THE CHEMISTRY OF INDIGENOUS TECHNOLOGY; APPLICATION OF THE AQUEOUS EXTRACT OF *PARKIA BIGLOBOSA* FRUIT HUSK IN FORMULATION OF MUD WALL PLASTER

by

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DECLARATION

I, Samson Abah Abagale, hereby declare that this submission is my own work towards the M.Sc degree and that, to the best of my knowledge, it contains no material previously published by another person or material which has been accepted for the award of any other degree of a University; where material has been taken, it has been duly acknowledged.

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ABSTRACT

Parkia biglobosa belongs to the family *Leguminosae* and the subfamily *Mimosoideae*. The aqueous extract of its fruit husk is well mixed with a sandy loam soil to obtain a uniform paste, and this is applied as a mud wall plaster on the walls of mud buildings to protect the walls against erosion by rain water.

Methods used in the project were Sohxlet extraction, TLC, HPLC, UV, IR, AAS, Flame photometry and X-ray analyses. To determine the chemical interactions of the constituents of a plastering material a simulated sample of the mud wall plaster was prepared and analysed. The water and ethanol extracts of the husk as well as the soil were separately analysed. The mass of extractable material from samples of husk harvested and stored for about a year (old husk) was compared with that of dry freshly harvested husk (new husk). Some organic constituents of the extract were identified and their interaction with metal constituents of the soil discussed.

The average weight recovery yield of dry extractable material from the husk by water was 37.77% compared to that by ethanol which was 30.83 %. Based upon quantitative extractable material, and neglecting the differences in extraction temperature, water was found to be a more efficient solvent than ethanol for the extraction of *Parkia biglobosa* fruit husk. Also water is generally cheaper and more accessible than ethanol hence recommended for extraction of the husk.

The storage duration of the husk (after harvesting) was practicably irrelevant to the amount of extractable material. Husks that have been harvested and kept for about a year produced almost the same yield of extractable material as freshly harvested husk. The respective amounts were: 38.31% / 37.22% weight recovered for old / new husk extracted

by water and 30.70% / 30.95% for old / new husk extracted by ethanol. Fractionation of the aqueous extract produced four components: weak acid, strong acid, basic and neutral fractions.

From the AAS and Flame analysis, the soil was found to contain: K (556.351 mg/Kg), Mg (230.054 mg/Kg), Fe (419.499 mg/Kg), Ca (336.315 mg/Kg) and Si (1400.564 mg/Kg) as well as Na (97.585 mg/Kg), Ni (103.220 mg/Kg), Pb (17.531 mg/Kg) and Zn (58.050 mg/Kg). In addition, the husks were found to have substantial amounts of Fe (144.248 mg/Kg), K (962.832 mg/Kg) and Mg (246.018 mg/Kg).

Phenolics, anthraquinone glycosides, flavonoids, alkaloids and saponins were indicated in the aqueous extract by phytochemical screening and verified by indication of their functional groups in UV, HPLC and IR analyses. The functional groups present included -OH, C=O, $-CH_3$, -NH and C=C/C=N.

The UV analysis indicated the presence of conjugated systems in the aqueous husk extract. The crude water extract as well as the weak acid and the basic fractions all absorbed predominantly in the visible region whilst the strong acid fraction absorbed mostly in the UV region.

The IR of the formulated plaster using the crude water extract indicated that the plaster contains a number of organic complexes and organometallic compounds such as methoxides, ethoxides and n-butoxides complicated by C-O and C-C coupling of Fe, Co, Al, Si and Zn. There were also $SiPh_4$ at 1100 cm^{-1}, $Si(CH_3)_4$ at 800-600 cm^{-1}, $Si-CH_3$ between 1280-1255 cm^{-1}, trialkoxy silanes $[(RO)_3SiH]$ between 840-800 cm^{-1} as well as tetraoxides of silicon indicated around 880-720 cm^{-1}. These were confirmed by associated absorption due to CH_2-rocking which occurred at 725 and 720 cm^{-1} (w).

From the spectra of the plasters of all the fractions, those of the acidic fractions were predominated by bands due to organometallic compounds very similar to those of the plaster formulated using the crude water extract. The plaster of the weak acid fraction had more identical bands with the plaster of the water extract. Therefore, the organic components of the acidic fractions were identified to have played key roles in the reactions leading to the formation of relevant organometalloids.

IR spectra of the formulated plaster attributable to aluminum complexes and trialkylboranes which are unaffected by water at ambient temperatures have also been observed at 1170, 1135 and 1120 cm^{-1}.

TABLE OF CONTENTS

CHAPTER THREE

CHAPTER FOUR

LISTS OF TABLES

LISTS OF FIGURES

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DEDICATION

This thesis work is dedicated to Diana, my wife, for the unflinching support and to my lovely Mary-Ann Azangyire Abagale and Francine-Macrina Awetonga Abagale. It is also dedicated to my mother, Adjoa Abagale and father Abagale Bole especially for their wonderful support to their children and grand children.

CHAPTER ONE

1 INTRODUCTION

Investigations into the local perceptions of trees in West Africa have revealed *Parkia biglobosa* as one of the species preferred among fruit-bearing trees conserved in farmlands and forests by farmers (Teklehaimanot, 2004). The tree is also a precious and convenient resource for producing traditional medicines. Various parts of it are used to make tonics and ointments to treat many different ailments (Banwo, *et. al.*, 2004).

The most significant product from *P. biglobosa* is food. Increasing awareness of *Parkia* products has resulted in a large increment of consumption of the *Parkia* seed condiment and pulp. In February and March, young green whole pods are roasted and eaten by men. In March and April, the beginning of 'hunger season' when other foods are becoming scarce, mature pods are collected for food. The seed is fermented into a spice called "dawadawa" (Campbell-Platt, 1980; Shao, 2002). *Parkia* food products have thus become important food supplements, the greatest economic value being derived from the fermented seed product which is used as flavoring but also adds protein to a protein-deficient diet. The pulp that surrounds the seeds is also an important source of carbohydrates and energy. As more seed and pulp is consumed, greater amount of husk (empty seed pod) is equally generated and put to various uses.

BACKGROUND

Preliminary investigation shows that *Parkia biglobosa* fruit husk is widely used in rural communities of West Africa. In developing countries like Ghana, using the aqueous *Parkia* husk extract to enhance resistance to rain washing of plastered laterite and as natural paint has remained cultural. Mucilage extract and the decoction of the husk are used to treat mud walls, pottery, floors and roofs to improve their quality and protect them against erosion by driving rain (Awindor, 2006).

In Europe and America, mud is effectively regarded as dirt. However, as part of its culture, earth has always been the most widely used material for building in India, and approximately 55% of all Indian homes still use raw earth for walls. Also, in rural Africa (as in so much of the world) earth is the most common of building materials with which everybody has direct contact. In the sparsely populated Sahel plains of the Western Sudan, traditionally built forms in mud are the most striking representations of human creativity and a unique part of the culture (Morris and Blier, 2003). In Ghana, about 90% of rural community lives in purely mud buildings designed, constructed and decorated with indigenous skills (CraTERRE, 1998). Among other benefits, using earth for construction offers thermal insulation, easy availability of raw material and beauty of the structure.

A good building, must satisfy three conditions; comfort, firmness or stability and appeal. Hence the materials and technical ability used for building must provide a means of achieving these particular results. Weathering of mud walls may be due to effect(s) of

frost, temperature variations, wind or rain on materials of the building causing change of appearance by gradual erosion and producing disfiguration and eventual collapse of the building. The degree to which this effect can go depends on many interacting variables including the type and amount of atmospheric pollution with exposure of the building to wind, rain, frost, snow and solar radiation. Resistance to these factors is determined by the characteristics of the materials used in building, including their capacity or otherwise to absorb moisture as well as surface profiles. Early structures were built from a wide variety of materials that were close to hand including clay, suitable earth, chalk and even dung mixed with sand. Straw or fibre was added as a reinforcing agent. But they suffered from the common problem of being vulnerable to water erosion (Bob, 1997; Slessor, 2004). The quality of nearly any inorganic soil as a building material can improve remarkably with the addition of the correct stabilizer in a suitable amount. The aim of soil stabilization is to increase the soil's resistance to destructive weather conditions in one or more of the following ways: By cementing the panicles of the soil together, leading to increased strength and cohesion, by reducing the movements (shrinkage and swelling) of the soil when its moisture content varies due to weather conditions, by making the soil waterproof or at least less permeable to water.

A great number of substances may be used for soil stabilization because of the many different kinds of soils. Stabilizers in common use include:

- Sand or clay
- Portland cement
- Lime

- Bitumen
- Pozzolanas (e.g., fly ash, rice husk ash, volcanic ash)

Many other substances may also be used for soil stabilization although their use is not well documented and test results are scarce. Sodium silicate or water-glass is best used to coat the outside of soil blocks as a waterproofing agent.

The future of mud buildings is hard to predict since mud is such a vulnerable material and there is an enthusiasm for building in concrete. Given the means, many would tear down their mud houses and build cement block replacements. This is a common practice in some countries and among people who can afford, and this brings a gradual process of extinction of mud buildings (Adarkwa *et. al.*, 2005). Already the extraordinary jelly mould houses of the Mousgoum people of Cameroon are gone and the Sakho houses of the Boso in Mali are all abandoned and in ruins whilst in other places they are gradually disappearing. It is quite possible that when West Africa emerges from below the poverty line there will be little of its mud built heritage remaining to be appreciated (Morris and Blier, 2003).

Also, forests and trees provide income, food, shelter, and health aid to rural as well as urban dwellers. They yield numerous products important to man: commercial timber, foods, pharmaceutical products, resins, rattan and tanning agents which all play significant role in the livelihood of mankind. Farmers know the qualities of trees, what they can be used for and the possibilities and limitations of combining trees with crops for various purposes and so conserve some of them on their farms (Haverkort *et. al.*, 2002; Teklehaimanot, 2004). *Parkia biglobosa* is one such tree named in several studies

as an important and beneficial tree species in Africa that can support sustainable rural development. In some of the areas that the tree grows, trees are culturally protected in sacred groves. The traditional belief is that ancestral spirits reside in the sacred grove and protect the community and so those trees are preserved. These sacred groves are also valuable reservoirs of biodiversity in an area where natural resources are rapidly being depleted. Currently, farmers do not actively plant the *Parkia biglobosa* tree. Yet, through enhanced usage of its seeds, humans play a major role in the decline of natural regeneration of the tree.

PROBLEM STATEMENT

Maintaining and resurfacing of mud buildings is part of the rhythm of the life of these buildings, and there is usually an ongoing and active refurbishment to support their continuing existence. These buildings emerge from the most basic of materials, earth and water. They are vibrant works of art with their own distinct and striking aesthetic, built in response to the qualities of African life, and the inherent properties of the mud. Often people attempt to cement the surface of these buildings, but not only does this destroy them physically, as they rot from within, but it also destroys their character.

In some traditional areas such as Sirigu, Mirigu, Kandiga, all in the Upper East Region of Ghana and several other communities, the empty fruit husks of *Parkia biglobosa*, obtained after using the seed and pulp for food, are boiled to make what is called "sour water". This water is mixed into mud and used to strengthen and waterproof the plaster on the walls of living rooms, huts, barns and other parts of the houses built with mud and mud bricks (Shao, 2002). It is also mixed with other components to make natural

paintings or murals to decorate the walls. This tradition dates back to at least one hundred (100) years when it was applied in the Navrongo Catholic Minor Basilica (CraTERRE, 1998; Awindor, 2006), now a national tourist monument. The husk extract has also been reported to contain a large amount of tannin that are used locally for tanning leather and dyeing cloth (Campbell-Platt, 1980). The Sirigu Women in Pottery and Art (SWOPA) is a non-governmental organization in Sirigu, in the Upper East region of Ghana. Among other things, the group applies *Parkia biglobosa* husk extract in mud wall plastering. They now operate the SWOPA VISITORS CENTRE, an important international tourist attraction that developed from cultural remnants of laterite plastering and wall painting. The works of SWOPA are replicated in most houses in the community and in other parts of Ghana and has attracted even international tourists to the area (Awindor, 2006).

Chemical studies on the empty fruit husk have thus become very imperative since its extract is used in several traditional processes.

Traditionally, the village communities of both Central Sudan and Northern Ghana used to take care of natural regenerating trees such as *Parkia biglobosa* that are of direct benefit to them. They developed knowledge and skills concerning the management and utilization of such trees (Millar, 2002). As a result, rural dwellers have found ways to generate additional income from products of *Parkia biglobosa* to their households. In markets of these communities, it is common to find the seedpods, dried bark, and many different products derived or harvested from trees being sold. These non–timber forest products have several cultural uses some of which have been investigated scientifically. As a result, some industrial values of these local trees have been discovered especially as

medicines. There is however no documentation on the chemistry of application of the *Parkia biglobosa* fruit husk extract.

This project also provides important interventions. It is usually assumed that the presence of manufactured and modern industrial products would conveniently replace existing home manufactured products. Traditional architecture, wall painting and sculpture are being replaced by modern practices in which cultural and spiritual values are marginalized (Haverkort *et. al.*, 2002). For instance, commercial bitumen has been mixed with mud and used for mud wall plastering as well as tamping floors. Cement is also another alternative that has been used in building of modern houses and also for plastering walls of mud buildings and making their floors. Regrettably however, the replacement of traditional products would divert precious cash for purchase of items that had little cost if home produced, reduce opportunities for income generation at the rural level and decrease the value local farmers had previously placed on some tree species. The industrial products are also expensive for most rural folks who, apart from being economically less endowed, are mostly characterized by subsistence farming, non-commercial animal keeping, inadequate scientific knowledge, and thus require scientific and technological interventions.

JUSTIFICATION

Most people in the tropics will continue to live in earth houses for sometime and it is important to take interest in providing ways and means by which at least, the rate of deterioration will be reduced and so make these earth buildings more durable and safe for habitation (Hagan and Osei-Frimpong, 2006). It has been possible to provide relative

protection against driving rain by applying a suitable external finish using the extract of *Parkia biglobosa* husk. The extract enhances appearance and durability which are important requirements for both external and internal plasters of a good building. Therefore, scientific studies on the application of the husk are relevant to understanding the chemistry. It is imperative to understand the chemistry involved in application of the aqueous extract of *Parkia biglobosa* fruit husk so that the ethnobotanical information available on the use of the extract in mud wall plaster could be given some scientific explanation.

Akobundu (1999) reported that research on expanded utilization of indigenous African useful plants should receive priority attention in order to promote plant conservation practices, increase their value and scientifically refine their uses. Ascribing scientific understanding to the local perception of trees and tree products as a resource is vital to enhancing their knowledge and use. The work creates general awareness of the husk, enhance knowledge of its uses and promotion of a sustainable natural resource management for *Parkia biglobosa*. When scientific investigations are conducted on the numerous uses of its products, it could create enough awareness for the tree to become a target for conservation and eventually its active cultivation as a cash crop. Cash crops such as the oil palm, rubber, cashew, cocoa and coffee trees were once derived from wild sources but now cultivated at lower cost to provide a reliable supply and improved quality as a result of numerous discoveries made on them from scientific studies (Gakou *et. al.*, 1994).

Ajaiyeoba (2002) presented his investigation, "*Phytochemical screening and antimicrobial studies of Parkia bicolor and Parkia biglobosa leaf extracts*" justifying it as being "in continuation of the study of *chemical constituents of different parts of Parkia bicolor* and *Parkia biglobosa.*" There is substantial literature on the uses of *Parkia biglobosa* seed and pulp, and their chemistry. There is also literature on ethnobotanical uses of the fruit husk of the tree. However, there is very little information on the chemistry of the "husk". Thus, this work augments the documented investigations conducted by other researchers on various aspects of the fruit of *Parkia biglobosa.* Finally, documentation of the scientific background to application of *Parkia biglobosa* fruit husk extract in traditional building practices could also enhance conservation of the tree or perhaps its active cultivation. Currently, people regard *Parkia biglobosa* only as an important local natural resource and this makes the tree persistent only on farmlands (Lykke, 2000; Berisavljevic, *et. al.*, 1999).

OBJECTIVES

This project therefore explored the chemical composition of the husk and the soil used in plastering mud walls and tamping of floors and roofs. It also sought to understand the chemistry of the plastering material. The project included:

a. (i) Extracting the husk using water and ethanol as solvents, carrying ouphytochemical screening of the extract and analyzing the extract by solubility tests, thin layer chromatography (TLC), high performance liquid chromatography (HPLC), infrared spectroscopy (IR), Flame photometer and atomic absorption spectroscopy (AAS).

(ii) Calculating the percentage yield of extract, identifying the better solvent for extracting the husk and fractionating the extract.

b. (i) Analyzing the sandy loam soil used in the traditional technology of mud wall plaster formulation using Flame photometry, AAS and X-ray diffraction for K, Na, Ca, Pb, Zn, Mg, Si, Ni and Fe which are cited by literature to have ability to form water resilient species and using IR to analyse for organic functional groups present in the soil.

(ii) Comparing the functional groups of the husk extract and the soil, and identifying the components of the soil and the extract whose interaction may contribute to water resilient properties of the plaster.

c. (i) Simulating the traditional formulation of the mud wall plaster and analyzing /reviewing the possible interactions between different organic components of the husk extract, as well as the interactions between the metals of the soil and organic components of the extract.

(ii) Analyzing the formulated plaster using IR and identifying components which contribute to water resilient properties.

d. Comparing (i) the functional groups of the extract and the fractions and identifying the fraction which contains most of the functional groups found in the extract.

(ii) the functional groups of the extract and plaster with metals of the soil and suggesting how the components of the plaster were formed.

SCOPE OF THE PROJECT

The project therefore led to discovery and documentation of some chemical constituents of the husk and soil that are used in mud wall plastering. The plaster was simulated and

enabled an understanding of the chemistry involved in the traditional technology of adding the aqueous husk extract in mud wall plaster.

Obviously it also increased awareness of the works of SWOPA as it delved into the chemical constitution and the underlying chemistry of materials used by the women in the traditional technology.

CHAPTER TWO

2 LITERATURE REVIEW

According to Shao, 2002, it is recorded that Michel Adanson, in 1757, first reported of the then new species, now *Parkia biglobosa* in his collection trips to Senegal and the Gambia. Adanson did not name the tree and in 1763 it was also reported by Nicolas Jacquin who published the name of the tree as *Mimosa biglobosa* from the West Indies. Palisot de Beauvois in 1816 also described the tree species as *Inga biglobosa* from Africa. Mungo Park had also discovered the tree species across Africa and in 1799 publish the local name *nitta*. In 1826, Robert Brown suggested renaming and reclassifying the species of the plants under the same genus *Parkia*, to commemorate Mungo Park. In 1842, Bentham included Asian forms of the tree into the genus Parkia.

The beauty, resilience and comfort of a building depend on its architecture and the composite materials. Earth building may be constructed using rammed earth, compressed earth blocks or with bricks. Bricks generally used for building, among other characteristics, have integral and durable colour and when properly constructed, are resistant to rain penetration. Stabilised mud bricks may contain materials such as straw, cement or bitumen that re-enforce them (CSIRO, 1995; Simmons and Gray, (Eds.)., 1996).

This chapter reviews *Parkia biglobosa*, its chemical constitution and applications, various types of building materials and their applications in architecture and analytical techniques used in the project.

2.1 BOTANY OF *PARKIA BIGLOBOSA*

Parkia biglobosa (Jacq.) Benth belongs in the family *Leguminosae* and the subfamily *Mimosoideae* (Hopkins, 1983). Other species in the same genus include *Parkia africana* R. Br., *Parkia intermedia* Oliver, *Parkia oliveri* J.F. Macbr., *Parkia clappertoniana* Keay, *Parkia pendula* and *Parkia bicolor*. *Parkia biglobosa* forms a crown and often grows as a shade tree for crops in the farms and along avenues (Okafor, 1999; Ajaiyeoba, 2002). Currently the described species within the genus *Parkia* number twenty-four, occurring in tropical South America, Asia, and in Africa (Hall *et al.*, 1997).

Figure 2.1 Picture of *Parkia biglobosa* tree on KNUST campus, Kumasi

2.1.1 Common Names

Common names of the plant include African Locust Bean, Fern Leaf, Monkey Cutlass Tree, Two-ball Nitta-tree all in English. In French West Africa it is commonly known as *Néré, Netto, Ulele, Séou,* and *Ouli* (Booth and Wickens, 1988) while in Ghana it is called Sungu in Kasem, Osonkorang in Twi, Dua in Nankani, and Ateomi in Ga. In Nigeria it is known in Yoruba as Igba or Irugba, in Hausa it is Dorowa and in Ibo Origili (Ajaiyeoba, 2002).

2.1.2 Morphology

Parkia biglobosa is a perennial, deciduous savannah tree reaching 7 – 20 m in height. The tree grows into tall, mostly gigantic, deciduous well-branched vegetation (Okafor, 1999). The crown or canopy is large and wide spreading with low branches on a stout trunk. Its pinnae are about 6 - 11 pairs and the leaflets up to 14 – 30 pairs (Andrew, 1956). The fruit or seedpod is the most widely used and most economically important part of the tree. Typically 20 to 25 pods arise from a single capitulum (Booth and Wickens, 1988).

When young, the fruits are green, fleshy, and pliable. They then mature and darken to a red-brown or brown colour and the hulls of the pods become hardened, smooth, and woody. The pod is sub-cylindrical and compressed laterally in shape (appendix 1). Its length ranges between 12 and 35 cm, having a width of about 15-25 mm. The pulp in the unripe fruit is white at first and turns to bright yellow as the fruit mature. Each pod contains 5 – 20 seeds, embedded in the spongy, yellow endocarp. Its pinnae is about 6 -

11 pairs with leaflets of about 14 - 30 pairs. *Parkia biglobosa* trees readily coppice after cutting. The trees are slow growing, and begin fruiting after 8 years; at 15-20 years it would produce 25-100 kg of pods per tree (Hall *et. al.* 1997).

2.1.3 Distribution

Parkia biglobosa has a wide distribution ranging across the Sudan and Guinea savanna ecological zones. The range extends from the western coast of Africa in Senegal across to Sudan. It is found in nineteen African countries: Senegal, The Gambia, Mali, Burkina Faso, Ghana, Benin, Niger, Nigeria, Chad, Zaire, Sudan, and Uganda among others (Hall *et. al.*, 1997). In Ghana, the tree is largely found in the North where it is regarded as a sign of traditional prestige due to its numerous applications. Dawadawa (*Parkia*) is found on arable lands in all three northern regions of Ghana and other parts of West Africa. It is a common species on farmlands and fallow lands and is shown to contribute to soil fertility (Bayala *et. al.*, 2006; Uyovbisere and Elemo, 2002). It is not felled but used as a regular source of fuel wood or other non timber products and almost all farmers in the community selectively preserve it. It is regarded as a traditional agro forestry and the tree is fourth (after *Vitelaria spp* , *Anogeissus leiocarpus* and *Azadriachta indica*) among twenty-two tree species on Ghana's priority list of trees species found in Northern Ghana (Berisavljevic *et. al.*, 1999). It is sparsely located in the south of the country, and its distribution conforms to common environmental factors throughout its range.

2.1.4 Uses

Parkia biglobosa is often used as a fodder source; branches are cut and fed to livestock. Non-timber forest products derived from *Parkia biglobosa* are food, medicine, glazes, soil amendments, charcoal, and firewood. The most significant product from *Parkia*

biglobosa is probably food. The unripe fruit is roasted on fire and the pulp with seeds is eaten as a meal. The food products collected from *Parkia biglobosa* are especially important due to the seasonality of their availability. During the lean season of the year (February to April) young green whole pods/fruits are roasted and eaten by humans (Shao, 2002). After roasting, the husk is peeled off its contents and the entire content (pulp + seed) is edible.

The pods of *Parkia biglobosa* ripen and dry up on the trees between May and June. They are normally harvested using a very tall go-to-hell but may also be harvested by hand when a person climbs up the tree. After removing and utilizing the edible seed and pulp, the husk is sold in the market for use in traditional mud wall plastering (Shao, 2002).

The pulp of the ripe fruit also serves as food source in the dry season and is used throughout West Africa. In the beginning of 'hunger season' when other foods are becoming scarce, mature pods are collected for food. It is pounded with a large pestle until the seeds are separated from the endocarp (making up the pulp). The endocarp is set aside using sieves and eaten raw, or used as flour to prepare a carbohydrate rich porridge (Hall *et. al.* 1997). It is sometimes used as a snack food though it sometime serve as an important food supplement (Becker, 1983; Ogbe, *et. al.*, 1999).

The seeds are used in preparation of *dawadawa*, a protein and fat rich food, for seasoning traditional soups (Ajaiyeoba, 1998). A survey on families in Burkina Faso on vegetable consumption and seasonality in two communities found that dawadawa was consumed in

78% and 85% of all meals (Mertz *et. al.* 2001). Also, the fermented seeds of *Parkia clappertoniana* and *biglobosa* are being produced commercially into cubes by industry (Alabi *et. al.*, 2004). In Nigeria, Cadbury Ltd. has used the seed extract to flavour cube spices called *Iru* and this enhances the saleability of the product, particularly among sophisticated housewives who do not want to buy the locally produced dawadawa balls. Uniliver Ghana Ltd. also produces large quantities of the cube flavour called ROYCO DAWADAWA for sale in Ghana and other West African Countries (Owusu *et. al.*, 1999).

Decoctions of the fruit husk extracted by boiling are used to impart water resiliency to floors, walls, and ceramic pots. The 'sour water' produced from steeping and boiling the husks is mixed with mud to plaster walls of houses in some rural communities. This plaster is also used to paint tamped earthen floors. The extract of the husk act to bind the soil and render the surface impervious to water (Shao, 2002).

Figure 2.2 Plastering mud rooms using mud/ *Parkia biglobosa* husk extract mixture

In Burkina Faso, Karaboro and Gouin potters splash their pots with a vegetal solution made from the pods and husks which act as a sealant and creates a dark, mottled surface (Cookery, 2000). The Raw Materials Research and Development Council reported that azo dyes have been synthesized by Putshaka and his co-workers using the water extract of *Parkia* fruit husk. A yellow dye soluble in water which was shown by spectroscopic (infrared and ultraviolet) and chromatographic analysis to have similar properties characteristic of conventional azo dyes has been produced from the water extract. The extract of the bark and husks of the pods of *Parkia biglobosa* are also used for dyeing and curing leather as well as for dying sculpture (Campbell-Platt, 1980).

Medicines derived from *Parkia biglobosa* are of value mostly to the rural communities that either cannot afford or have access to "modern medicine". The importance attached to the tree and its products as medicine is perhaps as a result of its large application. In Gambia, the leaves and roots of *Parkia biglobosa* are used in preparing a lotion for sore eyes (Irvine, 1961). The crude extract of bark and leaves has also been documented to be effective against bacteria. For infections, wounds, and fever the bark is boiled and applied topically.

Traditional herbalists have also claimed that the plant species cures diarrhoea and dysentery. To relieve diarrhea, the bark is boiled to make a tea (Ajaiyeoba, 2002; Banwo, *et. al.*, 2004). *Parkia biglobosa* is also known to provide an ingredient that is used in treating leprosy, and for treating hypertension while a decoction of the bark is used as a

bath for fever, as a hot mouthwash to stem and relieve toothache. The pulped bark is used along with lemon for wound and ulcers (Irvine, 1961).

Other authors have reported on the medicinal uses and treatments using this plant. Table 2.1 below gives a summary of some of these:

Table 2.1 Uses of different parts of the *Parkia biglobosa* tree

Source material	Preparation	Medicinal use
Leaves	Lotion preparation, Crushed	Sore eyes, Burns, Hemmorhoids, Toothache, Bronchitis
Flowers, Flower bud	Grilled and macerated, Infusion	Hypertension, Lumbago, Leprosy prophylactic
Bark	Gum extract, Macerated in bath, Decoction	Toothache, Diarrhea, Ear complaints Mouthwash, Leprosy, skin infections, sores, ulcers Bronchitis, pneumonia, Schistosomiasis, Rheumatism, Circumsion wounds, general wounds
Pulp		Diuretic, purgative, fever

Table 2.1 continued

Source material	Preparation	Medicinal use
Seeds	Pounded with salt, Fermented, Decoction	Tension, Mouth ulcers, Skin infections, Wasp and bee stings
Roots	Decoction	Diarrhea, dysentery, Eye infections, Guinea worm

Sources: (Abbiw, 1990; Booth and Wickens, 1988; Hall *et. al.*, 1997)

2.1.5 Regeneration

Parkia biglobosa is often used as a fodder source; branches are cut and fed to livestock (Hall *et. al.*, 1997). However, shoots and root suckers arise naturally from stumps after cutting. Antelopes, cattle, sheep, and goats are attracted to the nutritious pulp and also feed on the pods, in the process the seeds are ingested and dispersed. Baboons, monkeys, and chimpanzees also feed on the fruit and act as agents of dispersal. Feeding by primates can be more selective and seeds are often spat out after eating the pulp rather than passed through the gut (Campbell-Platt, 1980; Hopkins, 1983).

2.1.6 Chemical Composition

Parkia plants have also been identified as source of tannins, saponins, gums, fuel, glutamic acid, carbohydrates, glycosides and wood (Irvine, 1961; Ajaiyeoba, 2002).

The yellow starchy pulp is an important food supplement rich in Vitamin C and carbohydrates. It contains up to 60% carbohydrates, 10-24% of which is sucrose, and 291 mg of Vitamin C per 100 g of pulp (Campbell-Platt, 1980). It contains up to 29% crude

protein and has high oil content. The pulp is also rich in calcium, sodium, potassium and phosphorus.

Hall *et. al.* (1997) suggested that the bark contains 12-14% tannin while the husk contains 27-44%. Phenolic compounds such as tannin chelate metal ions after donating a hydrogen atom, making the compound become a resonance-stabilized radical which does not easily participate in other radical reactions. Metal chelators include some organic acids, ascorbic acid, polyphenols such as quercetin, carnosine, some amino acids, peptides and protein. They can convert metal ions into insoluble metal complexes or generate steric hindrance, which can prevent the interactions between metals and other moieties.

The chemical properties of some of the secondary metabolites probably contribute to the resistance of mud wall plaster to rain water erosion when the fruit husk extract is applied in the plaster. Alkaloids, tannins, saponins, flavonoids, terpenes, anthraquinones and anthocyanins are reviewed below.

