CHEMICAL AND MINERAL ANALYSIS OF RAW AND ACID-TREATED CLAYS FROM KANO PLAINS, KISUMU COUNTY, KENYA

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DECLARATION

I declare that this thesis is my original work and has not been presented for a degree in any other university or any other award

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DEDICATION

To Almighty God for wisdom and resources, my late mum Claris for prayers and encouragement, my wife Leah for moral and material support, my children Nelkon, Clara, Becky, Newton, Elemina, John Moses and Maxwell, my siblings John, George, Isaac and Patrobas and in-laws Irene, Everline, "Loices", Violet, Linet, Lilian, Lorna, Alfred, John and Sam for moral and financial support.

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ABBREVIATION AND ACRONYMS

AAS –Atomic Absorption Spectrometry

ANOVA- Analysis of Variance

CCMET- Canadian Centre for Mineral and Energy Technology

EDS- Energy Dispersive System

EDTA- Ethylenediaminetetraacetic Acid

ICRAF- International Centre of Research in Agriculture and Forestry

IR- Infra-Red Spectroscopy

JKUAT- Jomo Kenyatta University of Agriculture and Technology

KNBS- Kenya National Bureau of Statistics

LOI – Loss of Ignition

NIB- National Irrigation Board

SPSS- Statistical Package for the Social Sciences

WDS- Wavelength Dispersive System

XRD – X-Ray Diffraction

XRF –X-Ray Fluorescence

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ABSTRACT

Clays are aluminosilicate minerals which are widely spread in the earth's crust. They also naturally contain iron because of its high relative abundance of about 6.5% .They have many applications such as, use in manufacture of Portland Cement, ceramic products such as bricks, roofing tiles and high quality ceramic products as crockery. For the manufacture of high quality ceramic products, the level of iron in the clays should not exceed 1%. This study was done on clays of Kano plains, Kisumu County, Kenya to find out the elemental and mineral composition of the clays with special interest on levels of iron since it affected clays' use in making high quality ceramics. Further investigation was done on whether iron levels, if found to be high, would be lowered by mineral acids of different concentrations at different temperatures to improve clay quality for manufacture of high quality ceramics. Powdered raw clay samples dried at 105^oC for six hours in a desiccator, digested or pelleted were analysed by AAS, EDTA titrations and XRF for elemental composition, and by XRD and IR for mineral composition. The samples were then treated with mineral acids of different concentrations at room and boiling temperatures for 12 hours to remove as much iron as possible and the residual clay washed, dried and analysed for Fe, Al and Si contents. The percentage elemental composition for the raw clays by AAS were expressed as oxides and ranges of identified elements found to be 45.47 ± 0.18 to 64.70 ± 0.10 SiO_2, 12.54 ± 0.37 to17.95 ± 0.19 Al_2O_3, 3.74 ± 0.08 to $10.28\pm0.06Fe_2O_3$, 0.44 ± 0.01 to $1.17\pm0.01MgO$, 0.56 ± 0.02 to $2.34\pm0.01CaO$, 2.07 ± 0.013 to 11 ± 0.08 K_2O, 0.98 ± 0.1 to 1.86 ± 0.01 Na_2O, 0.92 ± 0.02 to 2.49 ± 0.01 TiO_2, 0.02 ± 0.01 to 0.25 ± 0.01 MnO and LOI of 9.77 ± 0.15 to 15.40 ± 0.10. The minerals in the raw clays, identified by XRD included Montmorillonite $(Ca,Na))_{0.3}Al_2(Si,Al)_4O_{10}(OH)_2.xH_2O$, Kaolinite $Al_2Si_2O_5(OH)_4$, muscovite, $KAl_2(Si_3Al)O_{10}(OH,F)_2$, Albite, $Na(AlSi_3O_8)$, Orthoclase $KAlSi_3O_8$ and Dickite $Al_2(Si_2O_6(OH)_4$. Acid-treated clays gave different mineral composition and saw Montmorillonite, Kaolinite, Muscovite and Quarts detected in raw samples disappearing completely, and Ilmenite $(Ni_{.25}Mn_{.25}Zn_{.25}Mg_{.25})TiO_3$ and $(Ni_{.5}Mn_{.5})TiO_3)$, the titanium ore, Microcline $KAlSi_3O_8$ and Calcite, $CaCO_3$, emerging after acid-treatment. The findings showed levels of iron reduced by minerals acids from average 8.25% to less than 1% achieved by boiling clays with 6-8 M sulphuric acid. The levels of aluminium were lowered sparingly from 15.9% to 13.7% while levels of silicon remained unchanged. Second finding was that acid treatment alters mineral composition and cause interconversion of the clay minerals. Further, mineral composition given by chemical formulae showed that iron in the clays was not in the mineral structure and existed as an accessory component. The findings led to the conclusion that iron levels in raw clays were high but were lowered to less than 1% by mineral acids which improved their quality for making high quality ceramics. Data analysis was done by SPSS software.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Clay soils have mineral groups like kaolinite, smectites, illites and palygorskite-sepiolite (Murray, 2004) with unique properties and industrial and economic uses other than farming. Other uses include manufacture of cement, making bricks and floor tiles, additive in medicinal ointments, catalyst in cracking reactions, manufacture of drilling clays, making lead pencils, fillers in paper industry, use in printing inks, and use in paints and making ceramic products (Murray, 2004).

Clay minerals are hydrous aluminosilicates with phyllosilicate structure and with very small-grained particles of less than 4µm (Mason, 1968). The classes of clay minerals includes smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). Clays have adsorption capabilities which result from a net negative charge on the structure of minerals and sorption properties attributed to their high surface area and high porosity (Alkan *et al*., 2004).

Clay minerals are composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalies and alkaline earths (Ralph, 1968). Atomic lattices of most clay minerals consists of two basic structural units, one consisting of closely

packed oxygens and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition, $Si_4O_6(OH)_4$ hydrated aluminium silicates with very fine particle size, usually $<$2mm (Ralph, 1968). A layered structure is formed by the tetrahedral sheet(s) linked to octahedral sheet through sharing of apical oxygens. The tetrahedra contain mainly Si(IV) as the central atom, while the octahedral sites are occupied mostly by Al(III), Fe(III) or Mg(II). If one tetrahedral and one octahedral sheet are bonded together the structure is called 1:1 layer silicate structure. The structure created from two tetrahedral sheets sandwiching an octahedral sheet is called 2:1 layer silicate.

Two types of octahedral sheets occur in clay minerals. The first type is di-octahedral where two-thirds of the octahedral sites are occupied mainly by trivalent central atoms like Al (III) or Fe (III), and the second type is tri-octahedral type, with most of the octahedral sites occupied by divalent central atoms, like Mg^{2+} or Fe^{2+}. Kaolinite and dickite are di-octahedral types with 1:1 layer silicates while crysotil types are tri-octahedral with 1:1 layer silicates. Kaolinite and dickite have identical chemical composition with mostly Al(III) and Si(IV) in the octahedral and tetrahedral positions respectively and structure of the individual layer. However, they differ in the layer stacking arrangement: kaolinite is a single-layer structure, while dickite is a double-layer polytype.

Kano plains are located in the western part of Kenya, Kisumu County and cover the sub-counties of Nyando, Nyakach and Kisumu East. The soils are fine-grained black and grey coloured, become plastic when wet and later become hard and form cracks during dry season. The soils are poorly drained and aerated when wet. The clays in the region are currently used for subsistence farming on a small scale and rice production under National Irrigation Board (NIB) on a large scale. The subsistence farming has frequent failures due to unreliable rainfall and floods that are most prevalent in March to May of each year.

Clays are classified into earthenware clay, mid-fire stoneware clay and high-fire stoneware clay depending on the temperature at which they are fired to reach maximum hardness (Barsoum, 2003). They can be modified to make ceramic matrix composite materials with superior characteristics than either of the components (Chawla, 1993). The practical effectiveness of several organic acids such as acetic, formic, citric and ascorbic acids used for dissolving iron from iron compounds have also been evaluated (Ambikadevi and Lalithambika, 2000). Oxalic acid was found to be the most promising because of its acid strength, good complexing characteristics and high reducing power, compared to other organic acids.

Some studies already done on Kano Plains include problems of alternating drought and floods (natural environment) on development of Kano Plains (Millman, 1973), Impact of Floods and Drought on development of Water Resources (Ongwenyi and Denga, 1993),

Rural water Supply and Sanitation program (MLA Engineers, 1988) and The Soils of Nyando Catchment Area – Reconnaissance Soil Survey Report (Waruru *et al.,* 2003). These studies have addressed the area as a whole with respect to natural catastrophes (floods and drought), improvement of water resources and sanitation and general soil survey. Other possible uses of clays like making Portland cement, floor tiles, high quality ceramics would be revealed if the chemical and mineral composition of the clays were known. However, such studies have not been done in Kano Plains' soils. The chemical and mineral composition of the clays explains properties which in turn determine industrial and other economic uses of the clays. Such have not been done on the clays yet its findings would reveal other alternative uses of the clays other than the current main use of rice production and subsistence farming as the only major economic uses.

Clay is one of the most important natural industrial substances (Cornelius and Cornelius, 1993) and one of the most versatile industrial minerals used in construction, agriculture, process industries and environmental applications (Murray *et al.,* 1993). Some industrial uses of clays include making of the floor and roofing tiles, pottery work, making high-quality ceramic products such as mugs and plates, manufacture of cement and a source of Al and Ti (Grimshaw, 1971). Kenyan clay industries import industrial grade clays from other countries yet Kenya has expansive clay deposits, Kano plains being just one of such areas. The elemental and mineral analysis of Kano clays shall establish their chemical and mineral composition. Acid washing of these clays with mineral acids should indicate

whether the level of iron can be minimised to a level which would render the clays high quality raw materials for manufacture of high quality ceramic products.

1.3 Justification of the Study

Clay contains many elements and minerals in different proportions which determine its ultimate properties and uses (Grimshaw, 1971). Clays are raw materials for ceramics but have impurities like organic matter, iron and other metal oxides that could be removed by use of distilled water, organic and mineral acids, magnetic separators and froth flotation to improve its ceramic quality (Norton, 1974 a; Reed, 1988; Richerson, 1992).

Almost all the high purity alumina required for the production of aluminum metal is manufactured by the well-known Bayer process utilizing high grade bauxite ores as raw materials. However, the reserves of bauxite are limited in comparison with aluminous raw materials such as clay, which occur in extensive deposits all over the world. There is evidence that demand for high quality clay is high. This is confirmed by revelation that Kenya spent 340,155,732.70 of shillings between 2007 and 2011 to import 15,093,418.0 Kg of clays and clay related minerals (KNBS, 2012). This is too costly for a country that is struggling to feed its population. It is also disturbing that a very huge tonnage of clay is imported yet Kenya has expansive clay soils in areas like Kano plains and Mwea. A study of the elemental and mineral composition of Kenyan clays would reveal their composition and properties which will help decide their suitability for use as raw materials in clay-products industries. It is also important to study the extent of removal of

iron, if any, from the clays using minerals acids so as to boost use of the clays as raw materials for high quality ceramics. The findings will relieve Kenya of cost of importing clays and help improve the economy.

1.4 Objectives

1.4.1 General objective

To determine elemental composition and identify clay minerals in raw and acid-treated clays from Kano plains, Kenya.

1.4.2 Specific objectives

i) To determine the percentage composition of SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O, Na_2O, MnO, CaO, TiO_2 and water in the clays using AAS, XRF, EDTA titrations and LOI

ii) To determine the percentage composition of SiO_2, Al_2O_3 and Fe_2O_3 in acid-treated clays

iii) To identify the clay minerals in raw and acid-boiled clay soils of Kano plains using XRD and IR

1.5 The Scope of Study

The study was conducted in the central parts of Kano plains. The analysis was restricted to identification of the clay minerals present, elemental composition and extent of acid-leaching of iron, aluminium and silicon from clays. Special interest was put on acid-leaching of iron to improve clay quality as raw materials for high quality ceramic products.

