in 50 ml volumetric flask and 5ml of Ammonium Antimony solution (prepared by dissolving 4.8 gm Ammonium molybdate and 0.1 gm potassium antimony tartarate in 400ml 4N H_2SO_4 and making the total volume to 500 ml with the same acid) and 2 ml of ascorbic acid solution (2 % w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 650 nm using spectrophotometer. A graph was plotted between phosphorus concentrations of the standards and optical density of samples The concentrations were obtained from this graph.

Sulphur:

% S content in the samples was determined using CHNSO Analyzer Model: Eura EA elemental Analyzer EA 3000 series based on Turboflash Combustion Technology installed in the CIF of School of Environmental Sciences. L-Cystine standard was used to calibrate the machine. The sample weighed in milligrams (approx. 35mg) housed in a tin capsule is dropped into a quartz tube at 950°C with constant helium flow (carrier gas). The standard deviation observed in the samples for S was 2.08%.

Total metal Analysis:

Analysis of heavy metals in the surface and core sediments as well as the analysis of grain size was carried out as per Shapiro (1975). 0.10 gm of finely ground sample were transferred to the Teflon crucibles and 2 ml of aqua regia (HNO_3 and HCl ratio 3:1) and 5 ml HF were added to each crucible, these were then sealed in metallic cases. The crucibles were heated for 30 minutes at 100°C and allowed to cool down to room temperature. 5.6 gm of Boric acid crystal (H_3BO_3) was dissolved in 2 ml distilled water and then added to bomb content which was made up to 100 ml. The solution was transferred to polypropylene bottles for storage. The sample was left undisturbed overnight to allow the formation and settling of borosilicate from the solution. This gelatinous precipitate was separated by 0.45 μm Millipore filter paper and the solution obtained was used for analysis of major and minor elements using Atomic Absorption Spectrophotometer (Thermo Scientific, M series AAS).

Standardization of AAS:

CRM 320 (BCR) riverine channel sediment standard, SRM 22.22 and VM-9 rock standards were digested as per the methods above. Heavy metals in the sediment extracts were analyzed by using Thermo Scientific, M series AAS. The instrument was standardized using elemental standard (Merck).

BCR Extraction Protocol

The extractants used, the extraction conditions and the metal species extracted are outlined in Table 1, and the extractions were performed as described below. The extraction procedure used in the present investigation was the modified BCR method

(Rauret et al., 1999). A batch of air-dried samples was used for BCR sequential extraction techniques. Blank extractions (without sample) were performed though out the complete procedure for each set of analyses. All extractions were performed by shaking in a mechanical, end-over-end shaker at a speed of 30 rpm at a room temperature (25-30°C).

Sequential extraction steps:

Step 1

A total of 40 ml of 0.11 M acetic acid was added to 1.0 g of air-dried IWS and CRM samples and this was then shaken for 16 h. The mixture was centrifuged to separate the extract from the residue.

Step 2

A total of 40 ml of freshly prepared hydroxyl ammonium chloride, adjusted with nitric acid to the pH 1.5, was added to the residue from Step 1, and the extraction was performed as above.

Table 4.1 BCR protocol for sequential extraction of metals

Step	Fraction	Extracting agent	Extraction conditions	
			Shaking time	Temperature
1	Exchangeable and acid-soluble	40 mL CH_3COOH (0.11 M, pH=7)	16 h	25–30°C
2	Reducible	40 mL NH_2OH–HCl (0.5 M, pH=1.5)	16 h	25–30°C
3	Oxidizable	10 mL H_2O_2 (30%, pH=2) and then 50 mL CH_3COONH_4 (1 M, pH=2)	1, 2, 16 h	30, 85, 30°C

Step 3

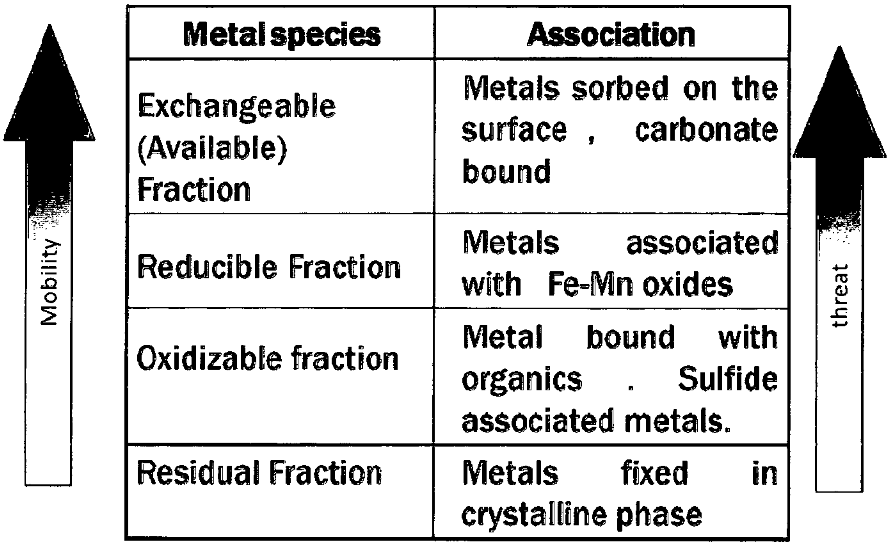
The residue from step 2 was treated twice with 10 ml 30% hydrogen peroxide, evaporated to near-dryness, and then 50 ml of ammonium acetate (adjusted to pH 2 with nitric acid) was added and the extraction was performed as above.

Between each extraction step, the residue was washed with ultrapure water, shaken for 15 minutes and centrifuged for 20 min at 3,000 rpm. The supernatant was carefully decanted and discarded to avoid the discarding any residue. This procedure was followed in order to remove any remaining reactants and metals present in the sediment residues from the previous extracts.

Table 4. 2 Association of different phases extracted

Metal Species	**Association**
Exchangeable (Available) Fraction	Metals sorbed on the surface, Carbonate bound
Reducible Fraction	Metals associated with Fe-Mn Oxides
Oxidizable Fraction	Metals bound with Organics and Sulfide
Residual Fraction	Metals fixed in crystalline phase

Table 4.3 Mobility potential of the metals in sediment



Metal species	Association
Exchangeable (Available) Fraction	Metals sorbed on the surface , carbonate bound
Reducible Fraction	Metals associated with Fe-Mn oxides
Oxidizable fraction	Metal bound with organics . Sulfide associated metals.
Residual Fraction	Metals fixed in crystalline phase

Step 4

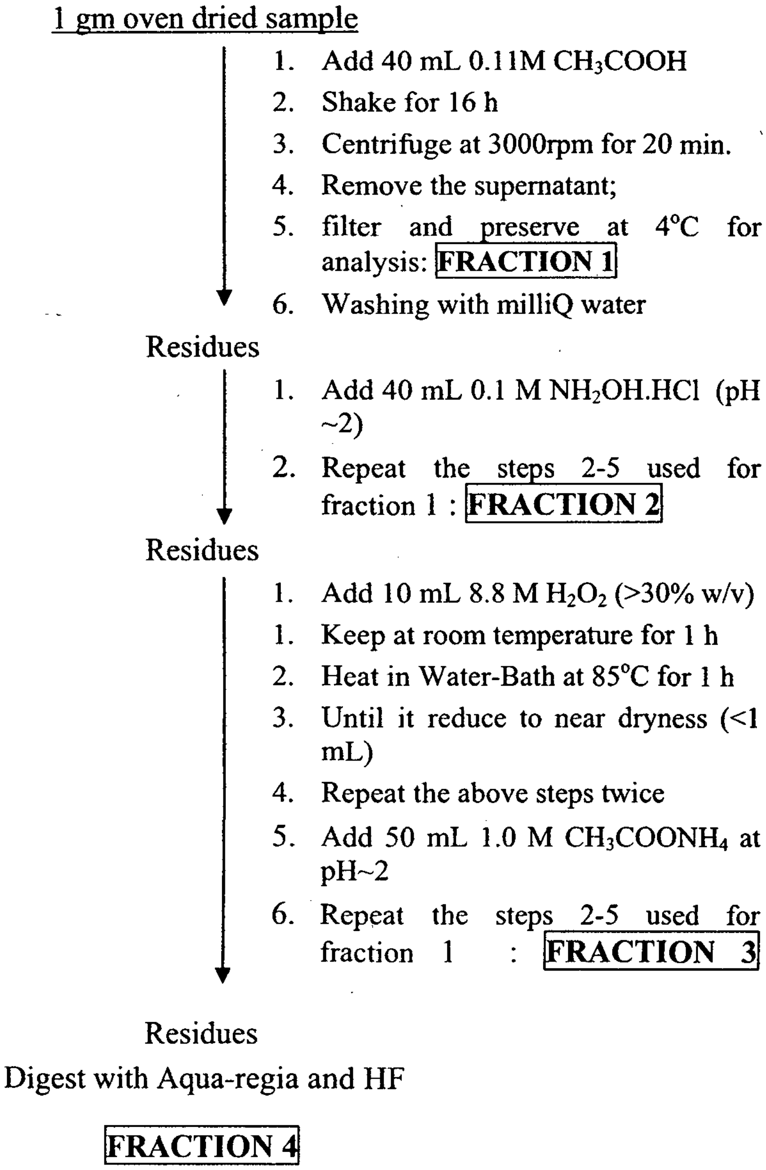
The residue from step III was digest by the method discussed for total metal analysis in sediments.

Softwares used

Study area map was geo-referenced by using Arcview GIS 3.2 package.

Statistical Analysis

With help of SPSS software different statistical analysis (factor analysis and Correlation matrix) have been done in order to well interpretation of data.



1 gm oven dried sample

1. Add 40 mL 0.11M CH_3COOH
2. Shake for 16 h
3. Centrifuge at 3000rpm for 20 min.
4. Remove the supernatant;
5. filter and preserve at 4°C for analysis: **FRACTION 1**
6. Washing with milliQ water

Residues

1. Add 40 mL 0.1 M $NH_2OH.HCl$ (pH ~2)
2. Repeat the steps 2-5 used for fraction 1 : **FRACTION 2**

Residues

1. Add 10 mL 8.8 M H_2O_2 (>30% w/v)
1. Keep at room temperature for 1 h
2. Heat in Water-Bath at 85°C for 1 h
3. Until it reduce to near dryness (<1 mL)
4. Repeat the above steps twice
5. Add 50 mL 1.0 M CH_3COONH_4 at pH~2
6. Repeat the steps 2-5 used for fraction 1 : **FRACTION 3**

Residues

Digest with Aqua-regia and HF

FRACTION 4

Figure 4.1 Flow diagram for Sequential extraction procedure for metals

Chapter 5

Results & Discussion

Granulometric Studies of the sediment core

Grain size analysis is an essential tool for classifying sedimentary environments. Grain size is the most fundamental property of sediment particles, affecting their entrainment, transport and deposition. Grain size analysis therefore provides important clues to the sediment provenance, transport history and depositional conditions (e.g. Folk and Ward., 1957; Friedman., 1979; Bui et al., 1990). Grain size distribution has been used for the determination of sedimentary environment with the help of log-probability studies. The entire grain size distribution is considered to be of several normal subpopulations representing the sediments transported by the process of rolling, suspension and saltation (Inman., 1949). Textural attributes of sediments and sedimentary rocks viz. Mean (Mz), Standard deviation (σ1), Skewness (SkI) and Kurtosis (KG) are widely used to reconstruct the depositional environments of sediments and sedimentary rocks (Amaral and Pryor, 1977). The size analysis of sediments from different depths in a core exhibits that more than 92% sand fraction in samples and in some cases even 100% of the samples come under the category of sand fraction while, a maximum of 12% of silt + clay fraction was observed in the sample (See Appendix-I).

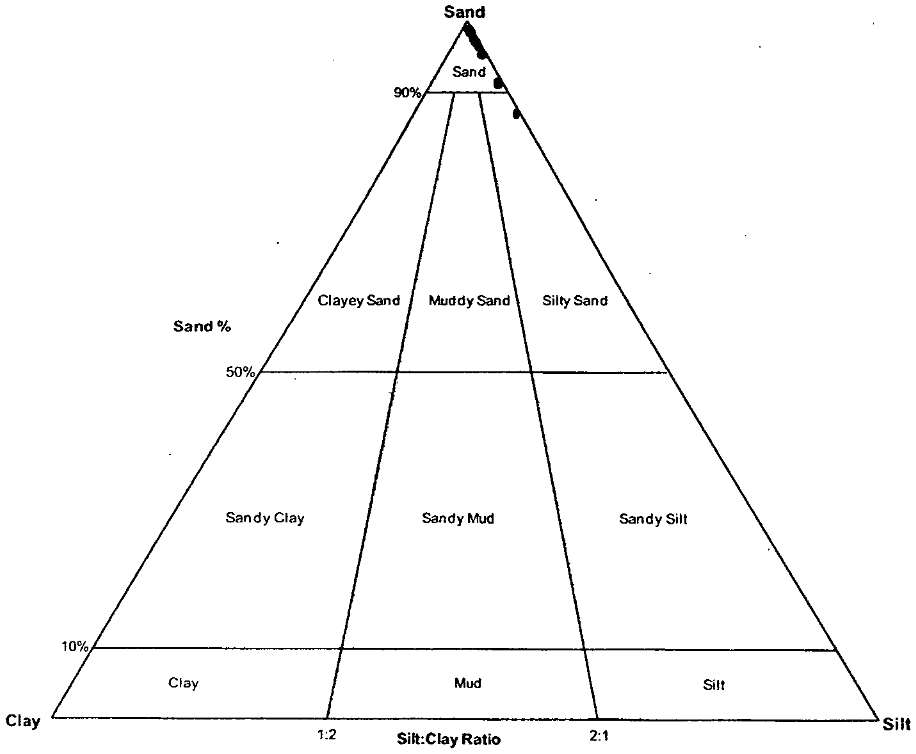


Figure.5.1: Sand, Silt and Clay ratio.

Mean (M_z)

It is the average size of the sediments and is influenced by the source of supply, transporting medium and the energy conditions of the depositing environment. Mean size indicates the central tendency or the average size of the sediment and in terms of energy; it indicates the average kinetic energy / velocity of depositing agent (Sahu., 1964).The average mean size (M_z) of all the sediment samples observed was 2.18ϕ while the maxima and minima values ranged from 3.53ϕ to 0.92ϕ respectively (See Appendix-I). The core sediments indicate the presence of coarse sand to very fine sand and the average size indicated the dominance of fine sand. The fine grain nature indicated the moderately low energy condition in the palaeo-flood plain deposits.

Standard Deviation

It is expressed by inclusive graphic standard deviation (σ_I) of Folk and Ward (1957), as it covers both the tails of the distribution. Standard deviation is a poorly understood measure that depends on the size range of the available sediments, rate of depositing agent and the time available for sorting. The sorting variations observed attributed to the difference in water turbulence and variability in the velocity of depositing current (Orton And Reading., 2006). The moderately well sorted character of the sediments indicated the influence of stronger energy conditions of the depositing agents or prevalence of strong energy conditions in the basin. The depth wise standard deviation values of the samples ranged between 0.47Φ to 1.32Φ. The average standard deviation value is 0.78Φ (See Appendix-I). About 28% of the sample indicates that they were poorly sorted and 45% shows moderately well sorted nature, while, 18% indicated moderately sorted nature and 9% showed well sorted nature. It indicates the episodic sediment deposition (recent Holocene) in the flood plains i.e. high discharges and low discharges over several decades in the region.

Skewness

It is used to determine the symmetry of the central part of the distribution. It reflects the symmetry or asymmetry of the frequency distribution of the sediments. It is the measure of particle size as it indicates that particles in excess of the normal distribution are present in coarser fraction or finer fraction, extremes of the distribution. If the skewness is negative, the sample is coarsely skewed, that is the mean is towards the coarser side of the median. When the skewness value is positive the sample is described as finely skewed. Coarsely skewed sample implies that the velocity of the depositing agent operated at a higher value than the average velocity for a greater length of time than normal and / or the velocity fluctuations towards the higher values occurred more often than normal (Sahu., 1964). The skewness values in the sediment samples ranges from a minima of -0.73Φ (at 24.5m) to 0.84Φ (at 33.5m) with an average skewness value of 0.12Φ (See Appendix-I). The values were indicative of very coarsely skewed and very fine skewed sediment samples. It also indicates the dynamic nature of flood plain deposits during monsoon and non monsoon period over the recent Holocene deposition.

Kurtosis

It is a measure of sorting of grain size. According to Folk (1966), it is also a function of internal sorting or distribution. The depth wise sediment kurtosis values ranges from a minima of 0.52 to a maxima of 6.19 with an average of 0.97. About 50% of the samples were very platykurtic, 32% are platykurtic, 9% are mesokurtic, 4.5% were leptokurtic and 4.5% were extremely leptokurtic in nature of distribution (See Appendix-I). The leptokurtic nature of the sediments indicated the higher kurtosis values and the mixing of a predominant population with very minor amounts of coarser and finer materials (Mason and Folk., 1958; Prabhakara Rao et al., 2001). The mesokurtic character of the sediments indicated moderate winnowing action of the depositing agent. The mesokurtic nature of the sediments in the study area suggested that the sediments achieved good sorting in the high-energy environment. Platykurtic nature indicated poor winnowing without any sorting, i.e. all size fractions jumbled up. The leptokurtic behaviour of the sediments also indicated the variations of the energy conditions of the environmental setup of depositions of the sediments. The leptokurtic character reflected the extreme skewness values, either positive or negative, indicating concentration of coarser and finer grained materials finally showing the impact of fluctuation of energy condition in the deposition of the sediments from most of the formations. The coarse grained character showed the influence of higher energy conditions and accumulation of finer materials show the influence of moderate to low energy conditions in the environmental setup showing the leptokurtic character of the sediments. Thus, it can be concluded that the aquifer sediments are dominated by silty fine sand material with little amount of coarse and medium sand and clay with less sorting and winnowing in the aquifer sediments.

Geochemical Characterization of sediment

Soil Moisture

The samples are oven dried at 105°C for 24 hours; the resulting loss in weigh of the samples gives the % soil moisture content in the sample. The soil moisture content varies with grain size of the sediments as the finer fraction like clay holds more water than the coarser fraction like sand this could be attributed to the less porosity of the sediments samples of finer fractions like clay and vice versa.

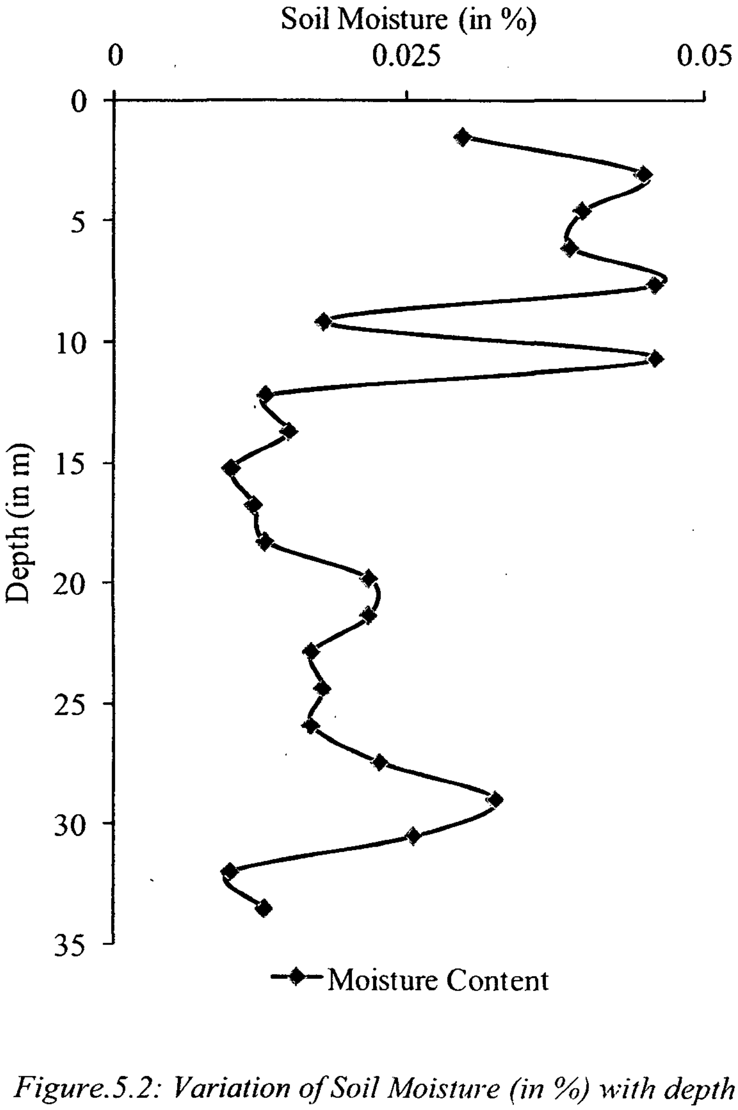


Figure.5.2: Variation of Soil Moisture (in %) with depth

As can be seen in the figure 5.2, the average value of % soil moisture observed was 0.024% while maxima and minima value observed were 0.046% and >0.01% at 7.62m and 32.02m respectively. The lower value of % soil moisture content could be attributed to its being directly in contact with the atmosphere thus contributing factors like evaporation from top surface layer could be the reason. From 12m to 26m there appears a constant decrease in the soil moisture which could be due to these layers being rich in sand and lower in clay content, while there appears a peak at 29m which is in conformity with % soil moisture content this could be attributed to the presence of patch of clay layer. The higher values observed in the samples up to a depth of 10.67m could be attributed to the fact that the site of drilling was earlier part of meandering of river Ganga and later there could have been the formation of ox bow lake, thus showing higher moisture holding capacity due to its being rich in clay fraction.

Organic Content

Organic content (OC) is an important soil constituent that influence physical properties, nutrient status and biological activity of soil. High content of functional groups, primarily Carboxyl, COOH renders OC capable of forming strong complexes with elements (Stevenson, 1994). Soil rich in OC has a high water holding capacity and was observed to sustain vegetative zones during dry summers, while soil with significantly less OC failed to do so (Kumpiene et al., 2005). Loss of OC is characteristic for contaminated soils (Viventsova et al., 2005), as toxic levels of metals hinder soil biological activity, vegetation development and generation of OC.

Figure 5.3 represents the variability of OC (% Organic content of the sediments). The average value of OC observed in the sediments was 3.01, while, the maximum and minimum values observed were 7.37 and 1.0 at 7.62m and 30.50m respectively. The top layer of the sediment sample is dry due to less % soil moisture content thus, decreasing the microbial activity in the region. The layers up to 7.62m are comparatively higher in organic content of the soil; this could be attributed to anoxic conditions (Weiner, 2000) finer grain size and due to the possibility of sampling site being part of the reclaimed natural pond which supports domestic sewage of the neighbouring houses. As can be seen in the figure 5.3, the values of OC is high up to the depth of 8m (i.e. approx. 25 feet) after this the value of OC continuously decreases except at a depth 29m. The decrease in the value of OC at 7.62m onwards could be attributed to the constancy in the grain size of the sediments in the core, as at these depths the % sand content is almost constant being around 99% while there appears an increase at a depth of 28.97m which is due to the presence of higher silt and clay content at this depth. Since, silt and clay fractions are finer in grain size thus have higher surface area which provides higher capacity to hold more organic content than the coarser fraction like sand (Hiscock, 2005; Singh et al., 1998). Clay, can increase the element retention capacity of OC by forming ternary clay-metal-organic matter complexes (Arias et al, 2002).

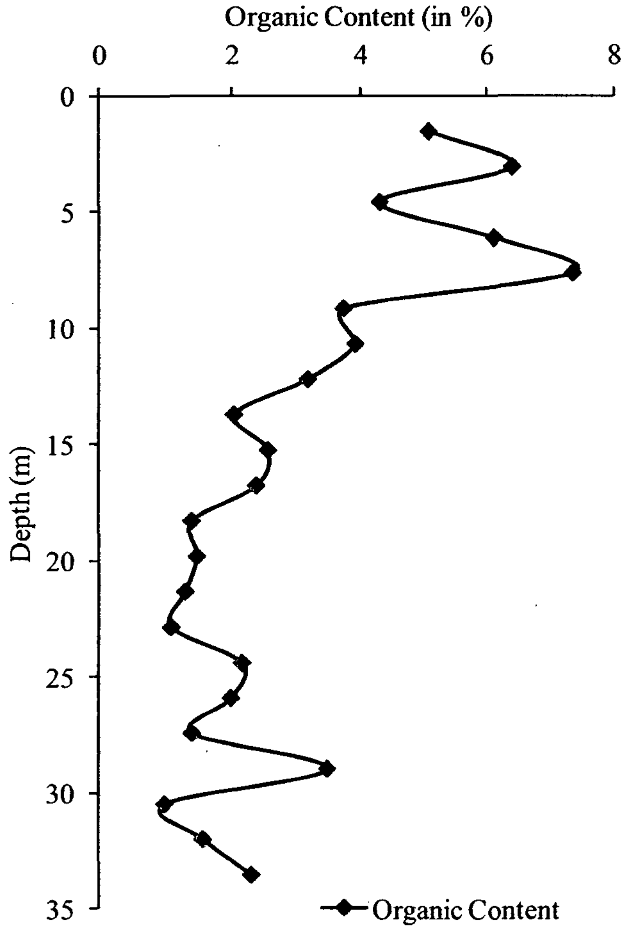


Figure. 5.3: Variation of Organic content (OC; in %) with depth

Carbonate content of the core sediments

Figure 5.4 depicts the variability of the % carbonate content with depth in the sediment samples. As can be seen in the fig, the value of %Carbonate content increases continuously from 21m to 33.5m. The average % carbonate value obtained is 3.97% in the samples while the maximum attained % carbonate in the samples is 13.83% while, the minimum is 0.53% at 33.55m and 9.15m respectively. The carbonate concentration is increasing in deeper layers but there appears a minima at 29m which means that at this depth the %carbonate content is low while the % Organic content is high at this depth which conforms with the presence of clay layer there, as the % soil moisture and %organic content is also high at this depth. The higher carbonate content in the deeper layers suggests net kankar domination due to deposition and also indicative of drier period that might have existed in the past in that region.