2.1.6.1 Alkaloids

Many of the earliest isolated pure compounds with biological activity were alkaloids due to the ease of isolation. Alkaloids have been defined in various ways, but one definition comes fairly close to actuality. An alkaloid is a plant-derived compound that is toxic or physiologically active, contains one or more nitrogen atoms in a heterocyclic ring, having a complex structure and is of limited distribution in the plant kingdom.

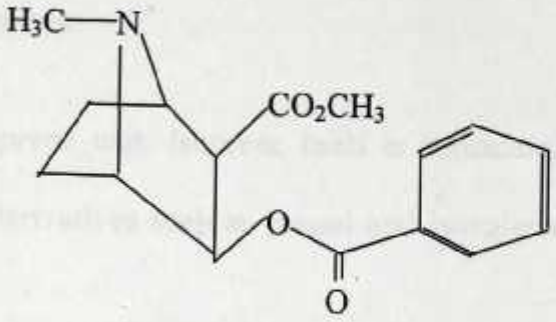
Among the most famous of the alkaloids are the Solanaceae or tropane alkaloids. Plants containing these alkaloids have been used throughout recorded history as poisons, but many of the alkaloids do have valuable pharmaceutical properties (Carey, 2006). Quinine, atropine, scopolamine, ergot and morphine are all examples of alkaloids.

Properties

Alkaloids are usually derivatives of amino acids and most of them have a very bitter taste. The nitrogen atom generally makes the compounds basic and so alkaloids exist in plants as a salt. Thus alkaloids are often extracted with water or mild acid and then recovered as crystalline material after treatment with base (Pavia *et. al*, 1995).

Scopolamine is an alkaloid that is used as a treatment for motion sickness. Also, cocaine, another member of this class from *Erythroxylum coca*, is closely related in structure and is active as a central nervous system stimulant. It has been used as a topical anesthetic in opthamology as well. Cocaine has been found to be a drug of abuse and has been outlawed. Atropine, the racemic form of hyoscyamine, comes from *Atropa belladonna* (deadly nightshade) and is used to dilate the pupils of the eye. Atropine is also a Central Nervous System stimulant and is a treatment for nerve gas poisoning. Originally isolated from *Cinchona succirubra*, quinine is one of 31 alkaloids with related structures and the principal antimalarial compound.

Structure of Cocaine



2.1.6.2 Terpenes

Terpenes are a large and varied class of hydrocarbons produced primarily by a wide variety of plants, particularly conifers, though also by some insects such as swallowtail butterflies which emit terpenes from their osmeterium. They are the major components of resin and of turpentine produced from resin. The name "terpene" is derived from the word "turpentine". Chemically modified (such as by oxidation or rearrangement of the carbon skeleton) terpenes are generally referred to as terpenoids. Some authors will use the term terpene to include all terpenoids. Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers. Essential oils are used widely as natural flavour additives for food, as fragrances in perfumery, in aroma therapy and in traditional and alternative medicines (Pavia *et. al*, 1995). Synthetic variations and derivatives of natural terpenes and terpenoids also greatly expand the variety of aromas used in perfumery and flavours used in food additives.

Classification

Terpenes are derived biosynthetically from units of isoprene, which has the molecular formula C_5H_8. As chains of isoprene units are built up, the resulting terpenes are

classified sequentially by size as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes and tetraterpenes.

Hemiterpenes consist of *a single isoprene* unit. Isoprene itself is considered the only hemiterpene, but oxygen-containing derivatives such as prenol and isovaleric acids are hemiterpenoids.

Monoterpenes consist of *two isoprene* units and have the molecular formula $C_{10}H_{16}$. Examples of monoterpenes are: geraniol and limonene.

Structure of Isoprene

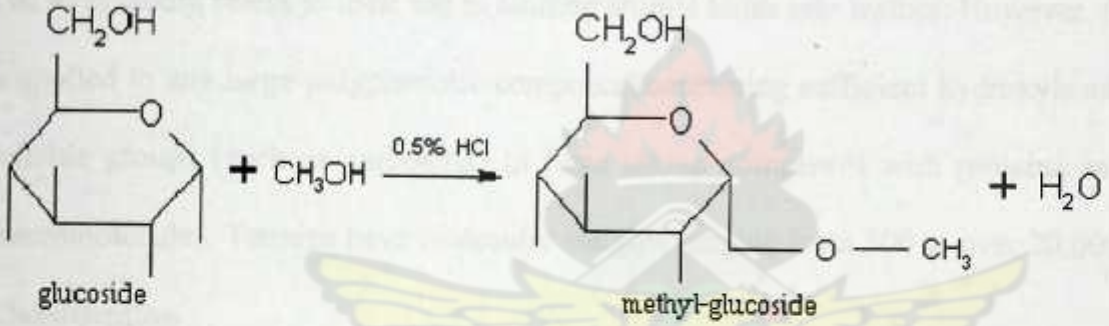
Sesquiterpenes consist of *three isoprene* units and have the molecular formula $C_{15}H_{24}$. An example of sesquiterpenes is farnesol.

Diterpenes are composed of *four isoprene* units and have the molecular formula $C_{20}H_{32}$. They form the basis for biologically important compounds such as retinol, retinal and phytol. Sesterterpenes are terpenes having 25 carbons in *five isoprene* units; triterpenes consist of *six isoprene* units and have the molecular formula $C_{30}H_{48}$ while tetraterpenes contain *eight isoprene* units and have the molecular formula $C_{40}H_{56}$. Biologically important tetraterpenes include the acyclic lycopene, the monocyclic gamma-carotene, and the bicyclic alpha- and beta-carotenes; polyterpenes consist of long chains of many *isoprene* units. Natural rubber consists of polyisoprene in which the double bonds are cis.

2.1.6.3 Glycosides

Glycosides are compounds containing a carbohydrate and a noncarbohydrate residue in the same molecule. The non-sugar component is known as an aglycone and the sugar components are called glycones.

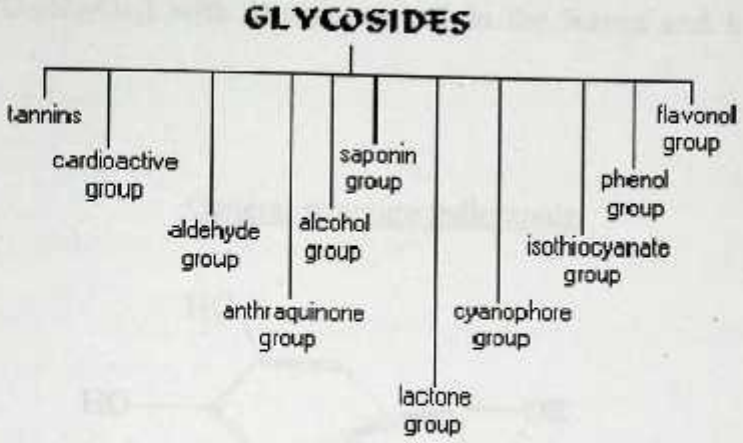
The carbohydrate residue is attached by an acetal linkage at carbon atom 1 to a noncarbohydrate residue or aglycone. If the carbohydrate portion is glucose, the resulting compound is a glycoside. An example is the methyl glucoside formed when a solution of glucose in boiling methyl alcohol is treated with 0.5% HCl as a catalyst.



The aglycone may be methyl alcohol, glycerol, a sterol, a phenol, etc.

Classification

Glycosides have been classified based on the glycone and aglycone residues. When the chemical nature of the aglycone group is used as the basis of systematization, the classification is as follows:



2.1.6.4 Tannin

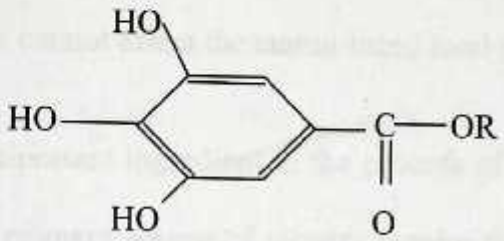
Tannins are astringent, bitter-tasting plant polyphenols that bind and precipitate proteins. The term tannin refers to their use in tanning animal hides into leather. However, the term is applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong complexes with proteins and other macromolecules. Tannins have molecular weights ranging from 500 to over 20,000.

Classification

Tannins are usually divided into hydrolyzable tannins and condensed tannins (proanthocyanidins). At the center of a hydrolyzable tannin molecule, there is a polyol carbohydrate (usually D-glucose). The hydroxyl groups of the carbohydrate are partially or totally esterified with phenolic groups such as gallic acid (in gallotannins) or ellagic acid (in ellagitannins). Hydrolyzable tannins are hydrolyzed by weak acids or weak bases to produce carbohydrate and phenolic acids. Condensed tannins, also known as proanthocyanidins, are polymers of 2 to 50 (or more) flavonoid units that are joined by carbon-carbon bonds, which are not susceptible to being cleaved by hydrolysis (Pavia *et. al*, 1995). While hydrolyzable tannins and most condensed tannins are water soluble, some very large condensed tannins are insoluble. Examples of gallotannins are the esters

of tannic acid ($C_{76}H_{52}O_{46}$) with glucose, found in the leaves and bark of many plant species.

General structure gallotannin



R = H gives gallic acid, R = $C_6H_{11}O_5$ gives glucogallin

Properties

Tannins may be employed medicinally in antidiarrheal, hemostatic and antihemorrhoidal compounds.

The tea plant (*Camellia sinensis*) is an example of a plant with naturally high tannin content. Green tea leaves are unquestionably a major plant source of tannins, as they not only contain the tannic and gallic acid groups, but also a proanthocyanidin (a type of flavanol) named prodelphinidin. When any type of tea leaf is steeped in hot water for an excessively long period it brews a "tart" (astringent) flavour that is characteristic of tannins (and other components). New varieties of *Camellia sinensis* have been specifically bred for lower tannin content. If ingested in excessive quantities, tannins inhibit the absorption of minerals such as iron into the body. This is because tannins are metal ion chelators, and tannin-chelated metal ions are not bioavailable. Modern winemakers take great care to minimize undesirable tannins from seeds by crushing grapes gently to extract their juice. Tannins play an important role in preventing

oxidation in aging wine and appear to polymerize and make up a major portion of the sediment in wine. Some persimmons are highly astringent due to the high level of tannins and therefore inedible when they are not extremely ripe. If eaten by humans (and many other animals), the mouth will become completely dry, yet the saliva glands will continue to secrete saliva which cannot affect the tannin-laced food (Templer *et. al.*, 2006).

Tannins are also an important ingredient in the process of tanning leather. Oak bark has traditionally been the primary source of tannery tannin, though synthetic tanning agents are also in use today. Each type of skin may be treated by several tanning processes. The process is chosen according to the use for which the leather is intended. The two principal tanning processes are mineral or chrome tanning and vegetable tanning. Chrome tanning often can be completed in a single day, whereas vegetable tanning requires many weeks or months. However vegetable tanning results in firmer leather with greater water and stretch resistance. Chrome tanning shrinks the stock and produces longer-wearing leather with greater resistance to heat. The processes are sometimes combined to derive the advantages of each (Templer *et. al.*, 2006).

2.1.6.5 Anthraquinones

Anthraquinones are condensed aromatic structures having anthracene as the parent compound. They are polycyclic aromatic hydrocarbon compounds containing two opposite carbonyl groups (C=O) at 9,10 position (formal IUPAC name: 9,10-dioxoanthracene). They are the most important quinone derivatives of anthracene, which is the parent substance of a large class of dyes and pigments. This highly crystalline aromatic hydrocarbon occurs in coal tar and melts at 218°C. It is insoluble in water but readily soluble in most organic solvents and halogenated solvents though anthraquinones

and their glycosides, along with other compounds, have been isolated and characterized from acetone:water (1:1) percolation of dried roots of some plants (Singh and Tanjali, 2005). Anthraquinones occur in various forms in plant material either as free anthraquinones or as glycosides. Research has shown that natural products also contain reduced derivatives of anthraquinones such as oxanthrones, anthranols and anthrones and compounds formed by union of two conthrone molecules.

In glycosides, the carbohydrate residue is usually attached by an acetal linkage at the first carbon atom to an aglycone. The aglycone may be methyl alcohol, glycerol, a sterol, a phenol, etc. If the aglycone is anthraquinone, the resulting compound is a glycoside called anthraquinone glycoside.

Properties

Anthraquinone aglycones are chloroform soluble whereas the glycosides are not and this has been applied with good results to the isolation of the aglycones and glycosides of cascara and senna. However, anthraquinones are usually soluble in hot water and dilute alcohol (Yung Su and Furguson, 1972).

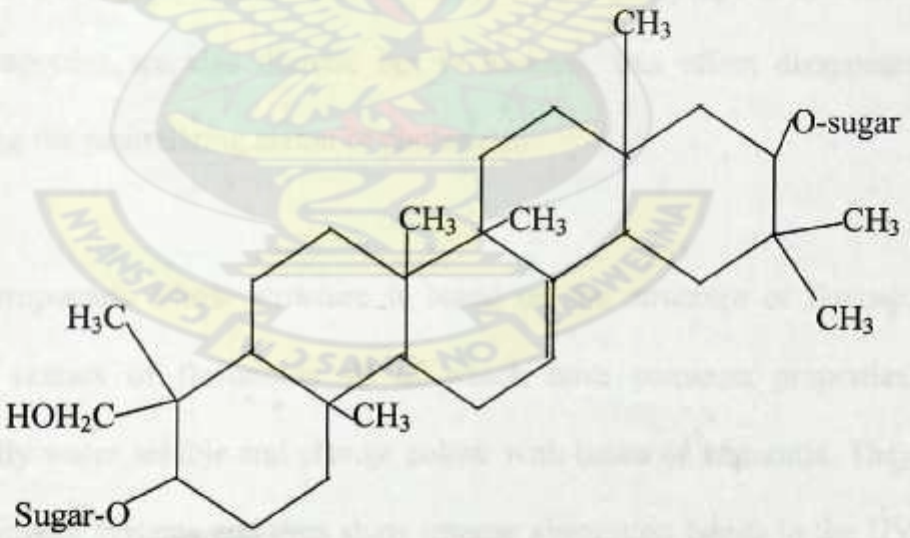
Upon oxidation of anthracene with potassium dichromate/sulphuric acid anthraquinone is obtained. Anthracene is highly toxic but on the other hand, anthraquinone is relatively non-toxic; the LD50-value (rat, oral) has been determined as 15g/kg body weight.

2.1.6.6 Saponin

Saponins are glycosides with a distinctive foaming characteristic. They are found in many plants, but get their name from the soapwort plant (*Saponaria*), the root of which was used historically as a soap. They are generally in tropical forage legumes, though

they are common in several temperate forage legumes. Several rangeland weeds including corn cockle (*Agrostemma githago)*, soapwort (*Saponaria officinalis*), cow cockle (*Saponaria vaccaria*), and broomweed (*Gutierrezia sarothrae*) cause serious toxicity problems for grazing livestock because of their saponins. Alfombrilla (*Drymaria arenaroides*) is a weed in northern Mexico containing 3% saponins that is responsible for cattle losses in Mexico. Yucca contains sarsaponins and is occassionally grazed by cattle. However, research indicates that sarsaponins might actually be beneficial to rumen digestion. Other plants containing saponins include christmas rose (*Helleborus niger*), Horse Chestnut trees (*Aesculus hippocastanum*), Asparagus fern (*Asparagus officinalis*) and Daisies (*Bellis perennis*). The aglycone is referred to as the sapogenin and steroid saponins are called saraponins. Saponins consist of a polycyclic aglycone that is either a choline steroid or triterpenoid attached via C3 and an ether bond to a sugar side chain.

General Structure



Properties

The ability of a saponin to foam is caused by the combination of the nonpolar sapogenin and the water soluble side chain. Saponins are bitter and reduce the palatability of livestock feeds. However if they have a triterpenoid aglycone they may instead have a licorice taste as glucuronic acid replaces sugar in triterpenoids. Some saponins reduce the feed intake and growth rate of nonruminant animals while others are not very harmful. Saponins found in oats and spinach increase and accelerate the body's ability to absorb calcium and silicon, thus assisting in digestion. Certain pasture weeds contain substantial quantities of dangerous saponins and result in life threatening toxicities for certain animal species. Historically, saponins have been blamed for the incidence of bloat in ruminants consuming fresh alfalfa. Bloat occurs in animals grazing temperate legumes that contain saponins. Humans generally do not suffer severe poisoning from saponins because cholesterin inactivates them so that only mucus membranes are affected. This is why saponins have been used in sneezing powders, emetics, and cough syrups to facilitate expectoration. Most saponins are also diuretic but in humans, this effect disappears within a week following the neutralizing action of cholesterin.

2.1.6.7 Flavonoids

Flavonoids include compounds whose structure is based on the structure of flavone. There are about ten classes of flavonoids all of which have common properties. Flavonoids are generally water soluble and change colour with bases or ammonia. They contain conjugated aromatic systems and thus show intense absorption bands in the UV and Visible regions (Andersen, 2006; Tuani and Sao, 1999). The term flavonoid refers to a class of plant secondary metabolites that can be classified as flavonoids, isoflavonoids

and neoflavonoids;

- *flavonoids*, derived from the 2-phenylchromone (2-phenyl-1,4-benzopyrone) structure.
- *isoflavonoids*, derived from the 3-phenylchromone (3-phenyl-1,4-benzopyrone) structure.
- *neoflavonoids*, derived from the 4-phenylcoumarine (4-phenyl-1,2-benzopyrone) structure.

Flavonoids are widely distributed in plants fulfilling many functions including producing yellow or red/blue pigmentation in flowers and protection from attack by microbes and insects. They have a large variety, are widespread and have relatively low toxicity compared to other active plant compounds. They have also been found in high concentrations in butterflies and moths sequestered from dietary intake at the larval stage and then stored in adult tissues.

Classification

Flavonoids are generally water soluble though can be extracted with 70% ethanol. They contain conjugated aromatic systems and thus show intense absorption bands in the UV and visible regions. They are generally in plants bound to sugar as glycosides. Flavonoids are also present in plants as mixtures and rarely found only as single flavonoid component in a plant tissue. Over 5000 naturally occurring flavonoids have been characterized from various plants. They have been classified according to their chemical structure, and are usually subdivided into 6 subgroups:

Flavones which use the 2-phenyl-4H-1-benzopyran-*4-one* skeleton;

Examples: Luteolin, Apigenin, Tangeritin.

Flavonols which use the 3-hydroxy-2-phenyl-4H-1-benzopyran-*4-one* skeleton;

Examples: Quercetin, Kaempferol, Myricetin.

Flavanones which use the 2,3-dihydro-2-phenyl-4H-1-benzopyran-*4-one* skeleton;

Examples: Hesperetin, Naringenin, Eriodictyol.

Flavan-3-ols use the 2,3-dihydro-*3-hydroxy*-2-phenyl-benzopyran skeleton;

Examples: Catechins (Catechin, Gallocatechin, Catechin 3-gallate.

Isoflavones which use the 3-phenyl-4H-1-benzopyran-4-one skeleton;

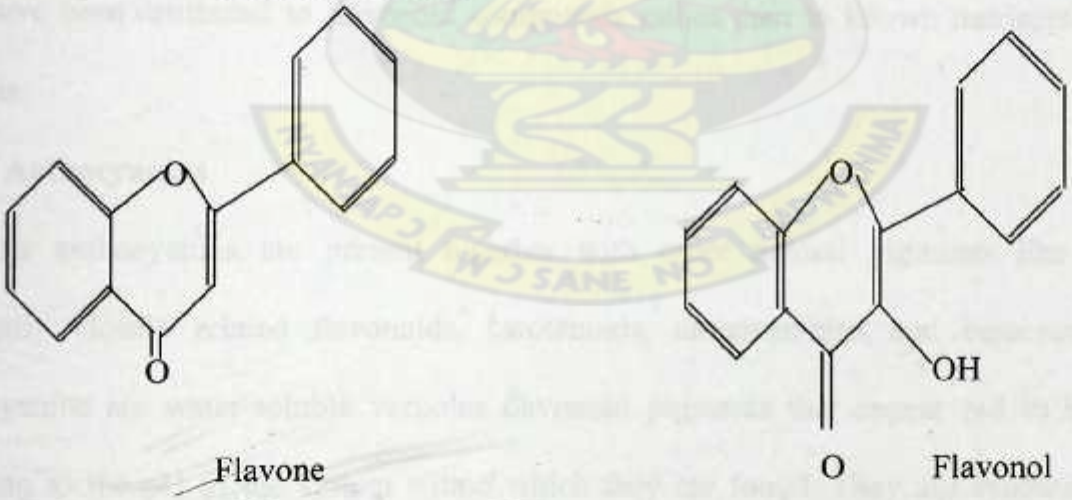
Examples: Genistein, Daidzein, Glycitein.

Anthocyanidins;

Examples: Cyanidin, Delphinidin, Malvidin.

Other important flavonoids include quercetin, epicatechin and oligomeric proanthocyanidins green tea polyphenols.

General Structures



Flavone Flavonol

Properties

Flavonoids are most commonly known for their antioxidant activity. They show anti-

allergic, anti-inflammatory, anti-microbial and anti-cancer activity. Plant extract may be brown due to extraction of flavonoid pigments and chlorophylls and their respective oxidation products. They are also commonly referred to as bioflavonoids. These terms are equivalent and interchangeable since all flavonoids are biological in origin.

Good sources of flavonoids include all citrus fruits, berries, onions, parsley, legumes, green tea, red wine, seabuckthorn and dark chocolate (that with a cocoa content of seventy percent or greater). A number of recent research articles have demonstrated the efficient production of flavonoid molecules from recombinant microorganisms. Such an approach opens the possibility of readily producing these compounds using renewable feedstocks and thus increasing the availability of rare flavonoid molecules for human and animal feed through dietary supplements (Spedding, 1989; Murray, 1996).

Consumers and food manufacturers have become interested in flavonoids for their medicinal properties, especially their potential role in the prevention of cancers and cardiovascular diseases. The beneficial effects of fruit, vegetables, and tea or even red wine have been attributed to flavonoid compounds rather than to known nutrients and vitamins.

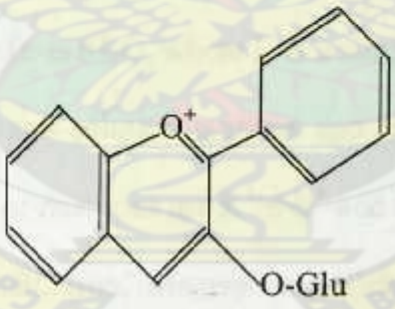
2.1.6.8 Anthocyanins

In plants anthocyanins are present together with other natural pigments like the chemically closely related flavonoids, carotenoids, anthoxanthins and betacyanins. Anthocyanins are water-soluble vacuolar flavonoid pigments that appear red to blue, according to the pH of the system within which they are found. They are synthesized exclusively by organisms of the plant kingdom and have been observed to occur in all tissues of higher plants, providing colour in leaves, stems, roots, flowers, and fruits. The

difference in chemical structure that occurs in response to changes in pH is the reason why anthocyanins are often used as pH indicator. They change from red in acids to blue in bases.

Plants with abnormally high anthocyanin quantities are popular as ornamental plants. The anthocyanins are subdivided into the sugar-free anthocyanidine aglycons and the anthocyanin glycosides. In the Caryophyllales, Cactus and *Galium mollugo* they are replaced by betacyanins. More recent literature puts the number of known anthocyanins at more than 550 different anthocyanins though not all land plants contain anthocyanin. Anthocyanin pigments are assembled from two different streams of chemical raw materials in the cell: both starting from the C2 unit acetate (or acetic acid) derived from photosynthesis, one stream involves the shikimic acid pathway to produce the amino acid phenylalanine.

General Structure of Anthocyanin



Properties

In flowers, anthocyanin pigments function as pollinator attractants, and in fruits, the colorful skins attract animals which will eat the fruits and disperse the seeds. In photosynthetic tissues (such as leaves), anthocyanins have been shown to act as a "sunscreen", protecting cells from photo-damage by absorbing ultra violet and blue-green

light, thereby protecting the tissues from photoinhibition or high light stress. This has been shown to occur in red juvenile leaves, autumn leaves and broad-leaved evergreen leaves that turn red during the winter. It is also thought that red coloration of leaves may camouflage leaves from herbivores blind to red wavelengths or signal unpalatability to herbivores, since anthocyanin synthesis often coincides with synthesis of unpalatable phenolic compounds.

In addition to their role as light-attenuators, anthocyanins also act as powerful antioxidants, helping to protect the plant during metabolic processes. This antioxidant property is conserved even after consumption by another organism, which is another reason why fruits and vegetables with red skins and tissues are a nutritious food source.

2.2 ELEMENTAL COMPOSITION

In complex or insoluble salt formation from a simple hydrate, different cation stability exists. The ligands in these complexes may be replaced by others in a reaction such as;

$M(H_2O)_n + L \longrightarrow ML(H_2O)_m + (n\text{-}m)H_2O$, where L is a simple anion or ligand. These reactions can occur in both solid and solution systems and if L is a very large anion (usually of a strong acid) the order of reactions are $K^+ > Na^+$ and $Ca^{2+} > Mg^{2+}$.

Arsenic, Chromium, Copper, Cobalt, Iron, Magnesium, Nickel, Silicon and Zinc are reviewed below.

2.2.1 Chromium

Chromium is a steel-gray, lustrous, hard metal that has a high melting point. It is also odorless, tasteless and is malleable. The most common oxidation states of chromium are

+2, +3 and +6, with +3 being the most stable whilst +1, +4 and +5 are rare. Chromium compounds of oxidation state +6 are powerful oxidants.

Chromium is passivated by oxygen, forming a thin protective oxide surface layer which prevents oxidation of the underlying metal. Trivalent chromium (Cr^{3+}) is required in trace amounts for sugar metabolism in humans and hexachromate is very toxic and mutagenic when inhaled. Cr (VI) has not been established as a carcinogen when not inhaled, but in solution it is well established as a cause of allergic contact dermatitis (ACD). Also it was recently shown, that the popular dietary supplement chromium picolinate complex generates chromosome damage. Chromium in the oxidation of +6 is highly toxic with limits of about 0.05mg/litre.

However, chromium complexes with various organic molecules into stable organometallic complexes. The element forms complexes with glutamine and methyl glutamine, cystein and other amino acids (Knochel and Twumasi, 1989).

2.2.2 Silicon

Silicon is a tetravalent metalloid that occasionally occurs as the pure free element in nature, but is more widely distributed in various forms of silicon dioxide or silicate. On earth, silicon is the second most abundant element in the crust. It has numerous known isotopes, with mass numbers ranging from 22 to 44. ^{28}Si (the most abundant isotope, at 92.23%), ^{29}Si (4.67%), and ^{30}Si (3.1%) are stable. Having four bonding electrons gives Si many opportunities to combine with other elements or compounds. The electron orbitals readily either donate or share four outer electrons allowing many different forms of

chemical bonding. Silicon does not readily participate in pi-bonding as its p-orbital electrons experience greater shielding.

Larger silicon compounds (silanes) are generally unstable owing to the larger atomic radius of silicon and the correspondingly weaker silicon-silicon bond; silanes decompose readily and often violently in the presence of oxygen making them unsuitable for an oxidizing atmosphere.

The metalloid is usually found in the form of silicon dioxide (silica), and silicate (various minerals containing silicon, oxygen and at least one metal). These minerals occur in clay, sand and various types of rock such as granite and sandstone. Though silicon does not have the tendency to form double and triple bonds it has many industrial uses. It is a very useful element that is vital to many human industries, and impacts much of modern life as a principal component in glass, concrete and cements of many kinds. Its silicates are also used in making enamels and pottery. Elemental silicon is the principal component of most semiconductor devices and integrated circuits or microchips.

Traces of silicon are also an essential element required for protection by animals. Silicic acid (a type of silica) forms the basis of the striking array of protective shells of the microscopic diatoms (Koch and Clement, 2007).

2.2.3 Cobalt

Cobalt is a hard silvery white metal used in metal mixtures and for colouring materials blue. Cobalt blue is a dark blue colour (Cambridge International Dictionary of English,

1996). It is found in various ores and is used in the preparation of magnetic, wear-resistant and high-strength alloys. Various compounds of cobalt have been used in many products including the production of inks, paints and vanish. Cobalt in small amounts is essential to many living organisms, including humans. Soil having 0.13 to 0.30 mg/kg of cobalt markedly improves the health of grazing animals. Cobalt is a central component of the vitamin cobalamin or vitamin B-12.

2.2.4 Iron

Iron is a lustrous, silvery soft, group 8 metal. It is notable as one of the heaviest elements which do not require a supernova or similarly cataclysmic event for formation. It is one of the most abundant metals in metallic meteorites and in the dense-metal cores of planets such as earth.

Iron is the most used of all the metals, comprising 95% of all the metal tonnage produced worldwide. Its combination of low cost and high strength make it indispensable, especially in applications like automobiles, the hulls of large ships, and structural components for buildings. It is mostly stably incorporated in the inside of metalloproteins, because in exposed or in free form it causes production of free radicals that are generally toxic. Steel is the best known alloy of iron. Iron in water has a number of harmful effects such as causing stains on clothing and also giving water an undesirable taste and colour (Dauphas and Rouxel, 2006).

Iron is essential to nearly all known organisms. Many animals incorporate it into the heme complex, an essential component of cytochromes, which are proteins involved in

redox reactions (including cellular respiration), and of the oxygen carrying proteins hemoglobin and myoglobin.

Iron binds avidly to virtually all biomolecules so it will adhere nonspecifically to cell membranes, nucleic acids, proteins etc..

2.2.5 Magnesium

Magnesium is the eighth most abundant element and constitutes about 2% of the earth's crust by weight. The free element (metal) is not found in nature.

Once produced from magnesium salts, this alkaline earth metal is used as an alloying agent to make aluminium-magnesium alloys, sometimes called "magnalium" or "magnelium". Magnesium ions are essential to the basic nucleic acid chemistry of life and thus it is essential to all cells of living organisms. Plants have an additional use for magnesium in that chlorophylls are magnesium-centered porphyrins. Many enzymes require the presence of magnesium ions for their catalytic action.

2.2.6 Zinc

Zinc in some historical and sculptural contexts, is known as spelter. Zinc is an essential element, necessary for sustaining all life. It is estimated that 3000 of the hundreds of thousands of proteins in the human body contain zinc prosthetic groups, one type of which is the so-called zinc finger. In addition, there are over a dozen types of cells in the human body that secrete zinc ions and the roles of these secreted zinc signals in medicine and health are now being actively studied. Intriguingly, brain cells in the mammalian forebrain are one type of cell that secretes zinc, along with its other neuronal messenger

substances. Cells in the salivary gland, prostate, immune system and intestine are other types that secrete zinc. Even though zinc is an essential requirement for a healthy body, too much zinc can be harmful. Excessive absorption of zinc can suppress copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish.