1.6 Limitations of the Study

Number of samples was limited to eight due to costs. Seasonal variation was not considered. Only names, chemical formulae and percentage of minerals in the clays was done and not the structural formulae.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition of Clay and Clay Minerals

Clay is defined differently by people in different disciplines and workers based of its use, the nature of operations involved in its use and the purpose of the definition (Grimshaw, 1971). Some definitions on such bases are; "Clay is plastic when wet" (Grim, 1962), "Clay is any fine-grained natural earthy argillaceous material" (Grim, 1968),"Clay is any material whose particles are finer than 4μ" (Moore and Reynolds, 1989). Clay implies an earthy, fine-grained material which develops plasticity when mixed with limited amount of water (Mason, 1968). A concise definition by the American Ceramic Society is, "Clay is a fine-grained rock which, when suitably crushed and pulverized, becomes plastic when wet, leather-hard when dried and on firing is converted to a permanent rock-like mass (Lawrence and West, 1982). The chemical definition of clay is that they are hydrated silicates of Al, Fe, or Mg, both crystalline and amorphous composed mainly of silica, alumina and water (Murray, 2004). Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalies and alkaline earths (Ralph, 1968). Clay mineral is defined as a stony or earthy mineral aggregate consisting essentially of hydrous silicates of alumina, plastic when sufficiently pulverized and wetted, rigid when dry, and vitreous when fired at a sufficiently high temperature (Murray, 2004). They are essentially hydrous aluminous sheet silicates that are fine-grained with variable composition and water content (Hans and Andrei, 2004). They are

crystalline in nature with layer silicates formed by condensation of sheets of linked $Si(OH)_4$ tetrahedra with those of linked $M_{2-3}(OH)_6$ octahedra, as the basic structure (M is either a divalent or trivalent cation) (Theng, 1974). The grains are plate-shaped and slide over each others' surface thereby contributing to the smooth feel. They contain impurities that contribute to plasticity, melt and colour (Zakin, 2001).

2.2 Properties of Clays

Clays have very fine particles that yield very large-specific surface areas that are physically sorptive and chemically surface-active. Many clay minerals carry excess negative electric charge owing to internal substitution of Si^{+4} by lower valent cations and thereby increase internal chemical reactivity in chemical combination and ion exchange. These characteristics contribute to the properties of clays which are of technical applications (Murray, 2004).

2.2.1 Plasticity

This is the property of a material that permits it to be deformed under stress without rupturing and to retain the shape produced under the stress, (Murray, 1979). The property enables the material to undergo permanent deformation in any direction without rapture under a stress beyond that of elastic yielding. The plasticity properties of clay are affected by the type of clay mineral, particle size and shape, organic matter content, soluble salts, adsorbed ions and the amount and type of non-clay minerals. (McGraw-Hill, 1992). It is

enhanced by the presence of fine particles in the clays (Zakin, 2001). The plasticity is determined by the following;

i)   Water of plasticity- the amount of water necessary to develop optimum plasticity or the range of water content in which plasticity is demonstrated.

ii)   The amount of penetration of an object into the formed plastic mass of clay which is frequently done by use of a needle or some special plunger

iii)   The stress necessary to deform the clay and the maximum deformation the clay will undergo before rapture at different moisture contents and with varying degrees of stress application (Murray, 2004).

2.2.2 Strength

This is the ability of clay to withstand the stress of forming without collapsing. It is influenced by a number of factors including thixotropy, particle size differentiation and clay body chemistry (Zakin, 2001). There are green and dry strengths of clays. Green strength is the strength measured as traverse breaking strength that prevails while the plastizing water is still present. The green strength increases continuously to a maximum as water is continuously added to dry clay. It varies with the composition of exchangeable cations in the clay and the type of clay minerals. Montmorillonites have the greatest green strength while kaolinites, illites and chlorites only have a slight green strength (Murray, 1979). Dry strength is measured as a traverse breaking strength of a test piece after drying long enough (usually at 105 $^{\circ}$C) to remove almost all the pore and

adsorbed water. It is reduced by large amounts of non-clay mineral components. It increases with a decrease in particle size and presence of organic materials in some clay. It is generally higher when Na is the adsorbed cation (Murray, 1979). It is also dependent on the proportion of fine particles present such that the larger the proportion, the greater the dry strength. Other factors that affect dry strength are the degree of hydration of the colloidal fraction, the method of forming the ware and the extent of drying (McGraw-Hill, 1992).

2.2.3 Shrinkage

This is the loss in volume in clay when it dries or when it is fired. There is thus both drying and firing shrinkage. Drying shrinkage is dependent on the water content, the character of clay minerals and the particle size of the constituents. It is high in very plastic clays and produce cracking and warping, and low in sandy clays or clays with low plasticity and tends to produce weak porous body. Firing shrinkage depends on the volatile materials present, the types of crystalline phase changes that take place during firing, and the dehydration characteristics of the clay minerals (McGraw-Hill, 1992)

2.2.4 Vitrification

Vitrification basically means glass formation. It occurs as a result of a process of gradual fusion in which some of the more easily melted constituents begin to produce an increasing amount of liquid which makes up the glass bonding material in the final fired

product. Vitrification range refers to the temperature range over which the fusion of the material takes place. Some clay minerals like montmorillonites, illites and chlorites have short vitrification ranges while others like kaolinites have long vitrification ranges. Vitrification temperatures are lowered by some nonclay impurities like calcite and feldspar which act as fluxes. The degree of vitrification depends on the duration of firing as well as the temperature attained (McGraw-Hill, 1992).

2.2.5 Colour

Natural colour of clays may be black, grey, tan, brown, white, red or greenish. The grey, brown, red or yellow clays contain iron in its many different forms (Glen *et al*., 2002). The Fe-containing clays produce red, tan or brown colours when fired. Raw clays that are either white or very light in colour are assumed to contain little iron and fire to light colour (Glen *et al*., 2002). Colour affects the aesthetic value and is important in most structural clay products. The colour of clay products depends on the oxidation state of iron, the state of division of the iron minerals, the firing temperature, and the degree of vitrification, the proportion of alumina, lime, and magnesia in the clay material and the composition of fire gases used during the burning process. The best white-burning clays contain less than 1 % Fe_2O_3, Buff-burning clays contain 1-5 % Fe_2O_3 while the red burning clays contain 5 % and more Fe_2O_3 (McGraw-Hill, 1992).

2.2.6 Firing Properties

Firing property refers to the fusion and hardening of clays when heated to higher temperatures. Heating clay materials to successive higher temperatures causes fusion. Shrinkage and loss of pore waters occur in the range of 100-105 $^{\circ}$C with attendant dimensional changes. Oxidation of sulphides present in the clays begins in temperatures of between 400-500 $^{\circ}$C, and loss of hydroxyl waters from clay minerals takes place at between 500-900 $^{\circ}$C. The loss of hydroxyl water is usually accompanied by a modification of the structure but not complete destruction of clay minerals. It causes shrinkage in the two layer minerals (Kaolinites and halloysites) but not in the three layer minerals (Murray, 1979). The structure of a clay mineral is destroyed in the temperature range of 800-950 $^{\circ}$C and major firing shrinkage develops. At temperatures above 900 $^{\circ}$C, new crystalline phases develop in all the clay minerals except those containing large amounts of Fe, alkalis, alkaline earths, for which case fusion may result after the loss of structure without any intervening crystalline phase.

2.3 Occurrence of the Clay Minerals

Clay minerals may be formed from weathering process, diagenesis, metamorphism or hydrothermal process (Grimshaw, 1972; Weaver and Pollard, 1973). The nature of the formation process significantly affects the crystallinity and purity of clay and its associated minerals. Clays that are deposited and found at the site of formation are called primary clays while those formed and eroded to a different site after formation are called secondary clays (Theng, 1979). Clay mineral deposits occur either as a relatively pure

concentration of the mineral or a mixture of clay minerals. The four major mineral groups with different chemical and mineral composition, physical structures, and crystal orientations include kaolins, smectites (or montmorillonites), illites, and palygorskite-sepiolite groups which occur in relatively pure concentrations (Hans and Andrei, 2004). Other mineral groups are chlorites and vermiculites which occur as mixtures with non-clay minerals such as shales (Murray, 2004).

2.3.1 The Kaolin Group

Kaolin is one of the widely used clay materials for a large number of applications such as in ceramics, paper coating, paper filling, paint extender, rubber filler, cracking catalyst or cements, oil refinery and water treatment (Belver *et al.*, 2002; Caulcante *et al*., 2005;Vaga, 2007; Salawudeen, 2007), cracking catalyst in the petroleum industry, use in water and oil-based paints, pencil heads, carrier of fertilizers, desiccants, and insecticides, among others (Murray, 2004). The percentage uses of kaolin in some of the technological industries are: paper filling and coating 45%; refractories and ceramic 31%, fiberglass 6%; cement 6%, rubber and plastic 5%, paint 3%, others 4% (Murray, 2002).

Kaolinite is the major mineral component of kaolin, which may usually contain quartz and mica and also less frequently feldspar, illite, montmorillonite, anastase, haematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite and halloysites. Kaolinite is a clay mineral with chemical composition $Al_2Si_2O_5(OH)_4$ (Belver *et al.*, 2002; Vaga,

2007) . It is a layered silicate mineral comprising of one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina (Deer *et al*., 1992). Rocks that are rich in kaolinite are called kaolin. Kaolinite has a low shrink-swell capacity and a low cation exchange capacity. It is a soft, earthy material, usually white mineral produced by chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world, it is coloured pink, orange or red by iron oxide giving it a distinct rust hue. Kaolinite, like other clays, are composed of fine grained minerals which are plastic at appropriate water content and harden up when fired (Stephen and Martin, 1995). They have varying chemical composition depending on both physical and chemical changes in the environment where they are found. The industrial utilization of kaolinite is closely related to its reactivity and surface properties and depends strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials with thermo-chemical treatment (Belver *et al.*, 2002; Vaga, 2007), or chemical activation (Coma *et al.,* 1990; Salawudeen,2007). The kaolin group of minerals includes kaolinites, dickite and nacrite. All these minerals have the molecular formula $Al_2Si_2O_5(OH)_4$. Other minerals from the group are Halloysites $(Al_2(Si_2O_5)(OH)_4$ and endellite, $Al_2O_3.2SiO_2.4H_2O$ (Grim, 1968; Hlavac, 1983 and Cornelis and Cornelius, 1993). The kaolin lattice consists of a two layer sheet comprising of one alumina octahedron, and a silica tetrahedron, hence described as a 1:1 layer.

2.3.2 The Smectites

This is a group of Na, Ca, Mg, Fe and Li aluminium silicates. The specific minerals include montmorillonites, saponite, nontronite, beidellite, and hectorite. They are the best-known clay minerals of the 2:1 layer type (Moore and Reynolds, 1989). Smectites are widely used in various branches of industry due to their high cation exchange capacity, swelling ability and high surface area. The main source of smectite minerals is the bentonite rock. The bentonites containing the smectite sodium montmorillonite as the major mineral component normally has a high swelling capacity, while the one with calcium montmorillonites as the major mineral component has a low swelling capacity (Murray and Elzea, 1994). Smectites have a three layer structure comprised of two silica tetrahedron sheets with a central alumina octahedron sheet, and is described as a 2:1 layer. Some industrial uses of smectites include making foundry binders (Grim and Guven, 1978), drilling mud, cat litter, sealants in ponds, slurry trench excavations to prevent caving, running of loose soils, absorbents for pesticides and insecticides to protect crops and human, suspension aids in the pharmaceutical, fertilizer and cosmetic industries to effect uniform spread of the chemical, bleaching clays to decolourise mineral, vegetable and animal oils, (Murray, 2004) and making nanoclays, the very strong and heat resistant composites used in automobiles and food wrappings and packaging (Beall, 1996).

2.3.3 Palygorskite and Sepiolite Groups

These are hydrated magnesium aluminium silicates that have an elongated shape. They have a large surface area, and are sometimes referred to as sorptive clays, also called Fuller's earth (Murray, 2004). The two groups are very similar but sepiolite has higher magnesium content while Palygorskite has higher aluminum content. They also have different crystal structures with palygorskite having a chain-like crystalline structure consisting of inverted ribbons of silica tetrahedron linked together by aluminium and magnesium octahedral to form a 2:1 layer structure. Some of the industrial uses of the palygorskite-sepiolite minerals include making oil-well drilling fluids that help in removing rock cuttings from the hole, making adhesives in production of corrugated paper, and making liquid suspension fertilizers among others.

2.3.4 Common Clay Group

This group includes a variety of clays and shales that are fine in particle size. The mineral composition is mixed, with illites and chlorites making the major mineral components. Illites are hydrated K, Fe- aluminium silicates while chlorites are hydrated magnesium iron aluminium silicate. Common clays are used in many structural clay products such as brick, tile, pottery, stoneware, among others (Murray,1994).