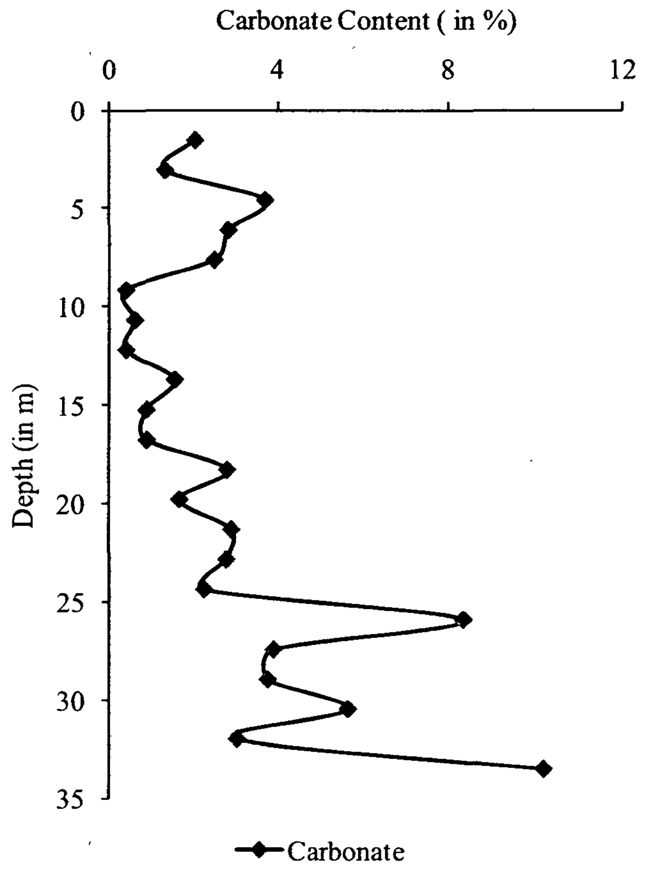


Figure. 5.4: Variation of Carbonate content (in %) with depth

Sulphur

In sediments, Sulphur exists as sulphate, sulphite and sulphides depending on the E_h and pH conditions of the soil. In sediments, precipitation of sulphides is considered the dominant mechanism limiting the solubility of many trace elements. Sulphide coordination is particularly strong for metals exhibiting chalcophilic character.

As shown in the figure 5.5, the highest concentration of Sulphur measured was 5.37 % at a depth of 7.6m while, the lowest concentration of sulphur measured was 0.44 at a depth of 19.4m. The average % of sulphur measured was 1.525% (See Appendix-II).

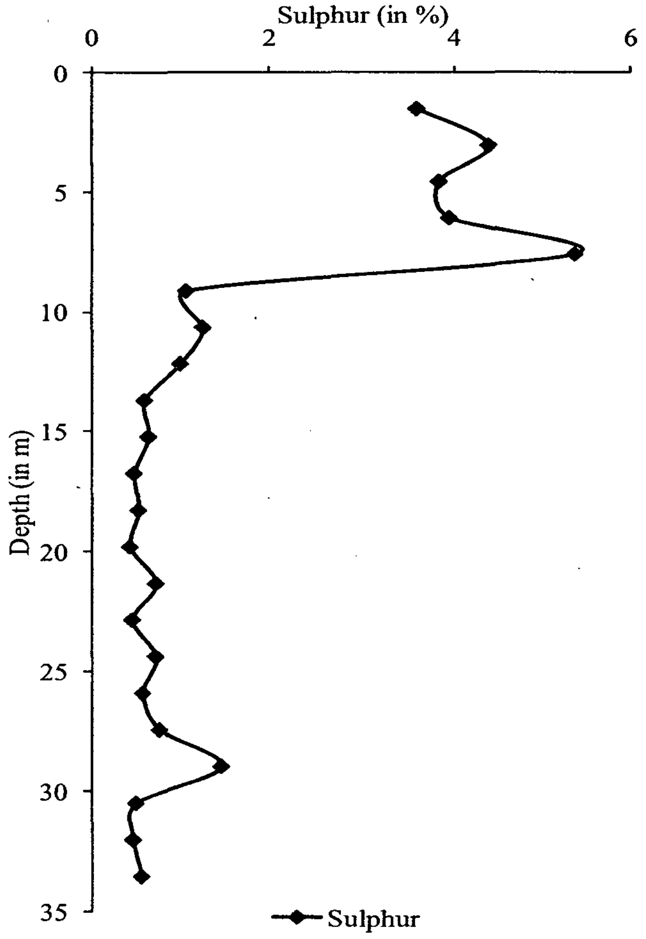


Figure. 5.5: Variation of Sulphur (in %) with depth

Sulphur and OC follow the same trend, thus, suggesting a common source. As can be seen in the figure, it is the upper layers where the availability of OC and redox conditions supplement each other thus, can be said to govern the Sulphur and OC concentration. The higher percentage of sulphur in the upper layers can also be attributed to the presence of high amount of clay and silt in the upper layers (as shown in the figure 5.6). Blackening of soils, wastewater, sludge, and sediments in locations with standing water, is an indication that sulphide is present (Essington, 2005). The black material results from a reaction of H_2S with dissolved iron and other metals to form precipitated ferrous sulphide (FeS), along with other metal sulphides (Essington, 2005). As the place of drilling is the region where, a portion of natural pond has been reclaimed, this increase in sulphur concentration could be attributed to presence of clay (as for the formation of a water body for holding water the prerequisite is the presence of clay in the top layers of the core whereas, in the deeper layers of the core the value of Sulphur decreases constantly except showing a peak at

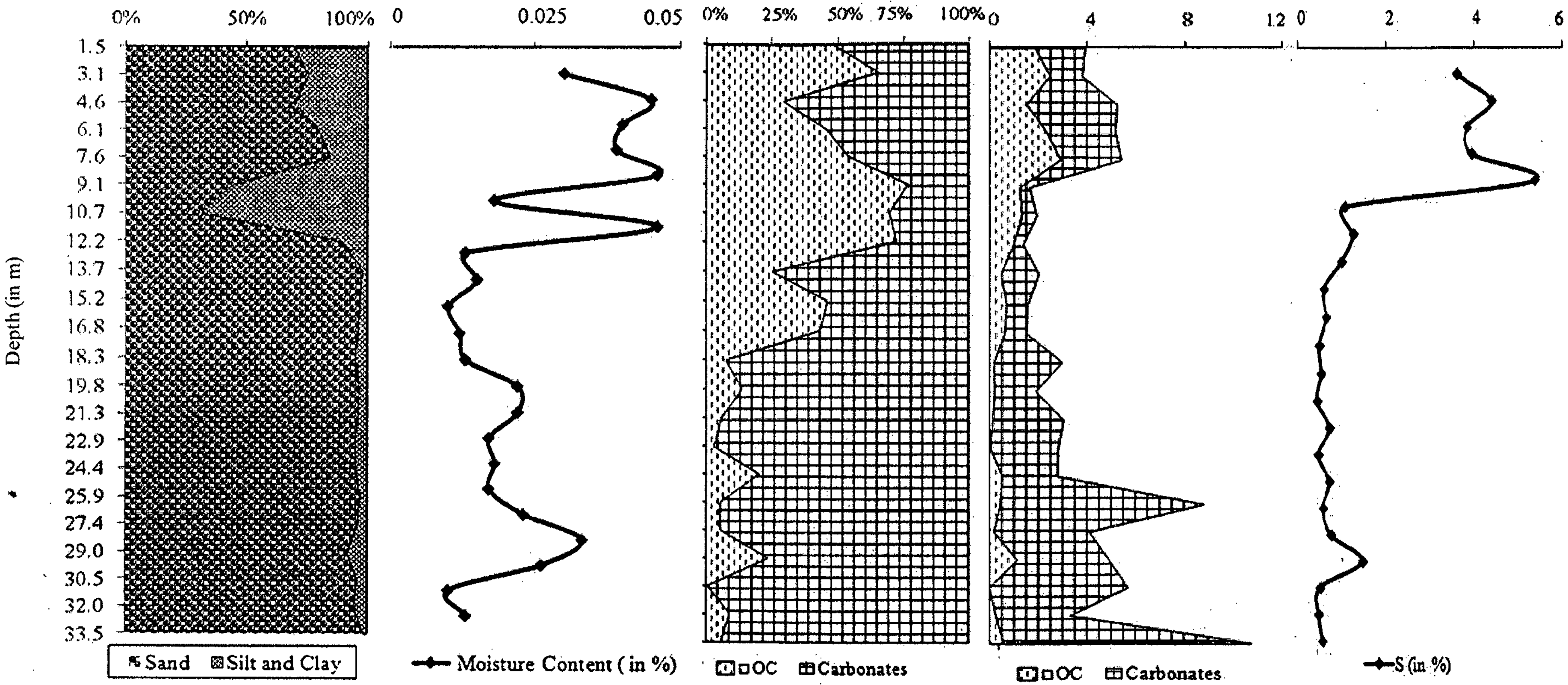


Figure. 5.6: Comparison of physico-chemical properties of sediments with depth

29m this could be attributed to a slight increase in the silt and clay content in that region in comparison to other deeper layers; this may suggest the presence of clay in that part of the core sediment.

As shown in the figure 5.6, the availability of % Moisture content in the soil, % organic content, % carbonate content and % Sulphur shows a well coordinated relationship with the grain size at different depths of the core sediments. As can be seen in the figure, there is higher % of silt and clay in the upper layers of the core sediments up to 12.2m and corresponding to this there is higher moisture content in combination with higher organic content and higher % sulphur content up to that depth. The variation in the graph after 12.2m follows the background concentration for % silt and clay in association with % moisture, organic content and % sulphur content. Thus, it can be said that the reason for such a variation could be due to the occurrence of coherent source. So, availability of sand, silt and clay fractions regulates the availability of moisture, organic content and sulphur along with the anoxic conditions in the sediment core.

Variation of Metals in core sediments

Variation of four metals and one metalloid (i.e. Fe, Mn, Zn, Cu and As) in the sediment core is shown in figure 5.7 indicating the variability of different metals in different fractions with respect to the depths at which the samples were taken. In total there have been five fractions which have been identified for each metal, out of these five the two Pseudo total and Residual have been extracted via digestion while the rest three Available or Exchangeable, Reducible and Oxidizable have been extracted via SM&T (formerly BCR) protocol for sequential extraction.

Iron (Fe) is one of the important elements in redox processes of a sediment-water system. This is not only due to their chemical reactivity, but also their abundance in natural waters and sediments. As can be seen in the figure 5.7, the variation in the concentration of Fe in the top layers of the core (up to 7.62m) could be attributed to the anthropogenic sources as it shows good association with sulphur content of the soil, thus being sulphide bound in the top layers due to this layer being rich in organic content. High levels of Fe are most likely due to chelation with natural organic matter (Koretsky et al., 2006). After the depth of 7.62m the Fe attains background concentration of the sediments and remains almost constant except a small peak at 30.5m. The high concentration of Fe at this depth could be attributed to

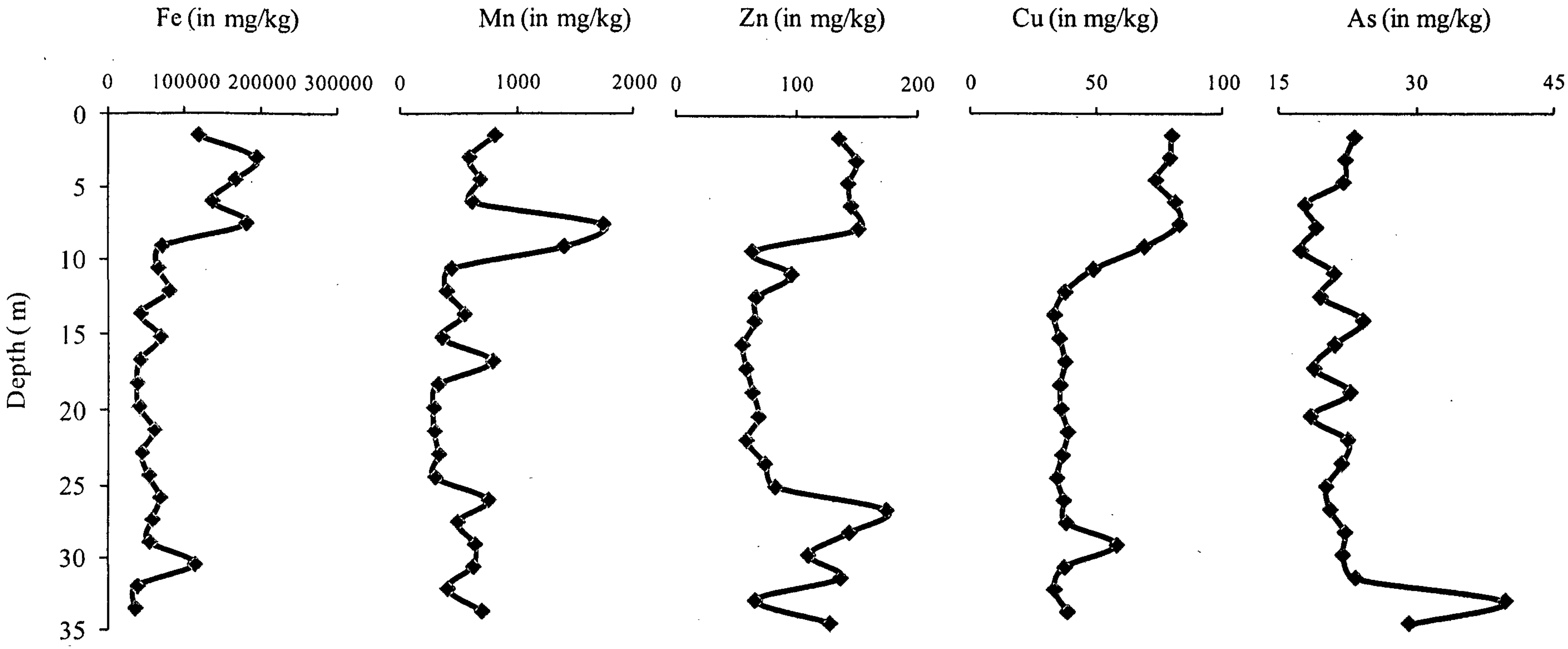


Figure. 5.7: Variation of metals (in mg/Kg) with depth

the presence of minerals siderite (e.g. Sphaerosiderite); this could be due to the fact that Fe shows strong correlation with carbonate at 30.5m and is not associated with sulphide as shown in the variation of sulphur with depth. Sphaerosiderite, a morphologically distinct millimeter-scale spherulitic siderite ($FeCO_3$), forms predominantly in wetland soils and sediments (Stoops, 1983; Landuydt, 1990; Ufnar, 2003). Sphaerosiderites are an important geochemical archive of 'greenhouse-world' palaeohydrological information (Ludvigson et al., 1998) and have been used to improve our understanding of mid-Cretaceous (Albian) humid continental palaeo-environments (e.g. Ufnar et al., 2001; White et al., 2001). Reductive dissolution of FMO (Fe-Mn Oxide) should mobilize associated metals, which, like Fe (II) or Mn (II) may diffuse upwards into a more oxidizing zone, where they could be reincorporated into fresh FMO (Koretsky et al., 2006).

Manganese (Mn) is a lithophile element. In suboxic or anoxic sediments, Mn is most often found in association with carbonate phases (Davison, 1993; Otero et al., 2003; Bottcher et al.,1998). The variation of Mn (see figure 5.7) in the sediment samples is in conformity with the Fe concentration and appears to be bound to the sulphur, thus sulphides due to the presence of high organic content in the top layers from anthropogenic sources like domestic sewage. In suboxic or anoxic sediments, Mn is most often found in association with carbonate phases (Davison, 1993; Bottcher et al., 1998 ; Otero et al., 2003). Mn is not typically associated with organic matter (Davison, 1993). Higher values of Mn from 25.92m onwards could be attributed to precipitation of reduced Mn (II) to form either rhodochrosite or a solid solution with calcite, as the concentration of Mn shows good correlation with Carbonates (see figure 5.6-5.7) at depths > 25.92m onwards.

Zinc (Zn) is a chalcophile and likely forms distinct sulphide phases, rather than being incorporated into pyrite (Huerta-Diaz, 1992; 1998; Achterberg, 1997, Morse, 1999).The concentration of Zn strongly follows the trend being followed by carbonates (see figure 5.6-5.7) in the sediments with depth this could be attributed to the fact that Zn under anoxic conditions is found in association with sulfides and carbonates (Davison., 1993; Bostick., 2001). Zn also has a strong affinity for organic matter (Achterberg et al., 1997; Warren., 2001; El Bilali et al., 2002).

Copper (Cu) is a chalcophile element with a very strong affinity for organic matter and sulphides (Stumm, 1996). In reducing sediments, Cu may form discrete Cu sulfide minerals (Balistrieri et al., 1992; Achterberg et al., 1997 and Morse et al., 1999) or may be associated with pyrite (Huerta-Diaz et al., 1992; Otero., 2003). Copper is frequently complexed to organic matter (Kadlec et al., 1986; Coetzee, 1993 and El Bilali et al., 2002). It is sometimes associated with FMO and may form ternary complexes with organic matter bound to FMO (Tessier et al., 1996). Thus, reductive dissolution of FMO can release Cu-organic complexes that subsequently associate with sulfides (Achterberg, 1997). As shown in the figures 5.6-5.7, the value of total copper varies in close coordination with the % sulphur content. The concentration of Cu continuously increases initially which could be attributed to its contribution from anthropogenic factors. The maximum concentration of Cu is observed at 7.62m then its concentration continuously decreases in the sediments and achieves background concentration, although their appears a peak at 28.97m which could be attributed to the presence of sulphide minerals of Cu as the variability of Cu is in good accordance with the %S content in the sediments, which could be contributing to the reducing conditions in the aquifer sediments. Thus, the presence of sulphide minerals of copper could be the reason of its abundance in the sediments.

As shown in the figure 5.7; the value of **Arsenic** (As) reaches maxima at 32.02m else there appears a discontinuous trend of increasing and decreasing concentration throughout the depth of the core sediments. The concentration of Arsenic in the soil matrix is considerably high in the soil as the concentration of As reaches as high as 40ppm at a depth of 32m, and the average concentration that is present in the sediment samples is equivalent to 21.5ppm. The concentration of As is in general not following any specific trend with the presence of Fe, Mn and % S content but it is geogenically associated in the aquifer sediments (Figure 5.6-5.7).

Statistical evaluation of the core sediments

Correlation analysis

The correlation plot shown above represents the correlation of total metals (Cu, Zn, Fe, Mn) and a metalloid As vs. Carbonate and Sulphur vs. OC of the sediment samples (Table 5.1). As can be seen in the correlation matrix above there exists a strong correlation of the sulphur with metals Fe, Mn, Zn and Cu as well as with that of OC; thus the correlation matrix suggests that the source of these metals could be the same in the sediment samples and are strongly affiliated to the source of organic content of the aquifer sediments.

Table. 5.1: Correlation matrix for core sediments (n=22)

	Fe	Mn	Zn	Cu	As	OC	Carbonate	Sulphur	T.P	Alumina
Fe	1									
Mn	0.47	1								
Zn	**0.65**	0.38	1							
Cu	**0.83**	**0.62**	**0.54**	1						
As	-0.25	-0.24	-0.07	-0.29	1					
OC	**0.82**	**0.60**	0.49	0.92	-0.29	1				
Carbonate	-0.10	0.04	**0.55**	-0.18	0.34	-0.25	1			
Sulphur	**0.92**	**0.54**	**0.60**	**0.93**	-0.22	**0.93**	-0.15	1		
T.P	**0.58**	0.46	0.30	**0.69**	-0.32	**0.64**	-0.48	**0.67**	1	
Alumina	0.38	0.02	0.36	0.34	0.29	0.41	0.09	0.45	0.12	1

The correlation matrix also shows the strong correlation of metal Iron with that of Zn, Cu and OC (Organic content) and % of sulphur in the sediment samples. Thus, such a trend confirms the presence of organic content in the aquifer sediments and its association with other metals as organic ligands enhance metal sorption to mineral surfaces through formation of ternary complexes (Arias et al, 2002). Similarly, Mn shows strong correlation with Cu, OC and S; while Zinc shows strong correlation with Cu, Fe, Carbonate, OC and S in the sediments. The reason for the association of Zn-Fe, Zn-Cu, Zn- OC and Zn- S can be attributed to the coherence of source of release of these metals in the sediments, while, the association of Zn- Carbonate can be attributed to occurrence of $ZnCO_3$ mineral. On the other hand, Cu shows strong correlation with Fe, Mn, Zn, OC and S in the sediments. Cu being a chalcophile has strong tendency to bind with sulphides. Cu can be easily mobilized when associated with dissolved OC of the sediments (Stumm, 1996).

Total phosphorus shows strong correlation with Fe, Cu, OC and Sulphur this clearly indicates that the Phosphorus present in the aquifer sediments is bound to the Fe hydroxide fraction. Phosphate has a strong tendency to interact with ferric iron to form a "mixed" ferric hydroxo-phosphate precipitate (Stumm and Morgan, 1970). The affinity of phosphate and other potential organic or inorganic ligands for Mn (IV) is less than for Fe (III) thus showing moderate correlation with Mn. Phosphate anions may be taken from water by alumina, kaolinites and monmorillonites (Chen et al., 1973) and also by precipitated ferric and aluminium hydroxides (Carritt and Goodall, 1954; Hsu, 1965). The strong correlation being shown by Total Phosphorus with Cu, OC and S suggests that the Total Phosphorus present is organically bound in the aquifer sediments and have a coherent source.

Principal Component Analysis

Principal components analysis (PCA) is an exploratory, multivariate, statistical technique that can be used to examine data variability. Multivariate techniques can consider a number of factors which control data variability simultaneously (Boruvka et al., 2005) and therefore offer significant advantages over univariate techniques, where errors associated with repeated statistical testing can occur (Manly, 1997). Environmental applications of PCA are varied and widespread and the technique has been applied to surface and groundwaters (e.g. Chen et al., 2007; Kuppusamy and Grirdhar, 2006), soils (Boruvka et al., 2005; Zhang, 2006), sediments (Emmerson et al., 1997; Spencer, 2002) and biota (Yawei et al., 2005). Typically, PCA has been used to examine the spatial variability of contaminants (Alvarez-Iglesias et al., 2003; Backe et al., 2004). However, increasingly it has also been used to discriminate between contaminant sources (Kim et al., 2006; Mudge and Duce, 2005) and to identify key variables for environmental monitoring purposes (Carlon et al., 2001; Shin and Lam, 2001)

Table.5.2: Principal Component Analysis of the core sediments

	Component		
	1	2	3
Fe	0.91	-	-
Mn	0.59	-	-
Zn	-	0.75	-
Cu	0.95	-	-
As	-	-	0.95
OC	0.95	-	-
% Carbonate	-	0.95	-
% S	0.98	-	-
% variance	57.34	20.22	9.96
Cumulative %	57.34	77.57	87.53

(n=24, Rotation Method: Varimax with Kaiser Normalization)

The first principal component, or factor, accounts for the greatest variability in the data, and there can be an infinite number of new factors with each accounting for less data variability than the previous (Webster, 2001). Factor loadings are correlation coefficients between the original variables and factors and are frequently used in the literature to investigate the processes that control data variability.

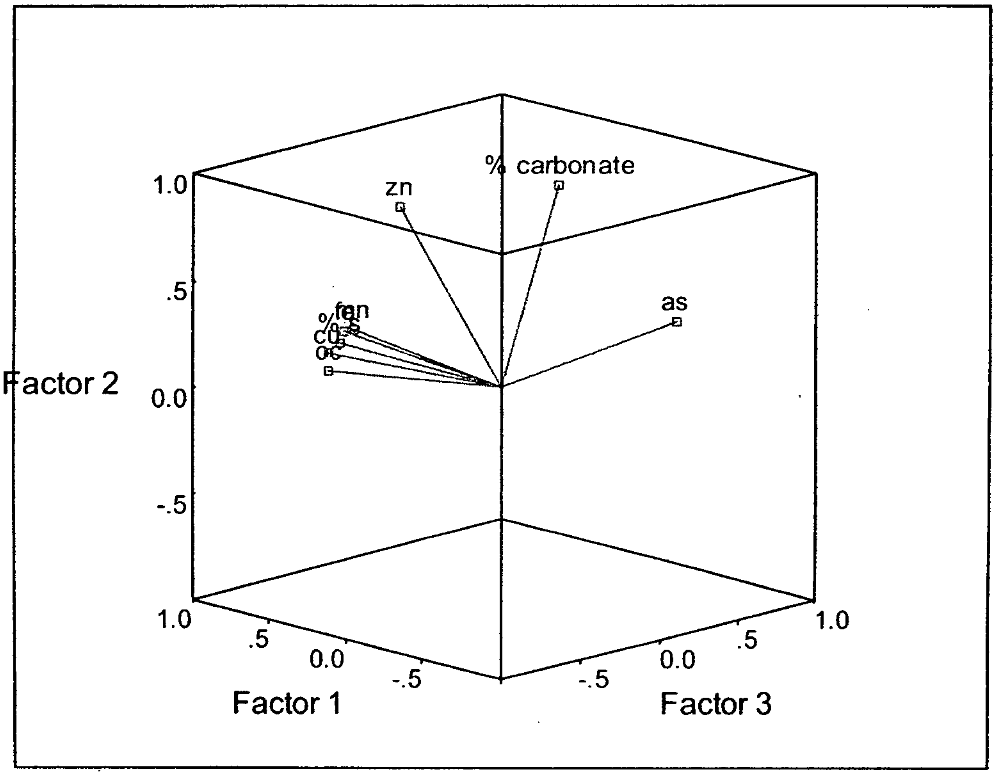


Figure.5.8: Component plot of the observed factors for core sediments.

Factor scores indicate how strongly individual samples are associated with each of the factors, and thus can be used to investigate similarity between samples, where samples with a similar composition will have similar scores and may therefore have similar contaminant sources and/or behaviour (Figure 5.8). Factor 1 explained 57 % variability of the data. It included Fe, Mn, Cu, As, OC, and % S. This suggested the apart from the presence of sulfide (due to prevailing redox condition), organic matter played an important role in controlling the metal concentration. Second factor explained 20% of the variability in data and suggested the zinc is mostly present as carbonate form. Third factor explained the 10 % of the data and included arsenic (Table 5.2).

Geochemical Indices

Index of Geoaccumulation (I_{geo})

In order to understand the level of contamination with respect to trace metals, the values of trace metals were utilized to find geoaccumulation index(I_{gco}) While computing the (I_{gco}) of sediments of the study region, world average concentrations of these elements reported for Shale (Turkian and Wedephol, 1961) were taken as the background values.

Possible sediment enrichment of metals was evaluated in terms of the I_{gco} of Muller (1979). The formula used for the calculation of

$$I_{geo} = \log_2 (Cn/1.5Bn),$$

where Cn is the measured content of element

''n'', and Bn the element's content in ''average shale'' (Turekian and Wedepohl, 1961). The geoaccumulation index (I_{geo}) was originally defined by Muller (1979) for a quantitative measure of the metal pollution in aquatic sediments (Ridgway and Shimmield, 2002)

Table. 5.3: Igeo values and assessment of sediment quality

Description of sediment quality	Igeo
Extremely Contaminated	>5
Strongly to extremely strongly contaminated	4 to 5
Strongly contaminated	3 to 4
Moderately to strongly contaminated	2 to 3
Moderately contaminated	1 to 2
Uncontaminated to moderately contaminated	0-1
Uncontaminated	<0

As shown in the table 5.4, the Geo Accumulation Index of the sediment samples shows that the Fe is responsible for moderately contaminating sediment quality at 3.05m, 4.57m and 7.62m. The sediment samples show uncontaminated to moderately contaminated sediment quality for all the metals.