Mixtures of metal alkoxides and silicones have been shown to have water proofing properties. It may be suggested that the metal alkoxides are very effective catalysts in the curing of silicone resins and this implies some chemical interaction between the metal alkoxide, silicone and substrate material (Seyferth *et. al.*, 1980).

The transition metal centre in an organometallic compound behaves as an electron sink for unsaturated groups attached to it. Both electronic interactions are ascribed to metal d-orbitals. The filled transition metal n-1 d-orbitals of proper symmetry are proposed to overlap with the available antibonding π-orbitals of attached carbonyl, vinyl or phenyl groups. Such back-bonding serves to disperse the accumulated negative charge on the metal and to enhance the electron density between the metal and carbon centers. This d_{π}-p_{π} bonding by a metal donor, significant in many transition metal alkyls and aryls, explains why unsaturated groups with electronegative substituents form stable C-M bonds. With transition metal organometallic compounds, the n-1d-orbitals can form hybridized orbitals with ns-, and np -orbitals having strong bonding properties. In forming Lewis complexes with some alkyl and aryl bases, transition metals often gain considerably in over-all stability. This stabilization of a transition metal alkyl or aryl by

coordination with suitable ligands involves rehybridization of orbitals so that the energy difference is increased between the lowest antibonding molecular orbital (M.O.) and the highest bonding M.O. For instance, tannins easily interact with iron to form stable iron-tannate. The donation of π-electrons by unsaturated groups attached to the metal could also be viewed as p_π-p_π or d_π-p_π bonding, depending upon the availability and energy of metal orbitals. The alkyls of group III metals and higher valence states of transition metals participate in p_π-p_π bonding. d_π-p_π bonding in transition metal alkyls and aryls (such as Mn, Fe, Co and Zn alkoxides) with unsaturated groups also form stable C-M bonds.

Also, spectroscopic and chemical properties of vinylsilanes support the importance of d_π-p_π secondary bonding in the ground state and in the transition states of these systems (Eisch, 1967). Silicon has no available 3s- or 3p-orbitals but highly electronegative ligands permit the attainment of higher coordination numbers, apparently by $3sp^3d^2$ hybridization. In addition, stabilisation of adjacent carbon-metal bonds can be facilitated by silicon due to availability of 'd' orbitals on silicon.

2.3 BUILDING MATERIALS

Materials for building purposes are diverse depending on the location and economic state of the developer. In urban areas, cement based buildings are in the majority whilst earth buildings are predominant in rural areas. Cement products are strong and durable but quite expensive beyond the reach of the average Ghanaian. Earth buildings are easier and cheaper to build but less durable (Obeng and Atiemo, 2006).

Using earth-based materials such as stone, brick and concrete for various types of buildings dates back to the beginning of human civilization and was done by the Mesopotamian and Babylonian empires. Drawing on huge geological riches of limestone, sandstone, alabaster, granite and porphyry, the ancient Egyptians were the first to use stone in building temples and pyramids on a scale that still astounds. The Romans invented concrete mixed from pozzolana, a volcanic ash which forms a natural cement when combined with lime. Lightweight aggregates such as pumice stone were also added to the mix, giving concrete its name derived from the Latin word concretus, meaning grown together or compounded. A number of chemicals are now commonly added to concrete to improve its properties.

2.3.1 Cement

Cement production requires a source of calcium and silicon while small amounts of bauxite and iron ore are added to provide specific properties. Limestone, marl and chalk are the most common sources of calcium in cement while common sources of silicon include clay, sand, and shale. Certain waste products, such as fly ash or *pozzolan*, are also used as a source of silicon whilst iron and aluminum are provided by iron ore and bauxite as well as recycled metals. Finally, about 5% of cement by weight is gypsum, a common calcium and sulfur based mineral. In Ghana cement is produced from imported clinker and gypsum (Lea, 1970; ER Gp., 1992). Cement and concrete are key components of both commercial and residential construction in Europe, North America and recently in developing countries. The Portland Cement Association estimated that United States cement consumption exceeded 100 million tonnes per year in 1997 while according to the

United States Bureau of Mines, the worldwide cement production totaled 1.25 billion tonnes in 1991 (Wilson, 1993).

2.3.1.1 Concrete

Concrete is produced by mixing cement with fine aggregate (sand), coarse aggregate (gravel or crushed stone), water and often small amounts of various chemicals called admixtures that control properties such as setting time and plasticity, pumpability, water content, freeze-thaw resistance, strength, and colour.

Concrete has traditionally been one of the most inert of building materials and thus very appropriate for chemically sensitive individuals. Its properties are determined by the type of cement used, the additives and the overall proportions of cement, aggregate and water (Terek, 1993).

2.3.1.2 Pozzolana cement

Pozzolans (clay) are heat treated to become pozzolanic. The Pozzolana is then blended with Portland cement to produce Pozzolana cement on site.

Pozzolanic activity of clay depends on the minerals present and the chemical composition. Clay minerals are tiny crystalline hydroxyl aluminium silicates. The clay contains 15-18% Al_2O_3, 4.5-9% Fe_2O_3 and 60-70% silica. The main components are kaolinite and quartz, small amount of chlorite and the red colour is due to goethite and hematite. CaO and MgO are very small (Momade and Atiemo, 2004).

Fly ash or pozzolanas are sometimes preferably used for construction because of their resistance to sulphate attack, improved workability, lower cost and reduced environmental pollution. Pozzolana can readily be substituted for 15% to 40% of the cement in concrete mixes for housing construction. For some applications fly ash content could be up to 70%.

2.3.1.3 Cement additives

Most concrete retarders are relatively innocuous sucrose (sugar) based chemicals, added in proportions of 0.03% to 0.15%. Air-entraining admixtures function by incorporating air into the concrete to provide resistance to damage from freeze-thaw cycles and to improve workability. These materials can include various types of inorganic salts (for example salts of wood resins and salts of sulphonated lignin) along with more questionable chemicals such as alkyl benzene sulphonates and methyl-ester derived cocamide diethanolamine. Workability agents or super plasticizers can include chemicals such as sulfonated melamine-formaldehyde and sulphonated naphthalene-formaldehyde condensates. Fungicides, germicides and insecticides are also added to some concrete (The National Concrete Masonry Association, 2006).

2.3.2 Earth/mud

Earth or mud is used to construct walls, floors, roofs and even furniture, fireplaces and ovens. The use of earth in construction is well-established as energy efficient. It is one of the oldest known building materials yet there is much about its properties and potential that remains undeveloped and poorly researched.

An earth structure could also be made as one continuous mass of compressed earth called "Rammed earth". Hand-operated presses have also been used for many decades to make bricks from various compositions of soil and dried at air temperature. More expansive clays like bentonite and hectorite give greater shrinkage on drying and therefore greater strength. Tests conducted have resulted in breaking strengths approaching 6,000 psi. Before that, and still today, some people make the blocks by beating soil with a stick into a wooden mold. Traditionally, mud wall construction varies enormously with topography, climatic conditions and needs of different regions.

Well constructed earth wall homes, according to international standards, have no damage in tremors, survive and are repairable in medium quakes and are damaged beyond repair but do not pose a threat to life in large quakes. Evidence from quakes in Newcastle, Meckering and New Zealand suggest that earth buildings coped well when compared with those built with other building materials (CSIRO, 1995).

2.3.3 Natural composite

There has been work to find ways to replace all of the lumber, concrete, steel and petroleum products used in new home construction with materials that have a decidedly lower environmental impact. Composite architecture refers to building without the use of lumber, concrete, steel or petroleum products. It is made from two components: A binder or adhesive, called a matrix, and a fibrous material of some type. The most recent sustainable architecture concept house uses a composite bentonite clay/cellulose fiber/straw-bale wall and roof system that eliminates the need for all structural lumber and steel.

2.4 SOME GHANAIAN ARCHITECTURE

Building of houses in Ghana from earth and earth-based materials can be put in five different categories across rural communities to urban cities: Earth building, traditional and modern mud and stick building, timber buildings, block work and concrete buildings, and modern buildings. According to the Ghana Statistical Service population and housing census 2002 report, brick houses constitute about 15% of total stock of houses in the country (Songsore, 2003).

About 70% of people in Ghana live in various forms of earth buildings. Currently, the country imports over 90% of its building materials. Manufacture of local building materials will cut down on building cost and generally help to keep pace with the housing needs (Hagan and Osei-Frimpong, 2006).

2.4.1 Earth (mud) building

Earth building is the practice of building using unfired earth material. These buildings meet the challenges of comfort and safety as well as have ease of heating and cooling. The common feature in all earth building techniques is that the earth material is subsoil that is composed of clay, silt, and sand where clay is the binder or cementing ingredient and the drying process is through the evaporative effect of sun drying. It is a technology that is ancient yet still most relevant. It is a building technology with an 11,000-year-old history and tradition which is utilised worldwide.

The material is durable, 100 – 400 years plus proven in Australia, Europe, England, Middle East, offering longevity rivaling modern western housing. It is adaptable, being used for footings, floors, walls and roofs utilising many techniques. It is raw and natural and non toxic, non allergenic, controls humidity, is fire, rot and termite proof and therefore can be used to create safe and healthy buildings. Studies reveal that earthen walls moderate the humidity within the building adding to comfort levels. They also take up and filter toxins from the out gassing of plastics and will shield electromagnetic radiation (Silverberg, 1997).

2.4.1.1 Rammed earth (pise)

Rammed earth or pise is damp or moist earth with or without any additive that is rammed (tamped) in place between temporary moveable formwork. It is a solid masonry wall which does not have, and does not need any cavity. Australia leads the world in modern rammed earth construction, both in quality and volume of projects built (Silverberg, 1997).

2.4.1.2 Compressed earth blocks

Compressed Earth Block (CEB) is the name given to earthen bricks compressed with hand-operated or motorized hydraulic machines. The choice to use CEB is dependent on several factors including culture, labour force, financial ability and most importantly, the preference of the homeowner.

Compressed Earth Block is often used in Africa and other places around the world. Modern equipment, with hydraulics driven by diesel, gas or electric motors, may be useful in urban areas or for large multi-house sites. A favorite hand-operated press is the

simple and inexpensive "TEK" produced from The Kwame Nkrumah University of Science and Technology, Ghana. A similar French machine is greater and as well simple to operate, but it costs more. Both machines create a CEB using only one operation (Dowton, 2004).

2.4.1.3 Earth/mud brick (adobe)

Mud brick is the most popular name used to describe bricks made from various compositions of soil and dried at air temperature in the brick production stage. Mud brick construction is often referred to as 'adobe' which is an Arabic and Berber word adopted into English. At its simplest, mud brick making involves placing mud in molds which, after initial drying, are removed to allow the bricks to dry slowly. Straw or other fibres that are strong in tension are often added to the bricks to help reduce cracking. Mud bricks are joined with a mud mortar and can be used to build walls, vaults and domes.

Molds can be made from timber or metal – anything that can be shaped to provide the desired size for the bricks. In New Mexico and other desert states, the soil used for mud brick making is mostly sand (70-90%) with varying amounts of clay and fine silts totaling from 10% to 30%. The individual sand grains (coarse and smooth) provide the "structure" which is bound together by the very fine and sticky clay particles. An ideal proportion for adobe bricks and mortar is 70% sand and 30% clay (Silverberg, 1997). It is estimated that up to a third to half the world's population is housed in earth homes. Brick houses are more aesthetically attractive and provide a better satisfactory indoor climate (Obeng and Atiemo, 2006).

2.4.2 Mud and stick building

These buildings are made out of mud walls, which are 'reinforced' with small sticks and covered with a bamboo, aluminium or grass roof. The mud is sometimes used for the roof. This way of building is mainly used in rural areas where resources are most limited.

2.4.3 Cob building

Another traditional building technique using earth mixed with water, straw and often sand is called Cob. It dries to hardness similar to lean concrete and is used like adobe to create self-supporting, load-bearing walls. Cob has been used for centuries throughout Western Europe, even in rainy and windy climates. Cob is very resistant to weathering and can withstand long periods of rain without weakening. In windy areas a lime-sand plaster is traditionally used to protect exterior Cob walls from wind driven rain. It is non-toxic, completely recyclable and well suited to cool damp climates, having resistance to rain and cold.

Influences from Africa and Latin America, and the conscious attempt to make Cob relevant to the third millennium, have created something quite different from other building techniques called Oregon Cob. Oregon Cob is very strong in compression and shear because carefully chosen ingredients are used; a high proportion of coarse sand to clay is mixed with lots of straw. The clay is pressure bonded onto every facet of the sand grains. The long-fiber straw, sewn from layer to layer, creates monolithic structures with high shear strength and walls without cracks.

2.4.4 Timber buildings

Timber buildings are commonly made of wooden walls and mostly consist of a timber structure and aluminium roof sheets. Aluminium sheets, timber and plate materials are sometimes used for the walls. This way of building is common especially for shops and houses for poor families in suburbs and slums.

2.4.5 Block work and concrete buildings

Block work is probably the most used technique to build houses for people with (some/a lot of) money and frequently used to build shops and offices in urban centres. Block work buildings are made of big blocks, which are produced at the building site by mixing sand, cement and water. The mixture is put in a small compression machine mostly operated by manpower only, which makes the production work a heavy job especially since the blocks are rather heavy. Block work and concrete buildings are improved and cost intensive types of buildings found mostly in the cities.

2.4.6 Modern buildings

The smallest group of all the buildings is the really modern ('high tech') buildings which use prefabricated structures. Only a small number of buildings, mostly governmental and a few well to do persons build using non-Ghanaian methods, such as steel or prefabricated structures. Modern buildings are expensive, the latest and fewest in the country. Also, baked bricks buildings are becoming popular now in Ghana (Obeng and Atiemo, 2006).

2.5 FINISHES

After brushing the wall to get a fairly even surface, the final finish is slurry, typically

finished by hand. This slurry may also be the final waterproofing coat on the wall or it may have a further clear coat of proprietary waterproofing material. Typical finishes are wall plasters, renders and aliz. The stability of these finishes against environmental factors enables them to provide protection to the walls. Laterite soils, which are widely distributed throughout the tropical and subtropical regions, generally give very good results, especially if stabilized with cement or lime. Laterite soils can be best described as highly weathered tropical soils containing varying proportions of iron and aluminium oxides, which are present in the form of clay minerals, and usually large amounts of quartz. Their colours range from ochre, through red, brown or violet to black.

2.5.1 Wall Plasters

The term plastering is usually applied to interior walls and ceilings to give jointless, hygenic and usually smooth surfaces often over uneven backgrounds. As the final layer, wall plasters (cement or mud) must be able to check wetness of buildings as it limits environmental factors to the wall. A mud plaster with high clay content and lots of straw mixed to a slippery, easily spreadable consistency is used on rough cob or adobe. It makes lots of little cracks on drying and provides a perfect surface for the next layer to adhere.

The plaster is a very effective method of protecting walls susceptible to erosion. Wetness of buildings constitutes a potential hazard to health and comfort and is a source of aesthetic and material damage. The thermal resistance of external walls is reduced by water content and this lowers the internal surface temperature, increases the likelihood of condensation and causes thermal discomfort. Very humid conditions that leave surfaces

of walls damp can also lead to fungal growth since potential changes in humidity provide favorable conditions for the activities of fungi. Extensive wetness, by volume over time, may eventually lead to the collapse of the building (Amos-Abanyie, 2006).

2.5.1.1 Earth/mud plasters

The final coat, before the aliz, on the adobe, cob, rammed earth, pumice-crete or straw/clay walls is mud slurry and this may be the only layer of plaster needed. This slurry may be the final waterproofing coat or it may also have a further clear coat of proprietary waterproofing material. The plaster is easily workable, sticky enough to adhere well to the dampened wall, and wet enough to trowel on easily but not so wet that it is hard to pick up.

In some cultures, boiled linseed oil and turpentine brushed on several coats are used to provide a final finish. There is even the option of using the 'natural plastic' of cellulose, processed by bovine beasts to create mud and manure (eg. a mud and cow dung mix) slurry. Finishes can also range from rustic to smooth forms and this typical flexibility of approach is one of the material's many appealing qualities (Simmons and Gray, (Eds.), 1996). Plaster dirt should be at least 20% clay because clay is essential for stickiness. Even at this percentage, architects may wish to add manure or flour paste to make it stickier. Many other variables in natural materials that can be added include the additions like psyllium husk extracts, cactus juice, natural fibres (e.g., grass, straw, sisal, sawdust), sodium silicate (water-glass), resins, gypsum and cow dung. According to Shao, (2002) and Awindor, (2006), the aqueous extract of *Parkia biglobosa* fruit husk has also been used for the same purpose. In India, the Middle East, and other places, it was discovered

that old stinky mud works better than fresh mud, so the mud is mixed in a pit with animal manure and other wastes and left to "ripen". This causes the molecules of clay to line up as closely as they can, improving wet plasticity and dry toughness. The plaster is scooped onto the trowel and applied to the dampened wall like icing on a cake.

In many parts of Ghana, Nigeria and other West African countries, bitumen has been added to mud to produce durable plasters. Bitumen (or asphalt) emulsion and cutback are mainly used to improve impermeability of the soil, and keep it from losing its strength when wet, but may cause some decrease in dry strength. They are only used with very sandy soils, since it would be very difficult to mix them with clayey soils. Bitumen in its natural form is too thick to be added to soil without heating, so it is thinned with other liquids such as water or kerosene to make it workable. After the emulsion has been added to the soil the water will separate leaving a bitumen film on the soil grains (Brandt, *et. al.*, 1985, Adebiyi and Omode, 2007).

If the bitumen emulsion is fast-settling, i.e., the water separates too quickly before it is mixed into the soil, the bitumen is instead dissolved in kerosene or naphtha. This mix is called cutback and is handled with care since it represents a fire hazard and explosion risk. After a soil has been treated with cutback it is spread out to allow the kerosene to evaporate. The bitumen content used is 2 to 4% since more of it may seriously reduce the compressive strength of the soil. This plaster enhances durability of mud wall making it a non-erodible (Brandt, *et. al.*, 1985, Adebiyi and Omode, 2007).

These plasters may require maintenance on a regular basis, which is similar to giving a house a fresh coat of paint. Also, some of the challenges of wetness of walls, especially in cold and damp climates, centre on finding ways to get the building materials to dry faster. Recently gypsum plaster has been added to the mixes to accelerate the drying process. Sodium silicate has also been used as sealers.

2.5.1.2 Cement plasters

Stabilizers such as cement, gypsum, fly ash, lime and the liquid types have been used in the body or on the surface of the bricks of buildings. It is less costly to make a soil block with no cement and then use cement for the mortar joints of the wall, and a cement plaster which adheres to the mortar joints. Cement plaster does not stick well to unstabilized earth bricks, so the mortar joint is used to hold the plaster.

2.5.2 Earth Renders

Exterior plastering is usually called exterior rendering. A good render must be vapour permeable and marginally weaker than the structure. A common cause of failure can be attributed directly to the inappropriate application of hard cement render and impervious paint. If denied the absorption of moisture from the atmosphere, an earth structure will slowly dry out to the point of sudden collapse. Earth structures survive by retaining sufficient moisture to maintain the integrity of the binder. Thus it is vital that they are allowed to 'breathe'. Lime mortar just like cement mortar, due to the change in the weather, expand and contract at different rates with mud wall and consequently do not work well together. Almost all historic buildings rely on the ability to breathe in order to survive and any interference by way of an impervious membrane could, at best, be harmful and, at worst, disastrous.

Lime rendering has been applied in one, two and even three coats, although normally a dubbing out or scratch coat is followed by a finishing coat. The first coat is usually prepared from one part matured slaked lime putty mixed with three parts of a well-graded aggregate. To reduce the initial suction of a dry wall, the substrate will need to be made wet before the application of each coat.

2.5.2.1 Non hydraulic lime renders

When lime was adopted as the principal binder in mortars, plasters, renders and washes, the integrity of the structure improved. This is because as non-hydraulic lime (calcium hydroxide) cures, it absorbs carbon dioxide from the air and slowly reverts back to calcium carbonate, which is more resistant to water erosion. The application of a lime wash, often modified by the inclusion of water-resisting agents such as tallow, raw linseed oil, animal glues, casein and even common salt, has proved very successful in further extending the life of lime render.

Carbonation is a slow process and several days often pass before the surface of the first coat is firm enough to take a finishing coat. Full carbonation often takes weeks, or even a year. The floating or finishing coat is usually prepared from one part lime putty to one to three parts well-graded aggregate. However, rapid drying out in hot weather can produce an early set with little carbonation, resulting in a weak render, which will be vulnerable to rain erosion.

2.5.2.2 Hydraulic lime renders

An earth render may be modified by the addition of animal hair or other modifications including the use of pozzolanic additives such as crushed brick, tile and other clay fired

products to form 'hydraulic' mortars to assist in reinforcing the render. With this addition, the render tends to take on an earlier set and sometimes produces a more weather-resistant finish.

Casein, egg, linseed oil, fresh blood, bees wax, tallow, beer and urine have all been used as additives to improve the performance of renders. Animal fats and oils improve the water-repellent properties of a render, while beer and urine act as air entrainers. Little use is made of the majority of these products today. Modern air entraining agents create air bubbles, which are distributed more uniformly throughout the mortar to assist in frost protection.

2.5.3 Aliz

A clay slip, known to some as an aliz, can be applied to an earth-plastered wall almost like paint is used on other surfaces. The purpose is to seal and beautify the surface, and after it has become soiled or damaged, another coat may easily be applied to renew its fresh look. Clay slips on the interior and mud plasters of the exterior allow an earthen structure to absorb moisture and then dry out again without creating major moisture problems.

For the final clay slip, a white Kaolin and ground mica are the major ingredients. Cooked flour paste is used as a binder in the proportion of 20% to 25% of the liquid. Gum Arabic and milk products also work well as a binder but buttermilk works best. In Taos, New Mexico, the favorite material used as aliz was a micaceous pearly-grey clay called tierra blanca.

2.5.4 The Chemistry of Finishes

Bitumen and cutback have been added to mud to produce durable plasters. Lemon juice, vinegar or urea have also been added to promote stability of finishes. The aqueous extract of *Parkia biglobosa* fruit husk has also provided good results. Deterioration of finishes normally occurs due to environmental factors such as rainfall.

In windy areas a lime-sand plaster is traditionally used to protect exterior Cob walls from wind driven rain. The use of lime to stabilize mud blocks significantly improves the water resistance and hence durability of earth buildings. Lime is a cementitious material, commonly used as stabilizer and plasticizer. The stabilizing effects depend on chemical reaction between the lime and clay minerals of the soil to form cementitious compounds such as calcium silicates (Hagan and Osei-Frimpong, 2006).

Bitumen (or asphalt) emulsion and cutback have also been used to improve impermeability of the soil, making it non-erodible to rain. The bitumen is mixed with hot water to produce a workable emulsion. Bitumen may also be dissolved in kerosene or naphtha to form a mix called cutback. The bitumen content used is 2 to 4% since more of it may seriously reduce the compressive strength of the soil. Bitumen is a mixture of paraffinic, aldehydric, naphthalmic and heteroatomic containing compounds with alkenes, aldehydes, anhydrides, polycyclic aromatics and amides all being present. Its elemental characterization also indicates presence of copper, nickel, lead, cobalt, vanadium, manganese and iron (Brandt, *et. al.*, 1985, Adebiyi and Omode, 2007).

Lemon juice, vinegar and urea also produce rain-erosion resistance. Ure, an organic compound of carbon, nitrogen, oxygen and hydrogen, having the C=O functional group, makes paint or glaze very water resistant. Urea is also a raw material for the manufacture of various glues such as urea-formaldehyde or urea-melamine-formaldehyde, which is waterproof.

Plaster dirt should be at least 20% clay because clay is essential for stickiness. Many other variables in natural materials that can be added include the additions like psyllium husk extracts, cactus juice, natural fibres (e.g., grass, straw, sisal, sawdust), sodium silicate (water-glass), resins, gypsum and cow dung. Other stabilizers are cement, gypsum, fly ash and lime. Minerals present in some of these additives are potassium, magnesium, iron, calcium, aluminum and silicon.

2.6 ANALYTICAL TECHNIQUES

The analytical methods or techniques namely solubility test, thin layer chromatography, ultraviolet spectroscopy, high pressure liquid chromatography, infrared spectroscopy and X-ray diffraction employed in this work are reviewed in the following subsection.

2.6.1 Solubility Test

This is a preliminary functional group determination process. Dried moisture free samples are dissolved in distilled water, 5% NaOH, 5% $NaHCO_3$, 5% HCl, conc. H_2SO_4 and organic solvents, and the extent of dissolution provide the basis for the preliminary assessment for the type of functional groups hence the compounds present in the sample.

Compounds not soluble in all these solvents are inert (hexane, benzene) whilst those soluble in water are further tested for their pH range in aqueous solution using a litmus paper. When compounds are soluble in water they are usually soluble in all aqueous solvents. A compound only slightly soluble in water may be more soluble in another aqueous solvent hence it is often necessary to determine the solubility of such compounds in all the solvents.

The tests reveal whether the compounds present are strong bases (amines), weak acids (phenol), strong acids (carboxylic acids), or neutral substances (aldehydes, ketones, alchohols, esters). Compounds not soluble in all these solvents are inert (hexane, benzene) (Pavia, *et. al.*, 1995).

2.6.2 Thin Layer Chromatography

Thin Layer Chromatography (TLC) is a widely-used form of preparative chromatography technique used to separate chemical compounds. It involves a stationary phase consisting of a thin layer of adsorbent material, usually silica gel, aluminium oxide or cellulose immobilized onto a flat, inert carrier sheet. A liquid phase consisting of the solute to be separated, dissolved in an appropriate solvent, is drawn through the plate via capillary action separating the experimental solution. Among other uses it can be used to determine the pigments a plant contains, to detect pesticides or insecticides in food, in forensics to analyze the dye composition of fibers, or to identify compounds present in a given substance. It is a quick, generic method for organic reaction monitoring because of its simplicity and speed and for the qualitative analysis of reaction products.

A small spot of solution containing the sample is applied to a plate, about 1cm from the base. The plate is then dipped in a suitable solvent and placed in a sealed container. The solvent moves up the plate by capillary action and meets the sample mixture, which is dissolved and is carried up the plate by the solvent. Different compounds in the sample mixture travel at different rates due to differences in their solubility in the solvent and due to differences in their attraction to the stationary phase. Results also vary depending on the solvent used. For example, if the solvent were a 9:1 mixture of hexane to ethyl acetate, then the solvent would be mostly non-polar. This means that when analyzing the TLC, the non-polar parts will have moved further up the plate. The polar compounds, in contrast, will not have moved as much. The reverse is true when using a solvent such as 1:9 of hexane to ethyl acetate that is more polar (Pavia *et. al.*, 1995). With these solvents, the polar compounds will move higher up the plate, while the non-polar compounds will not move as much.

The appropriate solvent in context of thin layer chromatography will be one which differs from the stationary phase material in polarity. If a polar solvent is used to dissolve the sample and the spot is applied over a polar stationary phase, the sample spot will grow radially due to capillary action. This is not advisable as one spot may mix with the other. Hence, to restrict the radial growth of sample-spot, the solvent used for dissolving samples in order to apply them on plates should be as non-polar or semi-polar as possible when the stationary phase is polar, and vice-versa.

In organic chemistry, reactions are qualitatively monitored with TLC. Spots sampled with a capillary tube are placed on the plate. A small (3 by 7cm) TLC plate takes a couple of minutes to run. The analysis is qualitative, and it will show if starting material has disappeared, product has appeared, and how many products are generated. The retention factor (R_f) is a quantitative indication of how far a particular compound travels in a particular solvent.

$$R_f = \frac{\text{distance moved by compound}}{\text{distance moved by solvent}}$$

The R_f value is a good indicator of whether an unknown compound and a known compound are similar, if not identical. If the R_f value for the unknown compound is close or the same as the R_f value for the known compound then the two compounds are most likely similar or identical (Pavia *et. al.*, 2005).

2.6.3 UV-Visible Spectroscopy

The main application of UV visible (UV-Vis) spectroscopy, which depends on transitions between electronic energy levels, is in identifying conjugated pi (π) electronic systems. The energy required to promote an electron from one electronic state to the next lies in the visible and ultraviolet range of the electromagnetic spectrum. The UV-Vis absorption wavelengths fall between 200–800 nm. UV-Vis bands are characterized by the absorbance (A), which is a measure of the quantity of the radiation that passes through the sample that is absorbed. The wavelength at an absorption maximum is referred to as the λ_{max} of the band. λ_{max} is affected by the solvent.

Absorption of UV radiation excites an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In compounds with

double bonds, such as alkenes and polyenes, the HOMO and LUMO are π type orbitals. The HOMO is the highest energy π orbital and the LUMO is the lowest energy π* orbital. Excitation of one of the π electrons from a bonding π orbital to an antibonding π* orbital is referred to as $\pi - \pi^*$ transition.

Another type of absorption in UV-VIS excitations in organic compounds is the n transition of the carbonyl (C=O) group. One of the electrons in a lone-pair orbital of oxygen is excited to an antibonding orbital of the carbonyl group. The "n" in $n - \pi^*$ identifies the electron as one of the nonbonded electrons of oxygen. This transition gives rise to relatively weak absorption peaks in the region of 270-300 nm (Carey, 2003, Daley and Daley, 1996; Pavia *et. al.*, 1979).

The structural unit associated with an electronic transition in UV-Vis spectroscopy is called a chromophore.

2.6.4 High Performance Liquid Chromatography (HPLC)

The essentials in this instrument include a solvent reservoir, a sample injection system, a pump, a pressure gauge, a column, a detector amplifier and chart recorder. In HPLC, a pump is used to force the solvent through the column parking and this increases the solvent flow rate while maintaining a better separation. The process is widely applied to problems where separations by ordinary column chromatography are unsatisfactory. In this instrument the column is packed with small particle size adsorbents and satisfactory separations are achieved even with pressures as low as 100 psi. The detector captures the

presence of a separated solute by its absorption of ultra violet light and the signal generated is amplified and recorded in the integrator. HPLC is an excellent analytical technique in which a mixture of compounds could be separated and may also be isolated. The reverse column can be used to separate ionic, nonionic and ionizable samples (Pavia, *et. al.*, 1995; Bishop *et. al.*, 1992). The method is mainly used for those classes of non-volatile compounds such as terpenoids, phenolics of all types, anthraquinones, alkaloids, lipids and sugars.