2.4 Structure and Composition of Clay Mineral

All clays are hydrous aluminosilicates with a phyllosilicate structure and with very small grain size of less than 4 µm. The basic phyllosilicates structure is the presence of SiO_4

tetrahedral linked by sharing of three of the four oxygens to form sheets of pseudohexagonal network (Mason, 1968). Clay minerals are sheet structures basically composed of fine grains of silica- tetrahedral layers and alumina octahedron layers (Figures 2.1 and 2.2)
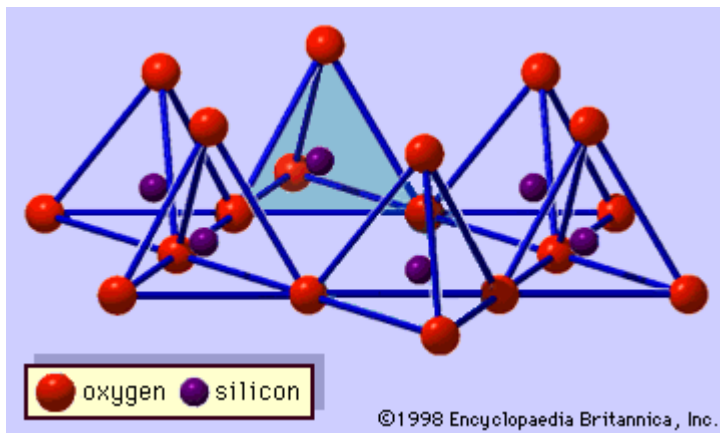
Figure 2.1. **Silica tetrahedral layers,** (Encyclopaedia Britannica, 1998)
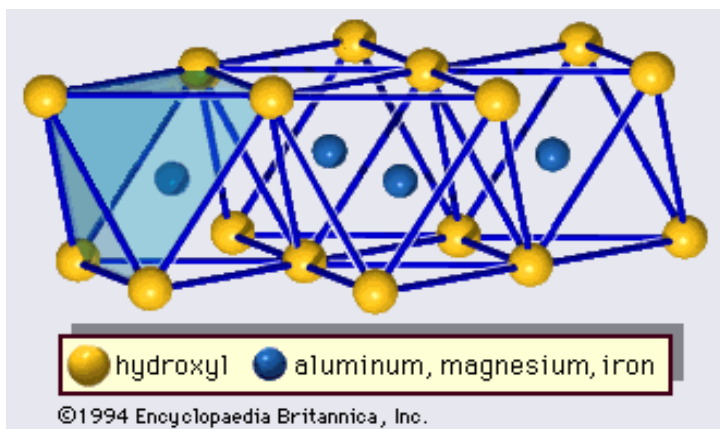
Figure 2.2. Alumina-octahedron layer, (Encyclopaedia Britannica, 1994)

The grains are plate-shaped and slide over each other's surface hence cause the slippery property of clays (Zakin, 2001). The silica-tetrahedron and alumina-octahedron layers are combined differently in each clay mineral and this forms the basis of their identification and differentiation by x-ray diffraction. Each tetrahedron consists of a cation, T, coordinated to four oxygen atoms, and linked to adjacent tetrahedra by sharing three corners (the basal oxygen atoms, Ob) to form an infinite two-dimensional 'hexagonal' mesh pattern along the **a**, **b** crystallographic directions (Figure 2.1). Common tetrahedral cations are Si^{4+}, Al^{3+}, and Fe^{3+}.
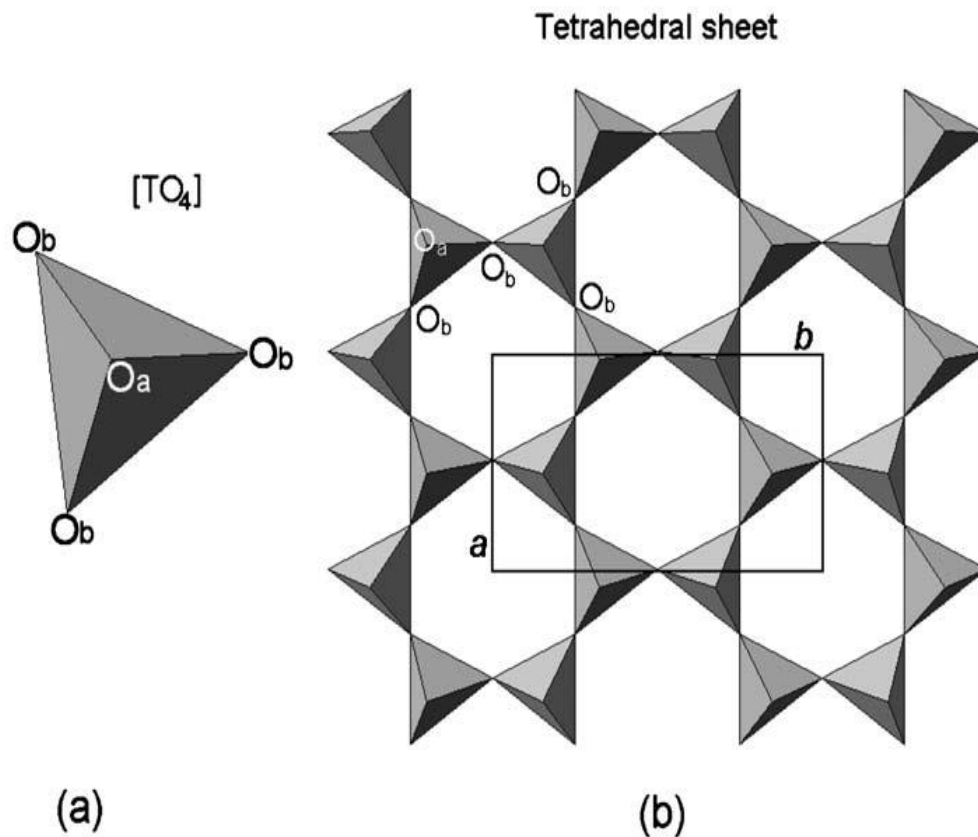
Figure2.3.
Coordination of cation, T, and oxygen atoms, O, in a tetrahedron and a tetrahedral sheet (a) Tetrahedron [TO4]; (b) tetrahedral sheet. Oa and Ob refer to apical and basal oxygen atoms, respectively. a and b refer to unit-cell parameters (Encyclopaedia Britannica, 1998).

In the octahedral sheet, connections between each octahedron, M, to neighbouring octahedra is made by sharing edges. The edge-shared octahedra form sheets of hexagonal or pseudo-hexagonal symmetry (Figure 2.2).

Octahedral sheet (M)

cis-octahedron

trans-octahedron

(a)

(b)
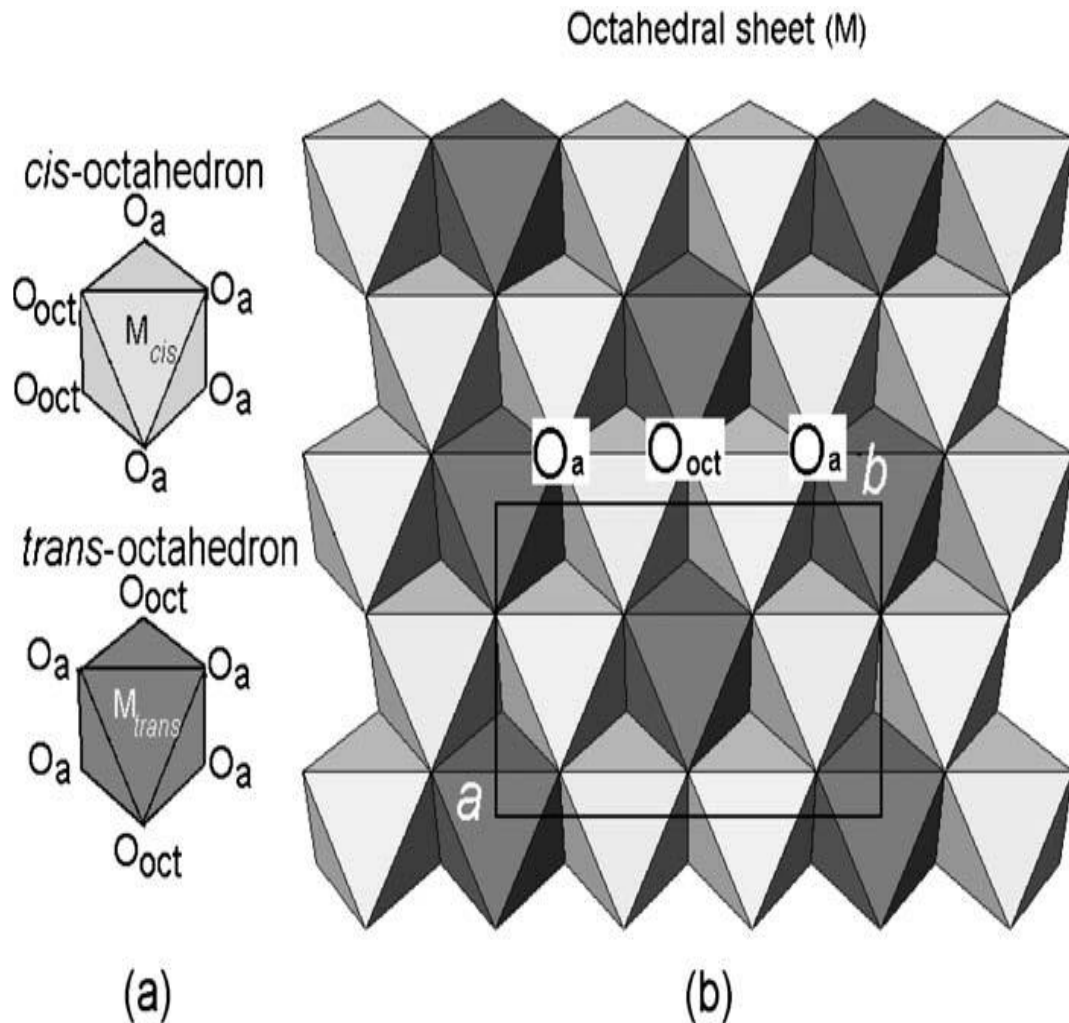
Figure 2.4. The Octahedron and the octahedral sheet (a) Ooct (OH, F, Cl) orientation in cis-octahedron and trans-octahedron; (b) location of cis- and trans-sites in the octahedral sheet. Oa and Ob refer to apical and basal oxygen atoms, respectively. a and b refer to unit cell parameters (Encyclopaedia Britannica, 1998)**.**

Octahedral cations are usually Al^{3+}, Fe^{3+}, Mg^{2+}, and Fe^{2+}, but other cations, such as Li^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, $V^{3+,}$ Cr^{3+}, and Ti^{4+} were identified. Octahedra show two different topologies related to (OH) position, i.e., the cis- and the trans-orientation (Figure 2.4). The free corners (the tetrahedral apical oxygen atoms, Oa) of all tetrahedra

point to the same side of the sheet and connect the tetrahedral and octahedral sheets to

form a

common plane with octahedral anionic position Ooct (Ooct ¼ OH, F, Cl, O) (Figure 4).

Ooct anions lie near to the centre of each tetrahedral 6-fold ring, but are not shared with

tetrahedra. The 1:1 layer structure consists of the repetition of one tetrahedral and one

octahedral sheet, while in the 2:1 layer structure one octahedral sheet is sandwiched

between two tetrahedral sheets (Figure 2.5).
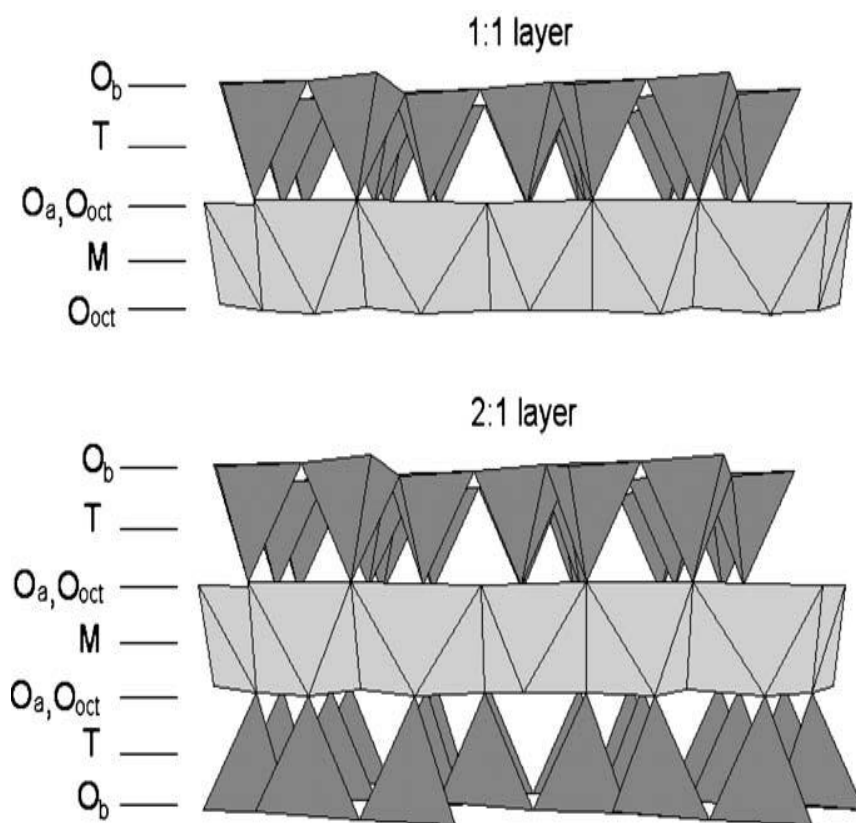
Figure 2.5. Models of a 1:1 and 2:1 layer structure. Oa, Ob, and Ooct refer to tetrahedral basal, tetrahedral apical and octahedral anionic position, respectively. M and T indicate the octahedral and tetrahedral cation, respectively (Encyclopaedia Britannica, 1998)**.**