Table. 5.4: Index of geoaccumulation (I_{geo}) for core sediments

Depth (in m)				I_{geo} Class			
	6	5	4	3	2	1	0
1.52						Fe, As, Cu	Mn, Zn
3.05					Fe	Cu, As, Zn	Mn
4.57					Fe	Cu, As, Zn	Mn
6.10						Fe, Cu, Zn, Mn	As
7.62					Fe	Cu, As, Zn	Mn
9.15						Mn, Cu	Fe, Zn, As
10.67						As	Fe, Mn, Zn, Cu
12.20						Fe, As	Mn, Zn, Cu
13.72						As	Fe, Mn, Zn, Cu
15.25						As	Fe, Mn, Zn, Cu
16.77							Fe, Mn, Zn, Cu, As
18.30						As	Fe, Mn, Zn, Cu,
19.82							Fe, Mn, Zn, Cu, As
21.35						As	Fe, Mn, Zn, Cu
22.87						As	Fe, Mn, Zn, Cu
24.40						As	Fe, Mn, Zn, Cu
25.92						Zn, As	Fe, Mn, Cu
27.45						Zn, As	Fe, Mn, Cu
28.97						As	Fe, Mn, Zn, Cu
30.50						Fe, As	Mn, Zn, Cu
32.02						As	Fe, Mn, Zn, Cu
33.55						As	Fe, Mn, Zn, Cu

Enrichment Factor

The enrichment factor (EF) was based on the standardization of a tested element against a reference. A reference element is the one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe (Reimann et al, 2000; Schiff et al., 1999 and Sutherland, 2000).

$$EF = \frac{(\frac{M}{Al})sediments}{(\frac{M}{Al})shale}$$

Where, M is the concentration of the element examined and Al represents the concentration of Aluminium in sediments and shale respectively. Five contamination categories are recognised on the basis of the enrichment factor (Buat- Menard et al., 1979).

Table.5.5: Enrichment Factor classification.

EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5- 20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Table.5.6: Enrichment Factors for core sediments.

Depth (in m)	**Fe**	**Mn**	**Zn**	**Cu**	**As**
1.52	11.23	4.27	6.4	7.94	8.04
3.05	4.87	0.82	1.87	2.08	2.04
4.57	3.38	0.77	1.44	1.56	1.63
6.1	5.98	1.5	3.17	3.73	2.86
7.62	7.23	3.86	3.01	3.47	2.78
9.15	19.38	21.37	8.72	19.82	17.46
10.67	1.88	0.7	1.38	1.46	2.2
12.2	18.85	5.31	7.94	9.28	16.94
13.72	3.98	2.87	3.07	3.23	8.21
15.25	4.52	1.34	1.84	2.43	5.08
16.77	2.75	2.89	1.93	2.56	4.5
18.3	1.98	0.95	1.66	1.92	4.3
19.82	12.62	4.97	10.65	11.64	20.92
21.35	-15.5	-4.2	-7.52	-10.32	-21.02
22.87	3.34	1.39	2.79	2.87	6.01
24.4	1.67	0.52	1.29	1.12	2.3
25.92	10.17	6.31	13.02	5.78	11.26
27.45	2.75	1.3	3.4	1.88	3.84
28.97	2.28	1.5	2.3	2.54	3.35
30.5	17.53	5.38	10.51	5.98	13.09
32.02	1.21	0.71	1.03	1.08	4.49
33.55	1.17	1.27	2.09	1.31	3.46

The metal enrichment factor for five metals was calculated and it was found that the values of these metals at different depths show considerable enrichment showing moderate to significant metal enrichment in the aquifer sediments. The sediment at the depth of 21.34m shows negative value for metal enrichment which may be due to absence of alumina for reaction kinetics at that depth. The values do not follow any specific trend but there is considerable capacity for metal enrichment in the aquifer sediments which may pose a threat in the future due to heavy enrichment.

Geochemical fractionation of metals (BCR Sequential Extraction)

Knowledge of total metal concentration in the sediments does not help in understanding their bioavailability and mobilisation in aquatic environment. Though the total metal concentration levels in sediments may be useful for global budget calculation, it provides little information on the potential availability of metals to biota under various environmental conditions. The mobility of trace metals, as well as their bioavailability and related eco-toxicity to system critically depends upon the chemical forms in which metals are present in the sediments (Davidson et al., 1994). Change in the environmental condition (such as pH and redox condition) may result in mobility of the metals in the sedimentary environment thus supporting the theory of chemical time bomb. Sequential extraction studies were undertaken to understand the present geochemical association as well as to predict the probable mobile fraction (if there is change in land use pattern or so).

Iron

Based on the geochemical characteristics of the samples at different depths the concentration of Iron in different extracted fractions follows following trend (see figure 5.9):

Residual > Reducible > Available > Oxidizable

The presence of Fe as residual fraction contributes > 91% thus, is the most dominant phase, while, rest other fractions i.e. Reducible, Available and Oxidizable together contributes 9%. The presence of Fe as residual fraction depicts that it is bound to the silicate and detrital material of the sediments.The concentration of heavy metals in the crystalline fraction is largely controlled by the mineralogy and the extent of weathering. Heavy metals in this form are not soluble under experimental conditions

Figure. 5.9: Geochemical fractionation of Iron (in mg/Kg) in core sediments

and hence may be considered to be held within the mineral matrix. (Tessier et al., 1993; Ure and Davidson., 1995 and Chakrapani et al., 2007).

The second most dominant fraction is Reducible phase. This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation (Bordas and Bourg, 2001) and acts as a significant sink for heavy metals. All the samples of the core follow a significant trend for the concentration of reducible Fe excluding the sample at the depth of 7.62m, the abnormally highly value of Fe at this depth falls in conformity with the concentration of % moisture as well as % S content in the sediments i.e. it shows strong correlation with LOI and %S content of the sediments thus, it can be assumed that the Fe at this depth is associated with the organic matter as well as Sulphur which may be in the form of Pyrite. Hence giving an abnormally high value for Fe at 7.62m else it follows a regular trend which could be the value of background matrix being contributed through primary or secondary minerals.

The third most dominant fraction in the aquifer sediments is Available phase; it is the phase which includes exchangeable as well as the Carbonate phase. The metals in this phase are weakly bound and are most bioavailable (Baruah et al., 1996). The concentration of Fe in the upper layers is lower than that of Oxidizable fraction, but in the deeper layers the available fraction is more than that of oxidizable fraction which is the least abundant phase (bound to organics and sulphides), this could be attributed to the correlation of Fe with LOI and % S content in the sediments and the presence higher % of finer grain particles (silt and clay) in the top layers of the sediments.

Manganese

Mn is abundant in the Earth's crust (Serife et al., 2000) and its abundance in different phases is follows the following trend (see figure 5.10):

Residual > Available > Reducible > Oxidizable

The most abundant phase for Mn observed is both residual as well as the available phase (avg. concentration being approx. equivalent), this could be due to the chemical probabilities of Mn (Wang Hal et al., 2002 and Liu Enfeng et al., 2005). The abundance of Mn in the available phase in BCR sequential extraction is due to the occurrence of both exchangeable as well as Carbonate bound fraction. The relatively high concentration of exchangeable manganese suggests that the metal exists in the

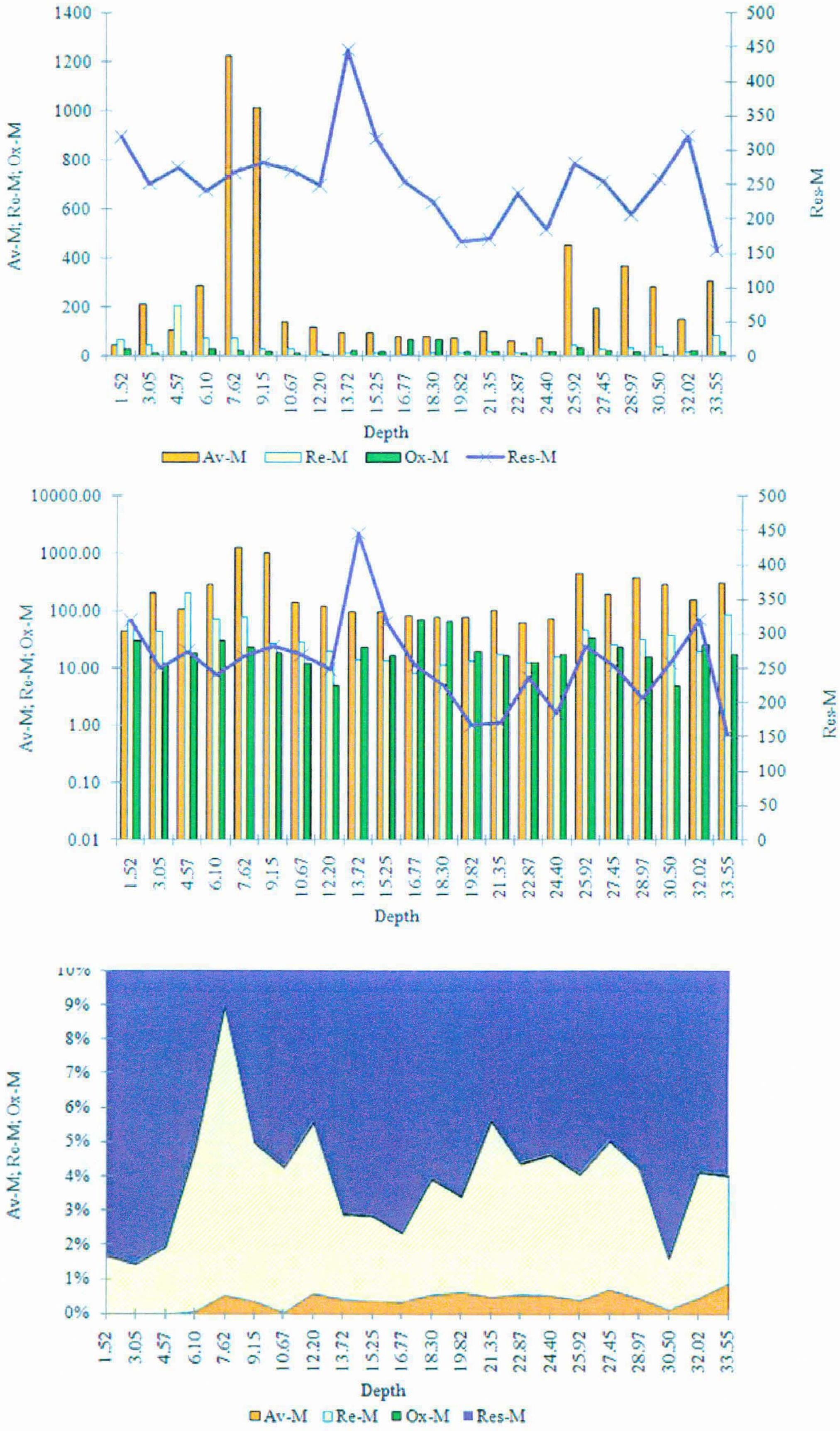


Figure. 5.10: Geochemical fractionation of Manganese (in mg/Kg) in core sediments

reduced form (Tessier et al., 1979). Mn^{2+} can easily be adsorbed on the surface of fine granules than other ions; the oxidation of Mn^{2+} is more relaxed than Fe^{2+}, and at lower pH (< 8) Mn^{2+} can be easily associated with carbonates (Liu Yingjun et al., 1984). Another feature is that the radius of Mn^{2+} (0.91) is similar to that of Ca^{2+} (1.08) and Mg^{2+} (0.8), so the replacement of Ca^{2+} and Mg^{2+} by Mn^{2+} is easier (Enfeng, 2005). Mn is a mobile trace metal that has great affinity to mix up with oxygen (Karbassi, 2004). All the above properties may be the reasons for higher Mn contents in the exchangeable/carbonate form in the sediments, while its abundance in the residual fraction represents that the metal is bound within the mineral matrix and remains attached to the silicate or detrital material of the sediments.

For Mn, after Residual and Available the most abundant phase is Reducible phase this is the phase which represents the association of metals with Fe-Mn (hydr)oxide the lower abundance of this could be attributed to less occurrence of finer grain particles (silt and clay) in the sediment samples, while, Mn has got least abundance in the Oxidizable phase, which suggests that the Mn is least associated in the Organic and Sulphide form fraction.

Zinc

The fractionation profile of Zn shows that the concentration of Zn in different extracted fractions follows the following trend (see figure 5.11):

Residual > Available > Reducible > Oxidizable

As per the fractionation profile of Zn the residual fraction is the most abundant thus is bound to the silicates and detrital materials in the sediments and cannot be remobilized under normal conditions encountered in the nature (Forstner, 1980; Ure, 1990; Jain et al., 2007).

The second most available fraction in the sediment profile is that of Available phase which includes the carbonate fraction as well, Carbonate association with Zn is due to the relatively high stability of $ZnCO_3$ under the pH - Eh conditions of common inland waters, as well as its characteristic co-precipitation with $CaCO_3$ (Salomons and Mook, 1978; Deurer et al., 1978) extremely important because it represents the proportion of heavy metals that can be easily remobilized by changes in environmental conditions such as pH, redox potential, salinity, etc. The relatively higher percentage of carbonate fraction for Zn is most likely the result of a similarity

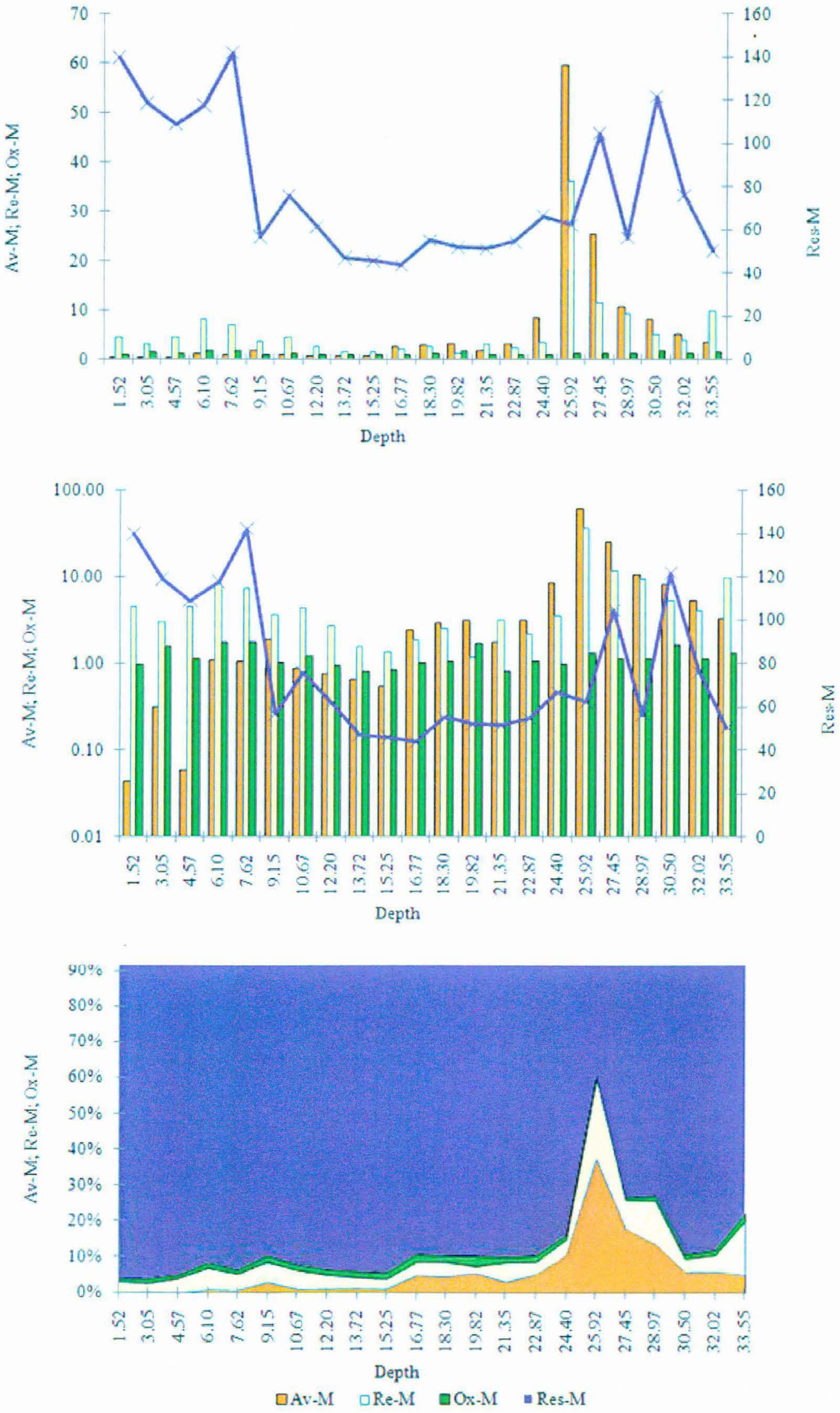


Figure. 5.11: Geochemical fractionation of Zinc (in mg/Kg) in core sediments

in their ionic radii to that of calcium in the carbonate phase (Pederson and Price, 1982; Zhang et al., 1988). The association of Zn with the carbonate fraction is also reported by many workers (Modak et al., 1992; Vaithiyanathan et al., 1993; Panda et al., 1995).

The relatively high concentration of exchangeable Zn may be due to the increase of clay and silt fractions, which act as an adsorbent, retaining metals through ion exchange and other processes (Riemer and Toth., 1970; Nriagu, 1979; Gupta and Harrison., 1981).

The third most abundant fraction in the sediments was that of Zn; Zn associated with the Fe-Mn (hydr) oxide bound fraction is caused by the adsorption of these metals by the Fe–Mn colloids ((Jenne, 1968) and there exists a considerably good correlation of Zn with Fe. The oxidizable fraction is least abundant for Zn thus not bound to sulphides and organics.

Copper

In the sediment profile of Cu for different extracted fractions follows the following trend (see figure 5.12):

Residual > Reducible > Available > Oxidizable

The most abundant fraction for Cu was observed in the Residual phase. The residual or lithogenic fraction is a major carrier of transition metals in most aquatic systems. The concentration of heavy metals in the crystalline fraction is largely controlled by the mineralogy and the extent of weathering. Heavy metals in this form are not soluble under experimental conditions and may therefore be considered to be held within the mineral matrix. Absolute concentrations of metals within this fraction are not affected by anthropogenic inputs (Gibbs, 1977).

The second most abundant fraction in the sediment profile for Cu was observed to be that of Fe-Mn hydr (oxide) i.e. the reducible phase of the sediments under oxidising conditions, constitutes a significant sink for heavy metals in the aquatic system (Gibbs, 1977). This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation and is sensitive to redox potential. The higher concentration of Cu associated with this fraction may be caused by the adsorption of these metals by the Fe-Mn colloids (Jenne, 1968). The dominant role played by Fe-Mn oxide phase in the heavy metal distributions of sediments has

Figure. 5.12: Geochemical fractionation of Copper (in mg/Kg) in core sediments

been reported for a number of rivers (Modak et al., 1992; Salomons and Forstner., 1984; Brook and Moore., 1988).

The third most abundant fraction for Cu is Available phase; Metals in this fraction are the most mobile and readily available for biological uptake in the environment (Gadde and Laitinen, 1974). The relatively higher percentage of carbonate fraction for Cu is most likely the result of a similarity in their ionic radii to that of calcium in the carbonate phase (Pederson and Price, 1982; Zhang et al., 1988).

The least abundant fraction for Cu is oxidizable, though the Cu shows strong correlation with organics and sulphides but for the sediments of this region they do not act as significant scavengers.

Arsenic

The fractionation profile of As shows that the concentration of As in different extracted fractions follows the following trend (see figure 5.13):

Residual > Reducible > Available > Oxidizable

The average arsenic content is 21.5 mg/kg, close to the ordinary level (typically 5–10 mg/kg) in modern unconsolidated sediments (Smedley and Kinniburgh, 2002), indicating that the high concentration of arsenic in groundwater is not due to abnormally enriched arsenic content in the aquifer sediment.

As per the fractionation profile of As the residual fraction is the most abundant thus is bound to the silicates and detrital materials in the sediments and cannot be remobilized under normal conditions encountered in the nature (Forstner, 1980; Ure, 1990; Jain et al., 2007). The second most abundant phase is that of Reducible As since, Iron oxyhydroxides in aquifer sediments were found to be the most important sorbents for arsenic. Both arsenite and arsenate show strong affinity for the surfaces of iron oxyhydroxides (Manning et al., 1998; Raven et al., 1998; Dixit and Hering., 2003; Root et al., 2007). Xie et al. (2008) proposed that Fe-oxyhydroxides are the major phase retaining As in the sediments and reduction of As-bearing iron oxyhydroxides is the primary reason for the occurrence of high arsenic groundwater. Iron rich mineral phases and iron oxyhydroxides are the major sequestrator of arsenic in aquifer sediments (Manning et al., 1998; Raven et al., 1998; Dixit and Hering, 2003; Root et al. 2007).

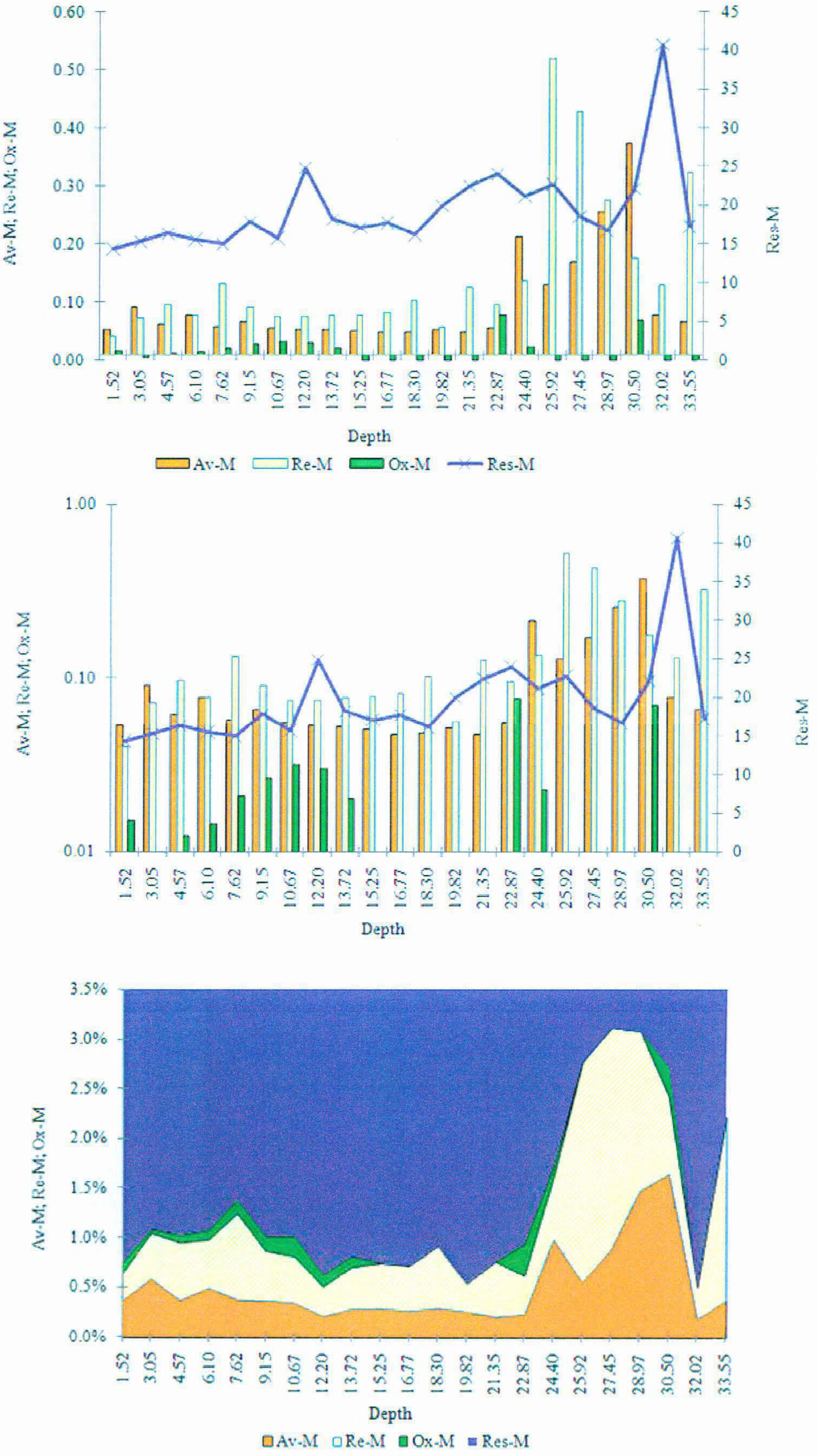


Figure. 5.13: Geochemical fractionation of Arsenic (in mg/Kg) in core sediments

As can be seen in the figure, a considerable % of As is present in the Available fraction which is easily exchangeable during the sediment-water interaction, thus, posing a threat for severe groundwater contamination in the future with changing redox conditions in the aquifer sediments. The oxidizable fraction occurs in significantly lower concentrations, thus indicating that As is not organically bound in the aquifer sediments.

Comparison with the aquifer sediments of Gangetic Bengal basin:

The aquifer sediment conditions in the region are very similar to that found in the deltaic plains of Ganges and Brahmaputra in the West Bengal and Bangladesh. The type of aquifer sediments are Holocene alluvial/deltaic sediments with abundance of solid organic matter in it with pH being neutral to slightly alkaline for water in the region. The affected aquifers are generally shallow (less than 100–150 m deep), of Holocene age and comprise micaceous sands, silts and clays deposited by the Ganges, Brahmaputra and Meghna river systems and their precursors. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. In most affected areas, the aquifer sediments are capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. This, together with the presence of recent solid organic matter deposited with the sediments, has resulted in the development of highly reducing conditions which favour the mobilisation of As.

The mobilisation has probably occurred by a complex combination of redox changes brought on by rapid burial of the alluvial and deltaic sediments, including reduction of the solid-phase As to As(III), desorption of As from Fe oxides, reductive dissolution of the oxides themselves and likely changes in Fe-oxide structure and surface properties following the onset of reducing conditions (BGS and DPHE, 2001). Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As because of competition for adsorption sites.