This method is an excellent analytical technique that provides preliminary information about the possible functional groups and hence compounds present in the extracts and fractions. It provides preliminary information about the number of compounds that would be indicated by their functional groups in the IR analysis.

2.6.5 Infrared Spectroscopy

Infrared (IR) spectroscopy was the instrumental method most often used to determine the structure of organic compounds. It is very important in identifying the presence of certain functional groups within a molecule. The fraction of infrared absorption of most use for structure determination lies between 2.5μm and 16μm in wavelength corresponding respectively to 4000 and 625 cm^{-1} in wavenumbers. The wavenumbers are directly proportional to energy.

IR spectra can be recorded on a sample regardless of its physical state. More commonly, a solid sample is mixed with potassium bromide and the mixture pressed into a thin wafer, which is placed in the path of the IR beam. In using IR spectroscopy for structure

determination, peaks in the range of 4000 - 1600 cm^{-1} are usually emphasized because this is the region in which the vibrations characteristic of particular functional groups are found. The region 1300 - 625cm^{-1}, known as the fingerprint region (Daley and Daley, 1996; Carey, 2003; Matthews, 2004), is the region in which the pattern of peaks varies most from one compound to another.

Reorganization of carbon-carbon bonds to form carbon-metal bonds result in increased wavenumbers. The resulting decrease in wavelengths can be used to assess the formation of organometallic compounds from organic counterparts in organic/inorganic (metal) interactions.

2.6.6 X-Ray Diffraction

X-radiation is an electromagnetic radiation that falls in the region between ultra violet and gamma radiation (0.1-100 pm), about the same size as an atom. It arises when matter is bombarded with a beam of high energy electrons. X-ray powder diffractometry utilizes a monochromatic beam of radiation to yield information about "d" spacings and intensities from a single crystal or crystalline powder. The X-ray diffraction occurs when an incident wave, initially confined to a single direction of propagation, is found (due to scattering effect) to be deflected so that it propagates in new and other directions. It results in a fractional decrease in intensity (I) of an X-ray beam as it passes through a substance. The decrease occur as a result of collision of X-rays with electrons of the atoms in the crystal and the diffraction is proportional to the distance (x) traversed by the beam, $-dI/I = \mu(dx)$. The constant μ is the linear absorption coefficient which is

dependent on the properties of the material of the absorber (Littlefield and Thorley, 1970; Masao and Nobutami, 1972).

X-rays primarily interact with electrons in the atoms of the target material and scattering occurs when an X-ray photon collides with one of the electrons of the absorbing element. When X-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they original traveled. If the wavelength of these scattered X-rays did not change (meaning that X-ray photons did not lose any energy), the process is called elastic scattering (or Thompson Scattering) in that only momentum has been transferred in the scattering process. Elastically scattered X-rays are said to be coherent and this radiation has the same wavelength as the incident beam. These are the X-rays that carry information about the electron distribution in materials and are thus measured in diffraction experiments. X-ray diffraction is a special case of coherent scatter. On the other hand, in the inelastic scattering process (Compton Scattering), X-rays transfer some of their energy to the electrons and the scattered X-rays will have different wavelength than the incident X-rays (Jenkins and Vries, 1970; Littlefield and Thorley, 1970).

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the

diffraction pattern therefore enables deduction of the distribution of atoms in a material (Tinoco *et. al.*, 1995).

The technique is also used widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials). The intensity of the diffracted beams depends on the arrangement and atomic number of the atoms in the repeating motif, called the unit cell. Thus, the intensities of diffracted spots calculated for trial atomic positions can be compared with the experimental diffraction intensities to obtain the positions of the atoms themselves.

X-ray diffraction is for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification and X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state, the inter-atomic distance and angle, etc. (Tinoco *et. al.*, 1995)

The Bragg's Law is one most important law used for interpreting x-ray diffraction data. If the wavelength and the inter-atomic distances are roughly the same the diffraction patterns, which reveal the repeating atomic structure, can be formed. A pattern of scattered X-rays (the diffraction pattern) is mathematically related to the structural arrangement of atoms causing the scattering. Bragg recognized a predictable relationship among several factors:

1. The distance between similar atomic planes in a mineral (the inter-atomic spacing) called the d-spacing and measure in picometers.

2. The angle of diffraction called theta (θ) angle measure in degrees. For practical reasons the diffractometer measures an angle twice that of the theta angle. The measured angle is therefore '2-theta' (2θ).

3. The wavelength of the incident X-radiation, symbolized by the Greek letter lambda (λ), equal to 1.54 picometers.

The Bragg equation is: $2dsin\theta = n\lambda$,

where: n = an integer such as 1,2,3 .....etc, λ = wavelength in picometers, d = interatomic spacing (d-spacing) in picometers and θ = the diffraction angle in degrees (Tinoco *et. al.*, 1995).

In the cubic lattice system, the d_{hkl} is the interplaner distance $a / \sqrt{h^2 + k^2 + l^2}$ ---------- (1), where a = b = c, a is the edge length (lattice constant of a cubic unit cell).

The general equation of a lattice plane (hkl) is $h_x + k_y + l_z = a$

The distance of a point $x_1y_1z_1$ from the plane is d,

$$d = \left| \frac{hx_1 + ky_1 + lz_1 - a}{\sqrt{h^2 + k^2 + l^2}} \right| \text{ ---------- (2)}$$

The Brag reflection condition demands that the glancing angle (θ) and the wavelength (λ) must conform to one another. Monochromatic X-rays of wavelength λ which falls on a three dimensional crystal are generally not reflected.

In order to fulfil the Brag interaction or reflection condition;

$$2d\sin\theta = n \times \lambda \text{ or } 2d_{hkl}\sin\theta = \lambda \text{ ---------- (3), } [d_{hkl} = d/n]$$

either the wavelength or the angle must be varied.

From equations (1), (2) and (3);

$$\sin\theta = \lambda/2a(\sqrt{h^2 + k^2 + l^2}) \text{ ----------(4)}$$

Equation (4) shows a linear dependence of the refracting angle θ and the square root of the Miller indices because from equation (4);

$$\text{Sin}^2\theta = \lambda^2/4a^2 (\sqrt{h^2 + k^2 + l^2}) \text{ ---------- (5)}$$

and so $h^2 + k^2 + l^2$ is always a whole number. This means that for every distinct angle on the next plane, there is a measured value for $\sin^2\theta$ which is a whole number of the factor $\lambda^2/4a^2$.

With a certain wavelength λ, one can measure the edge length a, of a cubic elementary cell.

2.6.7 Statistical Analysis and Significant Test

Statistics is employed in quantitative work to assess the overall performance of the process. The mean of duplicate quantities normally represents a general expectation. Standard error of the mean and significant test are two further analysis used to test the validity of the mean.

The mean, also known as the arithmetic average, is the sum of the values, divided by the total number of the values. μ is used to represent the mean of a population and is given by: $\mu = (x_1 + x_2 + x_3 + \ldots\ldots + x_n)/n$, where n is the total number of values in the population. The mean is normally rounded up to one more decimal place than occurs in the raw data.

The standard error of the mean is the standard deviation of the sample mean values. It measures the dispersion of the mean (μ) around the true values (M). The difference between μ and M is the error and a measure of the tendency for the sample mean to

deviate from the true value, thus the confidence limits for the mean. It is interpreted as the average error encounted if the sample mean was used to estimate the population mean. The standard error of mean (SEM) decreases as sample size increases, and the mean of a large sample size is likely to be closer to the true mean than the mean of a small sample. In this project the true value (M) is the mass of an extract and the sample mean is the mean mass of the extracts (μ) = ($M_1 + M_2 + \ldots. M_n$)/n. SEM = $s/\sqrt{n}$, where s = standard deviation of the samples, n = number of samples statistics and $s = \sqrt{\{[(M_1 - \mu)^2 + (M_2 - \mu)^2 + \ldots.(M_n - \mu)^2]/n\}}$. The significant test is conducted in the form of the t test, a statistical test for the mean of a population. It is used when the population is normally distributed, the population standard deviation is unknown and the sample size is less than 30.

In making significant tests the truth of a hypothesis, also known as null hypothesis, is tested. The term null hypothesis is used to imply that there is no difference between the observed and known values other than that which is attributed to random variation. Statistical theory can be used to calculate the probability (P) that the observed difference between the sample mean and the true values arise solely as a result of random errors. Usually the null hypothesis is rejected if the probability of such a difference occurring by chance is less than 0.05 (i.e. $P < 0.05$) working at 95% confidence limit. In this case, the difference is said to be significant at 0.05 (5%) level.

In order to decide whether the difference between the true value (M) and the mean (μ) is significant, the following equation is applied: $\mu < M \pm t(s/\sqrt{n})$, where t = the test result

and $t = [(M - \mu)/(s/\sqrt{n})]$, M = observed value, μ = mean or expected value in this case and s = standard error of mean.

The critical values are used to derive the significance level or the probability that the differences in the means are due to chance. If the t-test is used to compare two means and the absolute value of the test result (|t|) statistic calculated exceeds the critical value, from statistical tables, then a significant difference is said to exist and the null hypothesis is rejected. One tailed critical values are used to test whether one mean is significantly greater or less than the other mean. Thus, the critical value separates the critical from non-critical regions, the critical region being the rejection region whilst the non-critical region is the non-rejection region where the null hypothesis in not rejected (Bishop, *et. al.*, 1992; Bluman, 2006).

CHAPTER THREE

3 MATERIALS AND METHODS

Materials (ie. samples, chemicals and equipment) employed in the project as well as experimental methods used are presented in this chapter.

3.1 MATERIALS

Materials used in the project are the *Parkia biglobossa* fruit husk and the soil samples for the preparation of the plaster, the chemicals/reagents for the extraction and analysis, and the glassware and equipment also used for extraction and analysis.

3.1.1 Husk and Soil Samples

Parkia biglobossa fruit husk were collected, authenticated, extracted, and the extracts fractionated for various analyses. Freshly harvested dry husk (hereafter referred to as new husk) and dry husk that has been harvested for about a year (hereafter referred to as old husk) were pulverised separately for extraction.

Dry soil sample was also obtained and brought to the laboratory for digestion and analysis.

Chemicals and reagents for the analyses were obtained from the Chemistry Department of KNUST and chemical suppliers.

Various equipment were also applied in the analyses to determine the amount of extract, secondary metabolites, functional groups, number of components, and elemental composition.

3.1.1.1 Collection and Authentication of Husk Sample

The pods of *Parkia biglobosa* ripen and dry up on the trees between May and June. Freshly harvested dry husk (hereafter referred to as new husk) and about a year old dry husk (hereafter referred to as old husk) were purchased from the Navrongo central market in the Upper East Region of Ghana. They were purchased from three women who collected them from various farmlands in their communities, namely Pungu, Chiana and Korania. The outer surface of the fresh husk looked shiny, the old husk looked dull and darker.

The purchased husk were collected separately into nylon sacks and transported to the laboratory for further processing.

Random samples were picked out of the bulk husk and were authenticated by Mr. Ben Yamba of the KNUST Experimental Farms, Anwomaso and Mr. Ahmed Iddirisu also of the Horticulture Department of KNUST. The authenticated samples were further confirmed by Mr. V. Sore, the Chief Technician at the KNUST Botanical Gardens.

3.1.1.2 Collection and Authentication of Soil Sample

A sample of the soil that has been used in traditional mud wall plaster technology was obtained from the Sirigu Women in Pottery and Art (SWOPA), a non-governmental

organization of women in Sirigu near Navrongo. This NGO has been doing traditional mud wall plastering and decoration for their community and beyond for several decades. The soil sample was offered by Madam Margarette, one of the leaders of the womens' group, from a stock pile previously identified and collected by members of the NGO. Madam Margarette, Lucy and Milani Kassise, who are leaders of the group, and have over two decades of experience in traditional mud wall plastering, authenticated the soil as that used for mud wall plastering. It was further authenticated by Mr. James A. Apasiko of the Savana Research Institute, Tamale as a sandy loam soil with little silt.

3.1.2 Chemicals

All reagents/chemicals used were of analytical reagent grade from the BDH Laboratory supplies Ltd, Poole, England. They were obtained from Revelation Products Ltd., agents of BDH laboratory supplies at Asafo market in Kumasi and from chemical stores of the Chemistry Department, KNUST. Doubly distilled water was used for the preparation of all solutions. The following chemicals were used for the project:

Acetic acid

Acetic anhydride

Acetone

Acetonitrile

Ammonia solution (dilute)

Antimony chloride

Cupper sulphate pentahydrate

Chloroform

Diethyl ether

Ethanol

Hydrochloric acid (conc.)

Iodine crystals

Iron (III) chloride

Lead acetate

Magnesium ribbon

Methanol

Mercury chloride

Nitric acid

Petroleum ether (40 - 60)

Phosphoric acid

Picric acid

Potassium bromide

Potassium hydroxide

Potassium Iodide

Potassium sodium tartrate

Sodium carbonate

Sodium chloride

Sodium hydroxide

Sodium hydrogen carbonate

Sodium sulphate and 98% sulphuric acid

3.1.3 Equipment

Equipment used in this work include the following:

Atomic Absorption Spectrometer (Buck Scientific Model 210 GP)

Flame Photometer (Spectronic 21, Multon Roy model)

Hellois Gamma/Delta UV-Spectrometer, (Thermospectronic Model by Thermo Electronic Corporation)

FTIR-8201A single beam laser Shimadzu Infrared Spectrophotometer

High Pressure Liquid Chromatography (with Pump 422, Detector 332 by Kontron Instruments)

X-ray diffractometer, at Intitute of Physical Chemistry, Hamburg, Germany

Büchi RotaVapor, R-114 (by Kontron Instruments)

Soxhlet set up and other glassware.

3.2 METHODS

The husk samples were powdered, extracted and fractionated for analyses. The masses of the crude extracts were recorded and subjected to statistical analysis. Also solubility tests, phytochemical screening, thin layer chromatography (TLC), ultraviolet (UV) spectroscopic scanning, high pressure liquid chromatography (HPLC), infrared spectroscopy (IR) and metal analysis were further conducted on extract. TLC, UV and IR were also carried out on the acidic, basic and neutral fractions of the water extract.

The soil sample was digested and analysed by atomic absorption spectroscopy (AAS), X-ray diffraction and IR spectroscopic analyses were carried out on the soil sample. Mud wall plaster was formulated and subjected to IR analysis.

3.2.1 Extraction of Husk Samples and Fractionation of Extractives

To eliminate traces of water, the dry husk were further air-dried for seven days in the laboratory to a constant weight. The moisture free husk were then pulverized in a mill at the Faculty of Agriculture- KNUST to obtain a coarsely powdered sample for Soxhlet extraction using water and 96% ethanol separately as solvents.

200.00g of air-dried coarsely powdered *Parkia biglobosa* husk sample was Soxhlet extracted using distilled water at boiling point until the solvent in the column of the Soxhlet was colorless. The extract was concentrated under reduced pressure in the rotary evaporator, collected into a weighed empty beaker and dried in the oven to a constant weight at 105°C. The process was repeated to obtain duplicate masses of new husk extract and also for extraction of the old husk.

Another 200.00g portion of powdered husk was weighed and extracted using boiling 96% ethanol as solvent in a Soxhlet. The extract was concentrated in the rotary extractor and dried in a weighed beaker at 80 °C in the oven. The process was repeated to obtain duplicate results for the new husk extract as well as for the old husk.

The crude aqueous extract was fractionated using the Bulk Transfer methodology into separated portions depending on their polarity.

Immediately after exhaustively extracting with ethanol, the marc obtained was further extracted using water and named "water after ethanol extraction".

100ml of 0.5 g/v of the extract was shaken with 20ml of 5% HCl and 10ml chloroform in a separatory funnel to obtain two layers. The aqueous layer, containing alkaline components in HCl was collected, neutralized with dilute NH_4OH and washed twice with chloroform and the washings added to the chloroform portion. The chloroform layer contained the acidic and neutral components. To this layer dilute NH_4OH was added gradually, the mixture shaken and tested with red litmus paper, until the extract mixture turned basic and the red litmus paper changed to blue. The strong acids had then extracted into the aqueous medium and this was collected separately. The organic layer was washed twice with distilled water and the washings added to the aqueous layer. To the remaining organic layer, 5% NaOH was added gradually with intermittent shaking (until the mixture was basic and red litmus turned blue) to extract the weak acids into aqueous solution. The aqueous layer was collected separately from the chloroform layer

containing the neutral fraction. Further washings of the chloroform layer with distilled water were added to aqueous fraction. The various solvents were then evaporated to obtain dry weak and strong acidic, basic and neutral fractions.

Aqueous solutions of portions of the extracts and fractionated components were made and tested for their reaction with litmus paper (Pavia *et. al.*, 1995).

3.2.1.1 Analysis of Extract

Both quantitative and qualitative analyses were carried out on the extract. The mean masses of the aqueous and ethanol extracts were determined and subjected to statistical analysis. Separate portions of the extracts were used for phytochemical screening, solubility tests, thin layer chromatography, UV visible spectroscopy, high pressure liquid chromatography and infrared spectroscopy. The fractions obtained from the aqueous extract were also subjected to solubility tests and infrared spectroscopy.

Statistical analysis

The mass of extract was determined on a chemical balance and recorded. The empty dried beaker was weighed and recorded as M_0. After drying the extract in the beaker, the beaker and its contents were weighed again and recorded as M_1 and the mass of the extract (m) was obtained as the difference of M_1 and M_0 (appendix 3a & 3b).

Using the masses of extracts obtained, the mean masses and percentage extractives of water as well as ethanol extracts were calculated with reference to the weighed laboratory-dried powdered husk.

The mean mass (μ) of the dried extract, its standard error and the null hypothesis test were determined according to procedures indicated in Miller and Miller, 1993.

The individual percentage extractive of weighed water and ethanol extractives of the husk were calculated using the formula: $\%\ \text{Extractive} = \frac{\mu\ (100\%)}{200}$

The standard error of mean (SEM) for each extract was calculated. In this project the true value (M) is the mass of an extract and the sample mean is the average mass of the extracts (μ) = $(M_1 + M_2 + \ldots M_n)/n$. Therefore SEM = $s/\sqrt{n}$, where s = standard deviation of the samples and n = number of samples statistics. $s = \sqrt{\{[(M_1 - \mu)^2 + (M_2 - \mu)^2 + \ldots (M_n - \mu)^2]/n\}}$.

Significant tests were then conducted. The significant test was given by: $\mu < M \pm t(s/\sqrt{n})$, where t = the test result and $t = [(M - \mu)/(s/\sqrt{n})]$, where M = observed value, μ = mean or expected value and s = standard error of mean (Bishop *et. al.*, 1992; Bluman, 2006).

Phytochemical screening

Standard tests were conducted for saponins, general glycosides, flavonoids, terpenes, tannins, alkaloids, anthraquinones and their glycosides and cyanogenitic glycosides. Solutions (appendix 4) for the phytochemical screening were prepared using doubly distilled water. The tests were conducted on the moisture-free aqueous Soxhlet extracts and then repeated on the ethanol extracts. Solutions prepared for phytochemical screening are presented in appendix 2.

Test for saponins

About 0.2g of dried aqueous extract was re-dissolved in 4ml of 96% ethanol and 2ml portion of the resulting solution put in a test tube. 3ml of distilled water was added and shaken vigorously.

Observation of a persistent foamy layer on top of the filtrate confirms presence of saponins.

Test for general glycosides

About 0.5g of dried aqueous extract was re-dissolved in 4ml ethanol. 2ml of the resulting solution was put in a test tube and 1ml of Fehling's (appendix 2) solution was added to the test tube and the mixture heated in a water bath for 15 minutes.

Observation of brick red coloration confirms the presence of general glycosides.

Test for flavonoids

About 0.3g of the dry aqueous extract was re-dissolved in 4ml ethanol and 2ml of the resulting solution was put in a test tube. 0.5ml of concentrated HCl and 3 pieces of magnesium turnings were than added.

Observation of a brick-red colour and effervescence confirms the presence of flavonoids.

Test for steroids and terpenes

5ml chloroform was added to re-dissolve about 0.5g of dry aqueous extract. 5 drops of acetic anhydride and 2 drops of concentrated sulphuric acid were then added.

Observation of a reddish-brown ring in the chloroform layer confirms the presence of steroids and terpenes.

Test for tannins and polyphenols

3ml of hot distilled water was added to about 0.3g of the dried aqueous extract. The mixture was stirred and allowed to cool to room temperature. 2ml of 10% sodium chloride solution was added to salt out the non tannin compounds. The mixture was filtered and the filtrate divided into two and placed in different test tubes. 4 drops of lead acetate solution were added to one of the test tubes and 4 drops of ferric chloride solution to the other.

Observation of a white precipitate and bluish-green coloration in the first and second test tubes respectively shows presence of tannins.

Test for alkaloids

10ml of 1% HCl was added to about 0.5g sample of the dried aqueous extract. The mixture was left to stand for 30 minutes with occasional stirring before filtering. 2ml portion of the filtrate was placed into a test tube and 3 drops of Mayer's reagent (appendix 2) then added to the content of the test tube.

Observation of a pinkish precipitate confirms presence of alkaloids.

Test for anthraquinones

About 0.5g of sample was boiled with 25ml of 0.5M KOH and 4ml of H_2O_2. The mixture was cooled, filtered and acidified with 3 drops of acetic acid and the resulting solution

extracted with 15ml of benzene. The resulting yellowish benzene layer was separated and shaken with 4ml NH_4OH.

Observation of reddish coloration confirms presence of anthraquinones.

Test for anthraquinone glycosides

About 0.5g of the aqueous extract was boiled with 20ml of dilute sulphuric acid, boiled and filtered hot. The filtrate was allowed to cool and about 10ml portion was taken into a test tube and shaken with an equal volume of benzene. The benzene layer was separated and shaken with about half its volume of dilute ammonia solution.

A coloured ammoniacal layer gives indication of presence of anthraquinone glycosides.

Test for cyanogenitic glycosides

About 2.0g of finely powdered plant material was weighed into a test tube, moistened with a few drops of distilled water and dilute HCl, stoppered and allowed to hydrolyse. A few drops of chloroform were then added and a small piece of sodium picrate paper (appendix 2) inserted into the test tube (making sure the picrate paper does not touch the inner sides of the test tube or come in contact with sample in it). The test tube and its content was warmed to 35°C for about 3 hours.

Red colouration of the picrate paper after the 3 hours indicated the presence of cyanogenetic glycosides.

Solubility test and acidity tests

This preliminary functional group determination process was applied to the aqueous and ethanol Soxhlet extracts as well as the fractionated components.

To about 5ml of distilled water, 5% NaOH, 5% $NaHCO_3$, 5% HCl and conc. H_2SO_4 solutions in separate test tubes, about 0.2g portions of the moisture-free water extract were added and the test tubes well shaken to dissolve. More solvent was added to portions that did not dissolve and shaken very well. The process was repeated for the ethanol extract and fractionated components (appendix 5a – 5f).

Aqueous solutions of extracts and components found to be soluble in water were tested for their acidity using litmus paper. A small portion of each fraction was placed in a clean dry test tube so that blue and red litmus papers were dipped, one at a time, into the solution to wet the litmus paper. The paper was then removed and observations of any colour change recorded (Pavia *et. al*, 1995).

Thin layer chromatography

Thin layer chromatography was performed on the crude water and ethanol extracts as well as the acid, base and neutral fractions of the water extract using various solvent systems. Standard 5cm x 10 cm silica pre-coated thin layer chromatography plates, from Macherey-Nagel GmbH & Co. KG, were used for the analysis.

Using a pencil a line, 1cm from the base of the plate, was drawn and a solvent poured into a beaker to 1cm height from its base. With the aid of capillary tube a dissolved

extract was spotted on the line drawn on the plate and the plate placed upright into the mobile phase solvent in a beaker, with the spots downwards, and the beaker then covered with aluminum foil.

The movement of the solvent was monitored as the solvent front ascended the plate until it was just about 1 cm to the end of the plate. The developed plate was then removed, dried and visualized in iodine fume. The distance moved by separated components and the solvent front were measured and the respective R_f values calculated according to standard procedures (Pavia *et. al*, 1995). This procedure was repeated using different portions and mixtures of distilled water, ethanol, methanol, chloroform, acetone, hexane and ethyl acetate as mobile phase solvent systems.

UV-visible spectroscopy

Solutions of the extracts and fractions were scanned using a Thermostronic model Hellois Gamma/Delta V 7.03, UVG 121108 UV-visible Spectrometer.

1:10 g/v solutions of dry crude extracts and fractions in distilled water were prepared and used for UV analyses. Distilled water was put into the cuvette as a blank and the cuvette inserted into the spectrometer to zero the instrument. The blank was then replaced with each prepared solution filled in the cuvette for scanning. Scanning was done through wavelengths of 190-800 nm, corresponding to the UV absorption region of 190–400 nm and the visible region of 400–800 nm. The absorbance of each solution and corresponding wavelengths were recorded. The wavelength of maximum absorption (λ_{max}) for each solution was then identified and recorded (Pavia *et. al.*, 1995).

High pressure liquid chromatography (HPLC)

HPLC analyses were carried out to ascertain the presence and number of classes of alkaloids, phenyl glycosides, phenolic acids, flavan-3-ol, flavonols and proanthocyanidins in the extracts. 1:10 g/v solution of the dried crude aqueous extract in distilled water was prepared and injected into the Rheodyne injector of the HPLC equipment fitted with Pump 422 and a UV detector lamp 322 at various wavelengths depending on the requirement for the particular analysis.

The compounds were monitored by the detector as they eluted off the column and signals generated were captured as data by a Waters 746 data module in a print out, using integrator model No. 54076. The columns were eluted at room temperature in the isocratic mode.

The analysis of alkaloids was done according to the method used proposed by Hong-Xia, 2002, using Spherisorb 5-C 18 column having dimensions of 250 x 4.6 mm, a detection UV set at 257nm employing a mobile phase mixture of methanol and water, (1:9 v/v), and water as sample diluent. The flow rate was 1.0 mL/min., at 27°C temperature and sample injection was 20µL (Hong-Xia *et. al.*, 2002; Turkmen and Sedat, 2007).

The number of phenolic glycoside components in the extract was determined using the method validated by Muller *et. al.*. The glycosides were monitored by applying a Synergi 4 µm Fusion RP 80 Å column, using 5% acetonitrile in methanol as mobile phase and a detection limit UV at 210 nm. The flow rate was 1.0 mL/min., temperature was set as

27°C, and the sample injection was also 20µL using water as sample diluent (Muller *et. al.*, 2006).

To determine the presence of phenolic acids, flavan-3-ols and flavonols or proanthocyanidin 20 μL of the prepared extract solution were injected, applying a SPHERI-5 RP-18 (5 µm) column at 35 °C and a flow rate of 1.0 ml min^{-1} on the HPCL equipment. The column was eluted by 82 % (v/v) acetonitrile (CH_3CN) to water and 4 % (v/v) phosphoric acid to water mixtures. The peaks were detected at a wavelength of 280 nm.

Infrared spectroscopy

The aqueous extract of *Parkia biglobosa* fruit husk and its fractionated portions were analysed using IR. To obtain moisture free samples, the rotary concentrated extract and fractions were dried at 105°C in the oven for 24 hours. Final traces of moisture were removed by drying the samples over 98% concentrated sulphuric acid in a desicator. The moisture-free aqueous extract, the strong and weak acids and the basic as well as the neutral components were then used for the IR analysis.

The dry samples were powdered using a mortar and pestle and prepared using a minipress apparatus for IR analysis. Ground KBr was mixed with the sample powder into the die of the press and compressed into a translucent pellet. The holder was slided in place and the die replaced in the slot. The optical path was then set to obtain the spectrum using the FTIR-8201A single beam laser Shimadzu Infrared Spectrometer (Pavia *et. al*, 1995).

3.2.2 Analysis of the Soil

A sample of the soil that is used in the traditional technology of plastering mud walls was air-dried for three days in the laboratory and sieved using a 76 micron diameter pore-space sieve to remove lumps and stones. The fine-grained soil obtained was ground further using mortar and pestle. A portion was acid digested for metal analysis, and another portion was prepared for X-ray diffraction and for IR analyses.

3.2.2.1 Metal analyses

The samples were acid digested and subsequently analysed using the UNICAM model 929 Atomic Absorption Spectrometer (AAS) or Flame Photometer.

1.0g portion of the dry soil sample was weighed into a digestion flask and moistened with 1ml of distilled water. 2ml of 1:1 proportions of HNO_3: $HClO_4$ mixture and 5ml of H_2SO_4 were then added and the flask was covered with a watch glass. The mixture was heated on a hot plate under the hood to $200^\circ C \pm 5^\circ C$ till the production of brown fumes had ceased. This took about 30 minutes. The hot digested sample was taken from the hot plate and allowed to cool to room temperature. More distilled water was added and the solution filtered through a funnel with a Whatman No. 41 filter paper into a 50ml volumetric flask. More distilled water was added with occasional swirling to make up to the 50ml mark of sample solution.

A mixture of 1ml distilled water, 2ml of 1:1 proportions of HNO_3 and $HClO_4$ and 5ml of H_2SO_4 without the sample but subjected to the treatment as described above was used as the blank. Iron, zinc, silicon, lead and nickel were analysed using AAS. The AAS

instrument was fitted with the iron, zinc, lead and nickel hollow cathode lambs to determine the respective metals, after which silicon was also done.

To analyse for iron, the iron lamp was set in place, the spectrophotometer was switched on to allow the lamp to warm up for 15 minutes whilst the wavelength and slit width were selected. The monochromator was then adjusted to obtain maximum light output and a white sheet of paper used to ensure that the radiation passes through the window to the photomultiplier. The absorbance was set at zero, the gas flow adjusted and the flame ignited. The burner was allowed to heat for 10 minutes while aspirating water.

The sample solution was then replaced and aspirated and the reading taken. The blank solution was also replaced and aspirated and the absorption recorded. The process was repeated by setting the cathode lamp to analyse for zinc, lead and nickel, and then subsequently for silicon.

Calcium, magnesium, sodium and potassium were analysed by Flame Photometry. The photometer was switched on for 10 minutes to warm. It was then adjusted to zero using distilled water before the sample solutions were replaced into the flame.

The amount of every metal was determined in triplicates and the mean concentration calculated.