In the 1:1 layer structure, the unit cell includes six octahedral sites with four cis- and two trans-oriented octahedral and four tetrahedral sites. Six octahedral sites and eight tetrahedral sites characterize the 2:1 layer unit cell. Structures with all the six octahedral sites occupied are known as trio-octahedral (Figure 6a). If only four of the six octahedra are occupied, the structure is referred to as dioctahedral (Figure 6b).
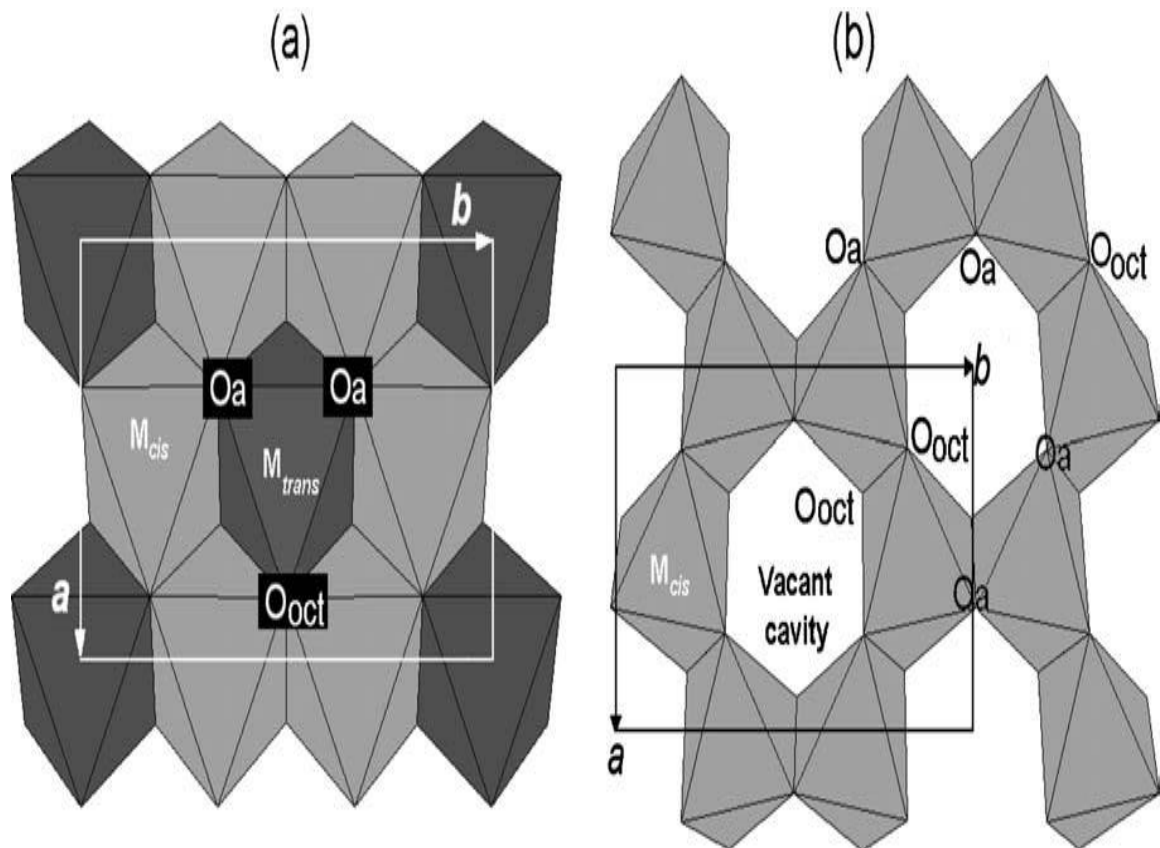
Figure 2.6. (a) Tri-octahedral sheet; (b) Di-octahedral sheet. Oa represents the apical oxygen atoms shared with tetrahedra and Ooct is the anionic site shared between adjacent octahedra, a and b (Encyclopaedia Britannica, 1998).

The structural formula is often reported on the basis of the half unit-cell content based on three octahedral sites.
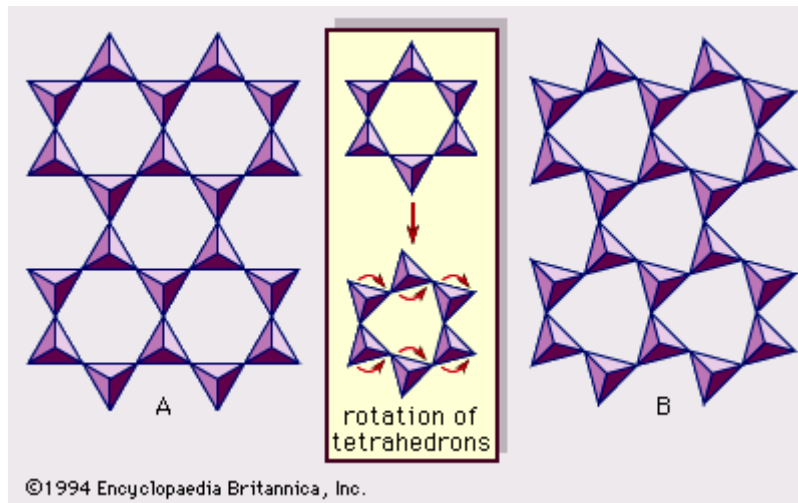
Figure 2.7. The octahedral sites
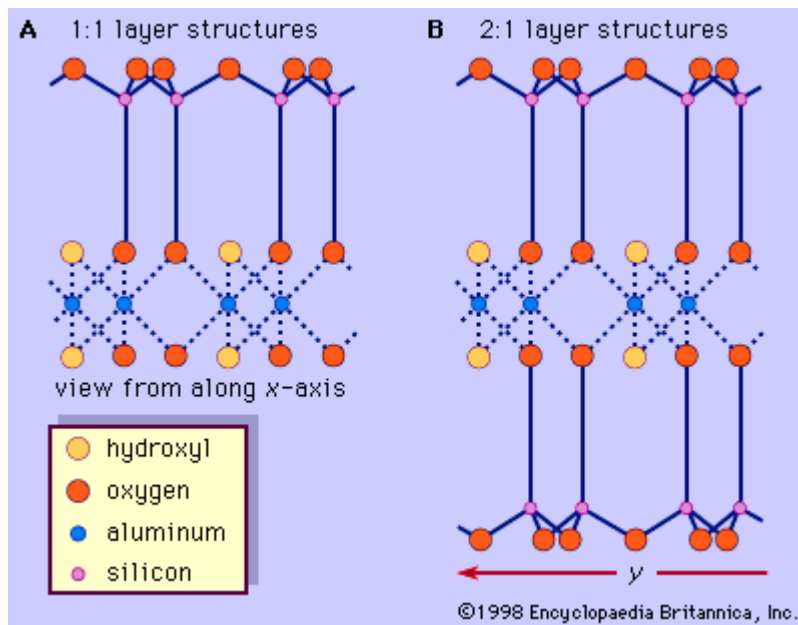
Figure 2.8. Views of 1:1 and 2:1 layer from x-axis (A) and y-axis (B)
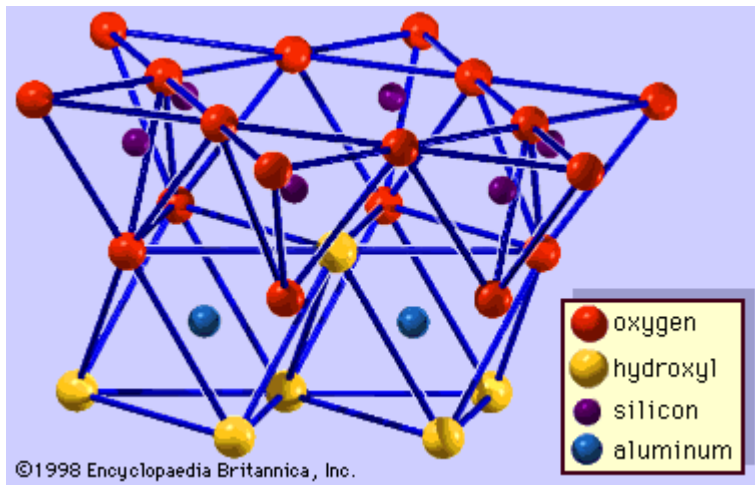
Figure 2.9. Silicate layer: 1:1 and 2:1 structures

2.5 Influence of Inorganic Acids on Clays

Inorganic acids may dissolve some constituents of clay soil in a structure. It has been reported that acids dissolve alumina, iron, alkali metals and alkaline earth metals (Grim, 1953). Clays contain large quantities of alumina and are consequently susceptible to partial dissolution by acids. The solubility of clays in acids depends on the nature of acid, acid concentration, the acid to clay ratio, the temperature and duration of treatment (Grim, 1968). The action of acid in clays is enhanced when the acid has an anion about the same size and geometry as a clay component and this in turn permit even weak acids to dissolve clay under some conditions. Studies have shown that percentage of iron and rate of leaching from clays depends on concentration of acid and temperature of leaching (Chawla and Horwitz,1991; Muriithi, 2012).

2.6 Clay as a possible Raw Material for Ceramics

Ceramics are solid compounds formed by application of heat, and sometimes heat and pressure, on materials comprising at least two elements provided one is a non-metal or a non-metallic elemental solid. Chemically, with exception of carbon, they are non-metallic inorganic compounds (Barsoum, 2003). Some considerations on physical properties of raw materials for ceramic processing includes fine particle size to provide improved plasticity for forming and higher thermodynamic driving force for sintering and sub micrometer particles that can be more easily packed and mixed in liquids (Murray, 2004). Other properties are ease of deformation without rapture and retention of imposed shape, a relatively non-reactive material that provides a rigid component and a high degree of fineness to make processing easy and give smooth finish (Disdane, 1986). Clays are fine grained in natural state and are aluminosilicates hence meets all the requirements for a raw material for ceramics. It is also naturally-occurring and provides a cheap raw material (Murray, 2002). It is however impure in natural state and require further purification.

2.7 Clay as a Source of Aluminium

Aluminium is very abundant in earth's crust but is rarely found in sufficiently high concentrations for direct extraction. Most clay contain between 10-40 % alumina which can necessitate ore beneficiation (Grimshaw, 1971). However, it is economical to use clays with higher percentages (> 40%) of alumina. Clay has also been used as a source of

Al in Korea and USA where non-bauxite aluminium bearing minerals like kaolin were used. The ore was calcined to 600 ºC for two hours and then leached with concentrated hydrochloric acid at 105 ºC for one hour. The resulting solution contains both Fe and Al and was subjected to a further purification where Fe was removed by solvent extraction. An aluminium value in the liquor was recovered as $AlCl_3$ hexahydrate, $AlCl_3.6H_2O$ by crystallisation. The chloride was then thermally decomposed and calcined at 110 ºC to produce alumina (Kyun *et al*., 1979).

Some of the properties of alumina that suit it for use in the clay products are its high melting point, resistance to chemical attack and desirable electrical and mechanical properties. These properties qualify alumina for use in making clay products like refractory components, crucibles, spark plugs, and substrates in electronic devices (Disdane, 1986)

2.7 Effect of Impurities on Properties of Clay

The impurities in clays are found in non-clay minerals that are mined or occur together with clay minerals. They add excess clay components which affect the properties of clays.

2.7.1 Effect of Silica

Silica occurs in clays as crystalline quartz or in amorphous form. Silica reduces plasticity, drying and firing shrinkage; it reduces firing strength, refractoriness and also causes increase in thermal expansion (Lawrence and West, 1982).

2.7.2 Effect of Alumina

Combined alumina occurs in feldspars, mica, hornblende, tourmaline, bauxite, laterite, diaspore and the clay minerals. When in accessory minerals, alumina reduces plasticity and increases refractoriness (Lawrence and West, 1982).