Average Variation of Metal fractionation

As shown in the Figure 5.14 and 5.15; all the metals (Fe, Zn, Cu, As) show their maximum concentration in the Residual phase thus are found to be bound to the silicates and remain in the mineral matrix and thus not easily available to the biota. Mn is the only metal with its availability being maximum in the Available

(Exchangeable) phase, suggests that the metal exists in the reduced form (Tessier et al., 1979). Mn^{2+} can easily be adsorbed on the surface of fine granules than other ions. Another feature is that the radius of Mn^{2+} (0.91) is similar to that of Ca^{2+} (1.08) and Mg^{2+} (0.8), so the replacement of Ca^{2+} and Mg^{2+} by Mn^{2+} is easier (Enfeng, 2005).

Although, as suggested by the concentration values for different heavy metals it is clear that after residual phase; reducible and available fractions are the phases which contribute significantly to the concentration of heavy metals in the aquifer sediments, these are the phases which are bound to Fe-Mn oxides and carbonate with labile phase respectively.

Recovery (Total metal digested vs. Sum total)

The plot shown in the Figure.5.16 shows, the relationship between the Σ metal observed after sequential extraction and the Pseudo total metal present in the sediment (via aqua-regia digestion). The graph show mild variability in the amount of Σ metal obtained and the pseudo total metal present in the samples this could be attributed to the over recovery and under recovery of metals during sequential extraction. The recovery of metal in the surface as well as core sediment was from 90% to 120%. The Davison et al. (1998) suggested that because of the extreme recovery of metal during fractionation, the sum total may far exceed the pseudo total, where as lower recovery might be due to various reason, such as sample loss during one fraction to other fraction extraction or during shaking (Tokalioğlu et al., 2000) or due to other technical error during analysis.

FTIR Spectra of core sediments

FTIR studies of these adsorbents help in the identification of various forms of the minerals present in the silt and clay fraction. Infrared (IR) spectroscopy has been for decades a frequently used method to investigate the structure, bonding and chemical properties of clay minerals. The coupled vibrations are appreciable due to the availability of various constituents. Nevertheless, observed bands (in the range, 4000–450 cm^{-1}) have been tentatively assigned. The kaolinite showed a characteristic peak between 3695- 3601 cm^{-1} and shoulder peak at 542 cm^{-1} while Illite was observed at 3441 cm^{-1} with supporting peak at 1042 cm^{-1}.

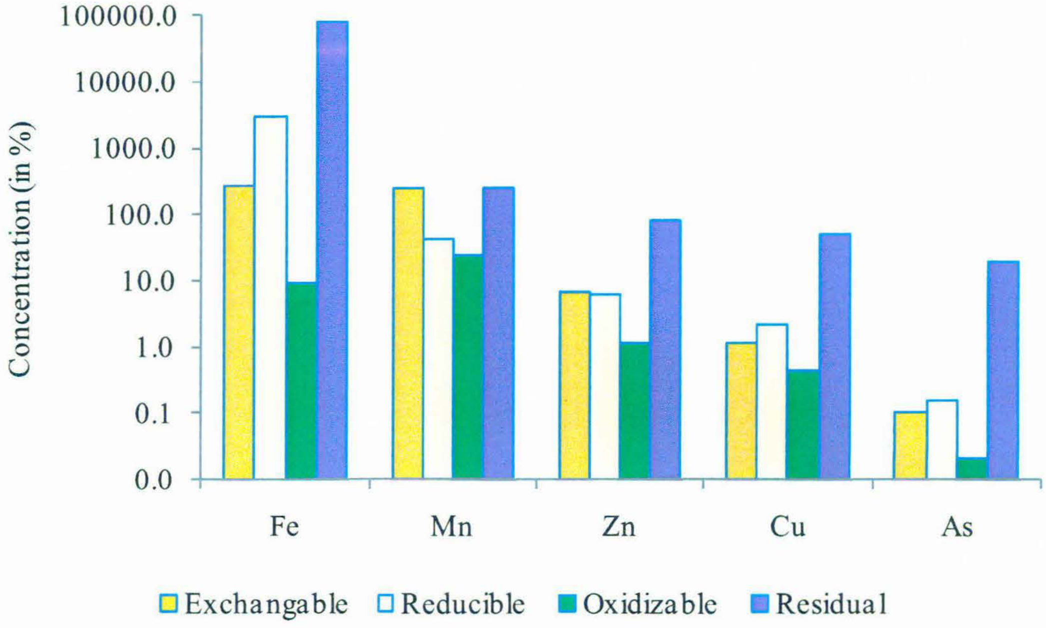


Figure.5.14: Average concentration (on log scale) of extracted fractions of Fe, Mn, Zn, Cu and As

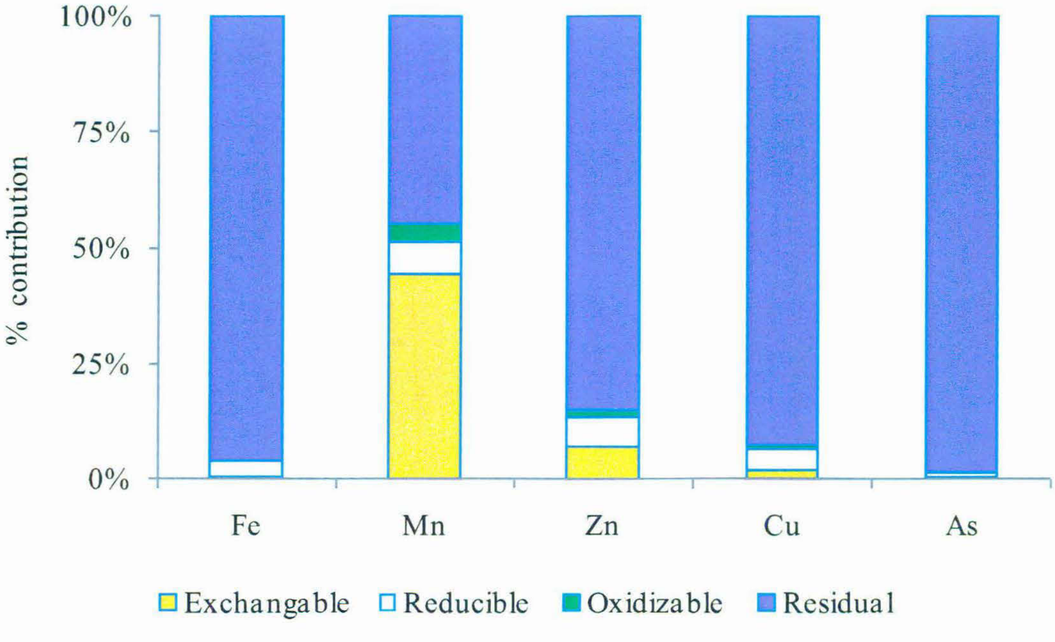


Figure.5.15: Average concentration (in %) of extracted fractions of Fe, Mn, Zn, Cu and As

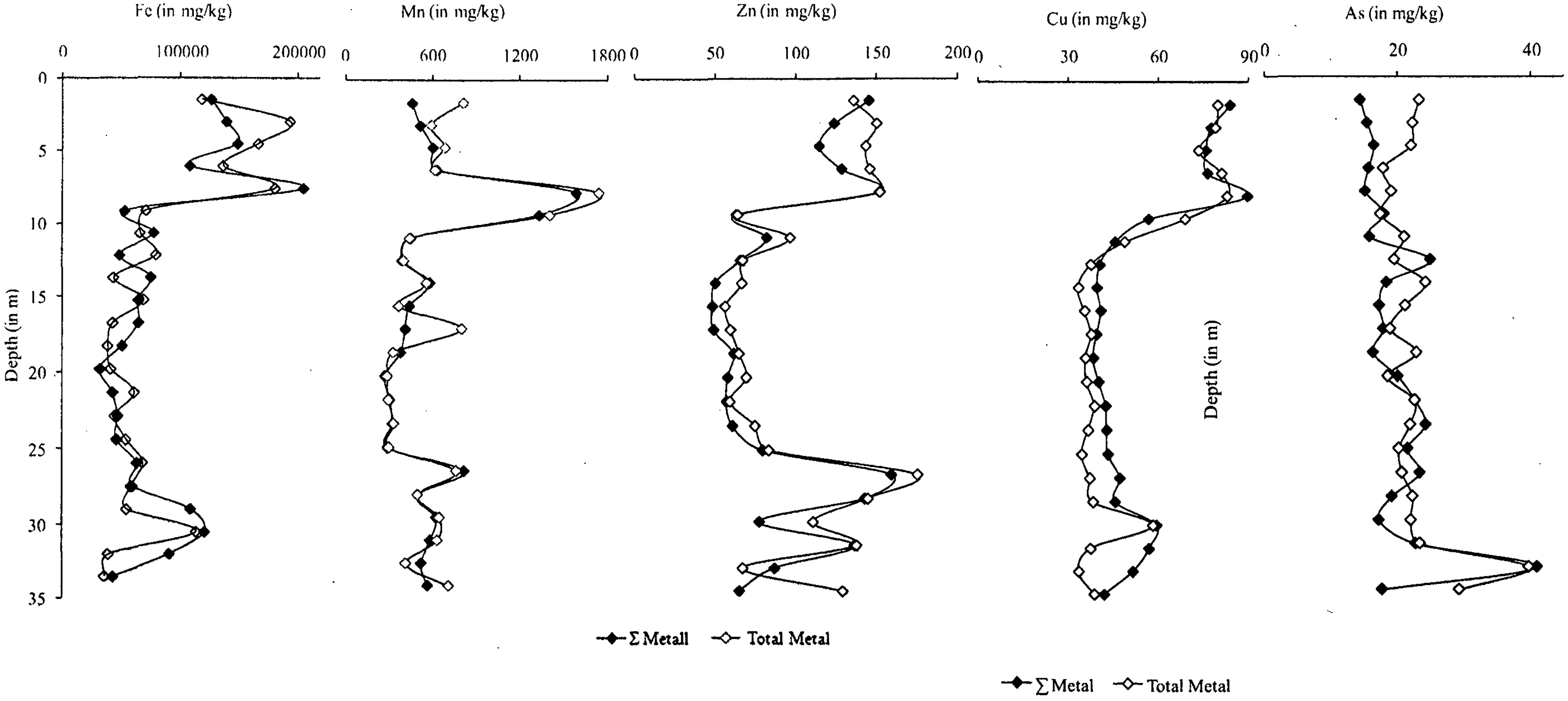
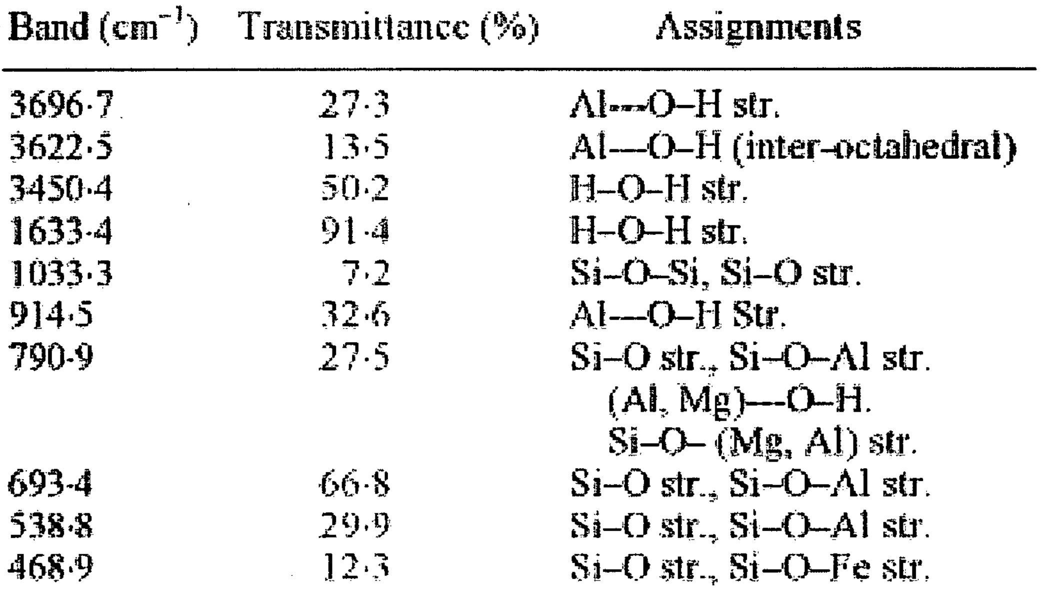


Figure. 5.16: Variation of Sum total (of sequential extraction) and Total Metal (in mg/Kg) in core sediments

The characteristics peak for calcite was 1732 cm^{-1}, The Pirotite occurs at 1450-1400 cm^{-1}, Montmorillonite at 1394 cm^{-1}, Quartz was recorded at 795 and 693 cm^{-1}, pyrite at 914 cm^{-1}, Orthoclase at 469 $cm^{-1}$and Chlorite at 751 cm^{-1} (Georges-Ivo, 2005). The dominant clay minerals present in the sediment are kaolinite, illite, organic matter, pyrite, quartz, pirotite and orthoclase.

Table.5.7: Important IR bands of clay along with their possible assignments.



Band (cm^{-1})	Transmittance (%)	Assignments
3696·7	27·3	Al—O–H str.
3622·5	13·5	Al—O–H (inter-octahedral)
3450·4	50·2	H–O–H str.
1633·4	91·4	H–O–H str.
1033·3	7·2	Si–O–Si, Si–O str.
914·5	32·6	Al—O–H Str.
790·9	27·5	Si–O str., Si–O–Al str. (Al, Mg)—O–H. Si–O– (Mg, Al) str.
693·4	66·8	Si–O str., Si–O–Al str.
538·8	29·9	Si–O str., Si–O–Al str.
468·9	12·3	Si–O str., Si–O–Fe str.

The FTIR spectra of the sediment samples (See Appendix-IV) shows, dominance of certain minerals like Kaolinite (in both ordered and crystalline form), Muscovite and Quartz. The occurrence of organic matter has also been adjudged from the FTIR spectra. Deeper down in the sediment samples the occurrence of Calcite can also be observed. Pyrite has also been detected in few samples. The Kaolinite showed a characteristic peak between 3695- 3601 cm^{-1} and shoulder peak at 542 cm^{-1} while Illite was observed at 3426 cm^{-1} with supporting peak at 1031 cm^{-1}. The characteristics peak for calcite was 1732 cm^{-1}, Pirotite occurs at 1450-1400 cm^{-1}, Quartz was recorded at 778 and 690 cm^{-1}, pyrite at 909 cm^{-1}, Orthoclase at 469 $cm^{-1}$and Chlorite at 751 cm^{-1} (Georges-Ivo, 2005). Therefore, the dominant clay minerals present in the sediment are Kaolinite, Illite, organic matter (presence of aliphatic chains between 2925- 2840 cm^{-1}), Pyrite, Quartz, Pirotite and Orthoclase although the peaks show slight shift from the standard peaks which could be due to peak overlaps thus showing slight shift.

The aquifer sediment shows Kaolinite, Illite, organic matter, Pyrite, Quartz, and orthoclase. Samples at deeper depths represent high amount of calcite, essentially represents the occurrence of kankar in the region brought by flooding in the past in the study area. The quartz represent minor fraction, which is the more resistant mineral towards weathering. The analysis revealed the presence of association of dominant Kaolinite with subordinate amount of Illite and Chlorite. The feldspars and other mafic minerals undergo chemical alteration, i.e. interact with water and form clay minerals. These feldspars are converted to clay minerals as Kaolinite, Smectite, Illite, Montmorllionite. Similar observations clay minerals from Brahmaputra basin, revealed the association of dominant Kaolinite with subordinate amount of Illite and Chlorite (Kotoky et al., 2006).

Chapter 6

Summary & Conclusions

Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Several researchers have undertaken studies on quantitative distribution of metals among various chemical phases of sediments under natural conditions to assess the ecotoxic potential. Sediments conserve important environmental information and are increasingly recognized as both carriers and possible sources of contaminants in aquatic system. Sorption and release, i.e., interactions, of heavy metals in the soil and sediment environment depend on their chemical forms and properties and their relative distribution in solution and solid phases. Until recently, analytical methods allowed analysts to determine total contents only, but it was soon realised that this analytical information was insufficient.

To study trace metal partitioning, different schemes have been proposed based on application of sequential procedures, yielding the so-called operational speciation (Tessier et al., 1979; Kersten and Forstner, 1989; 1995; Krishnamurti et al., 1995; Ure et al., 1993; Lylister and Probst ,1999; Gleyzes et al., 2002). The possibility of metal re-mobilisation from sediment materials will depend on the type of metal linkage to the sediment material and the possibilities of transformation in more labile species (Kersten and Forstner., 1989). The Fe–Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals. The release of the metals from the matrix is most likely to be affected by the redox potential and pH (Calmano and Forstner, 1993).

The aquifer sediment conditions in the region are very similar to that found in the deltaic plains of Ganges and Brahmaputra in the West Bengal and Bangladesh. The type of aquifer sediments are Holocene alluvial/deltaic sediments with abundance of solid organic matter in it with pH being neutral to slightly alkaline for water in the region. The affected aquifers are generally shallow (less than 100–150 m deep), of Holocene age and comprise micaceous sands, silts and clays deposited by the Ganges, Brahmaputra and Meghna river systems and their precursors. In most affected areas, the aquifer sediments are capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As because of competition for adsorption sites.

Preliminary works regarding the heavy metals pollution in the groundwater of the Semaria Ojhapatti area has been undertaken by Acharya et al., 1999; Chakraborty et al., 2003, especially in relation to Fe and As contamination, but none has identified the role of aquifer sediments for Fe, As, Phosphate and other heavy metals as contaminants in the middle Gangetic plain. This work qualitatively outlines the role of metals (Fe, As, Mn, Cu and Zn) in the enrichment and contamination of sediments. The summary of the results has been outlined below:

- The Mean size (M_z) for the aquifer sediments ranges from 0.92 Φ to 3.53 Φ (avg. 2.18Φ), this indicates that the sediments are very coarse to very fine sand and the average mean size indicating the dominance of fine sand; this indicates that the presence of Palaeo- flood plain deposit.
- The Average standard deviation of aquifer sediment is 0.78 Φ while its value ranges from 0.47 Φ to 1.32 Φ. With 45% samples of moderately well sorted nature, indicating the episodic sediment deposition (recent and Holocene) occurring in the flood plains i.e. high discharges and low discharges over the past few decades in the region.
- The average skewness for aquifer sediments is 0.12 Φ while its value ranges from - 0.73 Φ to 0.84 Φ thus sediment samples are very coarsely skewed to very finely skewed which indicates that the flood plain deposits are very dynamic in nature.
- The average value of kurtosis for aquifer sediments is 0.97 while the minima and maxima ranges from 0.52 to 6.19 with 50% of the samples being very platykurtic in nature, this indicating that the aquifer sediments are being dominated silty fine sand material with little amount of coarse and medium sand and clay which underwent less sorting and winnowing action during the formation of aquifer sediments.
- The occurrence of soil moisture, organic content, carbonate and sulphur lies in close accordance with grain size of the aquifer sediments with fine grained silt and clay portion holding more moisture, organic content and sulphur while the coarser grain fraction is mostly associated with carbonate fraction.

- The metal enrichment factor shows moderate to significant metal enrichment in the aquifer sediments which may be a real threat in the future.
- The Geo-accumulation index of metals for Fe shows that the metal lies in the range of moderately to strongly contaminated in the upper layers of aquifer sediments up to the depth of 7.62m; while on an average in rest of the sediment samples metals (Fe, Mn, Zn, Cu and As) show either uncontaminated to moderately contaminated or uncontaminated values. Thus showing that at some depths (especially the upper layers) sediments are contaminated and the groundwater in the region may become vulnerable in the future depending on the E_h- pH conditions and other anthropogenic factors.
- The FTIR studies show the dominance of minerals such as kaolinite, illite, muscovite, quartz, organic matter and calcite in the aquifer sediments.
- The metal fractionation studies show that the most dominant fraction in the aquifer sediments for all the heavy metals is the Residual fraction. The sequence of dominance of different fractions is as follows:
    - **Fe**: Residual > Reducible > Available > Oxidizable
    - **Mn**: Residual > Available > Reducible > Oxidizable
    - **Zn**: Residual > Available > Reducible > Oxidizable
    - **Cu**: Residual > Reducible > Available > Oxidizable
    - **As**: Residual > Reducible > Available > Oxidizable
- The statistical analysis shows that the Fe shows good correlation with Zn, Cu, LOI, Total Phosphorus and Sulphur while it shows moderate correlation with Mn. Similarly, Mn shows good correlation with Cu, LOI and Sulphur, while Zn shows good correlation with Cu, Carbonate and Sulphur; on the other hand Cu shows good correlation with Fe, Mn, Zn, LOI and Sulphur. Thus, most of the metals occur in association with organic content present in the silt and clay fraction and may be having coherent source. The strong correlation of total Phosphorus with Cu, OC, and S suggests that the phosphate is organically bound and have a coherent source.

Conclusion

Much work has been undertaken in the past by different authors on the contamination of groundwater in the region who have reported Arsenic contamination in the region but till now no work has been undertaken on heavy metals distribution in the aquifer sediments and its role in the groundwater contamination of Semria Ojhapatti area, hence, this work qualitatively underlines the role of different metals in the sediments and its relation to Arsenic contamination in the region. The work undertaken outlines that the metals Fe, Mn, Zn, Cu and As have the potential to severely contaminate the groundwater resources of the region as has been indicated by the metal enrichment factor and geo-accumulation index. . The Arsenic mobilisation in the region may be attributed to complex combination of redox changes brought on by rapid burial of the alluvial and flood plain deposited sediments, together with the presence of organic matter deposited with the sediments, has resulted in the development of highly reducing conditions which favour the mobilisation of As via reduction of the solid-phase As to As(III), desorption of As from Fe oxides, reductive dissolution of the oxides themselves and likely changes in Fe-oxide structure and surface properties. Enchanced concentrations of phosphate, bicarbonate, silicate and possibly organic matter can increase the desorption of As because of competition for adsorption sites. The moderately negative correlation of Arsenic with the Total phosphorus shows that the phosphate competes for the adsorption site in the aquifer sediments of the Semria Ojhapatti area. Thus, this study indicates the need for further study on Phosphorus fractionation studies in the aquifer sediments of the Semria Ojhapatti area. The need is to identify the relationship if any between Phosphorus and Arsenic in the aquifer sediments, which may help in defining the role of phosphorus in the Arsenic contamination of the groundwater in the Semria Ojhapatti, Bhojpur besides, the weathering of sulphide minerals and reductive dissolution of oxides of Iron and Manganese.

Chapter 7

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Appendices

APPENDIX-I

Table. I (a): Grain size distribution of Sediment samples

Depth\ Sieve size	600µm	300µm	250µm	125µm	63µm	37µm	25µm
1.52	12.82	25.35	14.08	17.43	22.30	7.61	0.22
3.05	11.96	27.42	18.27	18.05	21.49	2.74	
4.57	22.69	23.45	10.23	13.59	25.92	3.87	0.02
6.10	33.20	20.38	10.39	15.92	17.40	2.42	0.01
7.62	25.73	27.33	15.05	16.68	13.17	1.79	
9.15	1.83	5.34	3.10	33.93	47.24	8.16	0.02
10.67	1.88	5.76	3.66	20.11	55.68	12.51	0.06
12.20	1.03	21.02	29.46	37.23	8.37	1.75	0.14
13.72	0.50	7.70	43.58	45.81	1.38	0.25	
15.25	0.47	4.76	32.90	58.67	2.32	0.49	
16.77	0.51	10.70	31.68	34.15	2.26	0.41	
18.30	0.66	14.30	34.62	45.23	4.01	0.59	0.02
19.82	0.43	18.62	42.37	33.63	2.45	0.52	0.01
21.35	7.96	24.08	36.41	27.96	2.80	0.59	
22.87	0.11	17.86	30.59	46.19	4.19	0.49	0.03
24.40	1.34	9.23	23.93	60.49	3.69	0.54	0.03
25.92	57.22	17.52	11.64	10.85	2.40	0.31	
27.45	25.23	29.01	20.99	20.18	2.94	0.80	
28.97	23.80	22.15	17.34	19.15	5.57	1.72	0.02
30.50	30.81	27.43	21.04	16.18	3.50	0.37	
32.02	2.28	32.70	32.96	20.75	4.17	1.01	0.03
33.55	80.99	8.35	4.88	4.38	0.84	0.31	

Table. I (b): Depth wise % Sand and % V. Fine Silt & Clay Fractions in the sediments

Depth	% SAND	% V Fine silt and Clay
1.52	92.27	7.73
3.05	97.30	2.70
4.57	96.16	3.84
6.10	97.59	2.41
7.62	98.23	1.77
9.15	91.92	8.08
10.67	87.58	12.42
12.20	98.12	1.88
13.72	99.75	0.25
15.25	99.52	0.48
16.77	99.50	0.50
18.30	99.40	0.60
19.82	99.47	0.53
21.35	99.42	0.58
22.87	99.48	0.52
24.40	99.43	0.57
25.92	99.69	0.31
27.45	99.21	0.79
28.97	98.09	1.91
30.50	99.63	0.37
32.02	98.91	1.09
33.55	99.69	0.31

Table. I (c): Showing Depth wise classification of sediment samples as Sample type, Textural group and sediment name

Depth	**SAMPLE TYPE**	**TEXTURAL GROUP**	**SEDIMENT NAME**
1.52	Polymodal, Poorly Sorted	Sand	Poorly Sorted Medium Sand
3.05	Polymodal, Poorly Sorted	Sand	Poorly Sorted Medium Sand
4.57	Polymodal, Poorly Sorted	Sand	Poorly Sorted Medium Sand
6.10	Polymodal, Poorly Sorted	Sand	Poorly Sorted Coarse Sand
7.62	Polymodal, Poorly Sorted	Sand	Poorly Sorted Medium Sand
9.15	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Very Fine Sand
10.67	Bimodal, Moderately Sorted	Muddy Sand	Very Coarse Silty Very Fine Sand
12.20	Trimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
13.72	Bimodal, Well Sorted	Sand	Well Sorted Medium Sand
15.25	Bimodal, Well Sorted	Sand	Well Sorted Fine Sand
16.77	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
18.30	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
19.82	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
21.35	Trimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
22.87	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
24.40	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Fine Sand
25.92	Trimodal, Moderately Sorted	Sand	Moderately Sorted Coarse Sand
27.45	Trimodal, Moderately Sorted	Sand	Moderately Sorted Medium Sand
28.97	Polymodal, Poorly Sorted	Sand	Poorly Sorted Medium Sand
30.50	Trimodal, Moderately Sorted	Sand	Moderately Sorted Medium Sand
32.02	Bimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Medium Sand
33.55	Unimodal, Moderately Well Sorted	Sand	Moderately Well Sorted Coarse Sand

Table. I (d): Showing Mean, Sorting, Skewness, Kurtosis by Folk and Ward method and its description

FOLK AND WARD METHOD (ϕ)					**FOLK AND WARD METHOD (Description)**			
Depth	**MEAN (Mz)**	**SORTING (σI)**	**SKEWNESS (SkI)**	**KURTOSIS (Kg)**	**MEAN (Mz)**	**SORTING (σI)**	**SKEWNESS (SkI)**	**KURTOSIS (Kg)**
1.52	2.46	1.15	0.45	0.69	Fine Sand	Poorly Sorted	Very Fine Skewed	Platykurtic
3.05	2.42	1.09	0.46	1.00	Fine Sand	Poorly Sorted	Very Fine Skewed	Mesokurtic
4.57	2.12	1.32	0.26	0.62	Fine Sand	Poorly Sorted	Fine Skewed	Very Platykurtic
6.10	2.03	1.31	0.32	0.63	Fine Sand	Poorly Sorted	Very Fine Skewed	Very Platykurtic
7.62	1.78	1.10	0.20	0.66	Medium Sand	Poorly Sorted	Fine Skewed	Very Platykurtic
9.15	3.50	0.69	-0.65	1.04	Very Fine Sand	Moderately Well Sorted	Very Coarse Skewed	Mesokurtic
10.67	3.53	0.72	-0.65	1.14	Very Fine Sand	Moderately Sorted	Very Coarse Skewed	Leptokurtic
12.20	2.20	0.68	0.57	0.85	Fine Sand	Moderately Well Sorted	Very Fine Skewed	Platykurtic
13.72	2.23	0.49	0.56	0.54	Fine Sand	Well Sorted	Very Fine Skewed	Very Platykurtic
15.25	2.52	0.47	-0.71	0.52	Fine Sand	Well Sorted	Very Coarse Skewed	Very Platykurtic
16.77	2.22	0.51	0.52	0.55	Fine Sand	Moderately Well Sorted	Very Fine Skewed	Very Platykurtic
18.30	2.47	0.51	-0.65	0.55	Fine Sand	Moderately Well Sorted	Very Coarse Skewed	Very Platykurtic
19.82	2.17	0.52	0.55	0.55	Fine Sand	Moderately Well Sorted	Very Fine Skewed	Very Platykurtic
21.35	2.11	0.68	0.26	0.85	Fine Sand	Moderately Well Sorted	Fine Skewed	Platykurtic
22.87	2.46	0.52	-0.67	0.54	Fine Sand	Moderately Well Sorted	Very Coarse Skewed	Very Platykurtic
24.40	2.52	0.50	-0.73	0.57	Fine Sand	Moderately Well Sorted	Very Coarse Skewed	Very Platykurtic
25.92	1.07	0.71	0.82	0.87	Medium Sand	Moderately Sorted	Very Fine Skewed	Platykurtic
27.45	1.73	0.92	0.05	0.80	Medium Sand	Moderately Sorted	Symmetrical	Platykurtic
28.97	1.76	1.07	0.16	0.66	Medium Sand	Poorly Sorted	Fine Skewed	Very Platykurtic
30.50	1.70	0.92	0.06	0.80	Medium Sand	Moderately Sorted	Symmetrical	Platykurtic
32.02	2.10	0.66	0.67	0.83	Fine Sand	Moderately Well Sorted	Very Fine Skewed	Platykurtic
33.55	0.92	0.60	0.84	6.19	Coarse Sand	Moderately Well Sorted	Very Fine Skewed	Extremely Leptokurtic

APPENDIX-II

Table. II (a): Showing % Moisture, Organic Content (LOI_{550}), % Carbonate and % Sulphur content in the sediment samples.