3.2.2.2 X-ray diffraction

The aim of the X-ray diffraction was not to deliver a detailed structural information of the soil but to obtain information to help establish the interaction between some of the soil

constituents and the functional groups in the *Parkia biglobosa* fruit husk extracts. It was to serve as a supplement to the IR analyses of the extracts, the soil samples and the simulated plastering material meant to deliver information on the interaction of extract's functional groups and the constituents of the soil.

The Powder X-ray diffraction technique was used for characterizing the soil. X-ray analysis was conducted on the sieved and mortar-ground soil sample.

The sample was oven dried at 105°C for 24 hours and then ground to powder. The powder was exposed to X-rays at various glancing angles ranging from 0 to 100° and the diffraction patterns (the relative positions of the peaks) and intensities produced were then compared with reference standards for identification.

The relationship between the wavelength of the X-ray beam, the glancing angle θ, and the distance between each set of planes of the crystal lattice d, was established by the well known Bragg Law: $2d\sin\theta = n\lambda$; where n is the order of diffraction.

The angle of diffraction called theta (θ) is measured in degrees as 2θ, the d-spacing is measured in picometer and λ, the wavelength in picometer. n is an integer such as 1,2,3 .....etc.

3.2.2.3 Infrared spectroscopy

Infrared analysis was conducted on the soil sample. A portion of the soil sample sieved in section 3.2.2.2 above was treated with Nujol and analysed in the Nujol mull by Infrared spectroscopy.

To the ground soil in a mortar 2 drops of Nujol mineral oil was added and the mixture ground to very fine dispersion. The mull was placed between two plates using a rubber policeman, mounted in the holder of the spectrometer and the spectrum taken (Pavia *et. al*, 1995).

3.2.3 Formulation of Mud Wall Plaster

Simulations of the mud plaster were done using the water extract and the soil as well as the fractions and the soil. A hot aqueous extract of the husk was prepared by adding boiling water to the dry extract. The hot extract was then well mixed with the soil in a 1:2 weight to weight of extract to soil ratio to form a slurry as is done in the traditional technology of formulating mud wall plaster. The paste was spread into a thin sheet, on aluminum foil placed over a flat board and allowed to harden briefly. More extract was further sprinkled on the surface of the sheet of paste, such as pertains in the traditional technology. The formulation was then allowed to dry up completely in the sun for 72 hours. The process of plaster formulation was repeated using the fractions of the aqueous extract.

The dry formulated plasters were then analysed using IR.

3.2.3.1 Analysis of Formulated Mud Wall Plaster

A portion of each simulation was taken, ground in a mortar into powder and traces of water were removed by further drying in the oven at 35 °C for 36 hours. The moisture free powdered simulates were then pressed into KBr pellets (3.2.1.1.7) and analysed using the FTIR-8201A single beam laser Shimadzu Infrared Spectrometer.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

The results presented in this chapter, with some of their details presented as appendix, represent the various findings from the experimentation. The results of all the experiments performed on the extracts as well as on the soil and the simulated plaster are presented and discussed.

4.1 EXTRACTION OF HUSK

The results obtained for the extract (percentage yield), extract solubility tests, extract phytochemical screening, thin layer chromatography, high pressure liquid chromatography, infrared spectroscopic analysis of the extracts are presented and discussed.

4.1.1 Percent Yield of Extracts

The yield percent of the water and ethanol extractions are presented, put under statistical test and discussed. The mean masses were calculated from the masses of water and ethanol extractives of both the new (appendix 3.a.) and the old (appendix 3.b.) husk. The mean masses were then used to calculate for the percent extract. Statistical analyses were then conducted on the mean masses of extractives to assess the overall performance of the extraction process and to compare the performance of the solvents in the extraction.

Table 4.1 (i) Percent extractives (E) of new husk

Solvent used	Extract			
	E_1	E_2	Mean mass (g)	Percent mass (%)
Water	74.50	74.38	74.44	37.22
Ethanol	62.082	61.702	61.89	30.95
Water (after ethanol)	16.20	17.38	16.79	8.40

The mean mass of water soluble extractives (74.44g) of the new husk was greater than that of ethanol soluble extractives (61.89g). The percentage extractives using water as solvent was 37.2% whilst using ethanol as solvent yielded 31.0 % extract. Water is therefore a preferable solvent for extracting the new husk.

Table 4.1 (ii) Percent extractives (E) of old husk

Solvent used	Extract			
	E_1	E_2	Mean mass (g)	Percent mass (%)
Water	75.93	77.31	76.62	38.31
Ethanol	61.20	61.58	61.39	30.70
Water(after ethanol)	15.75	18.83	17.29	8.65

The mean mass of water soluble extractives (76.62g) of the old husk was higher than that of ethanol soluble extractives (61.39g). The percentage extractable material in old husk using water as solvent was 38.3% whilst using ethanol as solvent yielded 30.7 %. Water is therefore a better solvent than ethanol for quantitatively extracting the old husk. Table 4.2 below, compares the mass of extracts from the old and new husk.

The standard deviation (appendix 3.a.) and standard error (appendix 3.b.) of the mean of the new husk extracts and old husk were calculated on the mass of extract obtained and

the summary presented below on Table 4.3 (i) and (ii) respectively. The respective null hypotheses were then conducted.

Table 4.2 Comparison of masses of extracts of old and new husk

Husk	Percent (%) extract for respective solvents		
	Water	Ethanol	Water (after ethanol)
New	37.22	30.95	8.40
Old	38.31	30.70	8.65
Total yield	75.53	61.65	17.05
Average yield	37.77	30.83	8.53

From the table, the percentage extractive value by water (38.31% and 37.22%) for both old and new husk, representing an average yield of 37.77% was higher than that by ethanol (30.70% and 30.95%), representing an average of 30.83%. Using water to extract, the percentage extractive value of old husk (38.31%) was slightly greater than that of the new husk (37.22%). On the other hand, the percentage extractive value (30.70%) of the old husk using ethanol as solvent was only a little less than that of the new husk (30.95%). Using water to extract the samples after exhaustively extracting with ethanol offered the least values of extracts. The water soluble extractives (after ethanol extraction) yielded 8.65% from the old husk and 8.40% extract from the new husk. The total percentage of extracts using ethanol and then water afterwards was generally higher than that using only water to extract.

Though the percentages of the water soluble extractives were slightly higher for the old husk than for the new husk, the difference was insignificant. Generally polar solutes

dissolve in polar solvents and water is more polar than ethanol and will extract more solute than ethanol if the solute is very polar. Therefore the extractable materials are likely made up of very polar substances.

The total percentage yield of water extract of the new husk amounted to 75.53% and was higher than that by ethanol which amounted to 61.65%. Thus, the average extract by water (37.77%) therefore far outweighs the average extract by ethanol (30.83%) (Table 4.2) and so water was identified as a preferable solvent for extracting the husk quantitatively because it is cheaper and yields more extract than ethanol. Further analyses (quantitative and qualitative) were conducted on the water soluble extractives.

Table 4.3 (i) Results of statistical analyses of the extract of new husk

Extract	Standard deviation (s) of the mass of extracts	Standard error of the mean (SEM) mass of extracts
Water	0.06	0.0424
Ethanol	0.19	0.1344
Water (after Ethanol)	0.59	0.4171

On the t table, at 95% confidence level and 1 degree of freedom, the t_α value is 12.706 (Bluman, 2006). Thus, for the water extract, the 95% confidence interval of the mean $[\mu_w - t(s/\sqrt{2}) < \mu_w < \mu_w + t(s/\sqrt{2})]$ is: $74.44g \pm 12.706(s/\sqrt{2})g$

$74.44 - 12.706(0.06/\sqrt{2}) < \mu_w < 74.44 + 12.706(0.06/\sqrt{2})$

$74.44 - 0.539 < \mu_w < 74.44 + 0.5390$

$73.90 < \mu < 74.98$

Hence the 95% confidence interval contains the two extractive values (74.50g and 74.38g) of the water soluble extractives and the null hypothesis is not rejected. In principle, at 95% confidence level an extraction of new husk using water as solvent would always yield between 36.95% and 37.49% of extract (Bishop, *et. al.*, 1992; Bluman, 2006). The null hypothesis test, working at 95% confidence limit and probability (P), at $\alpha = 0.5$, indicated that the observed difference between the sample mean and the true values arise solely as a result of random errors.

Table 4.3 (ii) Results of statistical analyses of the extract of old husk

Extract	Standard deviation(s) of the mass of extracts	Standard error of the mean (SEM) mass of extracts
Water	0.98	0.69296
Ethanol	0.19	0.13435
Water (after Ethanol)	1.54	1.08894

On the t table, at 95% confidence level and 1 degree of freedom, the t_α value is 12.706 (Bluman, 2006). Thus, for the water extract, the 95% confidence interval of the mean $[\mu - t(s/\sqrt{2}) < \mu < \mu + t(s/\sqrt{2})]$ is: $76.62g \pm 12.706(s/\sqrt{2})g$

$76.62 - 12.706(0.98/\sqrt{2}) < \mu < 76.62 + 12.706(0.98/\sqrt{2})$

$76.62 - 0.693 < \mu < 76.62 + 0.693$

$75.93g < \mu < 77.31g$

The actual extractive values were contained within ± 12.706 of the mean (76.62g) and the null hypothesis is not rejected. In principle, the 95% confidence level of extraction of the old husk using water will have an extractive value within the range of 37.97% and 38.66% (Bishop, *et. al.*, 1992; Bluman, 2006). The null hypothesis test, working at 95% confidence limit and probability (P), at $\alpha = 0.5$, indicated that the observed difference between the sample mean and the true values arise solely as a result of random errors.

Generally polar solutes dissolve in polar solvents. The extract of the fruit husk therefore contains a large amount of polar compounds since a greater amount of solute (extract) was obtained using water.

Fractions obtained from the aqueous extract were strong and weak acids, basic and neutral. The litmus tests conducted on each of the fractions gave the following results: Red litmus paper remained unchanged in the weak acid, strong acid, and neutral fractions but turned blue in the basic fraction. Blue litmus paper turned red in the strong and weak acid fractions, but remained unchanged in the neutral as well as basic fractions. The acidity of the various fractions was thus confirmed.

4.1.2 Phytochemical Screening

Phytochemical screening performed on the water and ethanol extracts (appendix 4) indicated the presence of six metabolites. Saponins, flavonoids, tannins, anthraquinones, anthraquinone glycosides and alkaloids were present in *Parkia* fruit husk.

In formulating the plaster tannins would form stable water-insoluble co-polymers with alkaloids and proteins. They would also chelate the metals of the soil to form organometallic compounds. Hydrolysed tannins would produce tannic acid which combines with iron to form iron-tannate.

The saponins increase and accelerate calcium and silicon complexing processes and resin would be generated from terpenes whilst the conjugated double bonds of flavonoid units present in the extract would serve as electron sources for donation to metal sinks (Pavia, *et. al.*, 1995).

During the formulation of the plaster, these phytochemicals could therefore interact with metals in the soil to form relevant products.

4.1.3 Solubility Tests

The extent of solubility of the aqueous husk extract was done using standard methods prescribed by Pavia *et. al.*, 1995. Details of solubility test results are in appendix 5. A summary of suspected classes of compounds in the aqueous extract and fractions, after testing their solubility in distilled water, 5% NaOH, 5% $NaHCO_3$, 5% HCl and concentrated H_2SO_4 are recorded on Table 4.4 below.

Table 4.4 Suspected compounds in the moisture free extract/fractions

SAMPLE	SUSPECTED CLASSES OF COMPOUNDS
WATER EXTRACT	Low MW carboxylic acids, alkenes, alkynes, alcohols, ketones, aldehydes, nitro compounds, esters, ethers, amides
STRONG ACID FRACTION	Phenols, alkanes, alkyl halides, aromatic compounds
WEAK ACID FRACTION	Low molecular weight amines, alkenes, alkynes, alcohols, carbonyls, nitro compounds, esters, ethers, amides
BASIC FRACTION	Low molecular weight amines, alkenes, alkynes, alcohols, ketones, aldehydes, nitro compounds, esters, ethers, amides
NEUTRAL FRACTION	Low molecular weight neutral compounds; including alkanes, alkyl halides, aromatic compounds

Source: Pavia *et. al.*, 1995

From these results, the group of compounds of suspect in the water extract compared well with groups identified in the phytochemical screening of the extract and fractions.

Presence of acids, nitrogen containing compounds, alcohols, alkenes and esters in the aqueous extract were essentially due to functional groups associated with tannins, flavonoids, alkanoids, phenolics and glycosides. Presence of phenols and aromatic components would be due mainly to tannin whilst carboxylic acid groups due to tannic acid that comes from hydrolysis of tannins. Esters would be carbohydrate fragments from glycosides and unhydrolysable tannins.

The basic compounds represent nitrogen containing compounds such as alkaloids whilst the alkanes, alkyl halides and aromatic compounds are in the neutral fraction.

4.1.4 Thin Layer Chromatography

Thin layer chromatography results based on the distance moved by separated components and the respective measurement of solvent fronts, and the corresponding retention factor (R_f) values that have been calculated were recorded for the water, ethanol and water-after- ethanol extracts as appendix 6 and the fractions as appendix 7. A summary of solvent systems and extracts/fractions that produced highest number of separations is provided in tables 4.5 and 4.6 below respectively.

Table 4.5 Summary of solvent systems, number of components and R_f-values in TLC of the aqueous extract

Extract	Solvent system	Number of components	R_f
Water	Distilled Water	2	0.77, 0.42
	96% ethanol	2	0.86, 0.62
	2:1, Ethanol:Water	2	0.96, 0.67
	5:1, Ethanol:Water	2	0.80, 0.41
	3:2, Ethanol:Water	2	0.94, 0.26
	1:2, Ethylacetate:Ethanol	2	0.94, 0.22
	2:1, Ethylacetate:Ethanol	2	0.11, 0.07

The use of water, ethanol, acetone and chloroform separately as mobile phase in the TLC analysis gave varying results, water and ethanol producing a higher number of separations (appendix 6) of the aqueous extract than the others. For the mixtures of various proportions of the solvents used as mobile phase in the TLC of the aqueous extract, a 2:1 mixture of ethanol to water is less polar than water but more polar than a 3:2 ethanol to water mixture. The highest R_f value (0.96) was produced by 2:1 mixture of ethanol to water, 0.86 by water only and 0.94 by 3:2 ethanol to water mixture. Therefore,

the components of the extract were moderately polar. Generally the maximum number of observable separations in the crude extract was two, as indicated on table 4.5 above. Thus, compounds in the aqueous extract associated together in a minimum of two main groups generally represented by the two separations.

For the mixtures of various proportions of the solvents used as mobile phase in the TLC of the aqueous extract, a 2:1 mixture of ethanol to water is less polar than water but more polar than a 3:2 ethanol to water mixture. The highest R_f value (0.96) was produced by 2:1 mixture of ethanol to water, 0.86 by water only and 0.94 by 3:2 ethanol to water mixture. Therefore, the components of the extract were moderately polar, since the highest R_f was produced by a moderately polar solvent of 2:1 mixture of ethanol to water mixture.

A mobile phase of 2:1 ethylacetate : chloroform mixture produced the least R_f as well as separations (Appendix 6).

On the basis of the performance of the non polar solvents as mobile phases for TLC analysis, it can be concluded that the aqueous extract may not contain a good amount of non polar components.

Table 4.6 Summary of solvent systems, number of components and R_f-values in TLC of the fractions of the aqueous extract

Fraction	Solvent system	Number of components	R_f
Strong acid	Water only	2	0.14, 0.60
	1:2, Ethanol : Water	3	0.17, 0.60, 1.0
Weak acid	Ethanol only	4	0.07, 0.37, 0.78, 0.87
	1:2, Ethanol : Water	4	0.12, 0.31, 0.45, 0.687
Basic	Ethanol only	2	0.64, 0.86
	2:1, Ethanol : Water	3	0.44, 0.61, 0.76
	2:1, Ethylacetate : Ethanol	3	0.06, 0.55, 0.64
Neutral	Water only	3	0.06, 0.56, 0.82
	Ethanol only	3	0.035, 0.37, 0.70
	1:1, Ethanol : Water	4	0.14, 0.41, 0.56, 0.81
	1:2,Ethylacetate : Ethanol	4	0.06, 0.47, 0.68, 0.92

TLC results of the fractions showed that there were at least three components in the strong acid fraction, four in the weak acid fraction, three in the basic fraction and four in the neutral. The highest R_f values recorded for the various fractions were: 1.0 for 1:2 ethanol to water mixture in the strong acid fraction, 0.87 for ethanol only in the weak acid fraction, 0.86 for ethanol only in the basic fraction and 0.92 for 1:2 ethylacetate to ethanol mixture in the neutral fraction.

The TLC results of the fractions conformed to results of the solubility tests (section 4.1.3) of the fractions. The highest R_f value in all the fractions (1.0) registered for the strong acid fraction due to a polar mixture of 1:2 ethanol to water. This indicated that the most polar components were contained in the strong acid fraction. Also, the non-polar

components were contained in the neutral fraction which registered the lowest R_f value (0.06) for a mobile phase of 1:2 ethylacetate to water mixture.

4.1.5 Ultraviolet Spectroscopy

Results of UV-Visible scanning of aqueous solutions of the crude extract and fractions for the wavelengths ranging from 190 – 800nm are presented on table 4.7 below. From the scan results, the wavelengths of maximum absorbance (λ_{max}) and the corresponding absorbance for each solution have been abstracted and presented on table 4.8.

Table 4.7 Results of absorbance / wavelength (λ) of UV scan of water extract / fractions

WATER EXTRACT		FRACTION							
		STRONG ACIDS		WEAK ACIDS		NEUTRALS		BASICS	
Abs	λ	Abs	λ	Abs	λ	Abs	λ	Abs	λ
ND	234.0	ND	234.0	ND	193.5	ND	201.0	0.572	191.5
2.746	518.5	ND	329.5	ND	473.0	ND	204.5	1.445	194.0
0.417	731.5	2.073	334.5	2.518	487.5	ND	234.0	ND	198.0
0.399	744.0	1.453	336.5	0.614	630.0	ND	394.0	ND	234.0
0.364	774.5	1.369	339.5	0.288	724.0	3.672	400.5	3.189	482.0
0.362	787.0	1.204	342.0	0.202	779.0	2.885	410.0	2.302	497.0
0.361	794.5	0.921	351.0	0.203	787.0	3.910	439.5	0.315	724.0
--	--	0.712	365.5	--	--	2.990	445.0	0.298	731.5
--	--	0.246	427.5	--	--	3.012	448.0	0.290	737.5
--	--	0.226	609.0	--	--	2.839	454.5	0.246	787.5

Abs = Absorbance, λ = Wavelength, ND = Not detected

Table 4.8 Maximum absorbance and wavelengths (λ_{max}) of extract/ fractions

EXTRACT/ FRACTION	Peak Absorbance	Wavelength (λ_{max})
Water	2.746	518.5
Strong acid	2.073	334.5
Weak acid	2.518	487.5
Basic	3.189	482.0
Neutral	3.910	439.5

The crude water extract, the weak acid, the neutral and the basic fractions all absorbed predominantly in the visible region whilst the strong acid fraction absorbed mostly in the UV region. The wider range of visible absorption wavelengths in the basic (482.0 – 787.5) and weak acid (473.0 -787.0) indicated that the basic and weak acid fractions contained greater number of conjugated double bonds and/or polycyclic aromatic chromophores than the neutral and strong acid fractions. The strong acid fraction indicated only two bands at relatively low wavelengths (427.5, 609.0) in the visible region and therefore contained the least number of double bonds and polycyclic chromophores. The greater the number of conjugated double bonds, the lower the energy needed to move an electron from the π bonding to π^* antibonding orbital and therefore the higher the wavelength (Williams and Fleming, 1989; Matthews, 2004; Pavia *et. al.*, 1979). Also, longer conjugated systems give longer wavelength of absorption maxima. From table 4.8, the weak acid has longer λ_{max} hence longer wavelength, followed by the basic fraction, the neutral and then the strong acid whose λ_{max} falls within the UV absorption region.

Based on the results of the absorbance and the phytochemical screening the weak acid fraction contain unhydrolyzable tannins and flavonoids which gave rise to the extensive absorption in the visible region due to their conjugated systems and polycyclic aromatic rings. The strong acid fraction may contain hydrolysed tannins (tannic acid) and so have a lesser absorption in the visible region due only to the aromatic ring absorptions. Absorptions in the basic fraction were mainly due to the polycyclic aromatic rings of alkaloids.

4.1.6 High Performance Liquid Chromatography (HPLC)

HPLC analyses conducted on the aqueous extract determined the number of classes of alkaloids, phenolics glycosides, phenolic acids, flavonols and/or proanthocyanidins. The results are indicated on Figures 4.1 to 4.3 below.

4.1.6.1 Number of Classes of Alkaloids

Using the mobile phase mixture for separation of classes of alkaloids in aqueous solution (Hong-Xia *et. al.*, 2002; Turkmen and Sedat, 2007), one peak was indicated, with a retention time of 1.0.

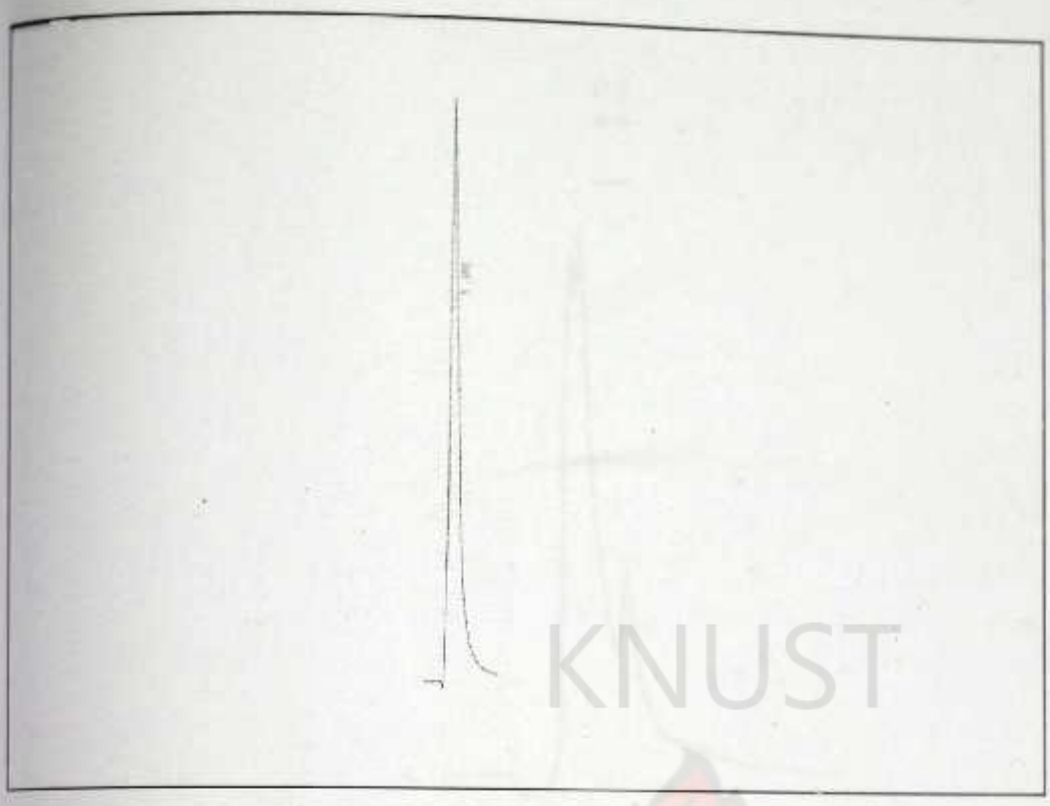


Figure 4.1 HPLC of alkaloids in the aqueous extract

One peak (in Figure 4.1 above) reveals that there was at least one class of alkaloids present in the extract and the sample for that matter.

4.1.6.2 Number of Classes of Phenolic Glycosides

Applying the mobile phase mixture for separation of phenolic glycosides, 5% acetonitrile in methanol (Muller *et. al.*, 2006), three peaks were produced. As shown below, the sample contains at least three classes of phenolic glycosides in the water extract. These were indicated by the three peaks as shown in Figure 4.2.

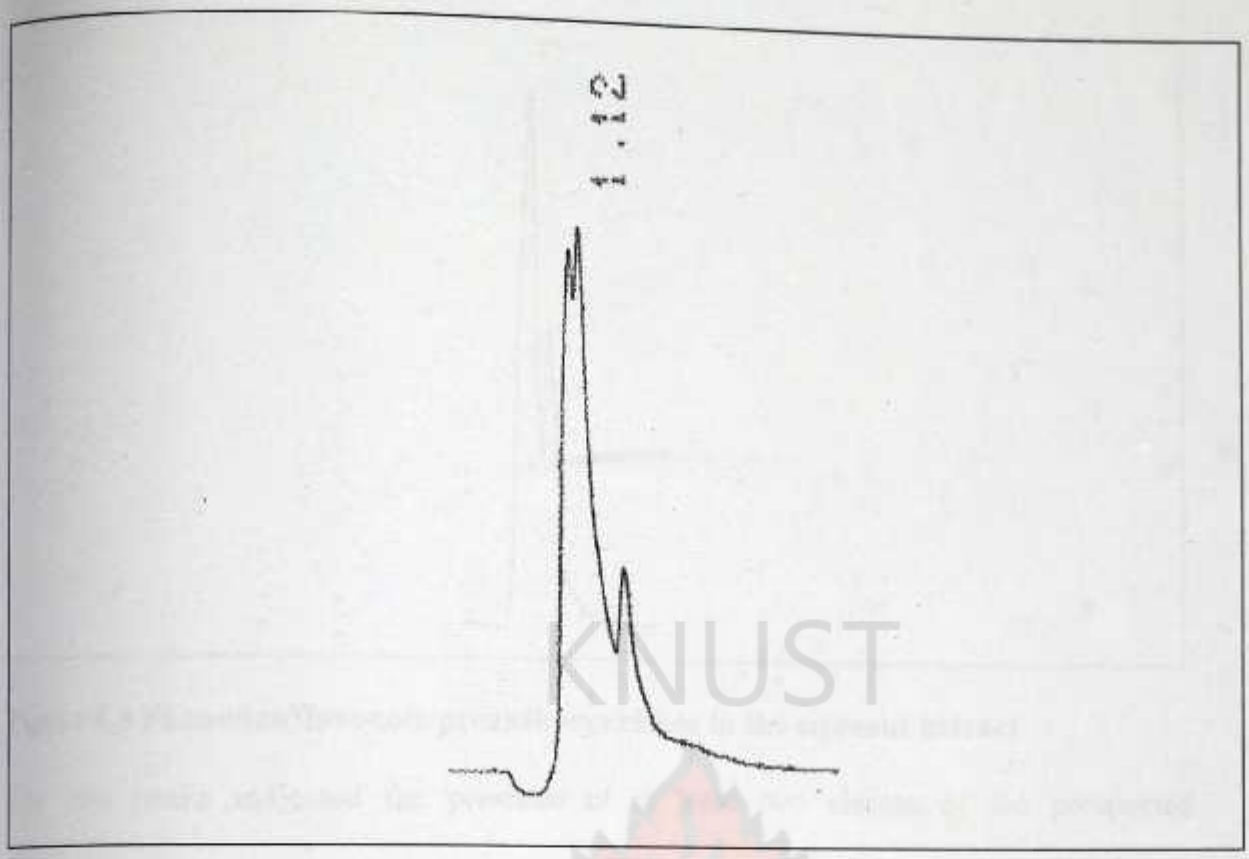


Figure 4.2 HPLC of phenolic glycosides in the aqueous extract

4.1.6.3 Number of Classes of Phenolics, Flavonols and/or Proanthocyanidins

The number of classes of phenolic acids, flavonols and/or proanthocyanidins, determined at 280 nm, were at least two. The result of the HPLC analysis performed on the extract containing using a combined mixture of 82 % (v/v) acetonitrile to water and 4 % (v/v) phosphoric acid to water mixtures as mobile phase is presented in Figure 4.3 below:

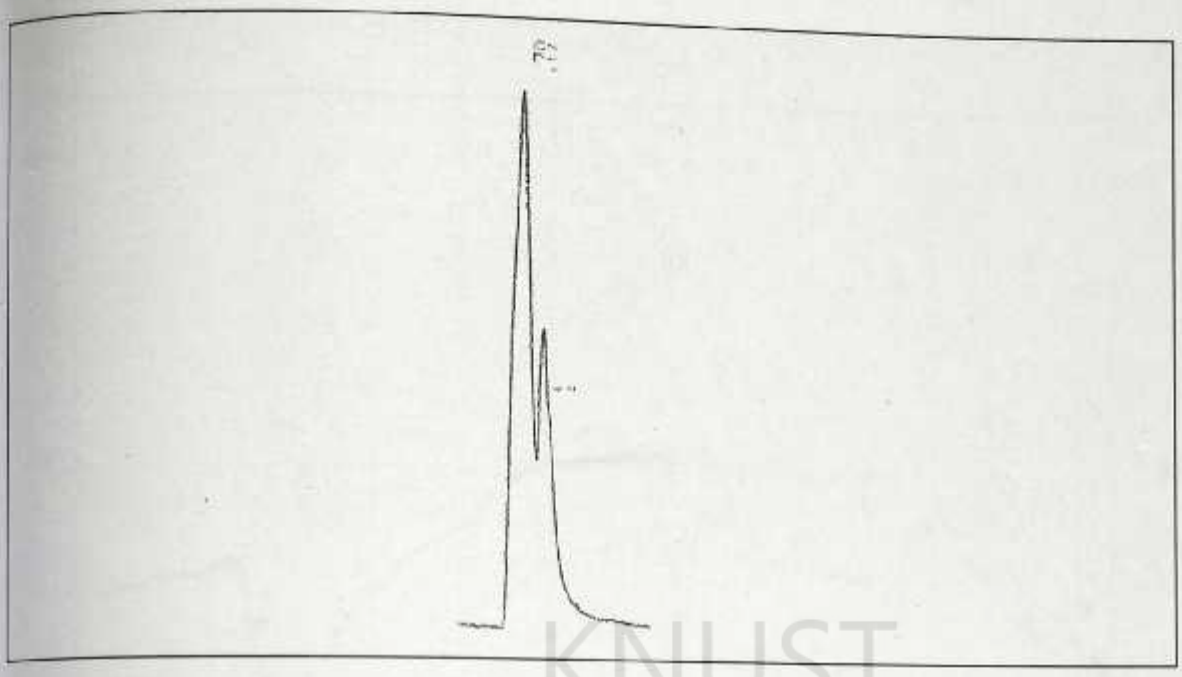


Figure 4.3 Phenolics/flavonols/proanthocyanidins in the aqueous extract

The two peaks indicated the presence of at least two classes of the prospected compounds. Hence two of the same or any two of the different groups of compounds may be present.