2.7.3 Effect of Alkalies

The principal alkali-bearing minerals are feldspars, micas and hydrous micas. They could also be present as adsorbed ions on the surface of clay minerals or in form of soluble chlorides and sulphates. Alkalies have strong fluxing action and reduce refractoriness, vitrification temperature and plasticity of clays. They on the other hand impose increase in glass formation which in turn increases the strength of the fired body (Lawrence and West, 1982). Presence of soluble alkalies in clays cause scum formation with soap. Lime is unstable in the atmosphere and takes water thereby causing swelling and breakage of fired product (Daniel, 1972)

2.7.4 Effect of Iron Compounds

Iron compounds in clays include iron oxides, sulfides, carbonates, hydroxides and phyllosilicates (Stucki, 2006). The Fe oxides are susceptible to oxidation-reduction

reactions which lead to colour changes and glazing temperatures. Fe_3O_4 in combination with silica starts glass formation at temperatures of 1455 ºC. If it gets reduced to FeO, then glass formation can start at a much lower temperature of 1180 ºC. Fe_2O_3 and FeO are brick red and black, respectively, and confer these colours on clay products (Lawrence and West, 1982).

2.7.5 Effect of Calcium Compounds

The calcium compounds found in clays include calcite, aragonite, $CaCO_3$ and gypsum $CaSO_4.2H_2O$ which decompose on heating to form CaO which acts as a flux. This then results in glass formation and lowers vitrification temperature. It increases the fired strength and reduces absorption of the product. CaO combines with iron minerals and bleaches the red colour to buff. If not fired to sufficiently high temperatures, CaO may remain as free lime which react with water after firing to form $Ca(OH)_2$ which causes large expansion and may develop sufficient pressure to disrupt the fired product (lime popping) (Lawrence and West, 1982).

2.7.6 Effect of Carbonaceous Compounds

Carbonaceous materials include peat, lignite and coal. Their presence in some clays cause a dark colour and an off-white colour on fired product. Large amounts of the compounds cause reducing conditions in the kilns and inordinate amounts affect colour, vitrification, and decomposition and redox reactions during firing (Lawrence and West, 1982).

2.8 Uses and Applications of Clay and its Minerals

Different clay minerals have different alumina octahedral and silica tetrahedral sheets which cause difference in physical and chemical properties hence differences in the ultimate applications. Particle size, shape and distribution, surface chemistry, area and charge, pH, plasticity, green, dry and fired strength, fired colour, refractoriness, colour and brightness determine the properties and ultimate use of clays (Murray, 2006). Other properties which qualify some clay minerals (more specifically Kaolin) are chemical inertness, white or near white colour, good covering and binding power, softness and non-abrasion, low conductivity of heat and electricity, low viscosity and ability to flow and ability to disperse readily.

2.8.1 Use of Clay in Ceramic Products

Ceramics can be defined as heat-resistant, nonmetallic, inorganic solids that are generally made up of compounds formed from metallic and nonmetallic elements. Although different types of ceramics can have very different properties, in general ceramics are corrosion-resistant and hard, but brittle. Most ceramics are also good insulators and can withstand high temperatures. These properties have led to their use in virtually every aspect of modern life (Barsoum and Michael , 1996). Clay consists of a large number of very tiny flat plates, stacked together but separated by thin layers of water. The water allows the plates to cling together, but also acts as a lubricant, allowing the plates to slide

past one another. As a result, clay is easily molded into shapes. High temperatures drive out water and allow bonds to form between plates, holding them in place and promoting the formation of a hard solid. Binders such as bone ash are sometimes added to the clay to promote strong bond formation, which makes the ceramic resistant to breakage. The common clay used to make flowerpots and roof tiles is usually red-orange because of the presence of iron oxides. White ceramics are made from rarer (and thus more expensive) white clays, primarily kaolin (Ball and Philip, 1997). Clay is used in manufacture of ceramic products like white ware, tiles, sanitary ware.

2.8.2 Use of Clay in Paper Industry

Clay is used as filler and a coating in the paper industry. As filler, Kaolin is mixed with pulp fibres to form a coating. Kaolin is mixed with water, adhesive and other additives and coated onto the surface of paper. It improves the opacity of the paper sheet, imparts smoothness to the surface and replaces some of the more expensive pulp fibres. As a coating, Kaolin imparts opacity, brightness, a glossy finish, smoothness and improved printing quality (Murray, 2004).

2.8.3 Use of Clay in Paints

Paint is essentially a fluid system in which solid bodies, usually identified as pigments, are suspended (Grim, 1962). Clays are used in both water and oil-based paints where it extends the much higher costly titanium dioxide opacifying pigment, controls the

viscosity so as to prevent the pigment from settling during storage, provides thixotropy so that the paint is easily applied yet does not sag or run after application, improves gloss, promotes film strength and aid in tint retention (Murray, 2004).

2.8.4 Use of Clay in Plastic and Rubber Industries

Kaolin is the only clay type used in plastic and rubber industries. It is used as an extender and functional filler. Calcined metal-kaolin is used in PVC wire insulator because it enhances electrical resistivity of the wire coating (Sekutowski, 1992).

2.8.5 Use of Clays in Inks

Kaolins are ingredients of printing ink where they act as extenders of the polymer present in ink, improve colour intensity, limit ink penetration into paper, control rheology and improve adhesion (Murray, 2004).

2.8.6 Use of Clay as Cracking Catalyst

Kaolins are used as raw materials to make zeolites and Al silicates for use as catalysts in refining of petroleum (Murray, 1994). Halloysites are used for manufacture of petroleum cracking catalyst (Murray, 2004).

2.8.7 Clay as a Chemical Raw Material

Air-floated kaolin is used as a chemical raw material to make fiberglass. Kaolin is also used in some cement plants to whiten the colour and to provide silica and alumina for cement reactions, and increase cement strength. Kaolin is used as a raw material for producing zeolites which are an ingredient in detergent (Murray, 2006).

2.8.8 Use of Clay in Pencil Leads

Kaolin is used as an additive to graphite in making pencil leads. Plasticity and fine particle nature of kaolin are useful in extruding the graphite-kaolin mixtures (Murray, 1961).

2.8.9 Use of Clays in Suspensions and Diluents

Kaolins are used as suspending agents in pharmaceuticals, cosmetics, enamels and medicines. Some pills use kaolin as a diluents and a binder in pressing pills (Murray, 2004).

2.8.10 Use of Clays in Fertilizers, Desiccants and Insecticides

Kaolin is used as a carrier for certain insecticides and fertilizers. It is also used as a desiccant to promote flow when mixed with highly deliquescent materials (Murray, 2004).

2.8.11 Use of Clay in Roofing Granules and Polishing Compounds

Roofing granules are produced by calcining coarse granular particles of white kaolin. Fine particle calcined kaolin of 3 µm is used in polishing compounds for automobiles, silver, copper, brass and other metals (Murray, 2004).

2.8.12 Use of Clay as Drilling Mud

Sodium montmorillonite is the major constituent of high swelling clays. The high-swelling property makes the clay a necessary ingredient in fresh water drilling muds in the world. Only 5% by weight of the high-swelling clay are required to produce the high viscosity, thixotropic fluid with low filter cake permeability necessary to meet the American Petroleum Institute (API) drilling fluid specifications (Murray, 2004).

2.9 Analytical Methods/Instruments

2.9.1 Atomic Absorption Spectrometry (AAS) analysis

This is an analytical technique used to determine the concentration of a specific metal element in a sample and can analyze concentrations of up to 70 different elements in a solution (Sperling *et al*., 1999). It involves atomizing the specimen by spraying a sample into a flame and then studying the absorption radiation from an electric lamp producing the spectrum of the element to be determined (Mendham *et al*., 2009). It is an analytical technique based on absorption of radiant energy by atoms of a sample (Khandpur, 2007).

2.9.1.1 Instrumentation of AAS

AAS instrument has four main parts namely, the hollow cathode lamp, the flame atomizer, the spectrometer and the signal read out. The hollow cathode lamp is the radiation source. It is cylindrical with a metal of choice as cathode or anode, and filled with argon or neon gas. A high voltage is applied across the cathode and anode to ionize the gas particles inside. As the voltage is increased, the ionized gas particles acquire enough energy to eject metal atoms from the cathode. Some of the ejected atoms are in an excited state and emit light with characteristic frequency to the metal under investigation. The sample is first dissolved and nebulized/aspired into the flame which vaporizes it and frees it from the atoms/ions of all the other elements present (Alkemade *et al*., 1982; L'vov, 2005).

2.9.1.2 Working Principle of AAS

A beam of light of a characteristic frequency is passed through vapourised ions in the flame. The ions absorb some of the energy and a series of absorbance bands are produced. Different ions produce characteristic absorption bands with a characteristic frequency and wavelength. The absorbance attained is proportional to the concentration of the atoms in the flame. Determining the wavelength of the absorbance bands gives the identity of the atoms present while determining the intensity of the absorbance band gives the concentration of the atoms in the sample. The measurements of absorbance are fed into Beer-Lambert law to determine concentration using the expression, $A = \varepsilon bc$,

Where; A = absorbance (No units), b = path length (cm), c = molar concentration (mol

dm^{-3}), ε = molar absorptivity (dm^3 mol^{-1} cm^{-1}). Calibration is done such that a given

absorbance gives a corresponding concentration.

2.9.2 X-Ray Diffraction (XRD) Analysis

XRD is a versatile non-destructive analytical technique that reveals detailed information

about the chemical composition and crystallographic structure of natural and

manufactured materials. It is a rapid analytical technique used primarily for phase

identification of crystalline materials and can provide information on unit cell

dimensions. XRD is the basic analytical tool used for identification and characterization

of clay minerals (Brindley and Brown, 1981).

2.9.2.1 Principle of XRD

X-ray diffraction is based on constructive interference of monochromatic X-rays and a

crystalline sample. X-rays are produced by the rapid deceleration of fast-moving

electrons as they impinge on matter (Klug and Alexander, 1974). X-ray diffraction

analysis uses monochromatic radiation. Intense X-radiation at a specific wavelength can

be produced when electrons from a source (e.g., tube filament) dislodge inner shell

electrons from the atoms of the metal target. Instantaneous replacement of the dislodged

electron by an electron from a specific lower energy shell results in the quantum release

of a packet of energy corresponding to a specific wavelength and termed *characteristic*

radiation (Figure 2.10), (Harris and White, 2007). These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength λ, of electromagnetic radiation to the diffraction angle θ and the lattice spacing d in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns (Moecher, 2004). The crystalline substances act as three dimensional diffractions gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice (Max von Lane, 1912). A crystal lattice is a regular 3-dimentional distribution of atoms in space with atoms arranged such that they form parallel planes separated by a distance d, which varies according to the nature of the material. Spectral peaks are produced which give the identity and intensity of the clay minerals (Chipera and Bish, 2001).

2.9.2.2 Instrumentation and Working of XRD

X-ray diffractometer consists of a cathode ray tube, a sample holder and an x-ray detector. X-rays are generated in the cathode ray tube by heating the filament to produce

electrons which are then accelerated towards the target material by applying a voltage

difference. The accelerated electrons bombard the target material and dislodge inner shell

electrons thereby creating a vacuum. Electrons from higher energy levels then release

energy and occupy void lower energy level and cause production of characteristic x-ray

spectra. The spectra produced comprises of several components, the most common being

K_α and K_β (Figure 2.10).
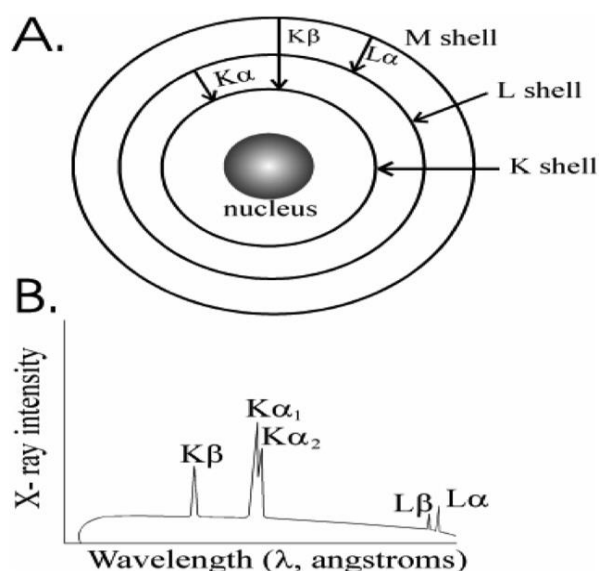
Figure 2.10 (A) Schematic of an atom, depicting electron shells and the energy transitions for Kα, Kβ, and Lα characteristic radiation. (B) Generalized depiction of an X-ray spectrum, showing peaks in intensity at wavelengths (energy levels) corresponding to characteristic radiation.