Depth (in m)	% Soil Moisture	OC	% Carbonate	% Sulphur
1.52	0.03	5.10	2.03	3.59
3.05	0.045	6.42	1.32	4.4
4.57	0.04	4.32	3.71	3.8
6.10	0.039	6.12	2.82	3.95
7.62	0.046	7.37	2.49	5.37
9.15	0.018	3.73	0.39	1.07
10.67	0.046	3.92	0.60	1.26
12.20	0.013	3.17	0.39	1.00
13.72	0.015	2.03	1.55	0.60
15.25	0.01	2.55	0.88	0.64
16.77	0.012	2.37	0.89	0.48
18.30	0.013	1.40	2.80	0.53
19.82	0.022	1.47	1.66	0.44
21.35	0.022	1.30	2.90	0.73
22.87	0.017	1.09	2.77	0.46
24.40	0.018	2.15	2.25	0.73
25.92	0.017	1.99	8.35	0.58
27.45	0.023	1.40	3.91	0.77
28.97	0.033	3.48	3.77	1.47
30.50	0.026	1.00	5.68	0.51
32.02	0.01	1.57	3.04	0.474
33.55	0.013	2.29	10.16	0.571

Table. II (b): Concentration of Total Phosphorus and Alumina

Depth (in m)	**Total Phosphorus (in ppm)**	**%Alumina**
1.52 (5 ft)	914	3.37
3.05(10 ft)	457	12.75
4.57 (15 ft)	489	15.79
6.10 (20 ft)	294	7.31
7.62 (25 ft)	685	8.02
9.14 (30 ft)	457	1.16
10.67 (35 ft)	457	11.15
12.19 (40 ft)	196	1.34
13.72 (45 ft	392	3.43
15.24 (50 ft)	98	4.84
16.77 (55 ft)	131	4.90
18.29 (60 ft)	228	6.18
19.82 (65 ft)	196	1.03
21.34 (70 ft)	bdl	bdl
22.87 (75 ft)	261	4.24
24.39 (80ft)	196	10.25
25.92 (85 ft)	228	2.13
27.44 (90 ft)	228	6.75
28.97 (95 ft)	196	7.64
30.49 (100 ft)	131	2.07
32.02 (105 ft)	98	10.24
33.54 (110 ft)	bdl	bdl

APPENDIX-III

Table. III (a): Concentrations of Iron (Fe in mg/kg) in different fractions of aquifer sediments

Depth (in m)	Total	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	118314	0.68	2104	10.50	124206
3.05(10 ft)	193905	6.91	1982	4.99	137228
4.57 (15 ft)	166691	0.75	2852	6.69	146013
6.10 (20 ft)	136628	66.20	5122	10.79	102807
7.62 (25 ft)	181001	1100	17337	8.22	186662
9.14 (30 ft)	70690	189	2420	6.87	49833
10.67 (35 ft)	65536	34.22	3248	8.38	73823
12.19 (40 ft)	79235	280	2393	7.73	45294
13.72 (45 ft	42606	300	1840	12.64	72034
15.24 (50 ft)	68397	236	1557	10.47	61786
16.77 (55 ft)	42132	220	1268	7.66	62393
18.29 (60 ft)	38222	270	1681	6.72	47980
19.82 (65 ft)	40719	198	879	6.39	30714
21.34 (70 ft)	60509	204	2159	13.36	39740
22.87 (75 ft)	44209	258	1768	10.12	44496
24.39 (80ft)	53564	241	1866	8.85	43434
25.92 (85 ft)	67872	244	2295	9.55	60255
27.44 (90 ft)	57909	416	2564	9.35	56269
28.97 (95 ft)	54341	492	4109	10.74	104034
30.49 (100 ft)	113673	152	1761	5.16	118841
32.02 (105 ft)	38797	417	3309	10.85	86591
33.54 (110 ft)	35872	372	1327	12.79	40775
Avg.	**80492**	**259**	**2993**	**9.04**	**78873**
Max.	**193906**	**1100**	**17337**	**13.36**	**186662**
Min.	**35872**	**0.68**	**879**	**4.99**	**30714**
S.D.	**48963**	**233**	**3347**	**2.4**	**41752**

Table. III (b): % availability of Iron in different fractions of aquifer sediments w.r.t. Sum Total Fe concentration

Depth (in m)	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	0.0005	1.66	0.008	98.32
3.05(10 ft)	0.005	1.42	0.003	98.56
4.57 (15 ft)	0.0005	1.91	0.004	98.07
6.10 (20 ft)	0.06	4.74	0.010	95.18
7.62 (25 ft)	0.53	8.45	0.004	91.00
9.14 (30 ft)	0.36	4.61	0.013	95.01
10.67 (35 ft)	0.04	4.21	0.010	95.73
12.19 (40 ft)	0.58	4.98	0.016	94.41
13.72 (45 ft	0.40	2.48	0.017	97.09
15.24 (50 ft)	0.37	2.44	0.016	97.16
16.77 (55 ft)	0.34	1.98	0.012	97.65
18.29 (60 ft)	0.54	3.36	0.013	96.07
19.82 (65 ft)	0.62	2.76	0.020	96.58
21.34 (70 ft)	0.48	5.12	0.031	94.35
22.87 (75 ft)	0.55	3.80	0.021	95.62
24.39 (80ft)	0.53	4.09	0.019	95.35
25.92 (85 ft)	0.38	3.65	0.015	95.93
27.44 (90 ft)	0.70	4.32	0.015	94.95
28.97 (95 ft)	0.45	3.78	0.009	95.75
30.49 (100 ft)	0.12	1.45	0.004	98.41
32.02 (105 ft)	0.46	3.66	0.012	95.86
33.54 (110 ft)	0.87	3.12	0.030	95.96

Table.III (c): Concentrations of Manganese (Mn in mg/kg) in different fractions of aquifer sediments.

Depth (in m)	Total	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	811	43.86	69.77	30.64	319
3.05(10 ft)	590	210	44.95	11.69	250
4.57 (15 ft)	685	106	205	17.92	274
6.10 (20 ft)	615	288	73.44	29.70	241
7.62 (25 ft)	1739	1224	75.894	23.44	267
9.14 (30 ft)	1403	1009	26.47	18.50	281
10.67 (35 ft)	441	140	28.80	12.02	269
12.19 (40 ft)	401	118	19.86	4.97	248
13.72 (45 ft	553	96.91	14.17	22.32	445
15.24 (50 ft)	364	93.33	13.01	16.77	316
16.77 (55 ft)	795	79.17	8.21	70.09	253
18.29 (60 ft)	328	78.23	11.11	66.69	223
19.82 (65 ft)	288	74.68	13.37	19.37	166
21.34 (70 ft)	295	102	17.76	16.03	170
22.87 (75 ft)	332	62.67	12.56	12.35	237
24.39 (80ft)	300	73.17	15.61	17.64	184
25.92 (85 ft)	758	453	47.73	33.19	281
27.44 (90 ft)	494	194	26.23	22.30	253
28.97 (95 ft)	643	369	32.49	15.72	206
30.49 (100 ft)	628	281	37.60	4.90	257
32.02 (105 ft)	410	152	19.02	25.10	320
33.54 (110 ft)	703	304	86.34	17.36	153
Avg.	**618**	**252**	**40.93**	**23.13**	**255**
Max.	**1740**	**1224**	**205**	**70.10**	
Min.	**289**	**43.86**	**8.21**	**4.91**	**153**
S.D.	**356**	**302**	**44**	**16**	**64**

Table.III (d): % availability of Manganese (Mn) in different fractions of aquifer sediments w.r.t. Total Mn concentration

Depth (in m)	**Available**	**Reducible**	**Oxidizable**	**Residual**
1.52 (5 ft)	9.46	15.04	6.61	68.89
3.05(10 ft)	40.63	8.68	2.26	48.43
4.57 (15 ft)	17.54	34.07	2.97	45.42
6.10 (20 ft)	45.56	11.61	4.70	38.13
7.62 (25 ft)	76.94	4.77	1.47	16.82
9.14 (30 ft)	75.58	1.98	1.39	21.06
10.67 (35 ft)	31.18	6.39	2.67	59.77
12.19 (40 ft)	30.33	5.07	1.27	63.33
13.72 (45 ft	16.74	2.45	3.86	76.96
15.24 (50 ft)	21.23	2.96	3.82	71.99
16.77 (55 ft)	19.25	2.00	17.04	61.71
18.29 (60 ft)	20.59	2.92	17.55	58.93
19.82 (65 ft)	27.28	4.88	7.08	60.76
21.34 (70 ft)	33.50	5.79	5.23	55.48
22.87 (75 ft)	19.30	3.87	3.80	73.02
24.39 (80ft)	25.16	5.37	6.07	63.40
25.92 (85 ft)	55.59	5.86	4.07	34.48
27.44 (90 ft)	39.22	5.28	4.49	51.01
28.97 (95 ft)	59.22	5.21	2.52	33.04
30.49 (100 ft)	48.43	6.47	0.84	44.26
32.02 (105 ft)	29.46	3.68	4.86	62.00
33.54 (110 ft)	54.23	15.37	3.09	27.31

Table III (e): Showing concentrations of Zinc (Zn in mg/kg) in different fractions of aquifer sediments

Depth (in m)	Total	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	135	0.04	4.55	0.96	139
3.05(10 ft)	149	0.31	3.01	1.56	118
4.57 (15 ft)	143	0.06	4.52	1.10	108
6.10 (20 ft)	145	1.07	7.98	1.74	117
7.62 (25 ft)	151	1.02	7.12	1.71	141
9.14 (30 ft)	63.99	1.85	3.65	1.02	56
10.67 (35 ft)	96.50	0.86	4.41	1.22	75
12.19 (40 ft)	67.17	0.74	2.66	0.93	61
13.72 (45 ft	66.27	0.66	1.54	0.80	47
15.24 (50 ft)	56.08	0.54	1.37	0.85	45
16.77 (55 ft)	59.36	2.43	1.89	1.01	43
18.29 (60 ft)	64.62	2.86	2.51	1.04	55
19.82 (65 ft)	69.14	3.17	1.17	1.65	51
21.34 (70 ft)	59.05	1.75	3.17	0.81	51
22.87 (75 ft)	74.48	3.16	2.15	1.03	54
24.39 (80ft)	83.02	8.32	3.53	0.97	66
25.92 (85 ft)	174	59.48	36.16	1.28	62
27.44 (90 ft)	144	25.39	11.58	1.13	104
28.97 (95 ft)	110	10.55	9.30	1.14	56.20
30.49 (100 ft)	137	7.99	5.13	1.60	121
32.02 (105 ft)	66.57	5.16	4.05	1.14	76
33.54 (110 ft)	128	3.27	9.75	1.31	50
Avg.	**102**	**6.39**	**5.96**	**1.18**	**77**
Max.	**174**	**59.48**	**36.16**	**1.74**	**141**
Min	**56.08**	**0.04**	**1.17**	**0.80**	**43.74**
Std Dev	**39.80**	**13.11**	**7.34**	**0.29**	**32.89**

Table.III (f): % availability of Zinc (Zn) in different fractions of aquifer sediments w.r.t. Total Mn concentration

Depth (in m)	**Available**	**Reducible**	**Oxidizable**	**Residual**
1.52 (5 ft)	0.03	3.13	0.65	96.18
3.05(10 ft)	0.25	2.43	1.26	96.05
4.57 (15 ft)	0.05	3.93	0.96	95.04
6.10 (20 ft)	0.83	6.21	1.35	91.60
7.62 (25 ft)	0.67	4.68	1.12	93.50
9.14 (30 ft)	2.92	5.78	1.61	89.67
10.67 (35 ft)	1.04	5.37	1.48	92.10
12.19 (40 ft)	1.12	4.04	1.41	93.41
13.72 (45 ft	1.31	3.07	1.59	94.02
15.24 (50 ft)	1.11	2.82	1.75	94.31
16.77 (55 ft)	4.94	3.85	2.05	89.14
18.29 (60 ft)	4.64	4.08	1.69	89.58
19.82 (65 ft)	5.48	2.02	2.84	89.64
21.34 (70 ft)	3.07	5.56	1.42	89.94
22.87 (75 ft)	5.20	3.54	1.68	89.56
24.39 (80ft)	10.50	4.45	1.22	83.81
25.92 (85 ft)	37.40	22.73	0.80	39.05
27.44 (90 ft)	17.80	8.12	0.79	73.27
28.97 (95 ft)	13.66	12.04	1.47	72.81
30.49 (100 ft)	5.86	3.76	1.17	89.19
32.02 (105 ft)	5.98	4.69	1.31	88.01
33.54 (110 ft)	5.06	15.06	2.03	77.84

Table.III (g): Concentrations of Copper (Cu in mg/kg) in different fractions of aquifer sediments

Depth (in m)	Total	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	79.8	0.18	2.80	0.13	80.6
3.05(10 ft)	79	0.74	2.76	0.30	73.6
4.57 (15 ft)	73.4	0.17	4.26	0.61	70.7
6.10 ft)	81.1	1.45	8.40	0.29	66.1
7.62 (25 ft)	82.9	4.73	9.10	0.30	75.4
9.14 (30 ft)	68.9	0.86	1.47	0.25	54
10.67 (35 ft)	48.6	1.09	3.22	0.19	40.9
12.19 (40 ft)	37.2	1.03	0.97	0.63	37.6
13.72 (45 ft	33	0.97	0.70	0.75	36.8
15.24 (50 ft)	35.1	0.71	0.80	0.51	38.5
16.77 (55 ft)	37.3	0.84	0.47	0.69	37.1
18.29 (60 ft)	35.4	1.08	0.74	0.4	35.8
19.82 (65 ft)	35.8	1.78	0.54	0.41	37.1
21.34 (70 ft)	38.4	1.42	1.06	0.40	39.3
22.87 (75 ft)	36.3	1.21	0.72	0.71	39.8
24.39 (80ft)	34.2	1.01	0.74	0.34	40.8
25.92 (85 ft)	36.8	0.15	1.40	0.55	44.7
27.44 (90 ft)	37.9	1.29	1.26	0.70	42
28.97 (95 ft)	57.9	3.02	4.69	0.29	51.1
30.49 (100 ft)	37	0.49	1.08	0.50	54.4
32.02 (105 ft)	33	1.01	0.83	0.59	48.6
33.54 (110 ft)	38.2	0.22	1.10	0.17	40
Avg.	**48.96**	**1.16**	**2.23**	**0.44**	**49.31**
Max.	**82.90**	**4.73**	**9.10**	**0.76**	**80.60**
Min	**33.00**	**0.15**	**0.47**	**0.13**	**35.80**
std dev	**18.85**	**1.02**	**2.43**	**0.19**	**14.52**

Table.III (h): % availability of Copper (Cu) in different fractions of aquifer sediments w.r.t. Total Mn concentration

Depth (in m)	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	0.21	3.34	0.15	96.29
3.05(10 ft)	0.95	3.56	0.39	95.08
4.57 (15 ft)	0.22	5.61	0.80	93.35
6.10 (20 ft)	1.89	11.01	0.38	86.69
7.62 (25 ft)	5.28	10.16	0.33	84.21
9.14 (30 ft)	1.52	2.59	0.45	95.42
10.67 (35 ft)	2.39	7.09	0.41	90.08
12.19 (40 ft)	2.55	2.41	1.56	93.45
13.72 (45 ft	2.46	1.77	1.92	93.83
15.24 (50 ft)	1.75	1.97	1.25	95.01
16.77 (55 ft)	2.14	1.21	1.77	94.86
18.29 (60 ft)	2.84	1.95	1.05	94.15
19.82 (65 ft)	4.45	1.34	1.02	93.16
21.34 (70 ft)	3.35	2.52	0.96	93.16
22.87 (75 ft)	2.84	1.69	1.68	93.77
24.39 (80ft)	2.34	1.73	0.80	95.11
25.92 (85 ft)	0.32	2.99	1.18	95.49
27.44 (90 ft)	2.84	2.78	1.55	92.81
28.97 (95 ft)	5.11	7.93	0.49	86.44
30.49 (100 ft)	0.86	1.90	0.88	96.34
32.02 (105 ft)	1.97	1.61	1.15	95.24
33.54 (110 ft)	0.53	2.63	0.42	96.39

Table. III (i): Concentrations of Arsenic (As in mg/kg) in different fractions of aquifer sediments

Depth (in m)	**Total**	**Available**	**Reducible**	**Oxidizable**	**Residual**
1.52 (5 ft)	23.35	0.053	0.040	0.015	14.32
3.05(10 ft)	22.37	0.091	0.072	0.005	15.29
4.57 (15 ft)	22.14	0.061	0.096	0.012	16.33
6.096 (20 ft)	17.98	0.078	0.077	0.014	15.54
7.62 (25 ft)	19.16	0.058	0.132	0.021	14.97
9.14 (30 ft)	17.53	0.066	0.091	0.027	17.86
10.67 (35 ft)	21.12	0.055	0.075	0.031	15.67
12.19 (40 ft)	19.60	0.053	0.074	0.030	24.80
13.72 (45 ft	24.23	0.053	0.077	0.020	18.17
15.24 (50 ft)	21.18	0.050	0.079	*bdl	17.11
16.77 (55 ft)	18.95	0.047	0.081	*bdl	17.72
18.29 (60 ft)	22.86	0.048	0.102	*bdl	16.14
19.82 (65 ft)	18.58	0.052	0.056	*bdl	19.91
21.34 (70 ft)	22.60	0.047	0.126	*bdl	22.44
22.87 (75 ft)	21.94	0.056	0.095	0.076	23.97
24.39 (80ft)	20.24	0.211	0.136	0.023	21.12
25.92 (85 ft)	20.70	0.129	0.518	*bdl	22.68
27.44 (90 ft)	22.28	0.169	0.427	*bdl	18.53
28.97 (95 ft)	22.04	0.254	0.275	*bdl	16.64
30.49 (100 ft)	23.38	0.373	0.176	0.069	22.01
32.02 (105 ft)	39.59	0.077	0.130	*bdl	40.60
33.54 (110 ft)	29.19	0.066	0.324	*bdl	17.20
Avg.	**21.50**	**0.098**	**0.148**	**0.000**	**19.50**
Max.	**29.19**	**0.373**	**0.518**	**0.076**	**40.60**
Min	**17.53**	**0.047**	**0.040**	**-0.066**	**14.32**
Std Dev	**4.60**	**0.083**	**0.125**	**0.022**	**5.63**

Where, *bdl stands for Below Detection Limit

Table.III (j): % availability of Arsenic (As) in different fractions of aquifer sediments w.r.t. Total Mn concentration

Depth (in m)	Available	Reducible	Oxidizable	Residual
1.52 (5 ft)	0.367	0.279	0.106	99.24
3.05(10 ft)	0.585	0.466	0.034	98.91
4.57 (15 ft)	0.372	0.582	0.075	98.97
6.10 (20 ft)	0.494	0.490	0.091	98.92
7.62 (25 ft)	0.379	0.867	0.138	98.61
9.14 (30 ft)	0.367	0.502	0.148	98.98
10.67 (35 ft)	0.347	0.472	0.199	98.98
12.19 (40 ft)	0.213	0.298	0.120	99.36
13.72 (45 ft	0.287	0.421	0.110	99.18
15.24 (50 ft)	0.293	0.456	bdl	99.25
16.77 (55 ft)	0.265	0.456	bdl	99.27
18.29 (60 ft)	0.296	0.624	bdl	99.08
19.82 (65 ft)	0.260	0.279	bdl	99.46
21.34 (70 ft)	0.210	0.556	bdl	99.23
22.87 (75 ft)	0.231	0.391	0.316	99.06
24.39 (80ft)	0.983	0.633	0.106	98.27
25.92 (85 ft)	0.553	2.22	bdl	97.22
27.44 (90 ft)	0.885	2.23	bdl	96.88
28.97 (95 ft)	1.47	1.60	bdl	96.92
30.49 (100 ft)	1.644	0.778	0.306	97.27
32.02 (105 ft)	0.189	0.318	bdl	99.49
33.54 (110 ft)	0.375	1.83	bdl	97.78

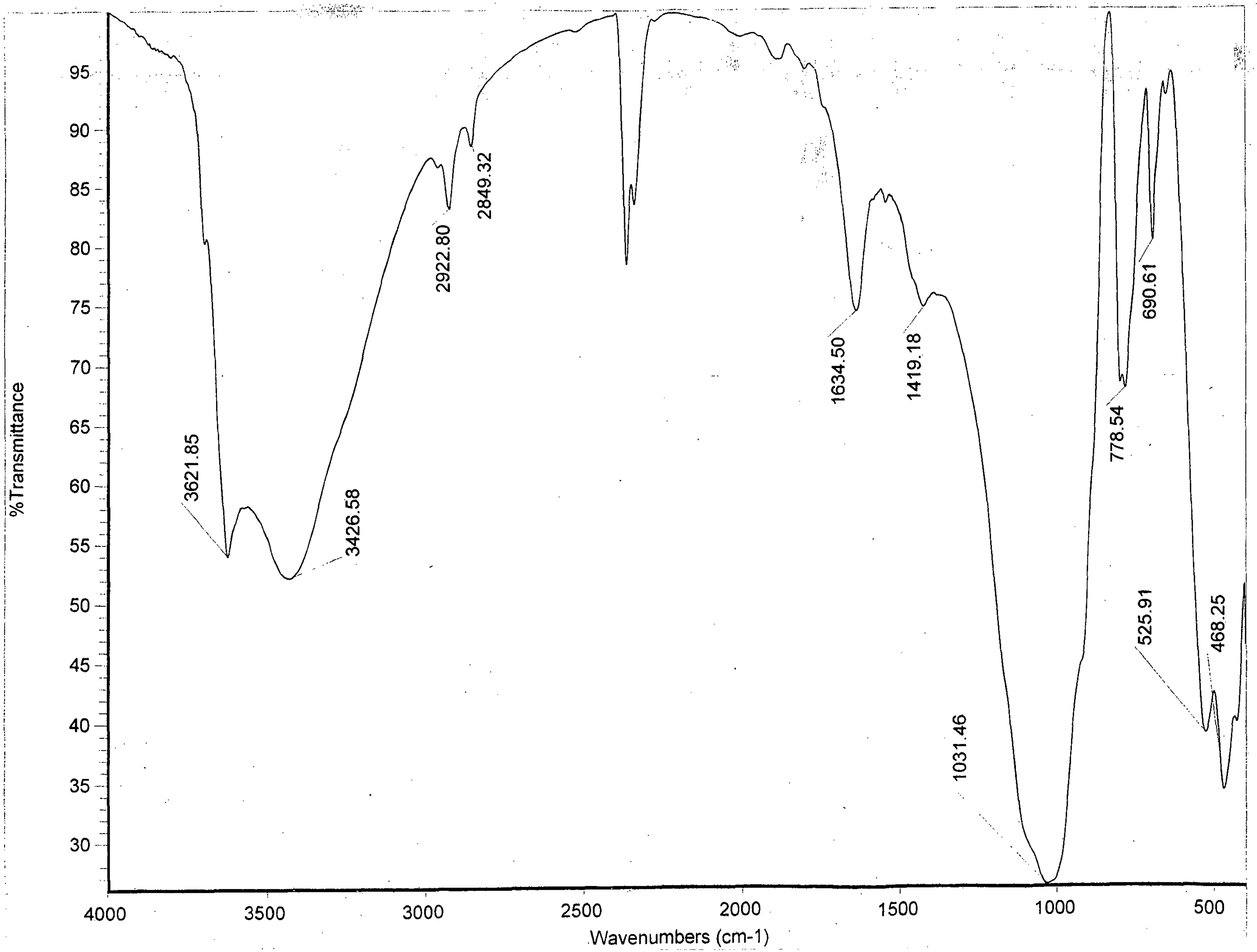
APPENDIX-IV

FTIR Table: Attribution of various wavelengths in FTIR analysis. (Source: Baddi et al., 2003)

Wave length	Attribution
3300 -3500 cm^{-1}	O-H vibrations of the hydroxyl groups of phenols, alcohols and carboxyl functions and N-H vibrations from amide ad amines.
2925 cm^{-1}	Symmetric CH stretching in-CH_3 and $-CH_2-$ of aliphatic chains
2840 cm^{-1}	Asymmetric CH stretching in $-CH_3$ and $-CH_2-$ of aliphatic chains
1725-1710 cm^{-1}	C=O stretching in carboxylic acids and /or in carbonyls, Ketones and aldehydes.
1654-1640 cm^{-1}	C=O stretching in quinones and /or in ketonic acids and primary amides
1540-1510 cm^{-1}	Aromatic C=C stretching and /or N-H deformation and C=N stretching in 2^0 amides
1460-1440 cm^{-1}	Aliphatic C-H deformation of structures such as fatty acids and waxes occurring in composts
1400-1380 cm^{-1}	O-H deformation, C=O stretching of phenols, anti- symmetric, COO- stretching and aliphatic C-H deformation.
1260-1200 cm^{-1}	C-OH stretching of aromatic groups and C-O-C stretching of aryl ethers and phenols.
1170 cm^{-1}	Alcohol function vibrations.
1080-1030 cm^{-1}	C-O-C stretching of carbohydrates
800-817 cm^{-1}	C-H deformation of substituted aromatic groups.