4.1.7 Infrared Spectroscopy

Results of the Infrared analyses of samples of the crude water extract and the fractions of the water extract are presented in the following subsections.

4.1.7.1 Water extract

The spectrum obtained from the infrared analysis of the crude water extract of the husk and deductions made from them are presented below.

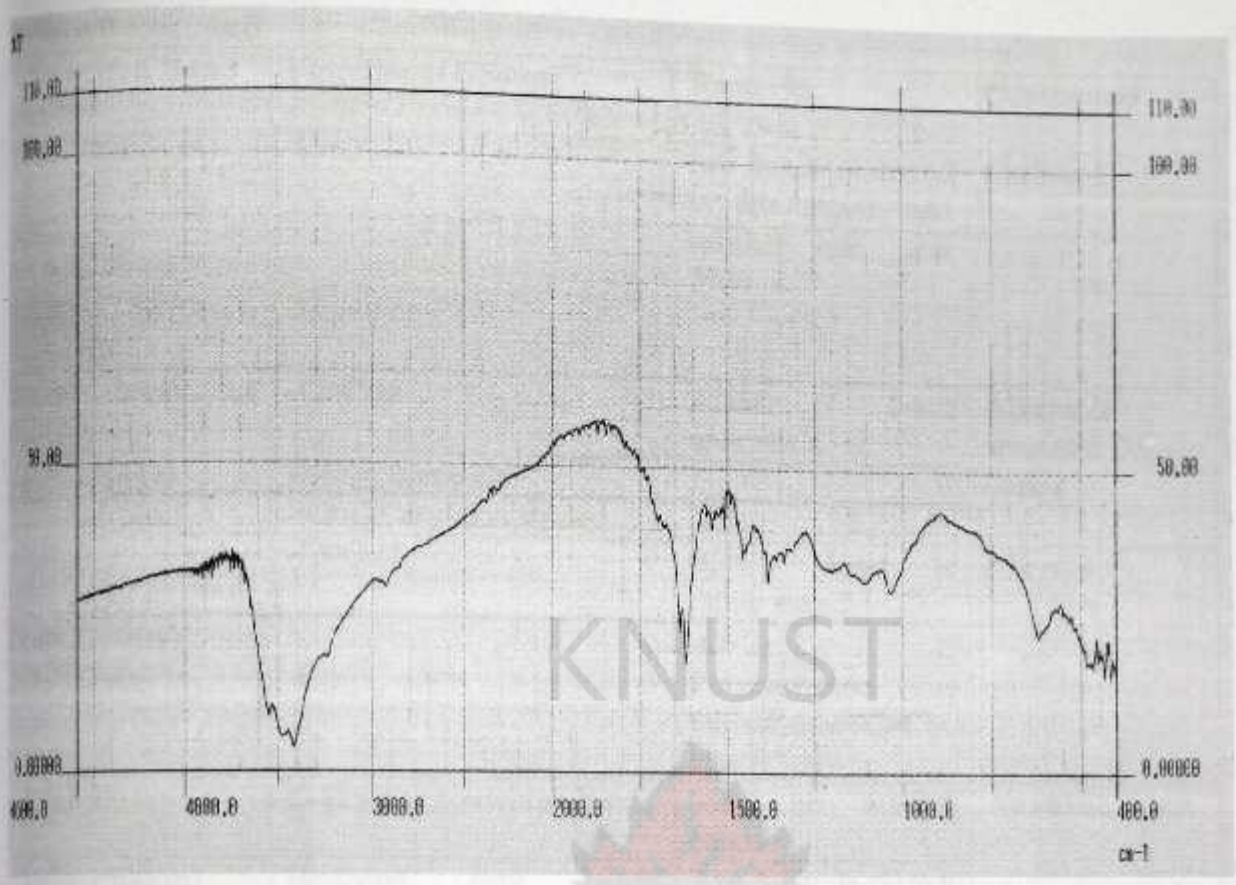


Figure 4.4 Infrared spectrum of the crude water extract in KBr

Table 4.9 Deductions made from Infrared spectrum of the crude water extract

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
3525, 3490, 3440, 3410(s)	Bonded O-H (Usually broad)	Three strong sharp peaks	Alcohol and Phenol
1150-1040 (s)	≥C-OH	C-O stretching	
3440, 3410 and 3300	-N-H symmetrical and unsymmetrical stretching	Two bands of primary amine peaks	Amine/amide
3300 and 3260	N-H of secondary amide	From $-CONH_2$	Amide
1640 and 1625(s)	Amide I give two C=O stretching bands	Amide I and amide II are both present As expected, amide I are overlapping	
2950, 2920 and 2850(s)	Saturated C-H and C-C in $>CH_2$ and $-CH_3$	Single bonds to hydrogen	Alkanes
1470-1430(m)	$>CH_2$ and $-CH_3$	C-H deformations	
≈720(vw)	$=CH_2$ rocking	CH_2	

Table 4.9 continued

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
1725-1705 (s-m)	C=O	two bands occurred at this region and another one near 2720	Carbonyl
1680, 1670(w), 1650(m)	Aldehyde C=O		
Sharp band at 3300(s)	-C=C-H	Alkene and aromatic C-H	Alkene & aromatic double bonds
1650, 1600(s)	Diene, triene etc.		
1640-1620(m)	>C=C< aryl conjugated		
3300(s)	-C≡C-H	(C≡C)- band is rather strong	Alkynes
2140-2100(w)		-C≡C-	
2260-2200(v)	-C≡C-, -C≡N	Polyacetylene vibration of (C≡C)-, also (C≡N)-	
~3030(v)	C-H weak stretching bands	May be several bands	Aromatic rings
~1600-1500(m)	Benzene ring bands characterized by C-H stretching, C=C (in ring) (2 bands) (3 if conjugated). ~1500(m) is usually the strongest of the 2 or 3 bands	2 or 3 bands shown by most six membered aromatic ring systems such as benzenes, polycyclic systems and pyridines	
Bands below 900	Out of plane C-H bending vibrations		

The series of overtone and combination bands at 2000 to 1600 cm^{-1} and weak aryl C-H bending band of isolated H atom in 1,3-disubstituted compounds may be due to aromatic compounds indicated at 875(w) cm^{-1}. The aromatic –H vibration is probably overshadowed by the symmetrical N-H and O-H vibrations (Williams and Fleming, 1989; Matthews, 2004). The sharp conjugated C=C band of medium intensity at 1620(m) further confirms the presence of a conjugated aryl groups. The above absorption bands coupled with the strong skeletal bands for aromatics and heteroaromatics in the 1600-

1300 cm^{-1} (Matthews, 2004) region therefore point quite conclusively to the presence of phenolic compounds, indicated by OH groups attached to a phenyl group. These compounds include tannins and flavonoids as indicated by phytochemical screening of the aqueous extract.

Three sharp bands suggesting the presence of N-H and O-H groups have likely been overshadowed by broad bands at 3550-3200 cm^{-1}. However, the strong C=O absorption at 1640-1620 cm^{-1} further suggests that the compound could be an amide or ketone since the absorption falls within the amide and carbonyl region. Presence of an amide is further confirmed by its $-NH_2$ and N-H absorptions in the regions 1650-1560(m) cm^{-1} and 1580-1490(w) cm^{-1} respectively. Aryl ketones are confirmed by bands in the region 1700-1680 cm^{-1}. Therefore, the C=O absorption likely comes from esters which absorb at 1750-1735 cm^{-1} (Hesse, *et. al.*, 2002; Matthews, 2004). Furthermore, the assignment of a C=O band could not be attributed to an aldehyde and ketones because of the absence of a pair of bands in the region of 2900-2695 cm^{-1}, that normally arise from the C-H stretching vibrations of the aldehyde group and 1725-1705 cm^{-1} for ketones.

Aliphatic compounds are indicated by weak symmetric C-H stretching bands at 2920 cm^{-1} and CH_3 symmetric deformations at 1390-1370(m) cm^{-1}. The corresponding C=C stretching frequencies at 1650-1600 cm^{-1} of reduced intensity indicate aliphatic conjugated groups (Matthews, 2004). The bands indicated in these regions suggest the presence of isoprene units of aliphatic flavonoid structures.

From the IR, the presence of functional groups of polycyclic compounds, esters and isoprenoid structures present a good basis to confirm the presence of saponins detected in the phytochemical screening.

From the IR of the crude extract, the functional groups indicated may include –OH of alcohols and phenols, -NH of amines/amides, C-H of saturated hydrocarbons and aromatics, C=C of alkenes and aromatics and C=O of esters. These are also functional groups associated with polyphenols and alkaloids detected by phytochemical screening.

4.1.7.2 Fractions

The acidic, basic and neutral fractions were all analysed but observations indicate similarity and hence resemblance of the strong and weak acid fractions to the crude water extract. Hence, the spectra, absorption bands and discussions of the strong and weak acid fractions are presented in this subsection. The spectra of the neutral and basic fractions are presented as appendix 8a. and 8b.

4.1.7.2.1 Weak acid fraction

The weak acid fraction turned blue litmus paper to red and did not change the colour of red litmus paper. The IR spectrum, the table of absorption bands and discussions are presented below.

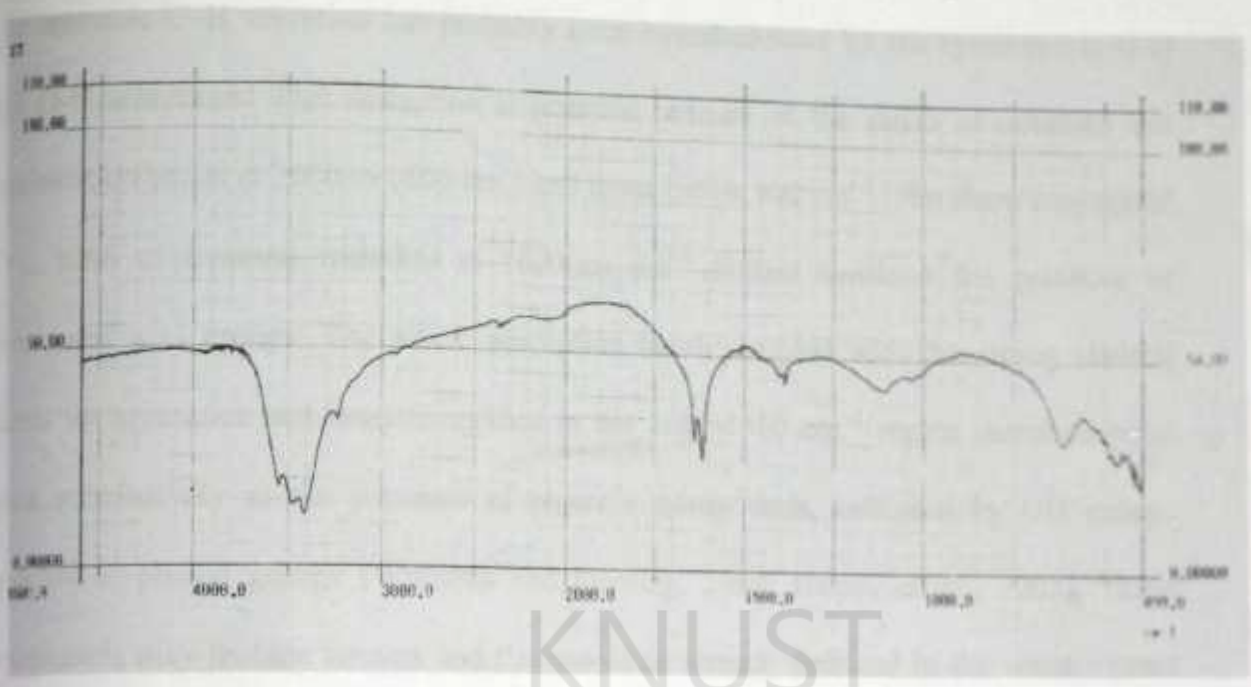


Figure 4.5 Infrared spectrum of the weak acid fraction in KBr

Table 4.10 Deductions from Infrared spectrum of weak acid fraction in KBr

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
3550(s)	O-H (free)	Sharp 'non-bonded' peak	Alcohols and phenols
3400-3200(m)	O-H	Hydrogen bonded	
1300-1000	C-O	Confirmation	
1410-1260(m)	-O-H	O-H bendings (in-plane)	
1150-1040(m)	≥C-OH	C-O stretching bands	
3000-2850	$>CH_2$ and $-CH_3$	Single bonds to hydrogen	Saturated C-H
≈1450 and ≈1375	CH absorptions		
≈1600-1500	C=C	Conjugated double bonds	Aromatic ring
1650-1450(m)			Aromatic ring
800-660	=C-H	Confirmation	
≈3500-3400(m)		Unsubstituted amide	Primary amide
1700-1640(s)			Amide
1640-1600(m)	C=O		Tertiary amide
1300-1000(s)			Alcohols, ethers, esters, carboxylic acids
3100-3000		Stretch	Alkenes/aromatics

The aromatic C–H vibration has probably been overshadowed by the symmetrical N-H and O-H vibrations. This deduction is possible because of the series of overtone and combination bands at 2000 to 1600 cm^{-1} and those below 900 cm^{-1}. The sharp conjugated C=C band of medium intensity at 1620(m) cm^{-1} further confirms the presence of conjugated aryl groups. The above absorption bands coupled with the strong skeletal bands for aromatics and heteroaromatics in the 1600-1300 cm^{-1} region therefore point quite conclusively to the presence of phenolic compounds, indicated by OH groups attached to phenyl groups (Williams and Fleming, 1989; Hesse, *et. al.*, 2002). These compounds may include tannins and flavonoids as already deduced in the water extract and by phytochemical screening.

Similar to that observed in the IR of the crude extract, there were weak symmetric C-H stretching bands at 2920 cm^{-1} and CH_3 symmetric deformations at 1390-1370(m) cm^{-1}, C=C stretching frequencies at 1650-1600 cm^{-1}, and ester absorption bands at 1750-1735 cm^{-1} (Hesse, *et. al.*, 2002; Matthews, 2004). Isoprenoid structures of aliphatic triterpenoids with ester linkages in the aqueous extract have been fractionated into the weak acid fraction. Thus, the fraction contains polycyclic compounds, esters and terpenoid structures indicating the presence of saponins .

There may be sharp bands to suggest the presence of N-H, overshadowed by broad bands at 3550-3200 cm^{-1}. The strong C=O absorption at 1640-1620 cm^{-1} suggest that the compounds may be amides but not aldehydes or ketones since the absorption falls outside the carbonyl region (1740-1705 cm^{-1}). The absence of a pair of bands in the region of

2900-2695 cm^{-1}, that normally arise from the C-H stretching vibrations of the aldehyde group further precludes them. Presence of an amide is however confirmed by its $-NH_2$ and N-H absorptions in the regions 1650-1560(m) cm^{-1} and 1580-1490(w) cm^{-1} respectively. Aryl amides are confirmed by the bands in the region 1700-1680 cm^{-1}. These bands generally occur as a result of amides and some alkaloidic groups.

The functional groups indicated therefore include –OH of phenolics and saponins, -NH and C=O of amides, C-H of saturated hydrocarbons and aromatics as well as C=C of alkenes and aromatics rings. Therefore, from the IR analyses of this fraction, the compounds likely present include alcohols and/or phenols, carboxylic acids, double bonded carbons of alkenes or aromatic compounds and amides.

Tannins, flavonoids, terpenes, saponins and amides were generally present in this fraction.

4.1.7.2.2 Strong acid fraction

The strong acid fraction had no effect on red litmus paper but turn blue litmus paper to red. The IR spectrum, the absorption bands and deductions are presented below.

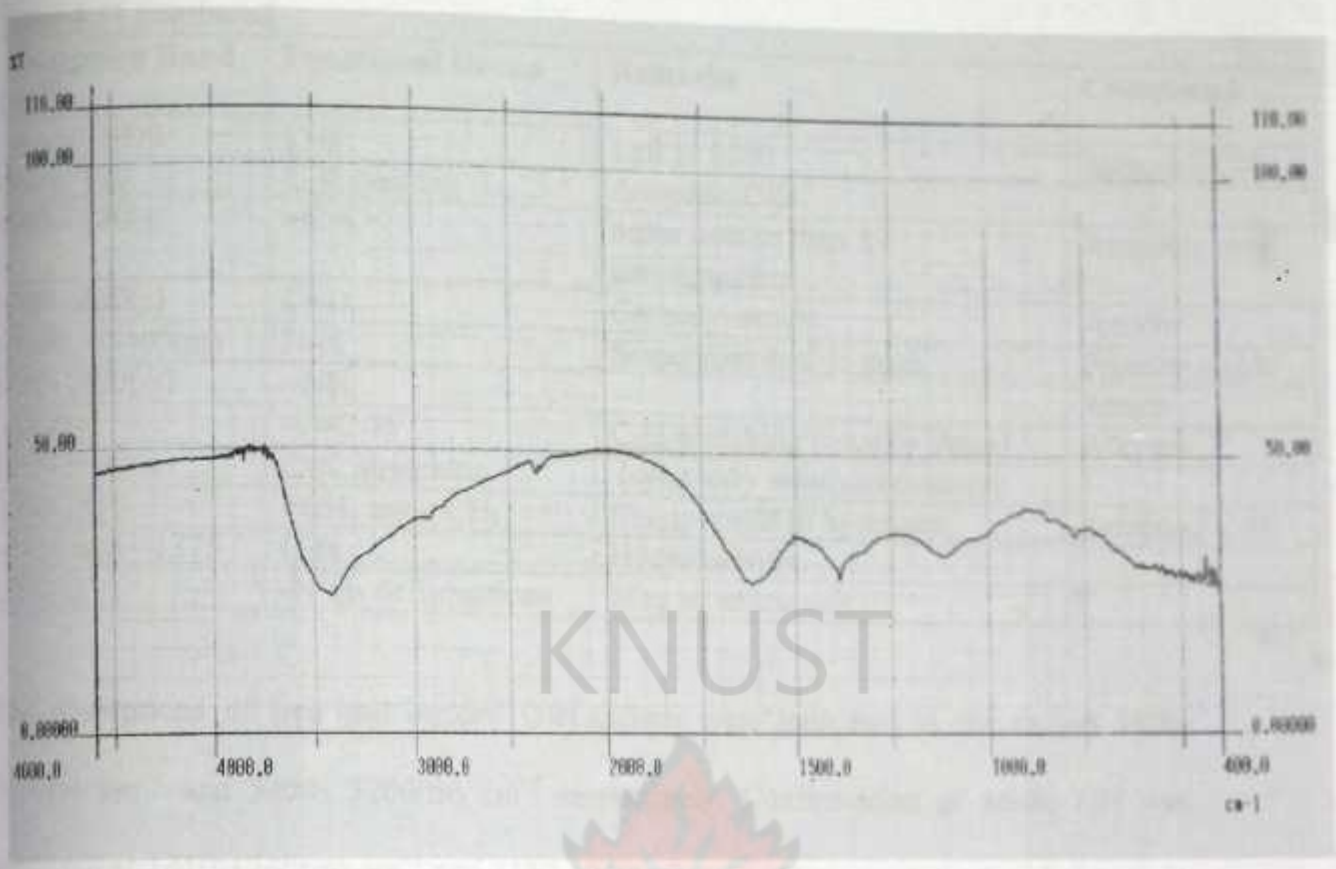


Figure 4.6 Infrared spectrum of the strong acid fraction in KBr

Table 4.11 Deductions made from Infrared spectrum of strong acid fraction in KBr

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
3550(s)	O-H (free)	Sharp 'non-bonded' peak	Alcohols and Phenols
3000-2500(m)	O-H	Stretching bands of acids	
1725-1700(m)	O-H	Carboxylic acid	
1300-1000	C-O	Confirmation bands	Acids
1410-1260(m)	-O-H	Series of O-H bending (in-plane)	
1150-1040(m)	≥C-OH	C-O stretching bands	
3500(m)	-N-H	Primary and secondary amines	
3300(s)	-C≡C-H, -O-H, $-CONH_2$	overlap C-H, O-H (very broad)	Carboxylic acids derivatives
1680-1600(m)	C=C		Alkene
1000-650	=C-H	Out of plane bending	
1600-1400(w)	C=C		Aromatic ring

Table 4.11 continued

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
Around 3000	C-H	Left of 3000	Aromatic CH
Below 900	C-H bending	Aromatic C-H	
1640-1620(s)	>C=C<	More intense than for unconjugation	Aromatic ring
1700-1640(s)	C=O	Carbonyl/amide	Amide
≈3500, ≈3400(m)	N-H	Sometimes double peak	Primary amide
1580-1490(w)	>NH		Amide
3300(s)	-C≡C-H	C-H stretching (usually sharp)	Alkynes
2250-2100(w)	C≡C stretching	(symmetry reduces intensity)	
3000-2850	$>CH_2$ and $-CH_3$	Single bonds to hydrogen	Saturated C-H
≈1450 and ≈1375	C-H	Hydrocarbons	
1600(s)	$-N^+H_3$ deformations	May be amino salt	

The absorptions of free and bonded O-H groups were indicated in the region 3600-3300(s) cm^{-1} and 3400- 3200(m) cm^{-1} respectively. Confirmation of acidic OH was indicated at 1410-1260(m) cm^{-1} and 1150-1040(m) cm^{-1}. Also, aromatic double bonds in rings were suggested by absorptions around 1650-1450(m) cm^{-1} and confirmed by the O-H absorption bands near 800-600 cm^{-1}. The bands below 900 cm^{-1} confirmed aromatic ring since non-aromatic C-H does not absorb below 900 cm^{-1} (Hesse, *et. al.*, 2002; Matthews, 2004). Acids present could be tannic acid groups from hydrolysed tannins since these contain the aromatic ring with OH groups.

There may also be sharp bands overshadowed by broad bands at 3550-3200 cm^{-1} to suggest the presence of N-H. The strong C=O absorption at 1640-1620 cm^{-1} suggest that the compounds may be amides. Presence of an amide was further confirmed by its $-NH_2$ and N-H absorptions in the regions 1650-1560(m) cm^{-1} and 1580-1490(w) cm^{-1} respectively. The compounds were aryl amides confirmed by the bands in the region 1700-1680 cm^{-1}.

The functional groups indicated therefore include –OH of alcohols and phenols and acids, -NH and C=O of amides, C-H of saturated hydrocarbons and aromatics as well as C=C of alkenes and aromatics rings. Therefore, from the IR analyses of this fraction, the compounds likely present include alcohols and/or phenols and carboxylic acids, alkenes, aromatic compounds and amides. Tannic acid and aryl amides may be present.

4.2 ANALYSES OF SOIL SAMPLE AND DRY AQUEOUS HUSK EXTRACT

The results obtained for the AAS metal analyses, X-ray diffraction and Infrared analyses conducted on the soil sample are presented and discussed below. The dry aqueous husk extract was also analysed using AAS and IR spectroscopic methods. The results obtained are also presented and discussed below.

4.2.1 Metal Analysis of the Soil Sample and Dry Aqueous Husk Extract

The soil sample and dry aqueous husk extract were analysed for the presence of Na, K, Ca, Mg, Fe, Si, Ni, Pb and Zn. The amounts of each metal determined in the soil sample and in the dry husk extract have been presented in Appendix 10a and 10b respectively. Calculated average values of duplicated measurements of the amount of the various metals have been presented below in Table 4.12 with the respective electronegativities of the metals.

Table 4.12 Average levels of metals in the soil and powdered raw husk

Metal	Electronegativity*	Average Amount (mg/Kg)	
		Soil	Husk
Na	0.9	97.585	77.611
K	0.8	556.351	962.832
Ca	1.0	336.315	532.743
Mg	1.20	230.054	246.018
Fe	1.80	419.499	144.248
Si	1.80	1400.564	0.786
Ni	1.80	103.220	124.956
Pb	1.90	17.531	113.097
Zn	1.60	58.050	58.053

* Source: (Silberberg, 2003)

The soil was found to have Potassium (556.351 mg/Kg), Magnesium (230.054 mg/Kg), Iron (419.499 mg/Kg), Calcium (336.315 mg/Kg) and Silicon (1400.564 mg/Kg) as well as smaller amounts of Sodium, Nickel, Lead and Zinc. In addition, the husk extract generally had lesser amount of the metals Iron (144.248 mg/Kg), Potassium (962.832 mg/Kg), Calcium (532.743 mg/Kg) and Magnesium (246.018 mg/Kg) being in greater quantities than the others.

With the same ligand Na^+ and Mg^{2+} are usually 6-coordinate and K^+ and Ca^{2+}, 8-coordinate. Mg^{2+} particularly has high affinity for nitrogen bases such as glycirate, chlorophyll and some dye stuffs due to its high charge density and thus ability to polarize. Mg^{2+} is bound preferentially (in $Mg^{2+}>Ca^{2+}>Na^+>K^+$) to nitrogen bases; Ca^{2+} preferentially to multidentate anions and strong acid anions; K^+ binds to large centres composed of neutral donors alone or neutral donors with a singly-charged strong- acid

donor; Na^+ to smaller centres of neutral donors and/or neutral donors plus one singly-charged donor which may be of a weak acid (Williams, 1971; Sawyer and McCarty, 1978; Margerum, 1978). Thus, alkaloids, tannins and other nitrogen bases in the extract would interact with these metals in the soil.

Silicon considered as a metal with dampened traits, forms bonds to carbon that are less polar than those formed by Groups I-III metals. Although silicon has no available 3s- or 3p-orbitals and hence organosilanes form no coordination compounds, highly electronegative ligands permit the attainment of higher coordination numbers, apparently by $3sp^3d^2$ hybridization. Since silicon was present in the soil and in large amount, it form organosilanes and other coordinated compounds with electronegative ligands.

Flavonoids identified by phytochemical screening and unsaturated C-C groups, whose presence was shown by UV analyses offer π electrons to the transition metal electron sinks.

4.2.2 X-ray Diffraction

X-ray diffraction pattern (figure 4.7 below) of the soil sample was taken. Data collected from the diffraction (Table 4.1.3) and deductions from the diffraction pattern are presented in this subsection.

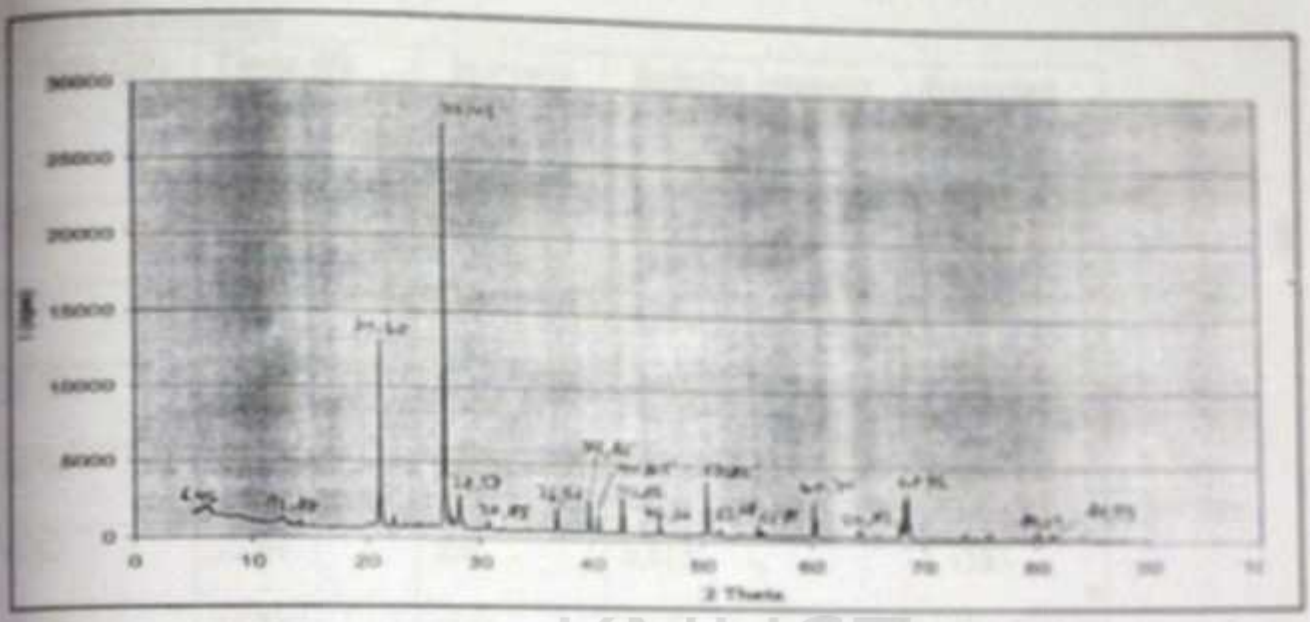


Figure 4.7 X-ray diffraction patterns

Table 4.13 X-ray diffraction results of the soil analysis

2 Theta (2θ)	Theta (θ)	Intensity (I)	Relative intensity (I/I_o)	d-spacing
6.46	3.23	800	2.963	13.684
12.88	6.44	500	1.852	6.8739
21.6	10.80	13000	48.15	4.1146
27.42	13.71	27000	100	4.2531
28.58	14.29	2000	7.407	3.1236
30.86	15.43	200	0.741	2.8978
36.91	18.46	1800	6.667	2.4356
39.85	19.93	1300	4.815	2.2624
40.65	20.33	1500	5.556	2.2197
42.86	21.43	2400	8.889	2.1102
46.20	23.10	1500	5.556	1.9651

Table 4.13 continued

2 Theta (2θ)	Theta (θ)	Intensity (I)	Relative intensity (I/I_o)	d-spacing
50.85	25.43	3800	14.07	1.7958
52.18	26.09	200	0.741	1.7531
55.79	27.90	750	2.778	1.648
60.74	30.37	2400	8.889	1.525
64.82	32.41	220	0.815	1.4385
68.76	34.38	2900	10.74	1.3654
80.69	40.35	300	1.111	1.1909
81.99	41.00	300	1.111	1.1753

The diffraction data collected provided information regarding the periodically repeating arrangement of atoms in the soil crystals. The symmetry of the diffractions corresponds to the symmetry of the atomic packing hence the inter-atomic spacings enabled identification of the crystals present in the soil under analysis.

Generally, only about 5% of the diffraction pattern could be identified clearly. The amorphous component of the sample could not be identified. Also, there were many peaks with very small intensities that could not be assigned. The d values (Table 4.13) deduced from the x-ray diffraction of the soil sample compared well with the standard diffraction data of pure silica (A.S.T.M., 1996) though the relative intensities do not exactly correspond.