The specific wavelengths are characteristic to the target material which can either be Cu,

Fe, Mo or Cr with Cu being the most commonly used target material for single crystal

diffraction. The x-rays are filtered to produce a monochromatic radiation, collimated and

directed into the sample. As the sample and detector are rotated, the intensity of the reflected x-rays is recorded and peak intensity is recorded when the geometry of the incident x-rays impinging the sample satisfies Bragg's equation and constructive interference occurs. The peak signal is recorded by the detector, processed and converted into a count rate which is then printed in the output device or computer. The geometry of an x-ray diffractometer is such that the sample rotates in the path of collimated x-ray beam at angle θ while the x-ray detector rotates at angle 2θ.

2.9.3 Infrared Spectroscopy (IR)

Infrared spectroscopy is a rapid and non-destructive physical method universally applicable to structural analysis. The technique is so versatile that it can be used both as a source of physical parameters of crystal lattice determination, and as a means of eliciting purely empirical qualitative relationships between specimens (Wilson, 1996). The technique investigates the vibrational energy levels of a molecule by measuring its infrared absorption spectrum (Whiffen, 1972). An IR spectrum can serve as a fingerprint for mineral identification, but it can also give unique information about the mineral structure, including the family of minerals to which the specimen belongs and the degree of regularity within the structure, the nature of isomorphic substituents, the distinction of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities. Generally, IR analysis of minerals yield useful information supplementary to that given by XRD and thermal studies (Farmer, 1968).

2.9.3.1 Principle of Infrared Spectroscopy (IR)

Infrared spectroscopy is an absorption spectroscopy arising from interaction of electromagnetic radiation with vibrating molecular bonds. Each vibrational motion of a molecule occurs with a given frequency which is characteristic of the molecule and the particular vibration. Clays have molecular bonds which stretch and undergo deformations asymmetrically during absorption of radiations hence enable analysis by IRS. Examples of active bonds in clay molecules are Si—O, Al—O, OH--, Al--Al--OH bonds, Al—Mg—OH, Al—O—Si, Al—Fe^{3+}--OH and others. The energy involved in a particular vibration is characterized by the amplitude of the vibration so that the higher the vibrational energy, the larger the amplitude of the motion (Khandpur, 2007). The molecule may be made to ascend to higher energy level by absorbing a quantum electromagnetic radiation. The molecule gains vibrational energy with a frequency equal to the frequency of that vibration. Absorption of this energy is manifested by an increase in amplitude. The frequency of absorbed radiation can be measured by determining the frequency of light absorbed by the sample. An IR spectrum is displayed as a plot of the energy of the infrared radiation expressed in wave numbers against the light transmitted by the compound. Transmittance is defined here as the radiant power of radiation incident to the sample divided by the radiant power transmitted by the sample. When an incident radiation I, interacts with the vibrating molecules in the clay, the molecules absorb some energy and the remainder is transmitted. The amount of energy absorbed by a sample is proportional to the amount of absorbing species. The intensity of transmitted radiation Io

is used to determine the concentration of the sample according to Lambert's law, **I = Io exp (-εcl),**

where, I = the intensity of incident radiation, Io = intensity of emitted radiation,

l = length of the sample, c = concentration of the specimen,

ε = constant characteristic with the transition

For identification of the minerals in clays, the infrared spectrum of the sample is used. The infrared spectrum for each mineral is characteristic and different from that of the other (Wilson, 1996).

2.9.3.2 Instrumentation in IR

Infrared spectrophotometers have three basic parts which comprises of the source of radiation which is commonly an inert solid body which is heated electrically to temperatures between 1500 ^{o}C and 2000 ^{o}C, the monochromator for dispersing the radiation and the detector which registers the residual intensity after selective absorption by the sample.

2.9.4 Ethylenediaminetetraacetic Acid (EDTA) Titration`

This is a complexation titration technique involving use of EDTA to complex with the metal cations in solution and produce a colour change on the indicator at the equivalent point. EDTA is assigned the formula H_4Y , its disodium salt Na_2H_2Y, and its complex-forming ion in aqueous solution represented as $[MH_2Y]^{n-4}$. EDTA reacts with all metal ions in a ratio of 1:1 thereby making calculations of the moles of metal ions possible. The

end-point for reaction with a specific cation is pH-dependent thereby making a given metal to be titrated at a specific pH. The efficiency of metal-EDTA complex formation is determined by concentration of the H_2Y^{2-} ion, the pH of the solution, the solubility of the metal hydroxide, and its solubility constant (Mendham *et al.,*1989).

CHAPTER THREE

MATERIALS AND METHODS

3.1 The Study Area

Kano plains are located in Kisumu County in the Republic of Kenya. The study area is found between latitude E $34^\circ25'$, E $35^\circ50'$ and longitude $0^\circ00'$ and N $0^\circ24'$ and is about 60 km^2 as shown in the map in figure 3.1.
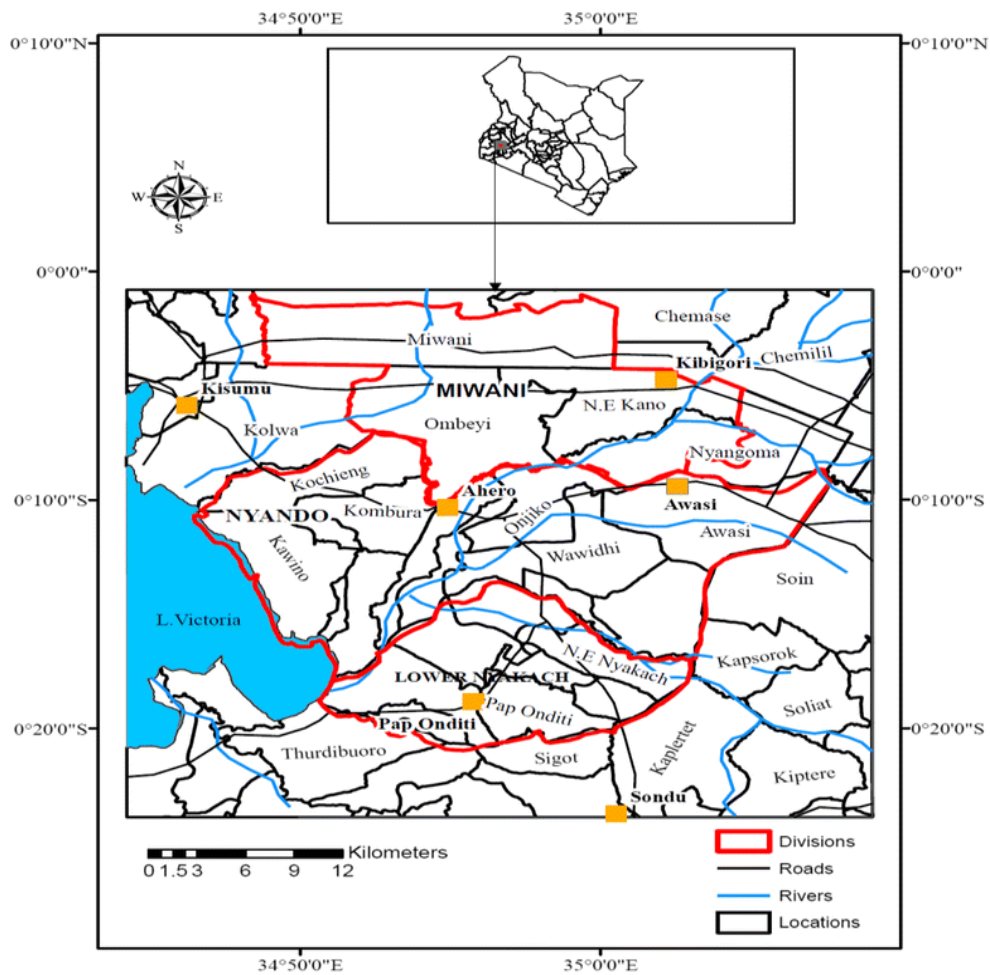
Figure 3.1 Map of Kano Plains, Kisumu County, Kenya
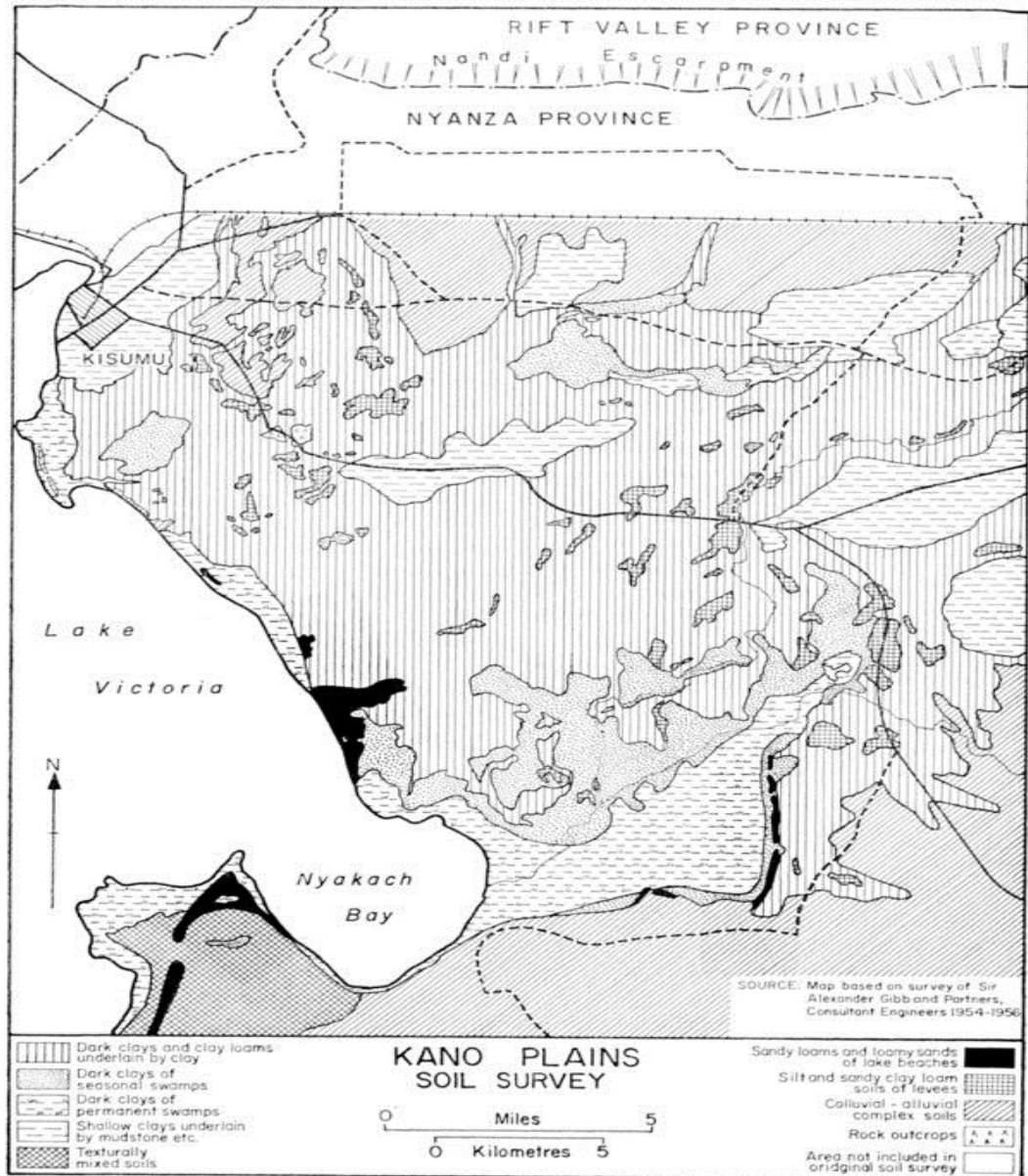
Figure 3.2 Soil survey map for Kano Plains, Kenya

Soil map of Kano Plains (Figure 3.2) reveal that the soils are majorly clay of different depths mixed sparingly with loams and a few areas with sandy soils. This is supported by physical clay characteristics of the soils such as plasticity when wet, poor drainage which partly lead to flooding due inability to absorb water leading to surface run-off, hardening and cracking of the soils during dry seasons.

3.2 Sampling

Eight sampling sites of about 5 Km apart were randomly selected within the study area. The sites were limited to eight due to costs involved in the experimentation processes. Three sampling points about 15 m apart were identified at each of the sites. The ground was cleared of vegetation and any organic matter and soil dug to about 60 cm (about 2 feet) depth to eliminate as much of the organic matter as possible and obtain set clay soils. About 500 g of clay was collected and kept in labeled clean, dry polythene bags. The samples were dried on a polythene sheet in the sun for six days and then mixed thoroughly and labeled to get a representative sample for the site (Christian, (2005). The procedure was repeated for the other sampling sites. The sampling sites were identified and numbered as in Table 3.1, and the sampling area shown in diagram 3.1.