Appendix V

FTIR SPECTRA (PLACED DEPTHWISE IN CHRONOLOGICAL ORDER)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Wavenumbers (cm-1)
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690.61
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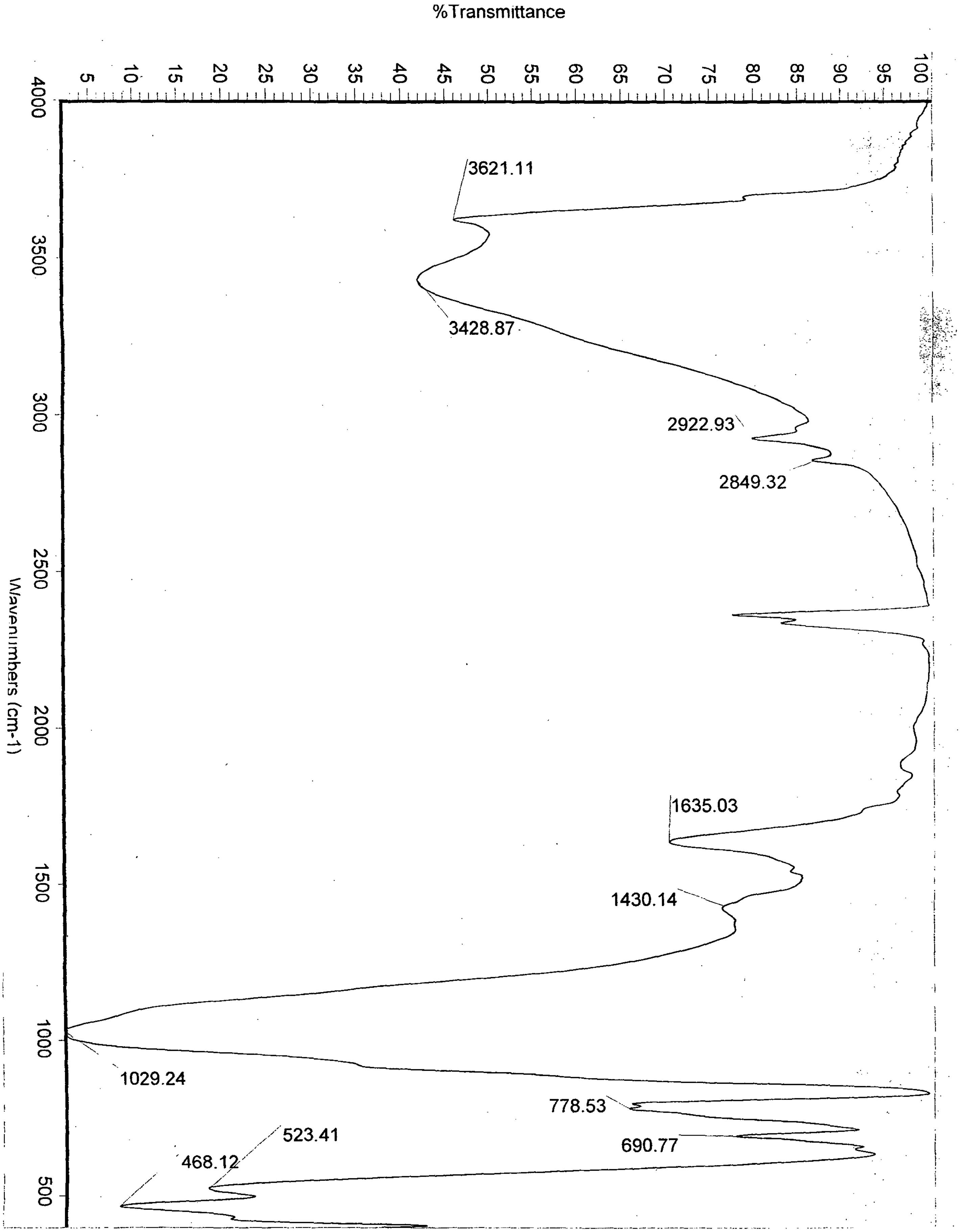
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Wavenumbers (cm-1)
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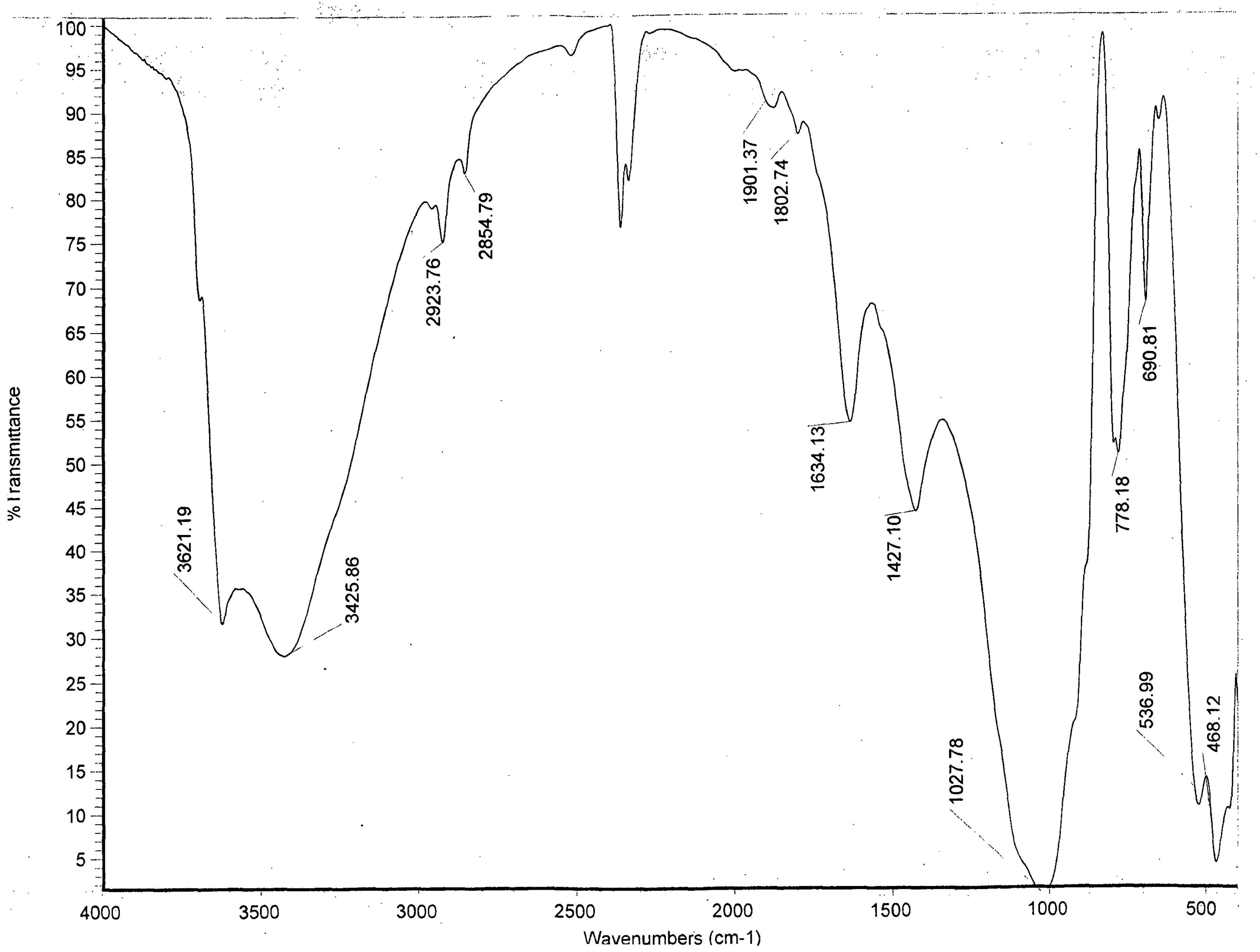