Table 4.14 Comparison of X-ray data of pure silica with that of the soil sample

d-spacing		Relative intensity (I/I_o)	
Sample	**Pure silica**	**Sample**	**Pure Silica**
4.1146	3.343	48.15	100
4.2531	4.55	100	20
2.4356	2.457	6.667	10
2.2197	2.281	5.556	10
2.1102	2.128	8.889	10
1.7958	1.818	14.07	10
1.525	1.541	8.889	10
1.3654	1.375	10.74	10

The changes in the relative intensities can be attributed to the interference from signal overlap with signals of other crystals. The peak with the highest count per second (cps) was identified as the peak for silica.

The X-ray patterns agree well with the mineralogy of the soil as exhibited by the high concentration of silica determined by AAS (Table 4.12).

4.2.3 Infrared Spectroscopy

The spectrum of Infrared analysis done on the soil sample is presented below (figure 4.8).

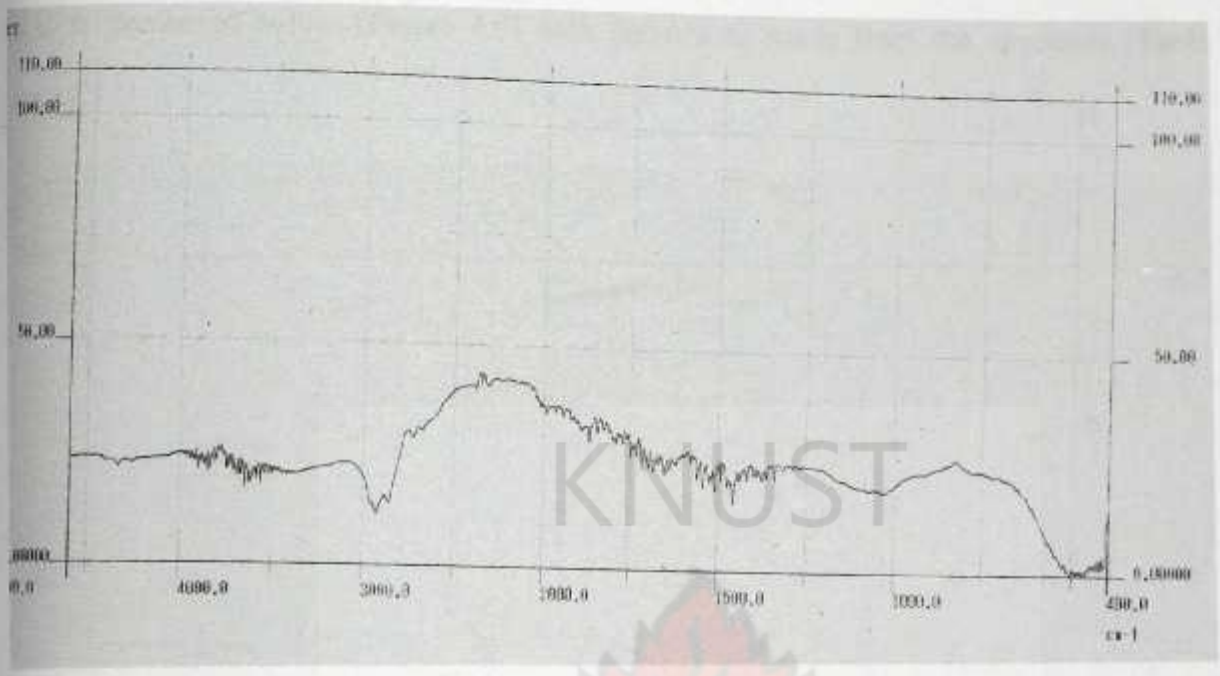


Figure 4.8 Infrared spectrum of the soil sample in Nujol

Comparing the spectrum of the soil sample in Nujol (figure 4.8) and that of pure Nujol (appendix 11) it indicates functional groups attributable to only the Nujol and the soil particles. The soil particles produced the series of bands with medium intensity from 2000-1250 cm^{-1} (Williams and Fleming, 1989; Hesse *et. al.*, 2002). Therefore, the soil may not contain organic matter of any significant variation with nujol.

4.3 FORMULATED PRODUCTS

The mud wall-plasters prepared from the crude water-extract and the soil, and from the fractions of the water-extract and the soil were analysed using infrared spectroscopy. The IR spectra of the formulated plaster samples and the deductions made from them are presented in the following subsections.

4.3.1 Simulations Using the Water-extract and the Soil

The Infrared spectrum of the formulated mud wall plaster from the water-extract and the soil is presented below (Figure 4.9) with deductions made from the spectrum (Table 4.14).

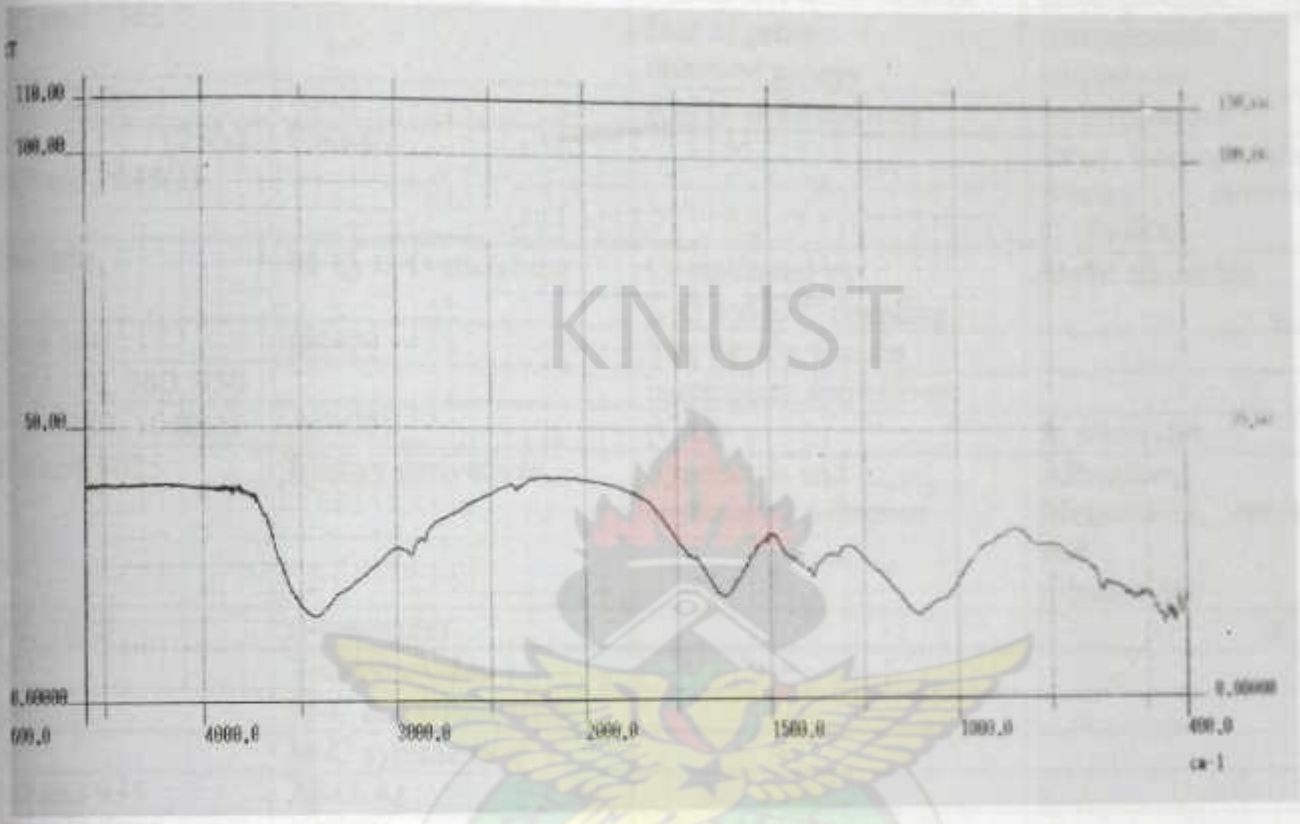


Figure 4.9 IR spectrum of simulated mud wall-plaster of the water extract in KBr

Table 4.15 Deductions made from the IR spectrum of simulated mud wall-plaster (from the water-extract) in KBr

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
1400(w), 1380(m), 1340(w)	O-H bending deformations (in-plane)		Alcohols & Phenols, Isopropoxides
1280-1255	$Si-CH_3$		Si-C
800-600	$Si(CH_3)_4$		
1200-1050	Phenyl derivative	$SiPh_4$ at 1100	
880-720, 780-640	Si-O Silicon tetraoxides	Band shifts to higher values when alkoxy group increases	

Table 4.15 continued

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
725, 720(w)	$>CH_2$	CH_2-rocking	Si-O Silicon tetraoxides
840-800	$(RO)_3SiH$	Position changes with polarity of σ-bonds	Trialkoxy silanes
1380, 1320(m)	$-CH_3$	Symmetric deformations	Isopropoxides
1375 and 1365		Due to germ-dimethyl groups	Isopropoxide derivatives
1320, 1210(m)	-O-H	(O-H)- deformations	Isopropoxides
1200(w), 1125(s), 1095(w), 1045(s)	C-O-C		Ether, Isopropoxides Ethoxy derivatives (1150-900)
1150-900	M-O, C-O stretching	Complicated by C-O and C-C coupling	Metal alkoxides
Below 600	(M-O)	Mn, Fe, Co, Cu, Zn	
1170,1150, 980, 950		Isopropoxy derivatives	
1100, 1080, 1040(s)	≥C-OH	(C-O)-	In alkoxides
1070 and 1025	Ethoxy derivatives	Symmetric and asymmetric vibration	Alkoxides: Methoxides, ethoxides and n-butoxides
1090, 1025	n-butoxides		
940	Tert-butoxides		
696	M-C antisymmetrical		
598	M-C symmetrical		
3340 and 935	Al-O-Al		
2079 and 1715	$Al(CO)_2$	2 broad bands	
1170,1135 and 1120	Isoproxy derivatives	Due to boron and aluminium isopropoxides	
Above 1000 and at 699-539	Al-alkoxides	Due to C-O stretching	

NB. M = metal

There were wavelength shifts of IR absorptions in the crude extract resulting in the wavelengths observed in the IR of the plaster simulate.

Carbonyl groups gave rise to bands in the region 2140-1800 cm^{-1}, doubly bridging groups at about 1850-1700 cm^{-1}, while triply bridging groups absorbed even far lower at about 1700- 1550cm^{-1}. C-O stretching vibrations in metal carbonyl complexes absorb at lower frequencies than the corresponding vibration in CO (2143- 1700 cm^{-1}). The pi-back

donation from metal into the pi star orbitals of CO reduces the C-O bond order. The higher the electron density on the metal, the more the back donation and the greater reduction in C-O bond order (Wiltshire, 1988).

The CO stretching frequencies appear as sharp and intense bands in a region where vibrational modes of most other ligands are generally absent. Thus the frequency range in which CO absorptions occur in a metal carbonyl generally provides an effective criterion for differentiating between terminal and bridging CO groups; these absorptions occurred in the range 2125-1850 cm^{-1} and 1860-1700 cm^{-1} respectively.

Isopropoxides and ethers as well as isopropoxide and ethoxy derivatives absorb around 1150-900 cm^{-1}. Symmetric deformations of $-CH_3$ in isopropoxides absorb at 1380 cm^{-1} and 1320(m) cm^{-1}, and deformation bands of (O-H)- in the isopropoxides shown around 1320 cm^{-1} and 1210(m) cm^{-1}. Germdimethyl groups of alkoxides were indicated at 1375 cm^{-1} and 1365 cm^{-1}. Metal alkoxides such as methoxides, ethoxides and n-butoxides complicated by C-O and C-C coupling of Mn, Fe, Co and Zn absorbed below 600 cm^{-1}. Silicon complexes such as phenyl derivatives absorb between 1200-1050 cm^{-1} and methyl silanes at 800-600 cm^{-1}. For example; absorption due to $SiPh_4$ occurred at 1100 cm^{-1}, $Si(CH_3)_4$ at 800-600 cm^{-1} and trialkoxy silanes $[(RO)_3SiH]$ between 840-800 cm^{-1}. Most alkoxy bands shift to higher values when the organic component increases in size. Other silicon associated bands include Si-H (2236-2150 cm^{-1}) and $Si-CH_3$ (1280-1255 cm^{-1} a very strong sharp band). The tetraoxides of silicon were also indicated around 880-720

cm^{-1} and absorption due to CH_2-rocking associated with these tetraoxides occurred at 725 and 720 cm^{-1} (w).

The stability conferred on the carbon-metal bond in organometallic compounds (R-M) depends on the unsaturation of R and its location. Carbon-carbon unsaturation at α,β- and β,γ with respect to carbon-metal (C-M) linkage is most significant as they can cause an increase or decrease of chemical stability in R-M depending upon the nature of the metal. Many C-M bonds are highly polar (C^-—M^+) and so the mutual alignment of such polar linkages in individual metal alkyl units might be pictured as the driving force. For α,β-unsaturation the stability of the potential carbanion in R-M parallels the assumed hybridization of the α-carbon atom (Eisch, 1967).

4.3.2 Simulations Using Fractions of the Water-extract

Below are IR spectra and deductions from the formulated mud wall plaster using the weak, and strong acid fractions. The spectra of the other formulations using the neutral and basic fractions of the water extract are presented as appendix 9a. and 9b.

4.3.2.1 Weak acid fraction

The IR spectrum of the formulated plaster prepared from the weak acid fraction and the soil, and deductions made from it are presented below.

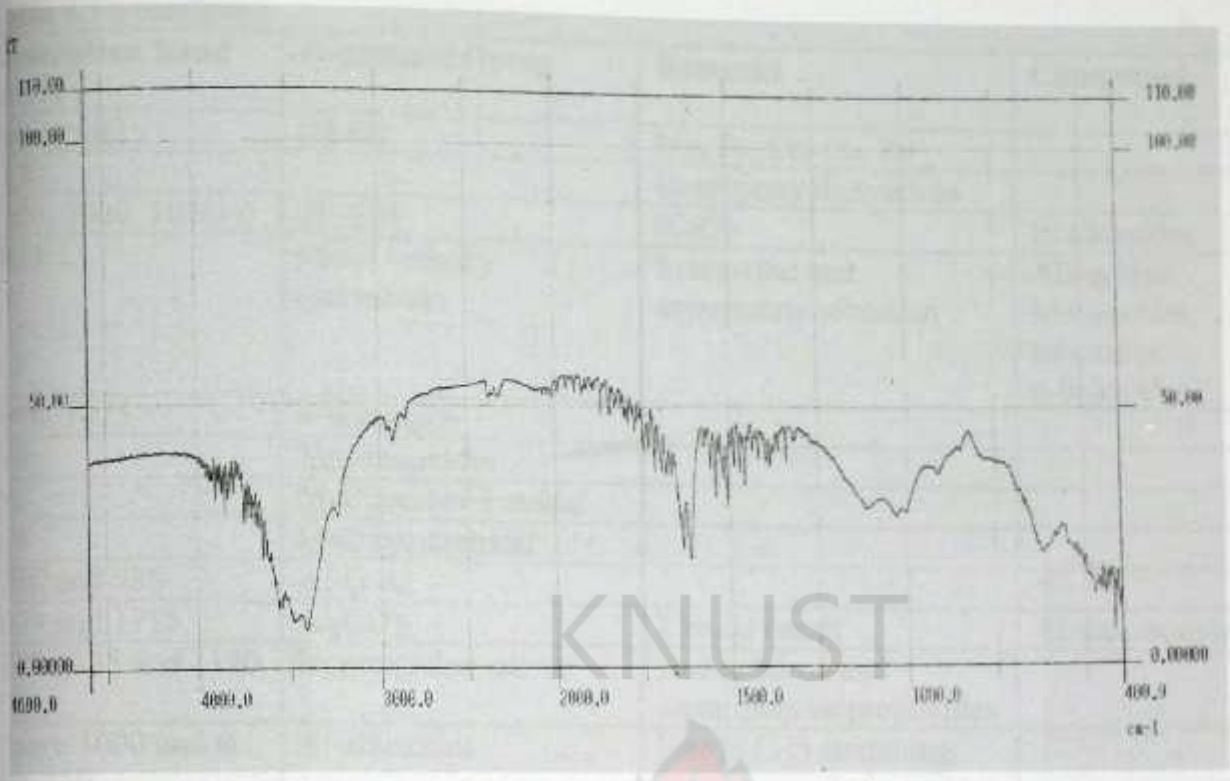


Figure 4.10 IR spectrum of mud wall-plaster simulation of the weak acid fraction in KBr

Table 4.16 Deductions made from the IR spectrum of mud wall-plaster simulation (from the weak acid fraction) in KBr

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
1280-1255	$Si-CH_3$		Si-C
800-600	$Si(CH_3)_4$		
1200-1050	Phenyl derivatives	$SiPh_4$ at 1100	
880-720, 780-640	Si-O Silicon tetraoxides	Band shifts to higher values when alkoxy group increases	Si-O
1380, 1320(m),	$-CH_3$	Symmetric deformations	Isopropoxides
1375 and 1365		Due to germ- dimethyl groups	Isopropoxide derivatives
1320, 1210(m)	-O-H	(O-H)- deformations	Isopropoxides
1200(w), 1125(s), 1095(w), 1045(s)	C-O-C	Ethoxy derivatives at 1150-900	Ether, Ethoxy derivatives, Isopropoxides
1150-900	M-O, C-O stretching	Complicated by C-O and C-C coupling	Metal alkoxides

Table 4.16 continued

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
Below 600	(M-O)	Mn, Fe, Co, Cu, Zn	
1170		Isopropoxy derivatives	
1100, 1080, 1040(s)	≥C-OH	(C-O)-	In alkoxides
1025	Metal –ethoxy derivatives	Symmetric and asymmetric vibration	Alkoxides: Methoxides, ethoxides, n-butoxides
1090, 1025	n-butoxides		
940	Tert-butoxides		
696	M-C antisymmetrical		
598	M-C symmetrical		
3340 and 935	Al-O-Al		
2079 and 1715	$Al(CO)_2$	2 broad bands	Al-dicarbonyls
1170,1135 and 1120	Isoproxy derivatives	Due to boron and aluminium isopropoxides	
Above 1000 and at 699-539	Al-alkoxides	Due to C-O stretching	

M = metal

Tannins, flavonoids and terpenes in the weak acid fraction reacted with metals of the soil to produce organometallic compounds detected by IR. C=O stretching vibrations in metal carbonyl complexes absorbed at lower frequencies than the corresponding vibration in C=O (2143 cm^{-1}). The pi-back donation from metal into the pi star orbitals of C=O reduces the C-O bond order. The higher the electron density on the metal, the more the back donation and the greater reduction in C-O bond order (Wiltshire, 1988). The absorption bands in this fraction were generally below 2143 cm^{-1}.

Also, chain polysiloxanes, $(R_2SiO)_n$, have water repellency and lubricity properties and others such as $R_2Si(CH_2CH_2CH_2\text{-}Phy\text{-}(OH)OCH_3)_2$ have cementing properties, $SiMe_3$ has lipophilic properties and is soluble in non-polar solvents (Mehrotra and Singh, 1992).

The surface effects of silicones also lead to useful applications. They derive from the presence of both polar Si-O and non polar hydrocarbon groups in the material. Materials treated with silicone oils become water repellent because the polar groups orient themselves close to the surface, presenting a hydrophobic hydrocarbon exterior. Water penetration into bricks, concrete and other building materials is greatly reduced by impregnation with silicones. Dimethyl and phenylmethylpolysiloxanes have also been used as paint additives to improve the water repellent properties of the painted surface as well as reduce the surface tension of the paint. Cross linking occurs through hydrosilation of $Si\text{-}CH{=}CH_2$ by Si-H (Wiltshire, 1988). A number of silicon complexes were indicated by IR of this fraction: $Si\text{-}CH_3$, (1280-1255); $Si(CH_3)_4$, (800-600); $SiPh_4$ (1100) and Silicon tetraoxides at 880-720, 780-640.

Methyl and phenyl silicon complexes formed in the mud wall plaster would contribute to durability of the plaster against rainfall.

4.3.2.2 Strong acid fraction and soil

The following IR spectrum and the deductions thereof show the functional groups of the chemical constituents of the mud wall plaster simulation using the strong acid fraction and the soil.

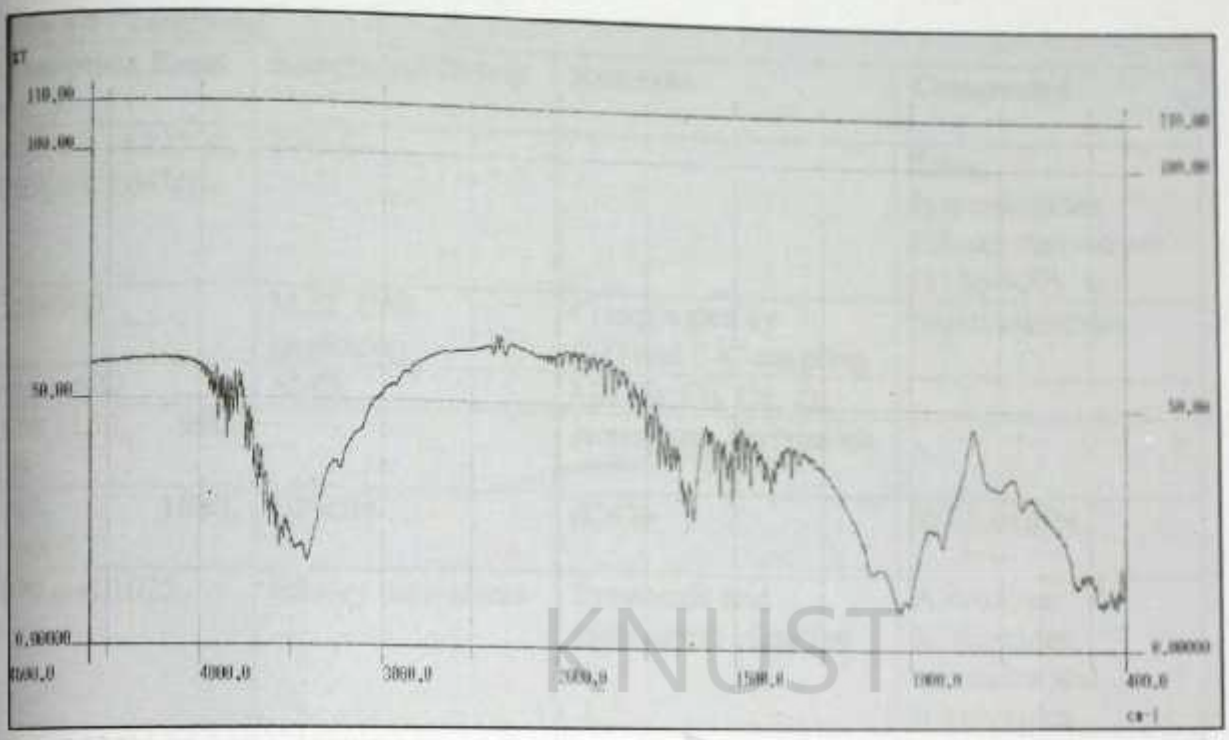


Figure 4.11 IR spectrum of simulated mud wall-plaster of the strong acid fraction in KBr

Table 4.17 Deductions made from the IR spectrum of simulated mud wall-plaster (from the strong acid fraction) in KBr

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
1280-1255	$Si\text{-}CH_3$		Si-C
800-600	$Si(CH_3)_4$		
1200-1050	Phenyl derivative	$SiPh_4$ at 1100	Si-Ph
880-720, 780-640	Si-OR and Silicon tetraoxides	Band shifts to higher values when alkoxy group increases	Si-O
725, 720(w)	$>CH_2$	CH_2-rocking	Si-O, Silicon tetraoxides
840-800	$(RO)_3SiH$	Position changes with polarity of σ-bonds	Trialkoxy silanes
1380, 1320(m),	$-CH_3$	Symmetric deformations	Isopropoxides
1375 and 1365		Due to germdimethyl groups	Isopropoxide derivatives
1320, 1210(m)	-O-H	(O-H)- deformations	Isopropoxides

Table 4.17 continued

Absorption Band (cm^{-1})	Functional Group	Remarks	Compound
1200(w), 1125(s), 1095(w), 1045(s)	C-O-C		Ether, Isopropoxides Ethoxy derivatives (1150-900)
1150-900	M-O, C-O stretching	Complicated by C-O and C-C coupling	Metal alkoxides
Below 600	M-O	Mn, Fe, Co, Cu, Zn	
1170,1150, 980, 950		Isopropoxy derivatives	
1100, 1080, 1040(s)	≥C-OH	(C-O)-	In alkoxides
1070 and 1025	Ethoxy derivatives	Symmetric and asymmetric vibration	Alkoxides: Methoxides, ethoxides and n-butoxides
1090, 1025	n-butoxides		
940	Tert-butoxides		
696	M-C Antisymmetrical		
598	M-C symmetrical		
3340 and 935	Al-O-Al		
2079 and 1715	$Al(CO)_2$	2 broad bands	
1170,1135 and 1120	Isoproxy derivatives	Due to boron and aluminium isopropoxides	
Above 1000 and at 699-539	Al-alkoxides	Due to C-O stretching	

M = metal

The strong acid fraction contains largely tannic acid, aliphatic organic acids and probably some alkenes and alkynes associated groups.

Aliphatic organic acids, phenols and hydroxamate siderophores are all aluminum binding ligands of concern in soils. The absorption bands at 1170 cm^{-1}, 1135 cm^{-1} and two broad bands at 2079 cm^{-1} and 1715 cm^{-1} are metal carbonyl [$Al(CO)_2$] absorption points (Robinson, (Ed.), 1993). Therefore aluminum carbonyl complexes were suspected though

the soil was not analysed for aluminum. Also, other complexes may have occurred around 1170, 1135 and 1120 cm^{-1} due to reaction of aluminum and boron with C=C, which easily forms π–complexes.

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATION

The project has been able to establish the level of efficiency of water as a solvent for extracting *Parkia* fruit husk as well as give some insight to the chemistry of mud wall plaster prepared from the aqueous extract of *Parkia biglobosa* fruit husk and the soil and its stability towards rain water. These are stated here as conclusions whilst recommendations for further work have also been made.

5.1 CONCLUSION

From the results and discussion it can be concluded that water is a better solvent for the extraction of *Parkia biglobosa* fruit husk than ethanol. The average yield of extractable material from the husk by water was 37.77% compared to that by ethanol which was 30.83 %. Also, water is generally cheaper and more accessible than ethanol hence water should be used for extraction of the husk.

The results also showed that the age (after harvesting) of husk is not relevant to the amount of extractable material. Husk that have been harvested and kept for about a year produced a total yield of 77.66% extractable material, having a negligible variation with that of the freshly harvested husk (76.57%).

The extract of the fruit husk contains a large amount of polar components, extractable by water.

The soil was found to contain various metals. Metals found in larger quantities in the soil are potassium (556.351 mg/Kg), magnesium (230.054 mg/Kg), iron (419.499 mg/Kg), calcium (336.315 mg/Kg) and Silicon (1400.564 mg/Kg) as well as smaller amounts of sodium, nickel, lead and zinc. In addition, the husk extract was found to have good amounts of iron (144.248 mg/Kg), potassium (962.832 mg/Kg) and magnesium (246.018 mg/Kg).

To a reasonable extent, the presence of polyhydroxy and carbonyl groups in the water extract has been confirmed alongside polyphenyl structures. Phenolics, anthraquinone glycosides, alkaloids and saponins indicated by phytochemical screening in the aqueous extract have been verified by UV, HPLC and IR analyses.

The UV analyses indicated conjugated groups likely to originate from tannins, flavonoids and terpenes whilst HPLC analyses indicated that at least one class of alkaloids, two classes of phenolic acids, flavonols and/or proanthocyanidins and three classes of phenolic glycosides were present in the aqueous extract. Phenolics, saponins, alkaloids and anthraquinones have functional groups comparable to aldehydic, naphthalmic, anhydride, polycyclic aromatics, paraffinic and amides in bitumen and polymers of urea such as urea-formaldehyde and urea-melamin-formaldhyde which are waterproof and have been used extensively and efficiently in mud wall plasters and glazes to bring about rain-erosion resistance as well as improve impermeability of soil, making it non-erodible to rain.

The tannins formed stable water-insoluble co-polymers with the alkaloids and proteins. The carboxyl and phenolic groups of tannins complexed with proteins and other macromolecules present. They also chelated the metals. Tannin that hydrolysed into tannic acid combined with iron present in the soil into iron-tannate.
Conjugated aromatic systems in flavonoids provided electrons for metal sinks such as cobalt and zinc.

Terpenoid alkaloids hydrolysed into terpenes and in combination with existing terpenes, bound to metal sites in the form of resin. This was probably facilitated by saponins which increase and accelerate calcium and silicon complexing processes.

The formulated plaster from the crude water extract was shown by IR to contain a number of organometallic compounds. Complexes formed are metal alkoxides such as methoxides, ethoxides and n-butoxides complicated by C-O and C-C coupling Fe and Zn. Organometalloids such as alkyls and aryls of group IV elements formed mainly by silicon are kinetically inert to hydrolysis and are partly responsible for the stability of the mud wall plaster to rain. They cannot be hydrolysed readily by acidic reagents such as rain water.

Water penetration into bricks, concrete and other building materials has been found to be greatly reduced by impregnation with silicon based complexes. Additionally, dimethyl and phenylmethylpolysiloxanes have been used as paint additives to improve water repellent properties. Silicon complexes such as phenyl derivatives and methyl silanes

were present in the mud wall plaster. These were $SiPh_4$ at 1100 cm^{-1}, $Si(CH_3)_4$ at 800-600 cm^{-1}, Si-CH_3 between 1280-1255 cm^{-1}, trialkoxy silanes [$(RO)_3SiH$] between 840-800 cm^{-1} as well as tetraoxides of silicon indicated around 880-720 cm^{-1}. These were confirmed by associated absorption due to CH_2-rocking which occurred at 725 and 720 cm^{-1} (w). Silicon forms bonds to carbon that are less polar than those formed by Groups I-III metals.

IR spectra of the formulated plaster attributable to aluminum complexes and trialkylboranes (Table 4.13), which are unaffected by water at ambient temperatures, are also suggested.