Table 3.1. The sampling sites and sample indexing

S/No.	Sample No.	Sampling Site	Grid Reference
1	3076	Nyaidho River Bank(Oren)	E 35º05', S 0º11'
2	3077	Chiga Kolwa Village	E 34º52', S 0º07'
3	3078	Thurgem Secondary School	E 35º01', S 0º18'
4	3079	Riat Market	E 34º51', S 0º15'
5	3087	Karanda Primary School	E 34º70', S 0º11'
6	3098	Okana Site	E 34º50', S 0º08'
7	3100	Anywang' River bank	E 34º50', S 0º05'
8	3104	Kobura Rice Scheme	E 34º75', S 0º10'

3.2 Apparatus, Chemicals and Materials

All apparatus and chemicals used were of analytical grade and had the standard specifications for the analyses. Specifications of additional apparatus and instruments used include;

i)   Jenway pH meter, Model 3510 manufactured in UK

ii) Sartorius top pan electronic weighing balance, Supplied by Acheles Kenya, Ltd, Nairobi

iii) Atomic Absorption Spectrometer named Spectro AA.10(Varian), Supplied by Labtec with calibrations done using SY-2 and MRG rock standards supplied by Canadian Centre of Mineral and Energy Technology (CCMET). SY-2 calibrations were used for analyses of all elements except Ti where MRG rock standards were used because Ti levels in SY-2 rock standards was low compared to those in MRG (Table 3.2).

Table 3.2 Percentage mineral composition of rock standards, (CCMET, 1991)

Rock standard	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
SY-2	60.07	12.15	5.92	2.66	8.03	4.37	4.52	0.15	0.33	0.07
MRG	39.09	8.46	17.94	13.55	14.71	0.74	0.18	3.69	0.03	0.09

The instrumental conditions for AAS analysis for different elements were set as indicated in table 3.3.

Table 3.3 Instrumental conditions and settings for AAS analysis (CCMET, 1991)

Element	Lamp current(A)	Slit width (nm)	Wavelength (nm)	Acetylene Flow(Psi)	Photomultiplier voltage(V)	Flame type
Si	7	0.2	251.6	4.5	359.3	N_2O-acetylene
Al	6	0.5	309.3	4.5	287.4	N_2O-acetylene
Fe	8	0.2	248.3	1.5	340.5	Air-acetylene
Ca	None	0.5	422.7	4.5	231.1	N_2O-acetylene
Mg	3	0.5	285.2	1.5	318.6	Air-acetylene
Mn	5	0.2	279.5	1.5	349.9	Air-acetylene
Ti	10	0.5	364.3	4.5	303.0	N_2O-acetylene
K	None	1.0	766.5	1.5	353.5	Air-acetylene
Na	None	0.5	589.0	1.5	365.5	Air-acetylene

iv)   X-Ray Fluorescence (XRF) spectrometer, Mini Pal 2 supplied by Philips

The voltage and current settings for analysis of different elements are done automatically by the Mini Pal software upon selection of the element Table 3.4). Calibrations for the analyses are also automated using Rock standard samples.

Table 3.4 XRF voltage and current settings for analysis of elements in clay samples

Element (in oxide form)	Voltage setting (kV)	Current setting (mA)
SiO and Al_2O_3	4.09	1.000
Fe_2O_3	20.00	0.010
MnO	8.00	0.100

v)   Infrared Spectroscopy (IRS)FTIR-8400 model Supplied by Shimadzu, Japan was used. Mini hand press Model MHP-1 was used to prepare pellet discs. Polystyrene mortar and pestle were used to mix and grind clay and KBr into powder. Chemical balance model AUY 220 from Shimadzu Corporation Japan was used in weighing clay samples and KBr.

vi)   X-ray diffractometer   Model D_2Phaser supplied by Bruker was used. Settings were 2θ, Cu operated at a voltage and current of 40 kV and 30 mA respectively.

vii)   Pulveriser: Name: SIEBTECHNIK, Model: TEMA B.V, Model T 5250 Jaw crusher Supplied by Denver, England.

viii)   **Furnace** Nabertherm TR 235-11z-1899 IEC 337/VDE 066, AC 21 220V ~ /16A Model N41/H 380 V 3N ~ 50 Hz 23 A

ix)   Pelleting machine Herzog, Type TP 2 OP Mazchinenfabric + Co, D – 49086 Osnabruck

–Germany

3.3 Sample Pre-Treatment and Analysis

3.3.1 Drying and Grinding Of the Samples

The samples were transferred into clean glass beakers, dried in the oven at 105 ºC for six

hours and then cooled in a dessicator. The dried samples were fed into the primary

crusher and then secondary crushers of the Siebtechnik model T 5250 ball mill steel

mortar and ground into powder sizes suitable for use in XRD, XRF instruments, and

digestion by inorganic acids for subsequent laboratory analyses (Norton, 1974,

Richerson, 1992).

3.3.2 Digestion for AAS Analysis

Exactly 0.1 g of dry powder was weighed in an electronic balance and transferred into a

clean Teflon bottle. An automatic liquid dispenser was adjusted and used to add 1.0 ml of

aqua regia solution. Another clean dispenser was used to add 3.0 ml of hydrofluoric acid

to the mixture. The bottle was then corked and the mixture allowed to digest for 12 hours.

Accurately measured 50.0 ml saturated boric acid was then added to the mixture and

allowed to digest for one hour. 46.0 ml of 1:1 boric acid: water mixture was then added to

the solution to make 100 ml sample. 10.0 ml of digested sample was accurately measured

in a clean automatic liquid dispenser and diluted to 100.0 ml in 100 ml volumetric flask in readiness for AAS analysis.

3.3.3 Pelleting for XRF Analysis

Oven dried clay powder of 10.0 g was accurately weighed in an electronic weighing balance and transferred into a clean dry porcelain crucible. Five grammes of starch powder was weighed and added to the sample. The mixture was ground and uniformly mixed into a fine powder using the pestle and then transferred into the pellet binder. The clay-starch mixture was placed into a compressor and compressed to 175 kN to form clay pellets. The pellets were then labelled and analysed for mineral composition.

3.3.4 Preparation of Alkali Halide Pressed Discs for IR Analysis

About 2.0 mg of dry powdered clay was mixed with about 170 mg of KBr crystals and ground for about 2 minutes in a polystyrene mortar with a pestle. The powdered mixture was fed into the "Mini hand press" and compressed into a disc. The disc was then placed in the sample holder of the IR spectrometer for mineral analysis.

3.3.5 Preparation for EDTA Titrations

3.3.5.1 Preparation of 0.05 M EDTA Solution

Analytical grade EDTA crystals of 18.60 g were accurately weighed and transferred into 1 L volumetric flask. About 600 ml of distilled was added and the mixture thoroughly

shaken to dissolve the crystals. More water was added to the mark and mixture shaken for homogeneity.

3.3.5.2 Preparation of Solochrome Black (Eriochrome Black T) Indicator

Accurately weighed dyestuff of mass 0.2 g was added to 15.0 cm^3 of triethanolamine and the mixture stirred to dissolve. A portion of 5.0 cm^3 absolute ethanol was then added to the mixture to reduce viscosity (Mendham *et al*., 1989).

3.3.5.3 Preparation of 0.01 M Zinc Sulphate Solution

 Hydrated zinc sulphate crystal weighing 2.8754 g was transferred into a clean I Litre volumetric flask. Distilled water was then added in portions with shaking till all the crystals dissolved. More distilled water was added to the mark and the mixture shaken for homogeneity (Mendham *et al.*, 1989).

3.3.5.4 Preparation of Standard 0.05 M Fe^{3+} Solution

Ammonium ferric sulphate, $(NH_4)_2SO_4, Fe_2(SO_4)_3$ weighing 24.12 g was transferred into a 1 L volumetric flask. Distilled water was then added in portions with shaking to dissolve the solid. More water was added to the mark and the mixture shaken to form a homogeneous solution (Mendham *et al.*, 1989).

3.3.6 Determination of Fe^{3+} and Al^{3+} In Raw and Acid-Treated Clays By EDTA Titration

3.3.6.1 Determination of Fe^{3+} in clay samples by EDTA titration

Using a pipette, 25 cm^3 portions of digested clay solution was placed in a conical flask and diluted to 100 cm^3 using de-ionized water. The pH was adjusted to 2-3 using ammonium hydroxide solution and hydrochloric acid complementarily. 5 drops of Variamine blue indicator was added and the mixture warmed to 40 ^{o}C. The solution was then titrated with approximately 0.05 M- EDTA solution till the blue colour turned grey just before turning yellow at the end-point. The experiment was done in triplicate and average titre used to determine the moles and later amount of Fe in the sample. [1 mole EDTA = 1 mole Fe^{3+}]. (Mendham *et al.*, 1989).

3.3.6.2 Determination of Al^{3+} In Clay Samples by EDTA Titration

Clean 25 ml pipette was used to transfer 25 cm^3 of clay solution into a conical flask and a slight excess of 0.01 M-EDTA added from a burette. The pH was adjusted to 7-8 using ammonium hydroxide and hydrochloric acid complementarily. The solution was boiled for a few minutes to ensure complete complexation of all Al, cooled to room temperature and the pH readjusted to 7-8. Solochrome Black/KNO_3 weighin50 mg was added to the mixture and the mixture rapidly titrated with standard 0.01 M-Zinc sulphate solution added from a burette till the colour changed from blue to wine red. Amount of Al in the sample was calculated using the difference between volume of 0.01 M EDTA from burette and 0.01 M zinc sulphate given that, [Every cm^3 difference between the volume of 0.01 M-EDTA added from a burette and the 0.01 M-Zinc sulphate solution

added from a burette used in the back-titration corresponds to 0.2698 mg Al] (Mendham

et al., 1989).

3.4 X-Ray Fluorescence Spectrophotometer (XRFS) Analysis

The prepared clay pellets were fed in the sample holders in the XRF spectrometer. The

setting for "application analysis" mode was selected from default program in the Mini Pal

software and the element of choice selected. The software has default calibrations for a

given element analysed and the analysis proceeds automatically on the press of a button.

The percentage composition of the element in oxide form is displayed on the screen. The

procedure as repeated for the other elements on test and the results recorded. The

application mode was used for analysis.

NB: The analysis for Fe was done based on "Ferric oxide" calibrations, while that for Al

was done using the "Alumina" calibrations.

3.5 X-Ray Diffraction (XRD) Analysis

Dried clay powder for each labelled sample was fed into the glass-walled sample holder

of the spectrometer. Each sample holder has a capacity that holds about 0.35 g of

powdered sample. The x-ray diffractometer was then set to rotate the sample holder

through angle θ while the detector rotates through 2 θ. X-rays of Cu α_k wavelength

1.54056×10^{-10} m was selected and used to scan the samples. The scans were taken

between 2 θ of 10° and 2 θ of 45° and increments of 0.04^o with a count time of 4 seconds

per step. The diffractometer produced signals on a screen and the names and formulae of the minerals printed. Clay mineral diffraction patterns contain a good deal of character. This character is manifested by the peak's position, intensity, shape, and breadth. Peak position is determined by the Bragg law which is written as $n\lambda = 2d\sin\theta$. If the analysis is one dimensional, l may be substituted for n and the equation rearranged to give $l\lambda/2d = \sin\theta$. Now we have two constants, $d = d(001)$ and λ, and if θ is small, the angle may be substituted for its sine and we have a working result of $\theta = l \times$ (constant). The importance of line breadth for qualitative analysis is that it tells us at a glance which reflections are due to clay minerals and which might be assigned to other minerals. In addition, all members of the $00l$ series from a given species have the same breadth (at low 2θ), so if your pattern contains broad (> 0.2 to $0.3°$) lines, some of which are broader than others, the sample contains more than one clay mineral types. Table 3.5 gives major d-spacings for some common minerals.

Table 3.5 Major d-spacings for some minerals that occur in soils, listed for each mineral in the commonly observed order of decreasing XRD peak intensity.

Mineral groups	Minerals	Major d-spacings $\overset{\circ}{A}$
Expansible phyllosilicates	Montmorillonite	18.0, 9.0, 4.49
	Vermiculite	14.4, 7.18, 4.79, 3.60
Feldspars	Albite	3.19, 4.03, 3.21
	Anorthite	3.20, 3.18, 4.04
	Microcline	3.24, 3.29, 4.22
	Orthoclase	3.31, 3.77, 4.22
Kaolins	Halloysite	0.7–10.0 (Hydrated), 7.6, 4.4, 3.4
	Kaolinite	7.17, 3.58,
Micas	Biotite	10.1, 3.37, 2.06
	Muscovite	10.1, 3.36, 5.04
Oxides, hydroxides	Anatase	3.51, 1.89, 2.38
	Gibbsite	4.85, 4.37, 2.39
	Goethite	4.18, 2.45, 2.70
	Hematite	2.69, 2.59, 1.69
	Ilmenite	2.74, 2.52, 1.72
	Quartz	3.34, 4.26, 1.82
	Rutile	3.26, 1.69, 2.49
Zeolites and related minerals	Analcime	3.43, 5.60, 2.93
	Palygorskite	10.4, 4.47, 4.26
	Sepiolite	12.1, 2.56, 4.31

3.6 Infrared (IR) Analysis

About 1-2 mg of dry, ground clay powder was mixed with about 170 mg of KBr in a polystyrene mortar and mixed uniformly with a pestle for 1-2 minutes. The mixture was then pressed into a disc using a hand press in readiness for analysis by Infared spectrophotometer (IRS) FTIR-8400 Model supplied by Shimadzu, Japan. The instrument was coupled to a computer programme that printed the spectra and recorded the wavenumbers of major clay mineral deformation bands in the region 4000-400 cm^{-1}.