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Wavenumbers (cm-1)
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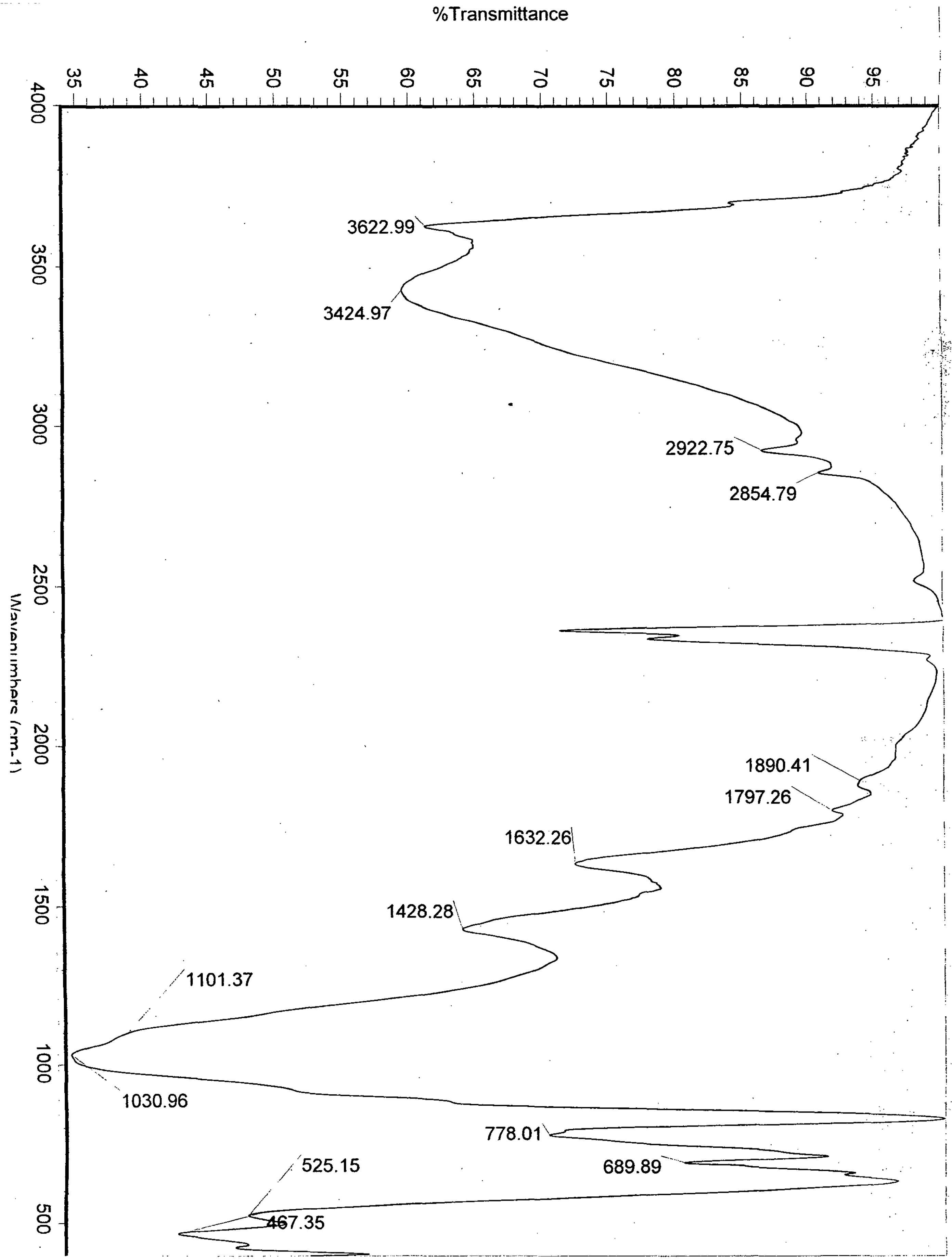
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Wavenumbers (cm-1)
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2922.75
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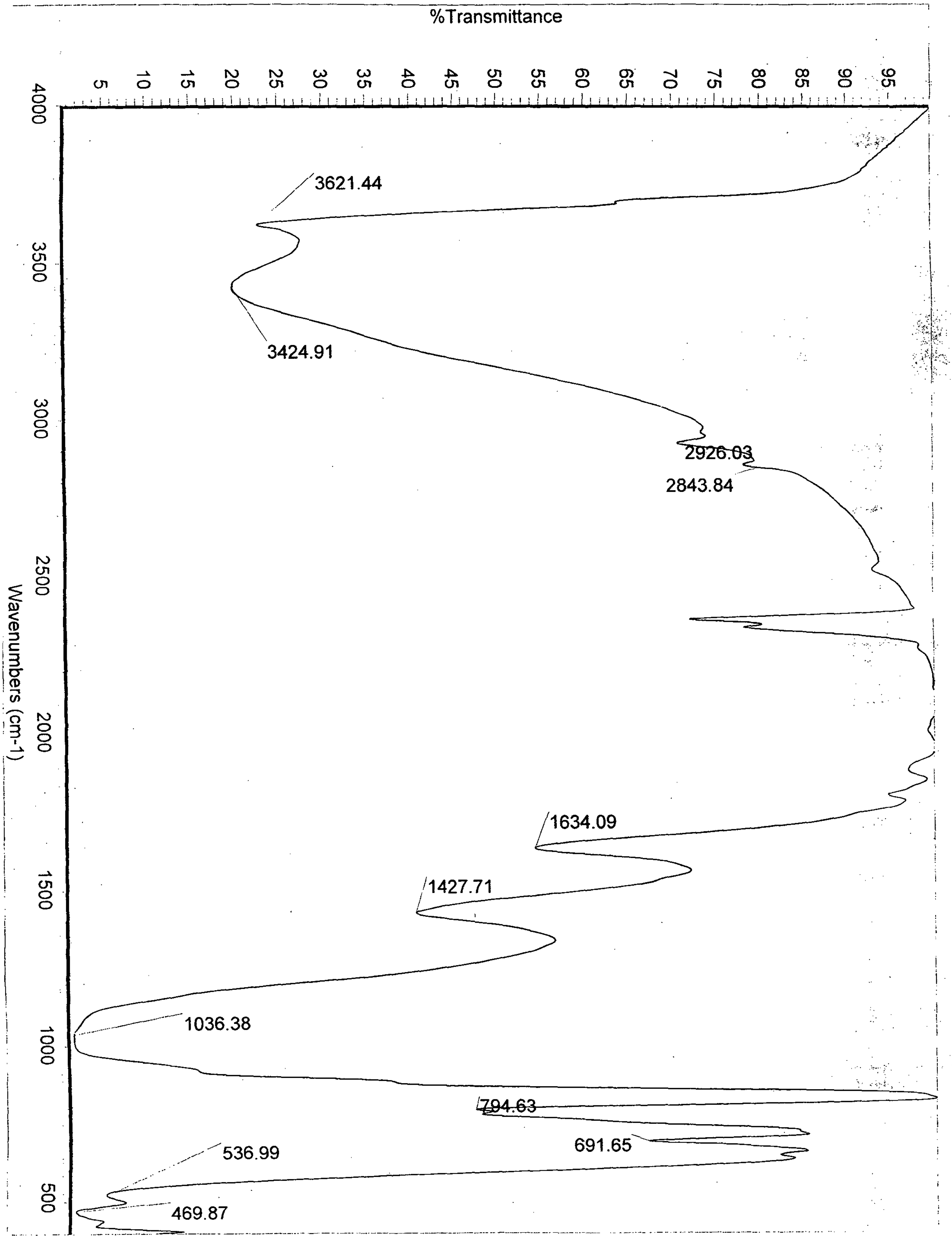
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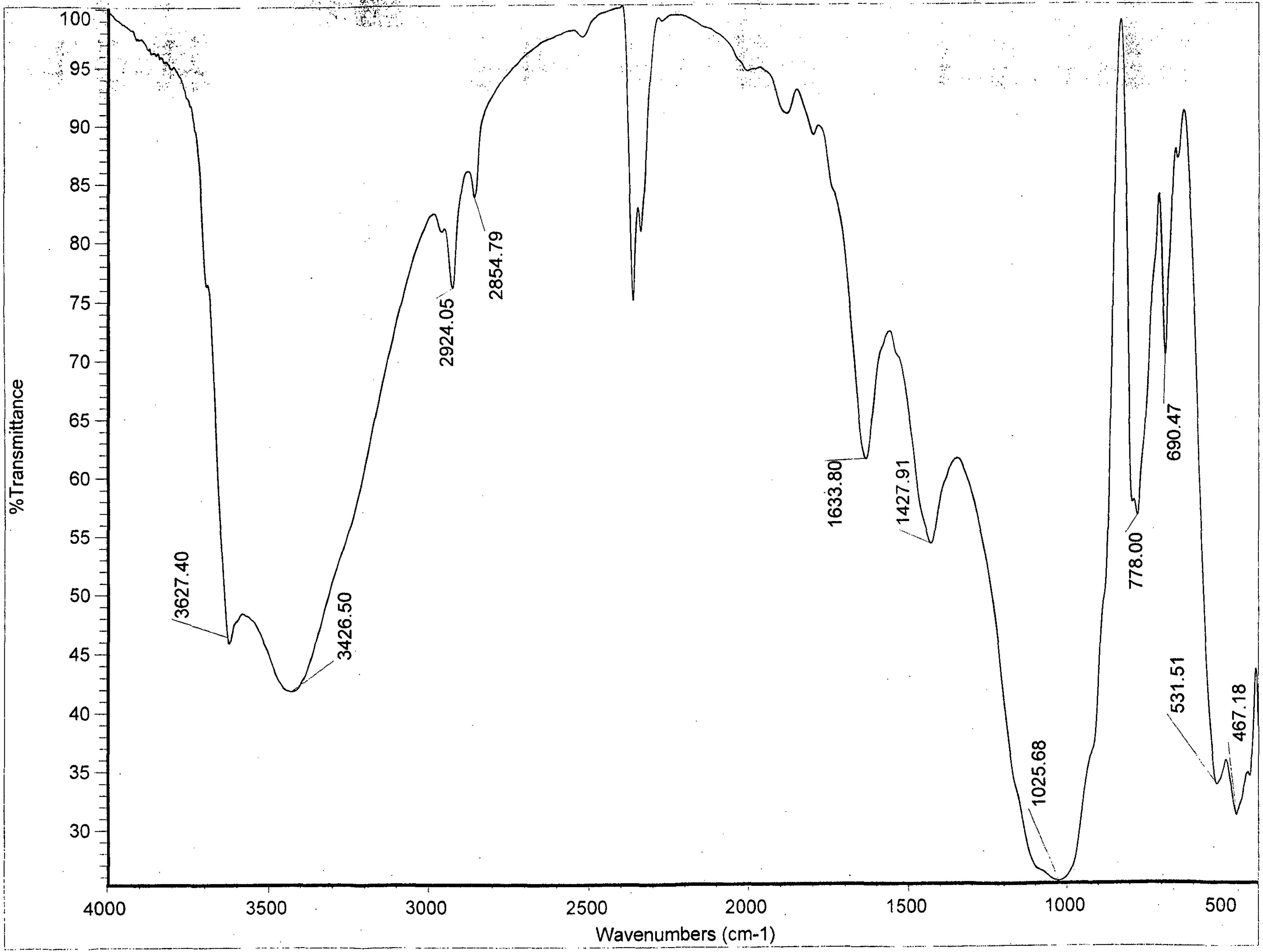
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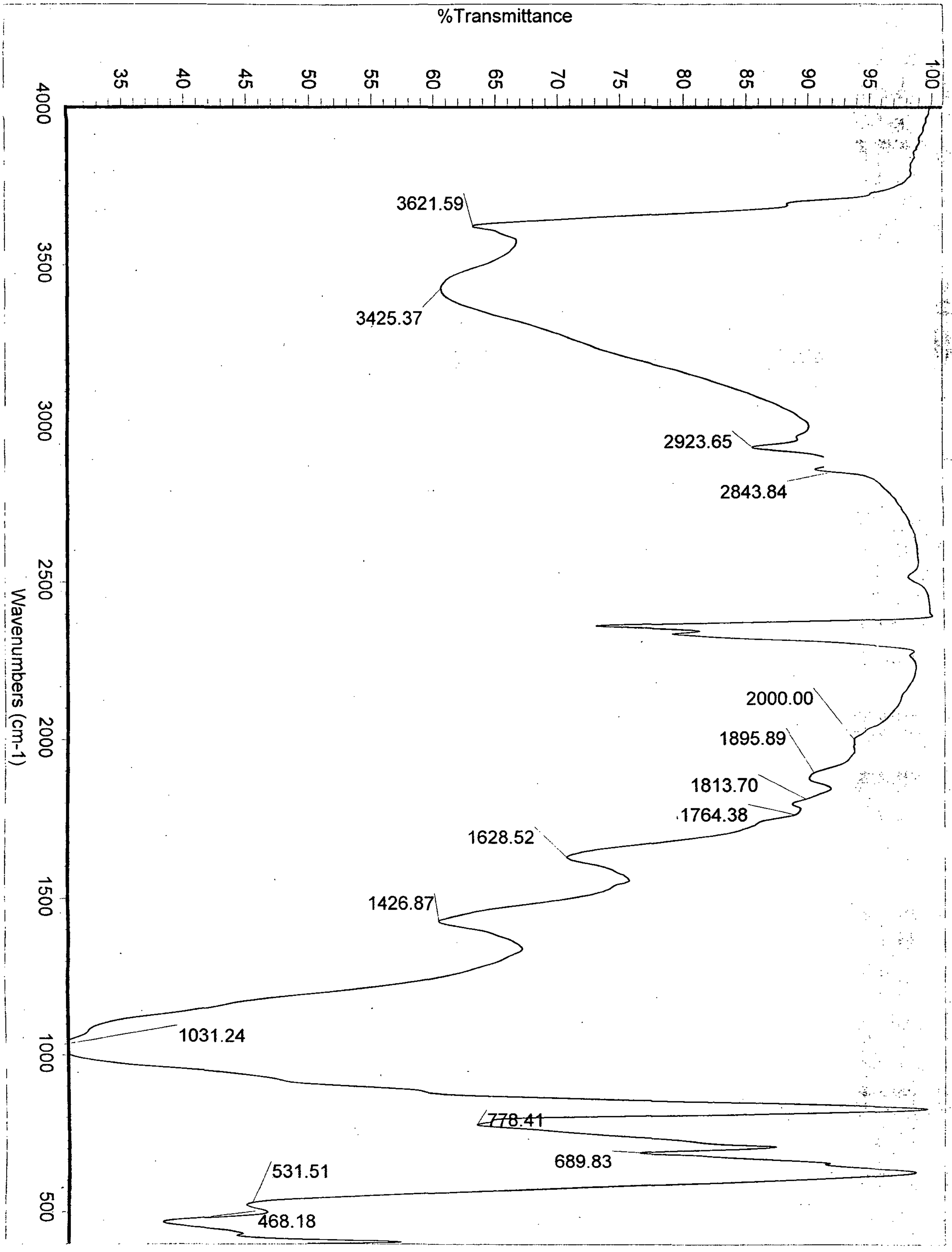
Wavenumbers (cm-1)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1000
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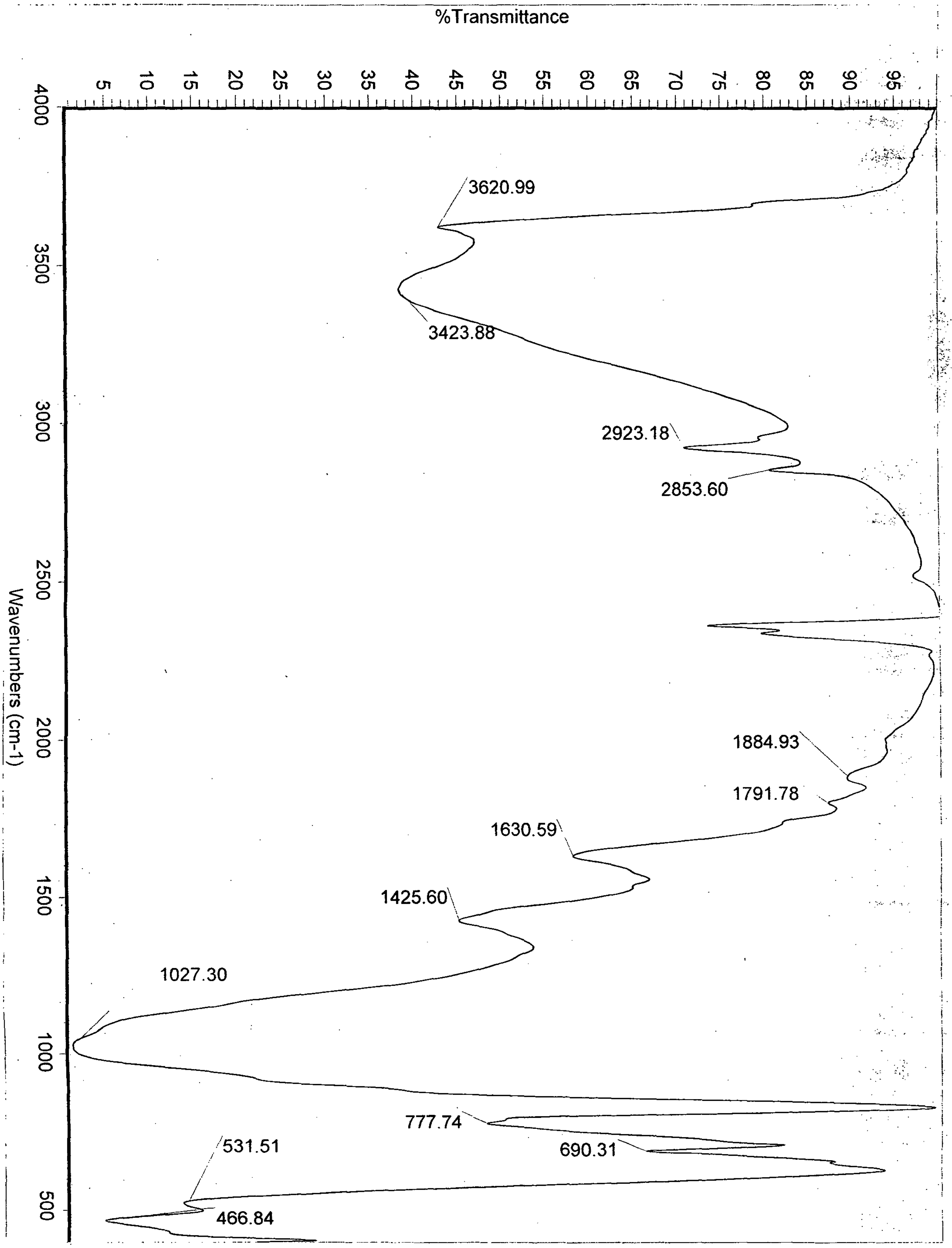
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Wavenumbers (cm-1)
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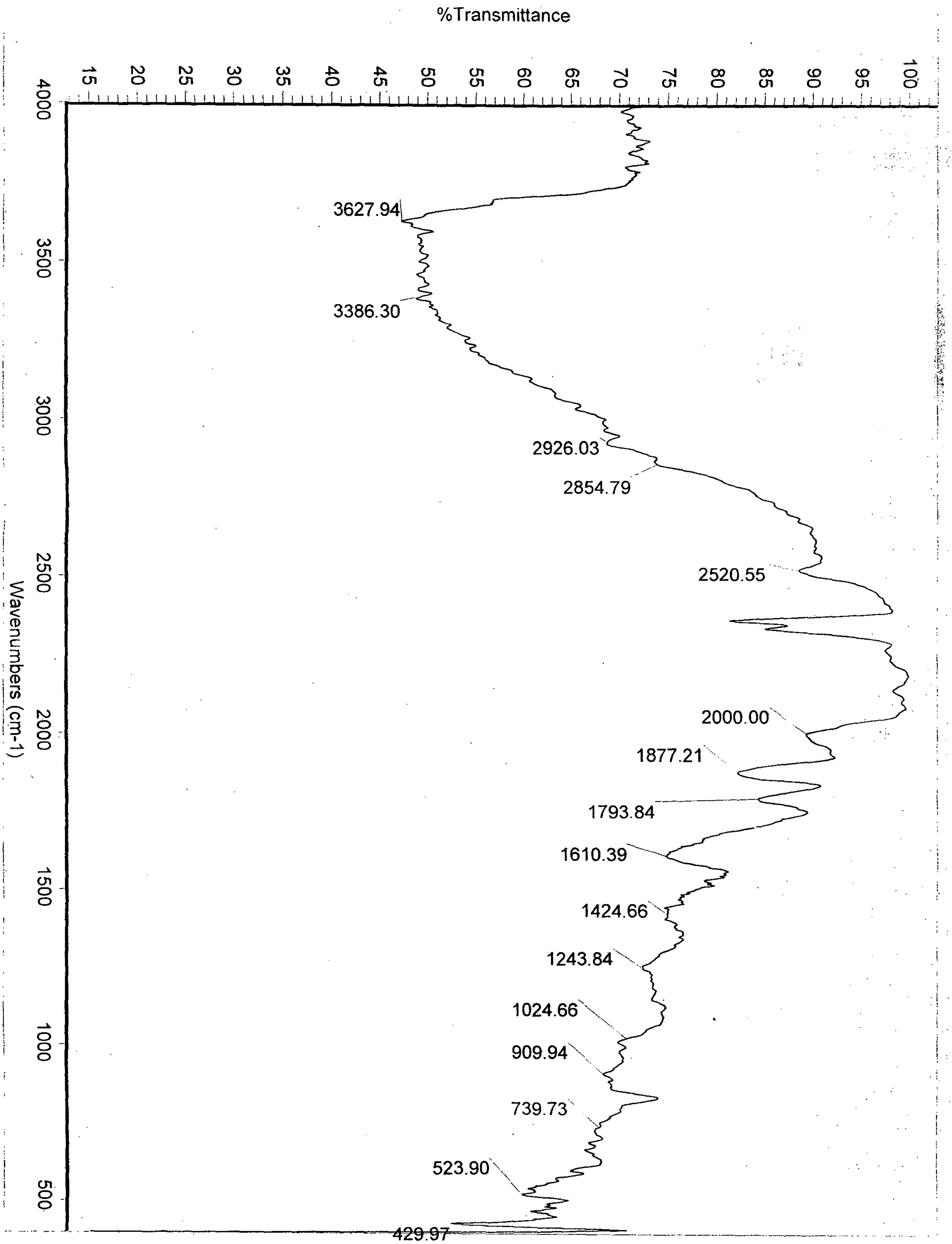
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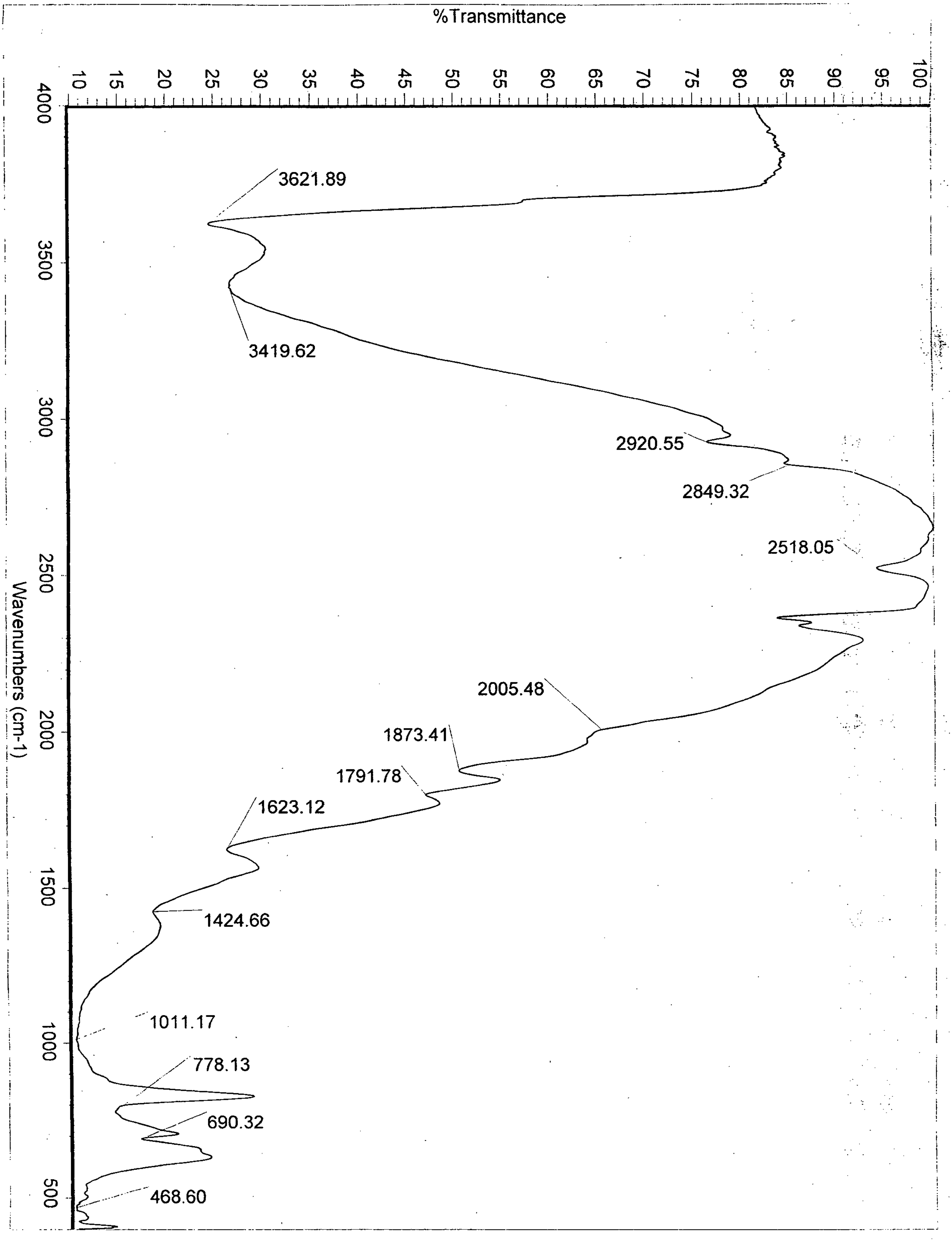
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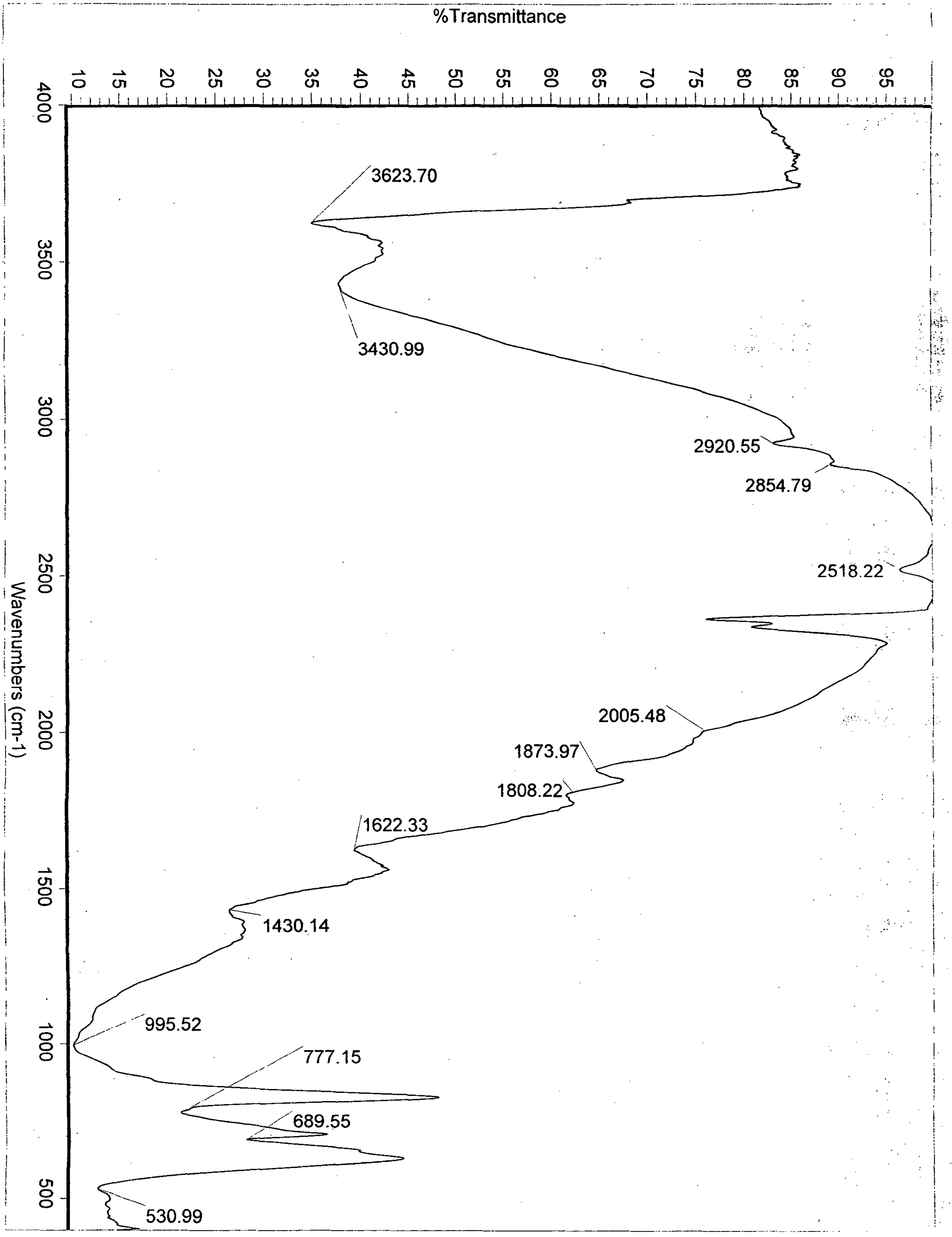
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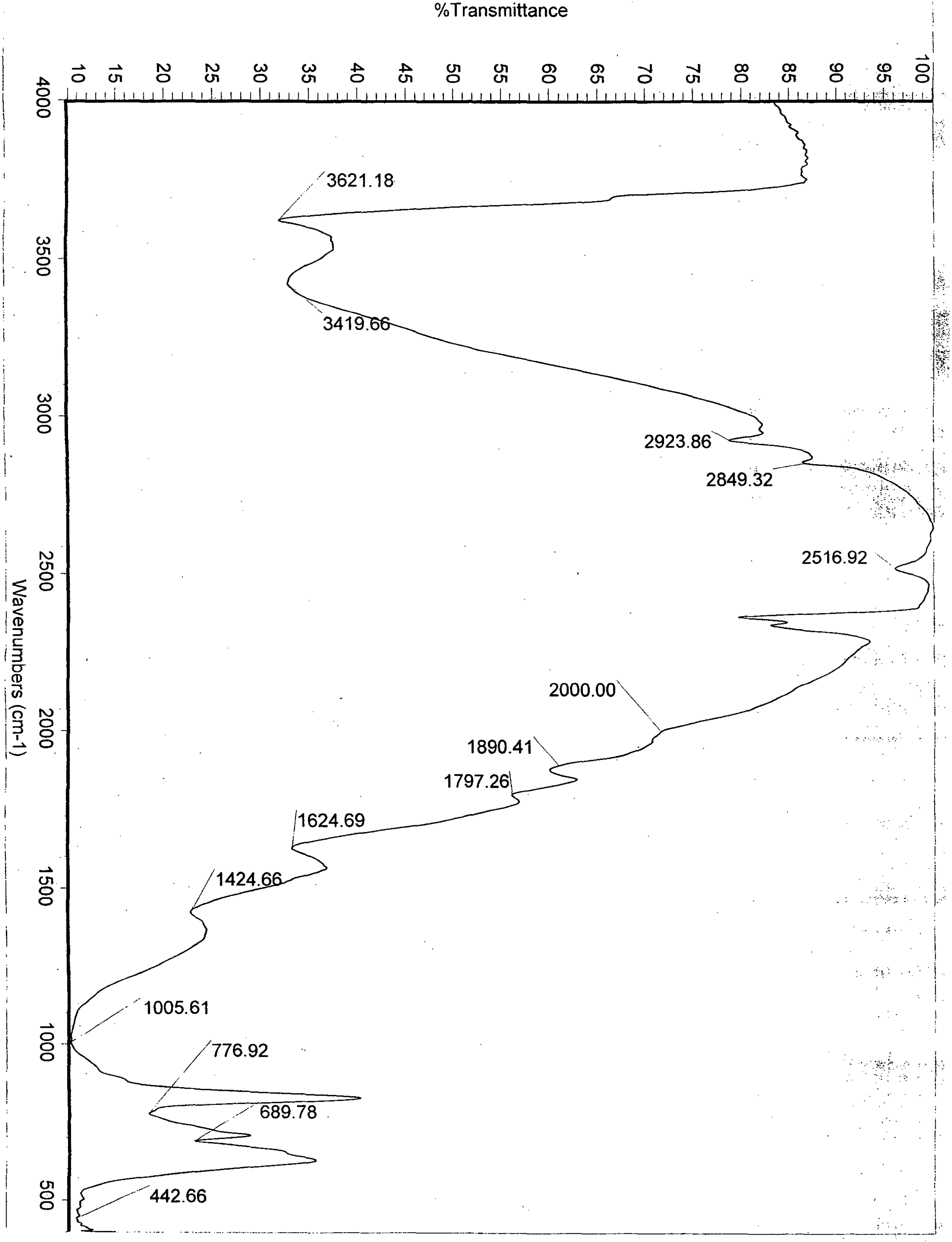