The UV analysis indicated the presence of conjugated systems in the aqueous husk extract. Subsequently, unsaturated organometallic compounds (Table 4.13) were also identified by IR in the formulated plaster. Unsaturated derivatives of organometallic compounds are less reactive and contribute to the resistance of mud wall plaster to erosion by rain water than their metal alkyls.

Bond polarity (C^--M^+) increases as the metal electronegativity index (X_m) decreases. The trend of X_m in the metals of the soil is Ni (1.75)>Si (1.74)>Zn (1.66)>Fe (1.64)> Pb (1.55)> Mg (1.23). Therefore organometallic compounds of Ni, Si, Zn, Fe, Pb and Mg respectively have increasing polarity. These facts support the stability of mud wall plaster because of the presence (shown by the existence of their absorption bands) of water insoluble complexes of the metals.

Four fractions (strongly acidic, weakly acidic, basic and neutral) of the aqueous extract were formulated into mud wall plaster and analysed by IR. Observing from the spectra of the plasters of all the fractions, those of the acidic fractions were predominated by bands due to organometallic compounds very similar to those of the plaster formulated using the crude water extract. The plaster of the weak acid fraction had more identical bands with the plaster of the water extract. Therefore, the organic components of the acidic fractions (Table 4.10 and 4.11) were identified as key participants to the reactions leading to the formation to relevant organometalloids and binding of the soil particles to bring about resilience of the plaster against rain water erosion. Unhydrolysable tannins in the weak acid fraction also bind the soil particles quite strongly, contributing to the properties of water resilience of mud wall plaster.

5.2 RECOMMENDATIONS

Stability properties of the mud wall plaster may be also attributed to mineral compounds formed from metals in the soil. Potassium, magnesium, iron, calcium, aluminum and silicon which are components of cement, lime, a number of stabilizers and pozzolanic clays are relevant metals in soils that are used in building materials and for wall plasters. Chemical reactions of these minerals of the soil may form cementitious compounds such as calcium silicates. Therefore, X-ray analysis should be conducted to check for cementitious compounds as well as confirm the complexes identified in the formulated plaster. The soil should also be investigated for presence of aluminum, boron and other group IV metalloids apart from silicon.

Also, there are numerous existing mud buildings in which the technology of incorporating the aqueous extract of *Parkia biglobosa* fruit husk and other materials have been applied. A more extensive research should be conducted on samples from the field applications of the various materials on existing mud buildings in order to test for the metals, mineral compounds and organometallic complexes using IR, AAS and X-ray analyses. This could lead to enhancing the formulation of cheaper but durable mud wall plasters that can extend the life span of mud buildings.

Even though the ethanol extract was quantitatively small, it is recommended that a formulated mud wall plaster using the extract should also be prepared and analysed to compare its resilience with that of the water extract.

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APPENDICES

1. Pictures of various developmental stages of the fruit of *Parkia biglobosa*

Stage I- Capitulum from which pods (fruit) develop

Stage II- Pods/fruit (coloured green) developing from capitulum

Stage III- Green, fleshy, pliable unripe pods/fruits

Stage IV- Dry matured fruits (contains edible pulp and seeds)

Stage V Empty husk (edible content of fruit removed)

2. Reagents prepared for phytochemical screening

Copper (II) sulphate:- 6.9g of $CuSO_4.5H_2O$ dissolved in distilled water and diluted to 100ml.

Dilute Ammonia solution:- Equal volumes of conc. ammonia and distilled water are added to make 50 ml of solution.

Lead acetate solution (0.5M, 1N):- 13.9g of $Pb(C_2H_3O_2)_2.3H_2O$ dissolved to make 100ml solution.

Fehling's solution:- Equal volumes of two previously prepared solutions were mixed; one containing about 7 grams cupric sulfate pentahydrate per 100 ml of solution and the other containing about 35 grams potassium sodium tartrate tetrahydrate (Rochelle salt) and 10 grams sodium hydroxide per 100 ml of solution.

Ferric chloride solution (0.5M, 1.5N):- 13.5g of $FeCl_3.6H2O$ dissolved in 100ml of distilled water containing 20ml conc. HCl.

Mayer's reagent (Potassium mercuric iodide):- 1.358g of $HgCl_2$ dissolved in 60ml of distilled water and added to a solution of 5g KI in 10ml distilled water, the mixture made up to 100 ml with distilled water.

Sodium picrate paper:– A strip of filter paper is saturated in a solution of 5.0g Na_2CO_3 and 0.5g of picric acid dissolved in 100ml of distilled water. The strip is then blotted dry.

3. a. Calculation of mean mass and standard error of mean of new husk extract

Solvent	Extract (E)	pH	Mass of extract and beaker (M)	Mass of beaker only (Mo)	Mass of extract only (M_1) ($M - M_O$)
Water	E_1	6.23	223.28	148.78	74.500
	E_2		367.28	292.90	74.380
Ethanol	E_1	6.48	415.902	353.82	62.082
	E_2		184.812	123.11	61.702
Water after Ethanol	E_1	6.35	370.02	353.82	16.20
	E_2		310.28	292.90	17.38

Mass of sample extracted = 200.00g

From table 1: Mean of M_1 (μ) = $(E_1 + E_2)/2$.

Mean mass of water extract, $\mu_w = (74.500 + 74.380)/2 = 74.440$g

Mean mass of ethanol extract, $\mu_e = (62.082 + 61.702)/2 = 61.892$g

Mean mass of water after ethanol, $\mu_{e/w} = (16.200 + 17.380)/2 = 16.790$g

Standard deviation, $s = \sqrt{\{[(M_1 - \mu)^2 + (M_2 - \mu)^2 + \ldots.(M_n - \mu)^2]/n\}}$:

Water extract, $s = \sqrt{\{[(74.5 - 74.44)^2 + (74.38 - 74.44)^2]/2\}} = \{\sqrt{[(0.06)^2 + (-0.06)^2]/2}\}$
$= \{\sqrt{[0.0036 + 0.0036]/2}\}$
$= 0.06$

Ethanol extract, $s = \sqrt{\{[62.082 - 61.892)^2 + (61.708 - 61.892)^2]/2\}}$
$= \sqrt{\{[(0.19)^2 + (-0.184)^2]/2\}}$
$= \sqrt{\{[0.0361 + 0.033856]\}/2}$
$= 0.1870$

Water after ethanol extract, $s = \sqrt{\{[16.20 - 16.79)^2 + (17.38 - 16.79)^2]/2\}}$
$= \sqrt{\{[(-0.59)^2 + (0.59)^2]/2\}}$
$= \sqrt{\{[0.3481 + 0.3481]/2\}}$
$= 0.59$

Standard error of mean, SEM ($s/\sqrt{n}$):

Water extract = $.06/\sqrt{2}$,
$= 0.0424$

Ethanol extract = $.19/\sqrt{2}$,
$= 0.1344$

Water after ethanol extract = $.59/\sqrt{2}$
$= 0.4171$

3. b. Calculation of mean mass and standard error of mean of old husk extract

Solvent	Extract (E)	pH	Mass of extract and beaker (M)	Mass of beaker only (Mo)	Mass of extract only (M_1) ($M - M_O$)
Water	E_1	6.32	368.23	292.30	75.93
	E_2		545.80	468.49	77.31
Ethanol	E_1	6.59	415.02	353.82	61.20
	E_2		530.88	469.30	61.58
Water after Ethanol	E_1	6.42	138.86	123.11	15.75
	E_2		167.61	148.78	18.83

Mass of sample extracted = 200.00g

From table 2, Mean of M_1 (μ) = $(E_1 + E_2)/2$:

Mean mass of water extract, M = (75.64 + 77.60)/2 = 76.62g

Mean mass of ethanol extract, M = (61.20 + 61.58)/2 = 61.39g

Mean mass of water after ethanol, M = (15.75 + 18.83)/2 = 17.29g

Standard deviation, s, of: $s = \sqrt{\{[(M_1 - \mu)^2 + (M_2 - \mu)^2 + \ldots.(M_n - \mu)^2]/n\}}$:

Water extract = $\sqrt{\{[(75.64 - 76.62)^2 + (77.60 - 76.62)^2]/2\}} = \sqrt{\{[(-0.98)^2 + (0.98)^2]/2\}}$
$= \sqrt{\{[0.9604 + 0.9604]/2\}}$
$= 0.98$

Ethanol extract = $\sqrt{\{[61.20 - 61.39)^2 + (61.58 - 61.39)^2]/2\}} = \sqrt{\{[(-0.19)^2 + (0.19)^2]/2\}}$
$= \sqrt{\{[0.0361 + 0.0361]\}/2}$
$= 0.19$

Water after ethanol extract = $\sqrt{\{[15.75 - 17.29)^2 + (18.83 - 17.29)^2]/2\}}$
$= \sqrt{\{[(-1.54)^2 + (1.54)^2]/2\}}$
$= \sqrt{\{[2.3716 + 2.3716]/2\}}$
$= 1.54$

Standard error of mean, SEM ($s/\sqrt{n}$):

Water extract = $0.98/\sqrt{2}$,
$= 0.69296$

Ethanol extract = $0.19/\sqrt{2}$,
$= 0.13435$

Water after ethanol extract = $1.54/\sqrt{2}$
$= 1.08894$

4. Table of results for phytochemical screening

SECONDARY METABOLITE	EXTRACT		REMARKS
	Water	Ethanol	
Saponins	+	+	Present in both extracts
General glycosides	-	-	Generally absent in both extracts
Flavonoids	+	+	Present in both extracts
Steroids and Terpenes	-	-	Generally absent in both extracts
Tannins and polyphenols	+	+	Present in both extracts
Alkaloids	+	+	Present in water extract
Anthraquinones	-	+	Generally absent in both extracts
Anthraquinone glycosides	+	-	Present in water extract, absent in ethanol extract
Cyanogenitic glycosides	-	-	Generally absent in both extracts

5. Tables of results of solubility tests to identify compounds present in extract

a. Results of the water extract

MOISTURE FREE WATER EXTRACT			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	Completely soluble	Blue litmus paper turned red, red litmus unchanged	Acidic; Low MW carboxylic acids
5% NaOH	More soluble		
5% $NaHCO_3$	Completely soluble		
5%HCl	Slightly soluble		
Conc. H_2SO_4	More soluble		Neutral compounds: Alkenes, alkynes, alcohols, ketones, aldehydes, nitro compounds, esters, ethers, amides

b. Results of the ethanol extract

MOISTURE FREE ETHANOL EXTRACT			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	More soluble	Blue litmus paper turned red, red litmus unchanged	Acidic; Low MW carboxylic acids
5% NaOH	More soluble		
5% $NaHCO_3$	Slightly soluble		
5%HCl	Insoluble		
Conc. H_2SO_4	Insoluble		Inert compounds: Alkanes, alkyl halides, aromatic compounds

c. Results of the strong acid fraction

MOISTURE FREE STRONG ACID FRACTION			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	Insoluble	Not required	
5% NaOH	More soluble		
5% $NaHCO_3$	Slightly soluble		Weak acid –phenols
5%HCl	Insoluble		
Conc. H_2SO_4	Insoluble		Inert compounds: Alkanes, alkyl halides, aromatic compounds

d. Results of the weak acid fraction

MOISTURE FREE WEAK ACID FRACTION			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	Completely soluble	Blue litmus paper turned red, red litmus unchanged	Basic: Low MW amines
5% NaOH	Completely soluble		
5% $NaHCO_3$	More soluble		
5%HCl	Slightly soluble		
Conc. H_2SO_4	Slightly soluble		Neutral compounds: Alkenes, alkynes, alcohols, ketones, aldehydes, nitro comps., esters, ethers, amides

e. Results of the basic fraction

MOISTURE FREE BASIC FRACTION			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	More soluble	Red litmus paper turned blue, blue paper unchanged	Basic: Low MW amines
5% NaOH	Slightly soluble		
5% $NaHCO_3$	Slightly soluble		
5%HCl	Completely soluble		
Conc. H_2SO_4	Completely soluble		Neutrals: Alkenes, alkynes, alcohols, ketones, aldehydes, nitro comps., esters, ethers, amides

f. Results of the neutral fraction

MOISTURE FREE NEUTRAL FRACTION			
SOLVENT	**SOLUBILITY**	**REACTION TO LITMUS PAPER**	**SUSPECTED FUNCTIONAL GROUPS**
Water	Completely soluble	No reaction on litmus	Neutral: Low MW neutral
5% NaOH	Slightly soluble		
5% $NaHCO_3$	More soluble		
5%HCl	Insoluble		
Conc. H_2SO_4	Insoluble		Inert compounds: Alkanes, alkyl halides, aromatic compounds

6. Table of results of thin layer chromatography (TLC) of crude water extract

EXTRACT	SOLVENT SYSTEM	NUMBER OF SEPARATION	R_f
Water Ethanol Water + Ethanol	Pure Water	2 1 1	0.77, 0.42 0.88 0.88
Water Ethanol Water + Ethanol	Pure Ethanol	2 2 1	0.86, 0.62 0.87, 0.51 0.89
Water Ethanol Water + Ethanol	Pure Chloroform	– – –	– – –
Water Ethanol Water + Ethanol	Pure Acetone	1 1 1	0.61 0.63 0.65
Water Ethanol Water + Ethanol	1:2, Chloroform:Methanol	1 1 1	0.214 0.90 0.014
Water Ethanol Water + Ethanol	2:1, Ethanol:Water	2 2 2	0.96, 0.67 0.97, 0.60 0.99,0.30
Water Ethanol Water + Ethanol	5:1, Ethanol:Water	2 2 2	0.80, 0.41 0.80, 0.56 0.81, 0.44
Water Ethanol Water + Ethanol	3:2, Ethanol:Water	2 2 2	0.94, 0.26 0.96, 0.25 0.85, 0.23
Water Ethanol Water + Ethanol	1:2, Ethanol:Methanol	1 1 1	0.71 0.80 0.82
Water Ethanol Water + Ethanol	2:1, Ethanol:Methanol	1 1 1	0.81 0.68 0.74

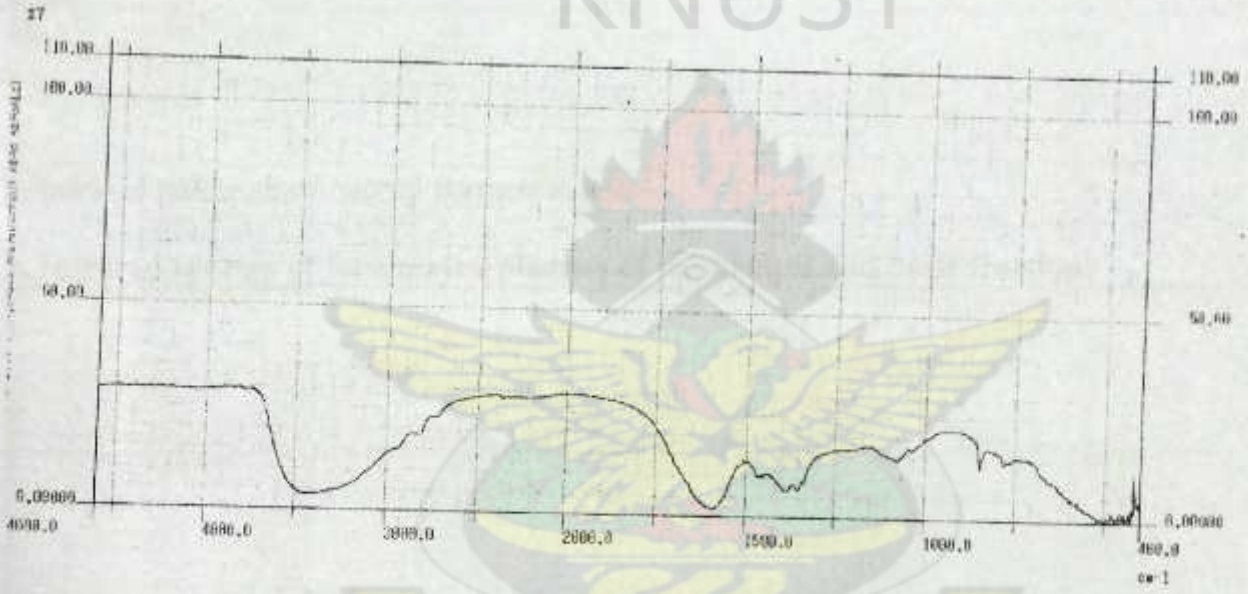
Water Ethanol Water + Ethanol	1:2, Acetone:Hexane	1 1 1	0.22 0.19 0.41
Water Ethanol Water + Ethanol	2:1, Acetone:Hexane	1 1 1	0.44 0.48 0.51
Water Ethanol Water + Ethanol	2:1 Ethylacetate:Chloroform	- 1 -	- 0.14 -
Water Ethanol Water + Ethanol	1:2 Ethylacetate:Ethanol	2 2 2	0.94,0.22 0.86,0.25 0.90,0.24
Water Ethanol Water + Ethanol	2:1 Ethylacetate:Ethanol	2 2 2	0.11,0.07 0.16,0.09 0.11,0.05

7. Table of results of TLC of fractions of the water extract

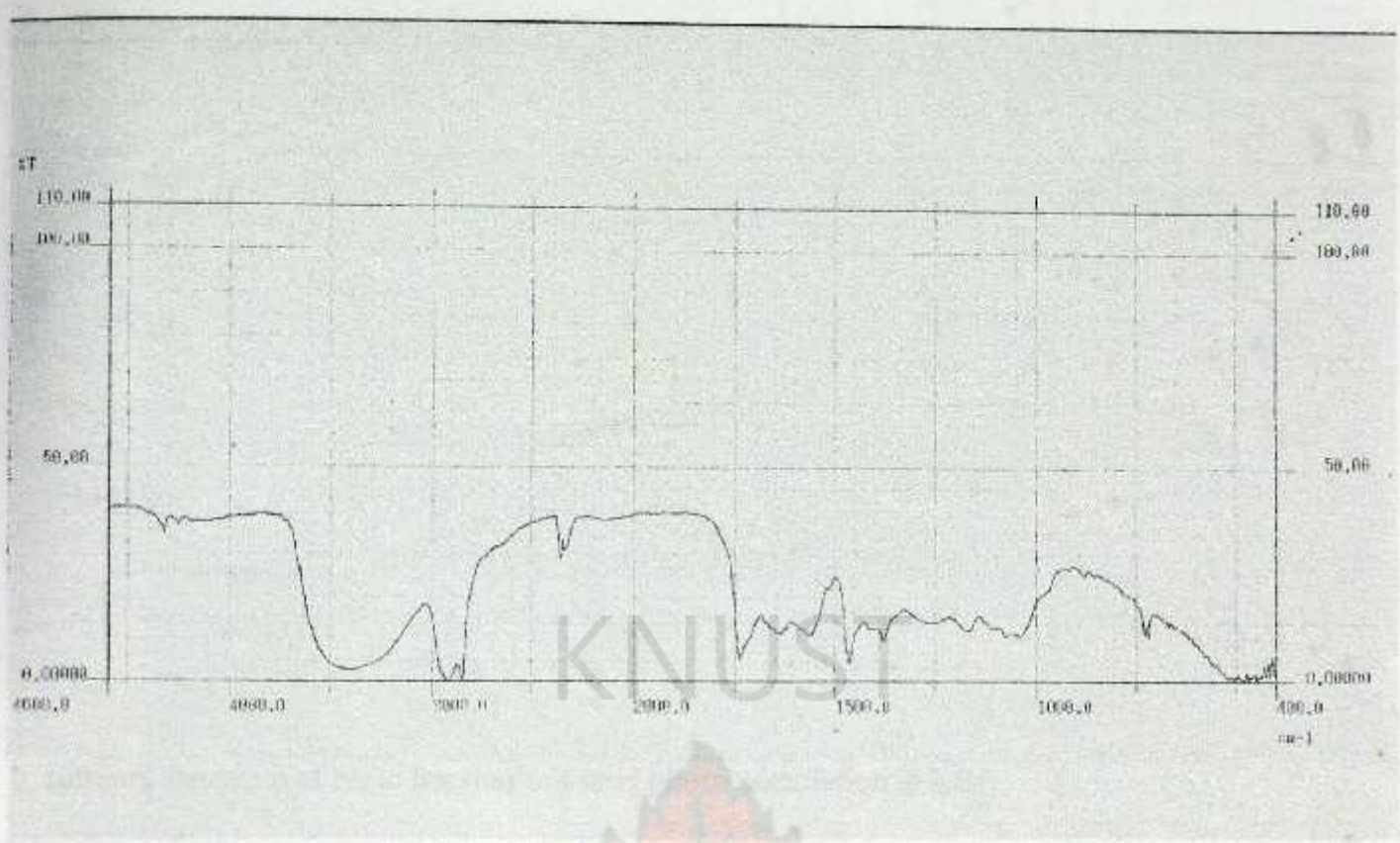
FRACTION	SOLVENT SYSTEM	NUMBER OF SEPARATION	R_f
Strong Acid Weak Acid Basic Neutral	Water only	2 3 0 3	0.14, 0.60 0.20, 0.50, 0.81 - 0.06, 0.56, 0.82
Strong Acid Weak Acid Basic Neutral	Ethanol only " " "	1 4 2 3	0.70 0.07, 0.37, 0.78, 0.87 0.64, 0.86 0.035, 0.37, 0.70
Strong Acid Weak Acid Basic Neutral	1:1, Ethanol : Water	1 3 0 4	0.78 0.07, 0.15, 0.64 - 0.14, 0.41, 0.56, 0.81
Strong Acid Weak Acid Basic Neutral	2:1, Ethanol : Water	1 2 3 3	0.87 0.32, 0.76 0.44, 0.61, 0.76 0.08, 0.28, 0.67
Strong Acid Weak Acid Basic Neutral	1:2, Ethanol : Water	3 4 - 3	0.17, 0.60, 1.0 0.12, 0.31, 0.45, 0.687 - 0.07, 0.48, 0.84
Strong Acid Weak Acid Basic Neutral	3:2, Ethanol : Water	2 3 2 3	0.51, 0.82 0.09, 0.35, 0.68 0.35, 0.58 0.09, 0.59, 0.81

Strong Acid Weak Acid Basic Neutral	1:2,Ethylacetate : Ethanol	1 2 2 4	0.88 0.29, 0.71 0.71, 0.81 0.06, 0.47, 0.68, 0.92
Strong Acid Weak Acid Basic Neutral	2:1, Ethylacetate : Ethanol	1 1 3 3	0.77 0.87 0.06, 0.55, 0.64 0.14,0.71, 0.82

8. Infrared spectra of basic and neutral fractions

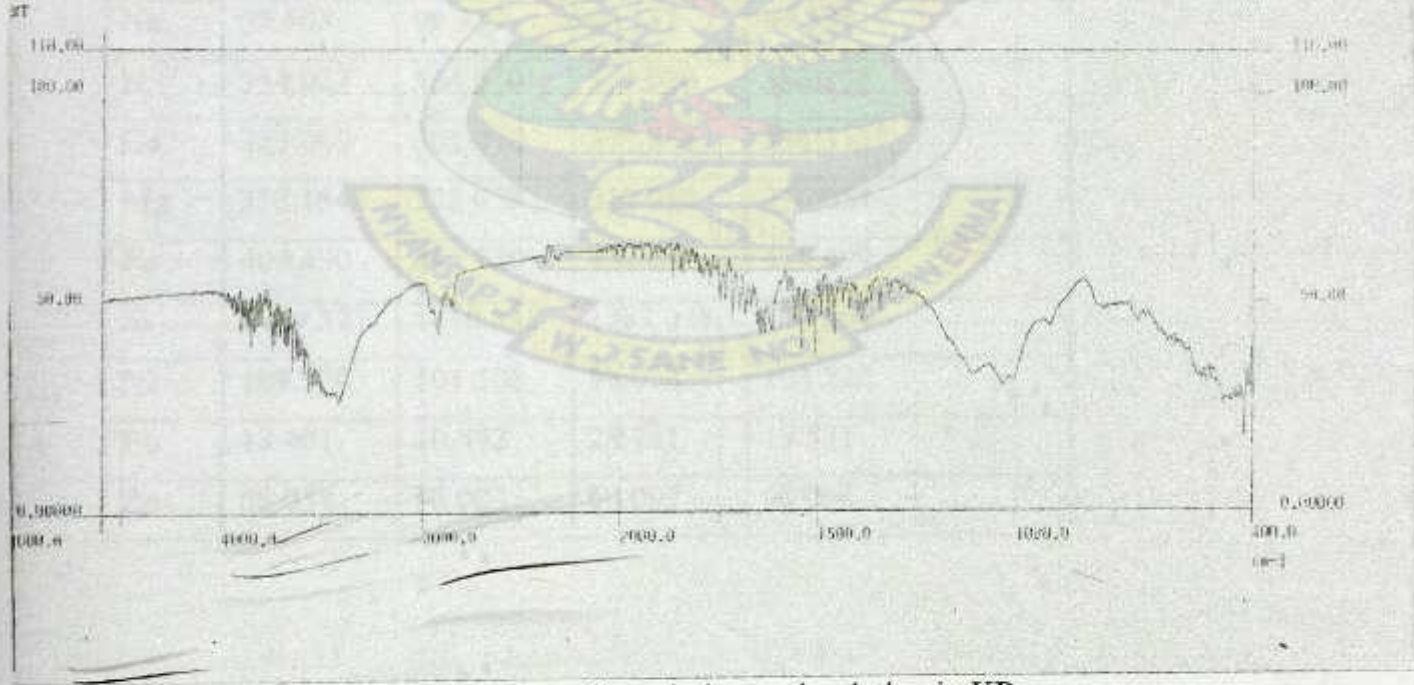


a. Infrared spectrum of basic fraction in KBr

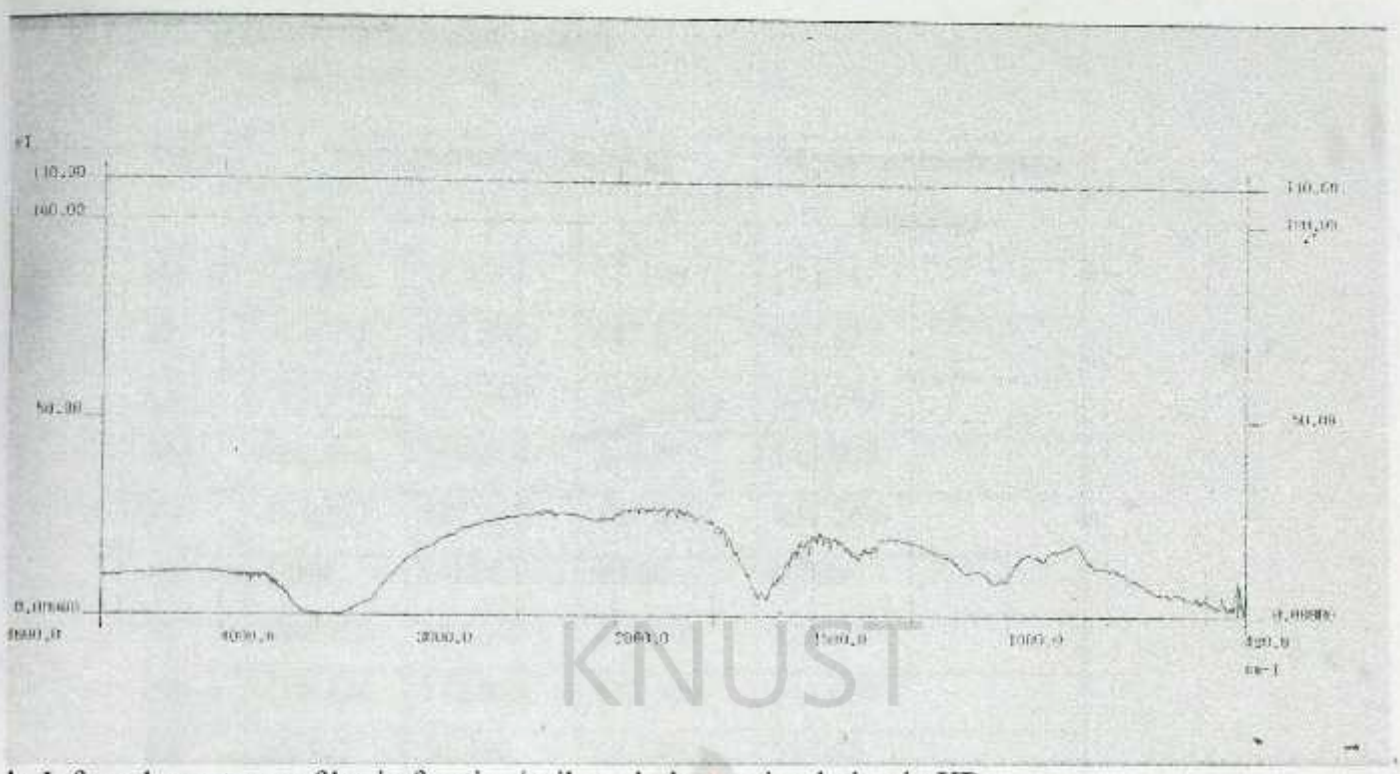


b. Infrared spectrum of neutral fraction in KBr

9. Infrared spectra of formulated plasters of the neutral and basic fractions



a. Infrared spectrum of neutral fraction/ soil mud plaster simulation in KBr



b. Infrared spectrum of basic fraction/soil mud plaster simulation in KBr

10. a. Levels of metals in soil sample

Mass of sample used = 1.0g

Metal	Concentration (mg/Kg)			Mean concentration (mg/Kg)
	1	2	3	
Na	97.505	99.139	96.112	97.585
K	554.023	564.010	551.020	556.351
Ca	335.009	301.070	372.866	336.315
Mg	232.154	228.058	229.950	230.054
Fe	409.490	411.940	437.067	419.499
Si	1409.321	1410.333	1382.038	400.564
Ni	109.320	101.508	98.038	103.220
Pb	13.401	10.432	28.761	17.531
Zn	58.051	56.003	60.097	58.050

10. b. Levels of metals in the husk sample

Mass of sample used = 1.0g

Metal	Concentration (mg/Kg)			Mean concentration (mg/Kg)
	1	2	3	
Na	77.600	77.827	77.100	77.611
K	962.832	962.833	962.831	962.832
Ca	532.743	530.700	534.786	532.743
Mg	246.016	244.028	247.015	246.018
Fe	103.241	111.233	181.259	144.248
Si	2.002	1.010	0.066	0.786
Ni	124.952	124.955	124.960	124.956
Pb	111.320	112.388	115.584	113.097
Zn	60.521	50.450	63.188	58.053

11. Infrared Spectrum of Nujol