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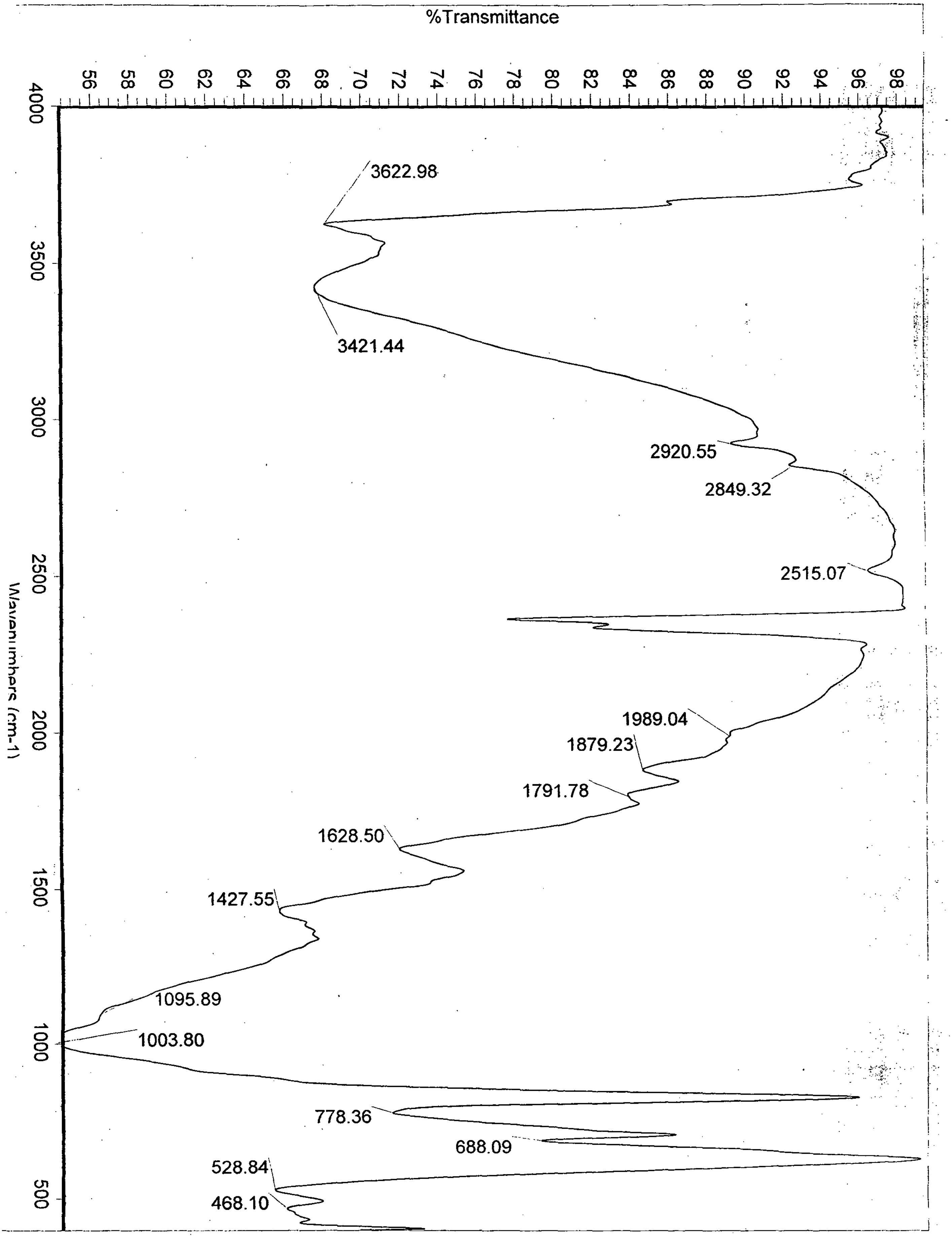
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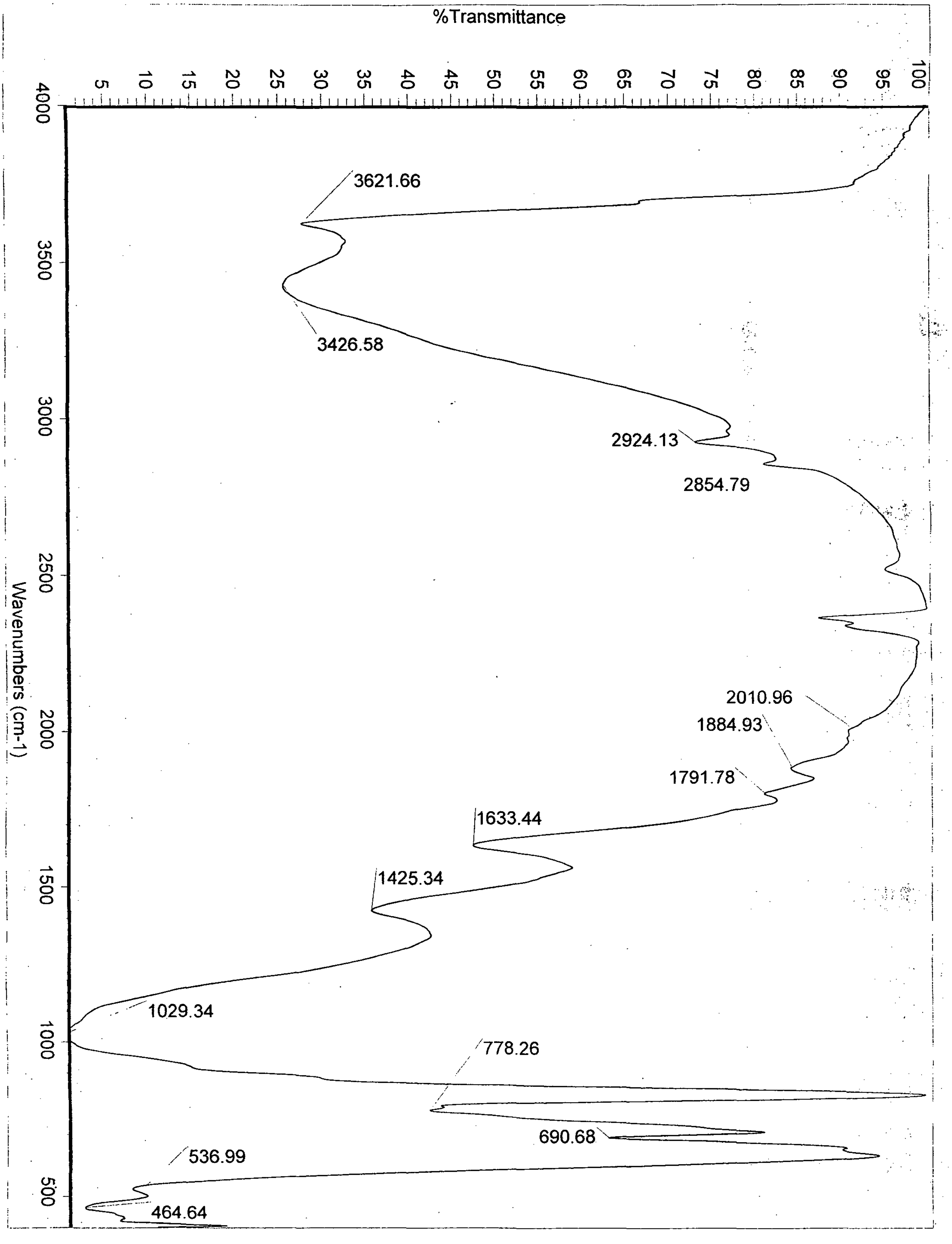
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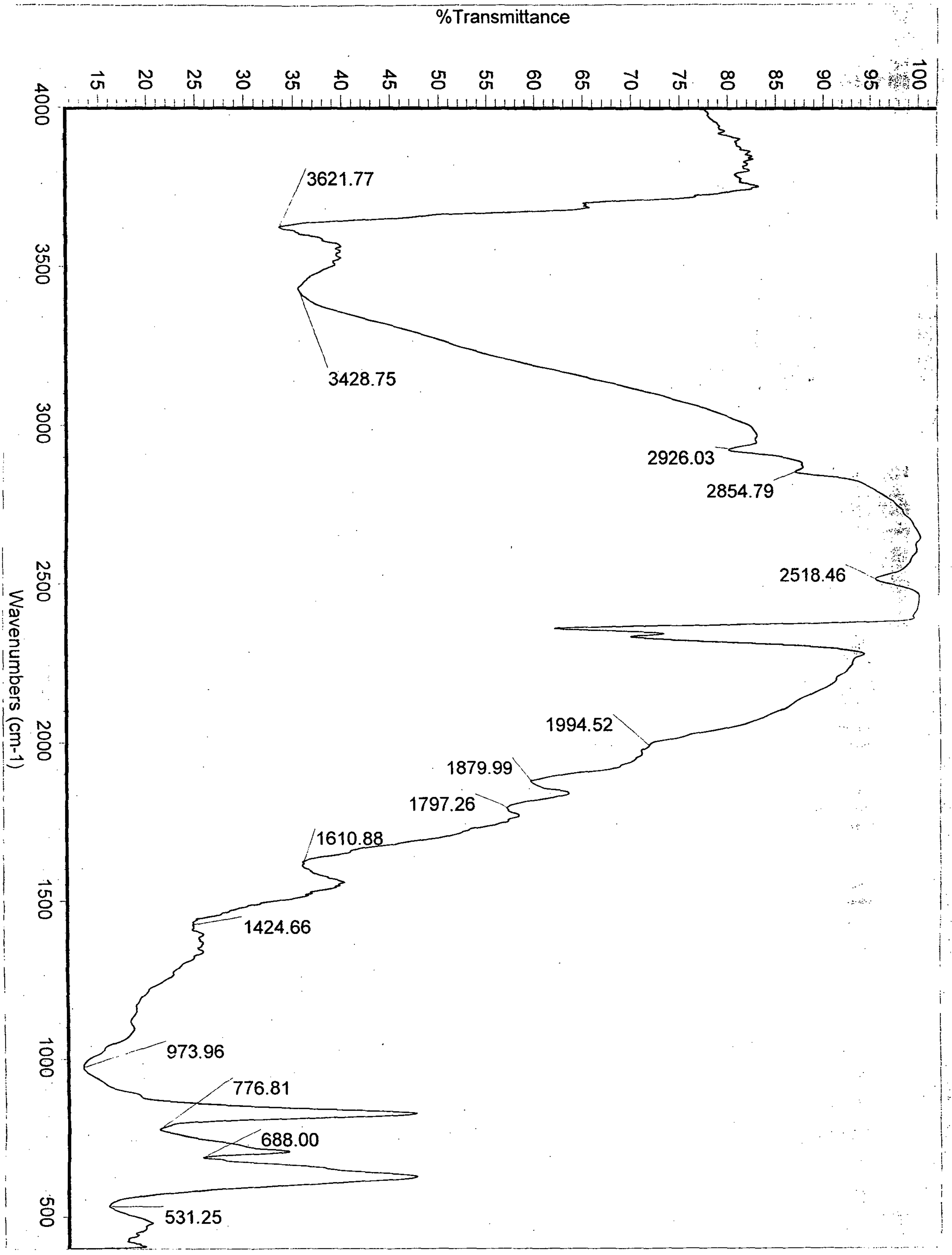
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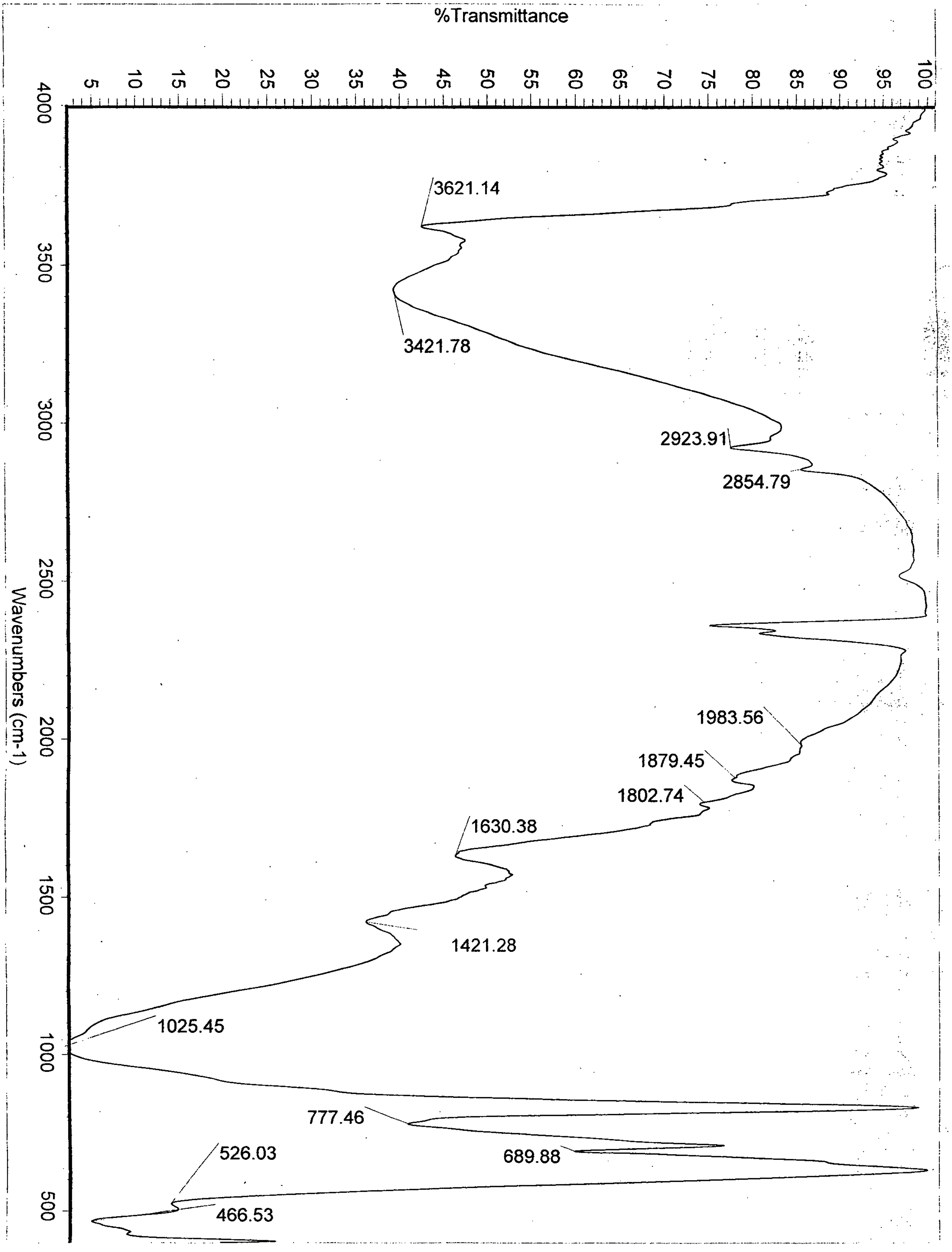
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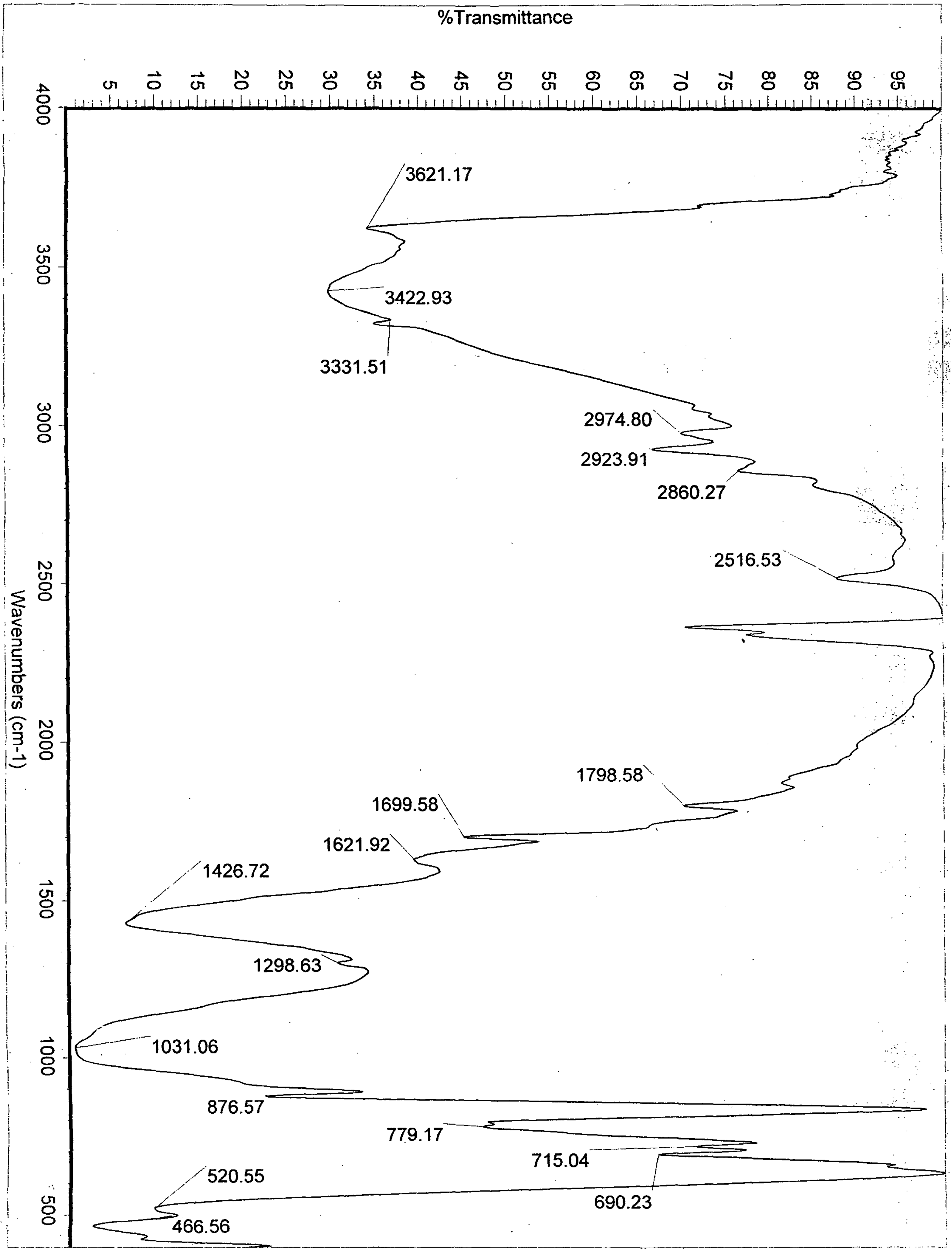
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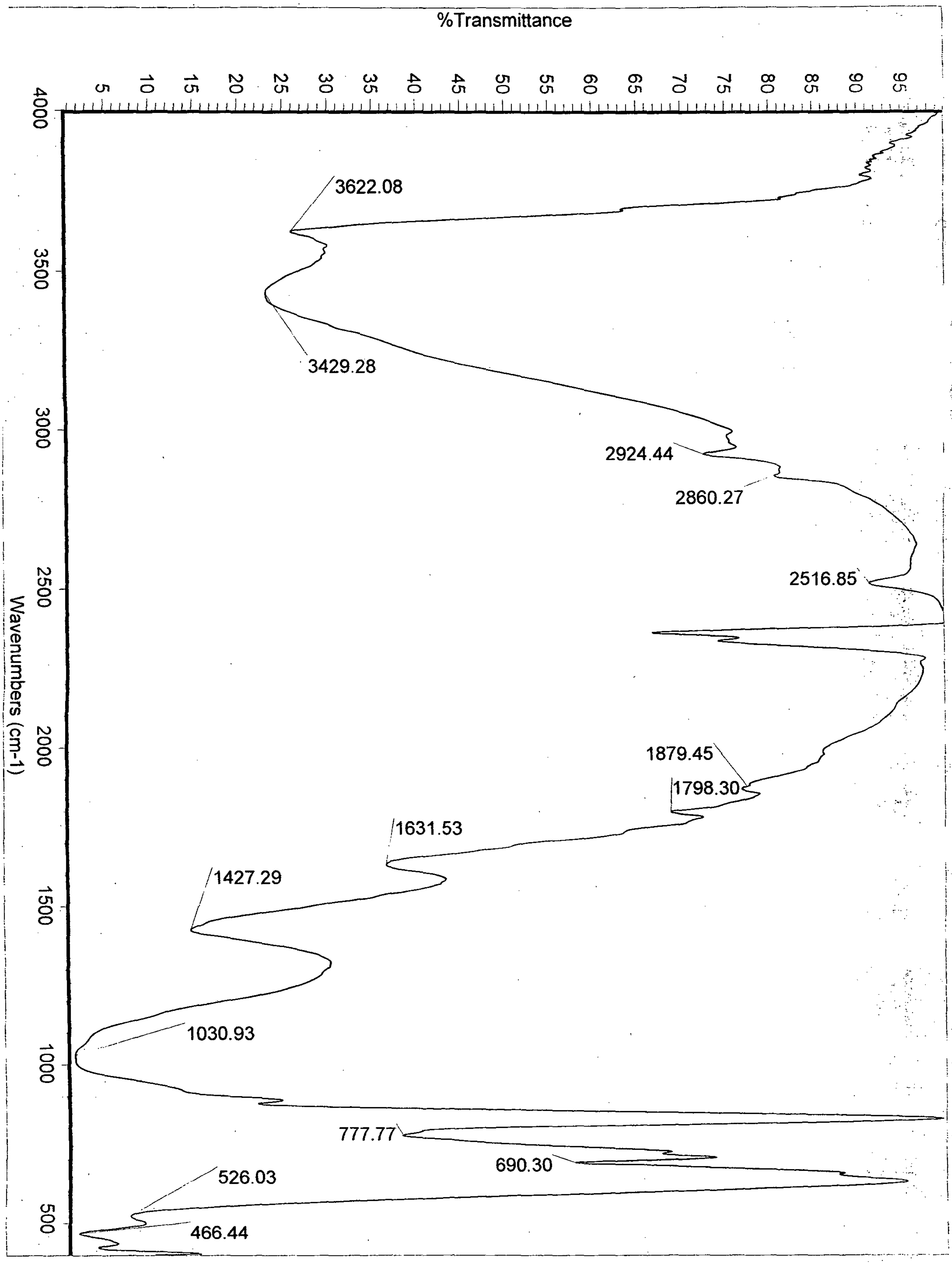
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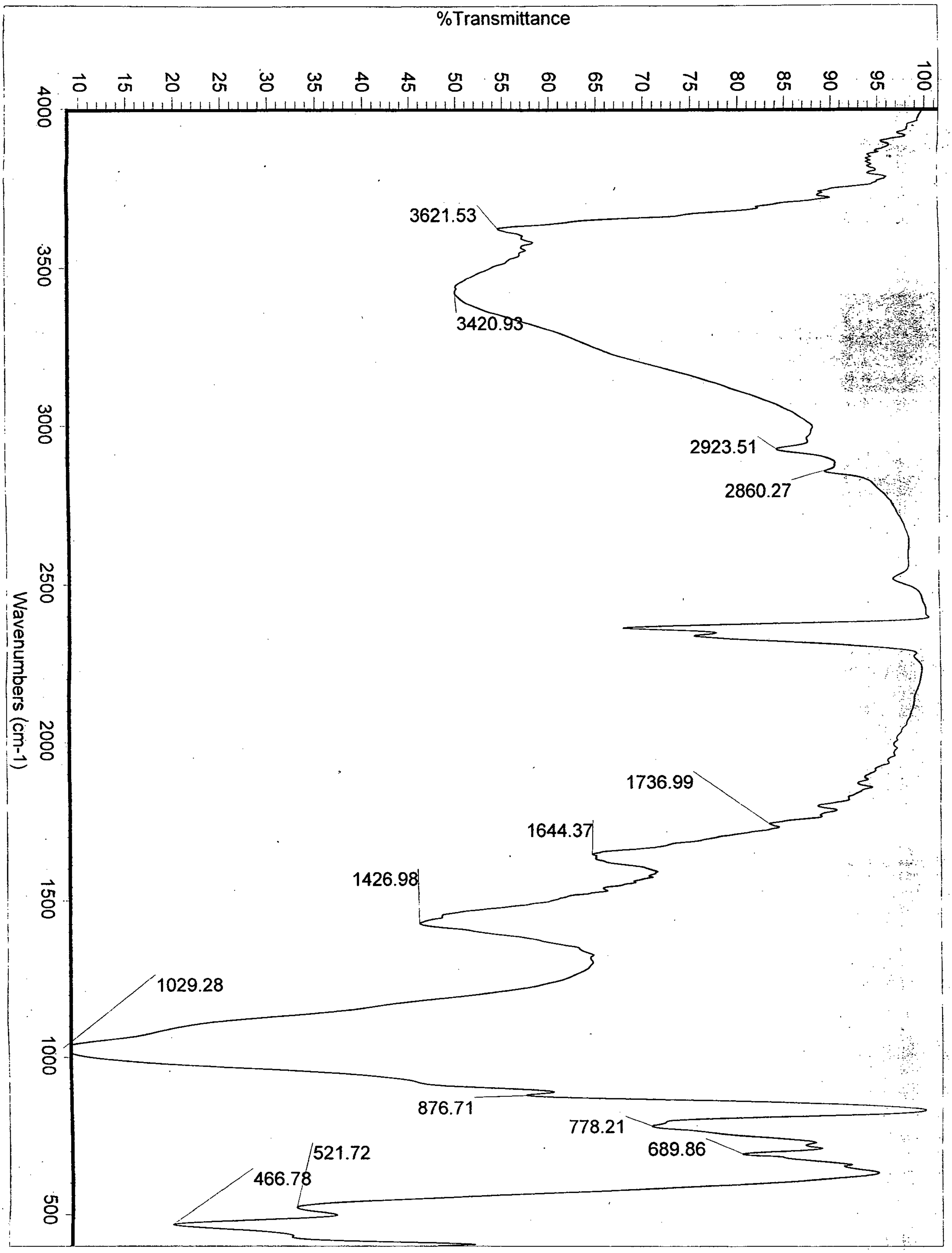
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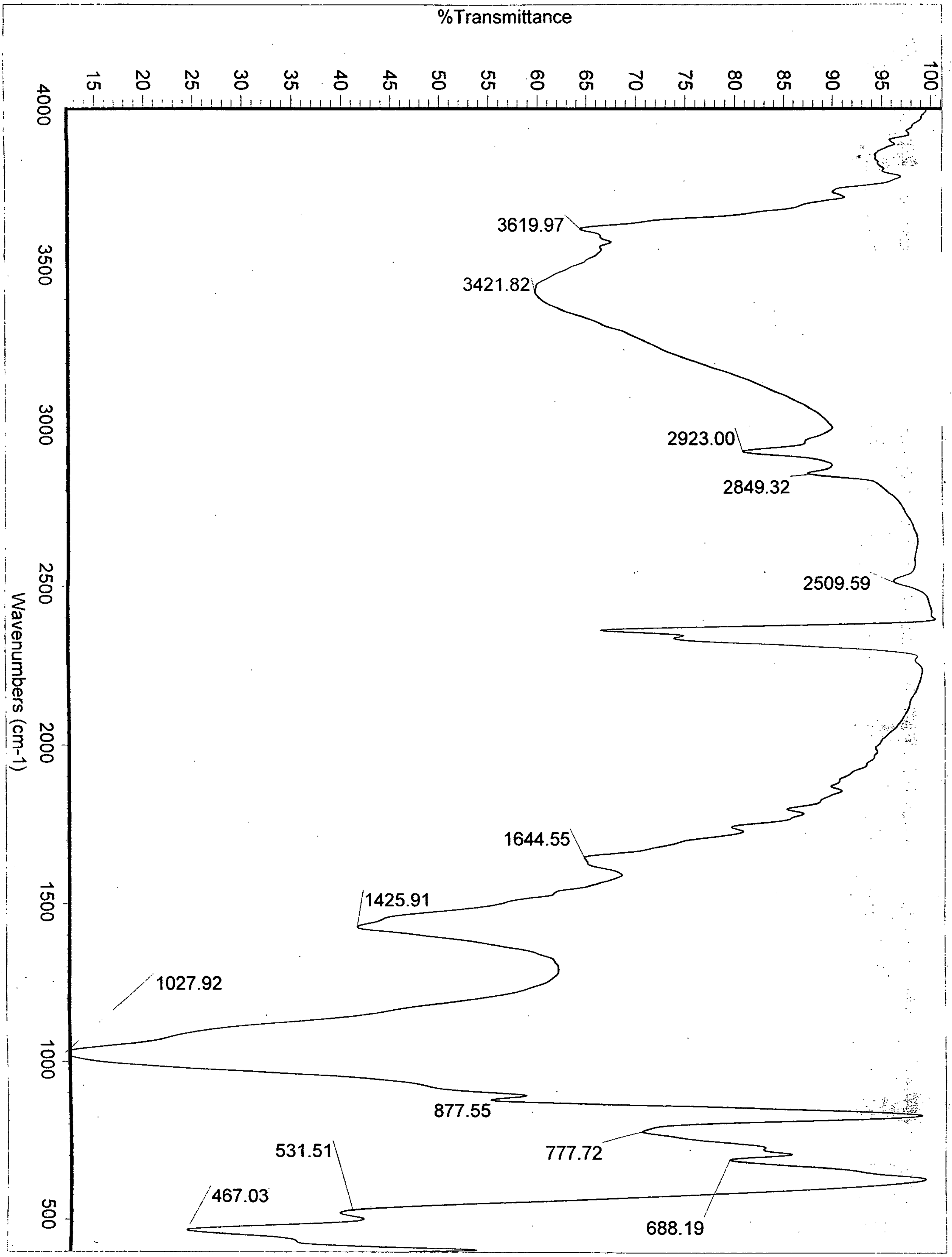
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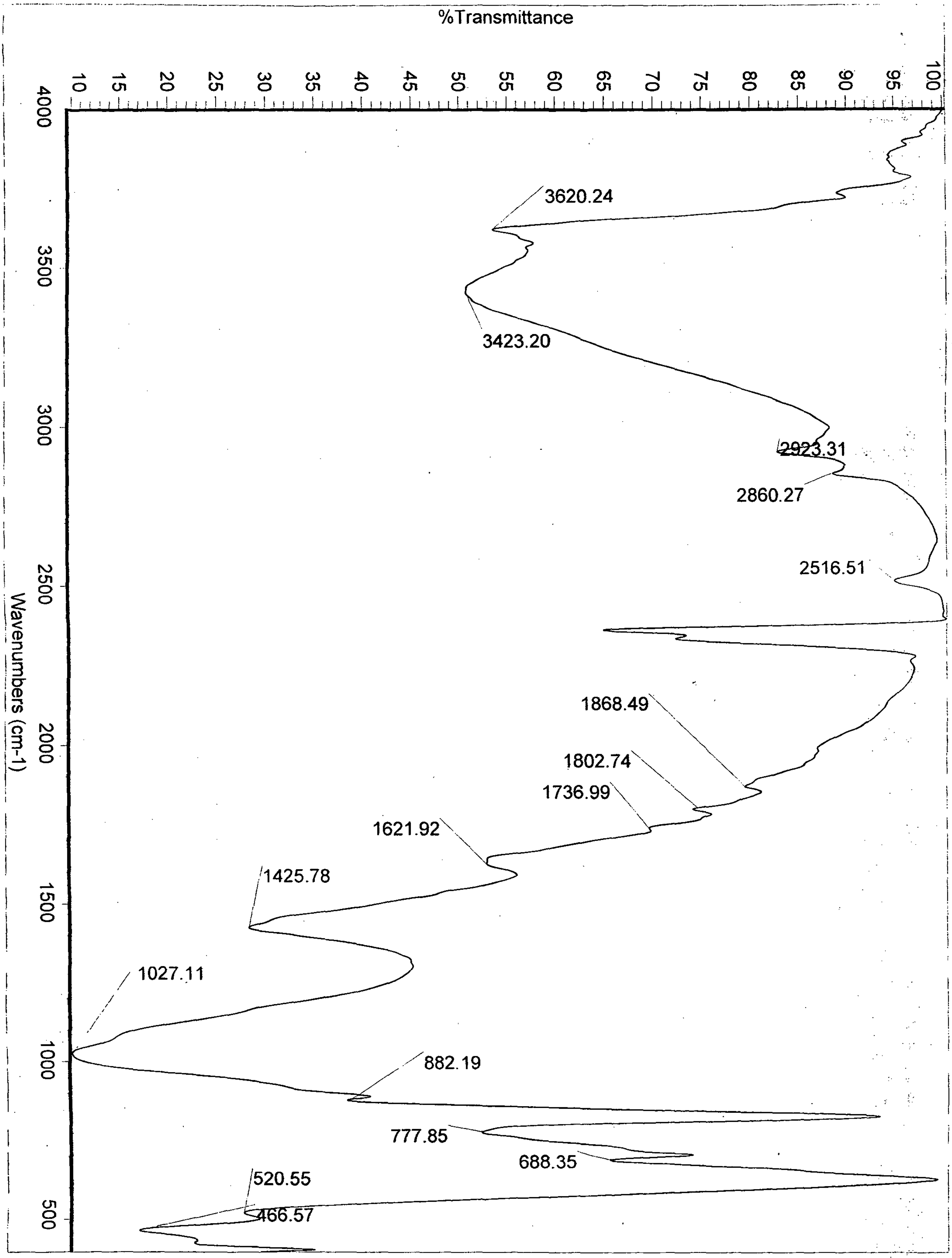
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Wavenumbers (cm-1)
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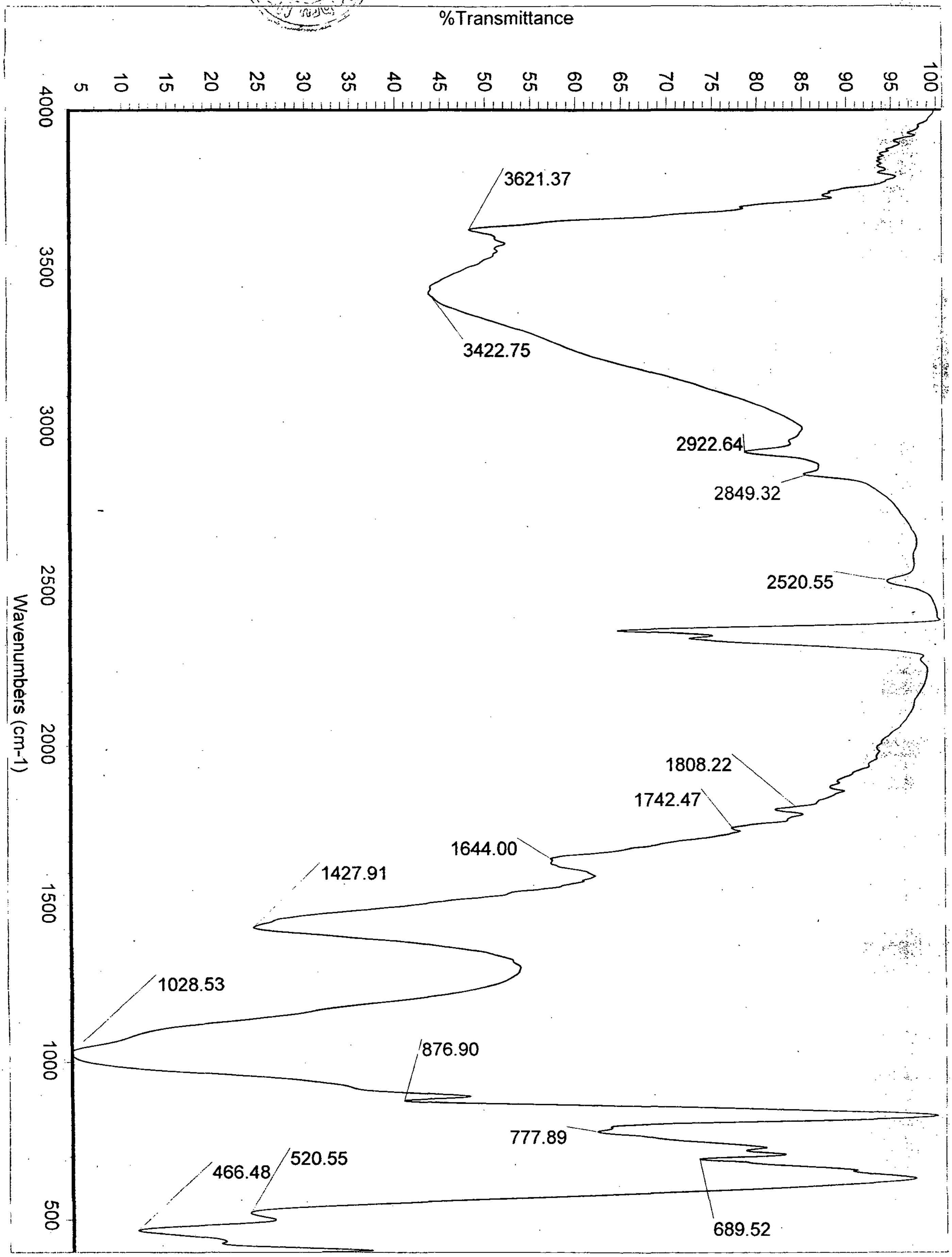
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Wavenumbers (cm-1)
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