The wavenumbers from the spectrum are then used to identify the corresponding minerals.

The appearance of ν (Si–O–Si) and δ (Si–O) bands also support the presence of quartz (Marel and Bentelspacher, 1976) a strong band at $3696 \cdot 7$ cm^{-1}, $3622 \cdot 5$ cm^{-1} and $3450 \cdot 4$ cm^{-1} indicate the possibility of the hydroxyl linkage. However, a broad band at $3450 \cdot 4$ cm^{-1} and a band at $1633 \cdot 4$ cm^{-1} in the spectrum of clay suggest the possibility of water of hydration in the adsorbent. The inter-layer hydrogen bonding in clay is assigned by a characteristics band at $3622 \cdot 5$ cm^{-1}. Most of the bands such as $3696 \cdot 7$ cm^{-1}, $3622 \cdot 5$ cm^{-1}, $3450 \cdot 4$ cm^{-1}, $1033 \cdot 3$ cm^{-1}, $914 \cdot 5$ cm^{-1}, $790 \cdot 9$ cm^{-1}, $693 \cdot 4$ cm^{-1}, $538 \cdot 8$ cm^{-1}, $468 \cdot 9$ cm^{-1} show the presence of kaolinite (Tuddenham and Lyon, 1960). The vibrations observed at $914 \cdot 5$ cm^{-1} indicate the possibility of the presence of hematite (Gadsen, 1975). The presence of bands at $3696 \cdot 7$ cm^{-1}, $3622 \cdot 5$ cm^{-1}, $3450 \cdot 4$ cm^{-1}, $2369 \cdot 8$ cm^{-1}, $1633 \cdot 4$ cm^{-1}, $1033 \cdot 3$ cm^{-1}, $914 \cdot 5$ cm^{-1} and $790 \cdot 9$ cm^{-1} indicate the possibility of the presence of illite (Wolf, 1963), whereas $3622 \cdot 5$ cm^{-1}, $1633 \cdot 4$ cm^{-1}, $1033 \cdot 3$ cm^{-1} are indicative of gypsum and $693 \cdot 4$ cm^{-1} shows the possibility of the presence of calcite (Gadsen, 1975). The corresponding values are given in table 4. Thus the results of IR are quite helpful in the identification of various forms of minerals present in the used sorbents. IR spectra of these sorbents show adsorption band at $3622 \cdot 5$ cm^{-1} of clay corresponding to H_2O vibrations, indicating the hydrous nature of these materials and the presence of hydroxyl linkage. The peaks which identify the various clay minerals are shown in table 3.6.

Table 3.6 IR Identification peaks for clay minerals

Mineral	Identification Peaks (cm^{-1})
Kaolinite	3696, 3670, 3654, 3620, 3440, 1111, 1032, 1009, 913, 794, 754, 698, 538 470, 431 cm^{-1}
Illite	3621, 3340, 3625, 3421, 1024, 912, 829, 799, 750, 527, 471, 434 cm^{-1}
Montmorillonite	3626, 3424, 3419, 1634, 1039, 915, 843, 796, 623, 522, 466 cm^{-1}
Muscovite	3624, 3621, 3435, 3431, 1026, 912, 820, 790, 753, 632, 629, 474, 417 cm^{-1}
Chlorite	3548, 3424, 1628, 985, 758, 649, 548, 453, 435 cm^{-1}
Feldspar	1146, 1090, 1034, 1011, 780, 693, 688, 533, 464, 428 cm^{-1}
Calcite	2672, 2513, 1719, 1422, 876, 711 cm^{-1}
Quartz	1871, 1171, 1082, 796, 779, 695, 514, 460 cm^{-1}

IR spectra have been published by(Moenke, 1962;   Van der Marel and Beutelspacher, 1976; Ferraro, 1982; Kodama 1985).

3.7 Leaching the Clays with Mineral Acids at Room and Boiling Temperatures

Exactly 50 g each of dry powdered samples were weighed and placed in eight separate beakers. 100 ml of hydrochloric acid of different molarities of 12 M, 10 M, 8 M, 6 M, 4 M and 2 M respectively were added to each clay sample. The mixture was allowed to stand overnight. Another set of eight separate samples of 50 g were weighed and treated similarly with 100 ml of HCl of the aforementioned concentrations but the mixture boiled for one hour. A third set of eight samples of same mass are again taken but treated with sulphuric acid of molarities of 18 M, 10 M,   8 M, 6 M, 4 M and 2 M respectively at room temperature. A fourth set was treated similarly with the stated concentrations of sulphuric acid and heated to boiling temperature for one hour. Each of the mixtures was then filtered using Whatman No. 542 in sintered glass crucible and the residue rinsed several times with hot distilled water to wash as much acid as possible. The residue was

then dried in the oven at 105 $^{\circ}$C for six hours, cooled to room temperature and then subjected to analysis of residual Fe, Si and Al using AAS, XRF and EDTA titrations (For Fe and Al only). The percentage composition of the elements, expressed as oxides were recorded in tables and graphs. Physical factors of the clay like particle size, clay-acid ratio and duration of leaching were kept constant. The room temperatures of 25°C were also kept constant.

3.8 Loss On Ignition (LOI)

Powdered, dry clay sample of 0.10 g, accurately weighed was placed in a porcelain crucible and heated to 1000 $^{\circ}$C in a furnace for one hour. It was then placed in a dessicator and cooled to room temperature in an oven and re-weighed. The difference in weights was then used to determine the amount of organic matter and both combined and uncombined water in the clays.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The findings from elemental and mineral analytical procedures are presented in tables, diagrams and and graphs. Detailed results and findings are found in the appendices. The elemental compositions are expressed in percentage of oxides of the respective elements for raw and acid-treated clays as given by AAS and XRF. For the acid-treated clays, elemental compositions of the three major minerals, silica, alumina and iron(iii) oxide are given for residual clay after acid treatment since special interest was to determine levels of iron in clays after acid-treatment. For mineral analysis, the name, formulae and percentage composition of minerals are given as determined by XRD for both raw and acid-treated samples. The IR analysis results are presented by spectra for selected samples. The spectra of peaks of identified minerals are shown together with a summary of percentage composition and elemental constitution of individual minerals.

4.2 Chemical Analysis of Raw Clays in the Study Kano Plains

The major elements present in clays of Kano Plains, expressed in oxide form, are silica, SiO_2, Alumina, Al_2O_3, Iron (iii) oxide, Fe_2O_3 and water, H_2O, which is represented as Loss On Ignition (LOI). The other elements present in appreciable levels are potassium oxide, K_2O, sodium oxide, Na_2O titanium oxide, TiO_2 and calcium oxide, CaO, while those present in trace amounts are magnesium oxide, MgO and Manganese oxide, MnO.

The individual percentage compositions of the elements in each sample as given from AAS full Assay analysis is given in Table 4.1. The clays were found to have percentage range composition of 50-56% SiO_2, 12-18% al Al_2O_3, 4-10% Fe_2O_3, 10-15 % H_2O, 2-3% K_2O, 0.5-2.3% CaO, 1-2.5% TiO_2, 1-2% Na_2O, 0.4-1% MgO and 0.02-0.25% MnO with individual mean values given in table 4.2.

Table 4.1 Full Assay analysis of clays from Kano Plains by AAS with percentage composition of elements expressed in oxide form

Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	Na$_2$O	TiO$_2$	CaO	MgO	MnO	LOI	TOTAL
3076	62.37±0.02	14.33±0.45	4.33±0.11	3.11±0.08	1.86±0.01	1.22±0.01	0.80±0.01	0.45±0.01	0.20±0.01	10.03±0.06	98.76±0.47
3077	64.70±0.10	13.65±0.08	3.74±0.08	2.40±0.05	1.16±0.02	0.92±0.02	0.56±0.02	0.44±0.01	0.02±0.01	10.99±0.10	98.58±0.31
3078	61.44±0.06	12.54±0.37	5.94±0.06	2.84±0.02	1.76±0.01	1.18±0.01	1.04±0.01	0.77±0.01	0.24±0.01	11.00±0.11	98.79±0.43
3079	49.85±0.28	17.21±0.27	10.28±0.06	2.43±0.15	1.08±0.02	2.49±0.01	1.67±0.01	1.12±0.02	0.23±0.01	15.40±0.10	101.75±0.73
3087	45.47±0.18	14.47±0.36	5.94±0.06	2.31±0.02	1.06±0.03	2.01±0.01	1.71±0.02	1.06±0.02	0.21±0.01	14.17±0.15	88.37±0.36
3098	53.37±0.09	16.53±0.30	10.28±0.06	2.07±0.01	0.98±0.01	2.23±0.01	1.69±0.01	1.15±0.02	0.21±0.02	12.67±0.01	101.06±0.23
3100	54.24±0.12	17.95±0.19	5.68±0.10	2.50±0.02	1.35±0.02	1.52±0.01	1.15±0.02	0.73±0.01	0.13±0.01	9.77±0.15	95.01±0.13
3104	49.76±0.23	15.75±0.15	9.79±0.03	2.78±0.01	1.28±0.01	2.35±0.01	2.34±0.01	1.17±0.02	0.25±0.01	15.11±0.10	100. ±0.22

Table 4.2 Ranges of percentage elemental composition, as oxides, from Full assay AAS analysis of raw clays from Kano plains

Element(Oxide)	Range of percentage composition of oxides
SiO_2	45.47±0.18- 64.70±0.10
Al_2O_3	12.54±0.37- 17.75±0.19
Fe_2O_3	3.74±0.08- 10.28±0.06
K_2O	2.31±0.0.02- 3.11±0.08
Na_2O	0.98±0.01- 1.86±0.01
CaO	0.56±0.02- 1.71±0.02
MgO	0.44±0.01- 1.15±0.02
TiO_2	0.92±0.02- 2.49±0.01
MnO	0.02±0.01- 0.24±0.01
LOI	9.77±0.15- 15.40±0.10

Comparison of percentage range of composition of elements as analysed by different instruments is given in table 4.3.

Table 4.3 Percentage mean composition of different minerals in raw clays by different methods

Element	Method	Range of % oxide(Site mean)	Overall mean
SiO_2	AAS	45.47±0.18 - 64.70±0.10	55.15±0.26
	XRF	47.53±0.23- 65.92±0.04	57.10±1.30
Al_2O_3	AAS	12.54±0.37 - 17.95±0.19	15.30±0.17
	XRF	14.68±0.20 - 19.55±0.30	16.62±0.35
	EDTA	13.30±0.10 - 18.57±0.06	15.78±0.38
Fe_2O_3	AAS	3.74±0.08 - 10.28±0.06	7.00±0.53
	XRF	5.18±0.15 - 11.54±0.07	8.63±0.46
	EDTA	4.16±0.06 - 10.56±0.08	7.48±0.51
Na_2O	AAS	0.98±0.01 - 1.86±0.01	1.32±0.01
K_2O	AAS	2.07±0.01 - 3.11±0.08	2.56±0.07
	XRF	2.33±0.02 - 3.41±0.06	2.86±0.07
MgO	AAS	0.44±0.01 - 1.17±0.02	0.86±0.01
MnO_2	AAS	0.20±0.01 - 0.25±0.01	0.19±0.01
	XRF	0.05±0.00 - 0.19±0.01	0.14±0.01
TiO_2	AAS	0.92±0.02 - 2.35±0.01	1.74±0.02
	XRF	0.77±0.01 - 2.23±0.01	1.50±0.11
CaO	AAS	0.56±0.02 - 2.34±0.01	1.37±0.05
	XRF	1.18±0.00 - 2.84±0.02	1.93±0.12

From the results, it is established that Iron content in raw clays of 4-10% is far above the recommended levels of below 1% required for use in making high quality ceramics but suitable for making low quality ceramics. This justifies the hypothesis that iron content in the clays is high.

The results obtained from XRF gave elemental compositions of almost same ranges but are consistently slightly above those obtained from AAS analyses because of strong and severe X-ray absorption and enhancement effects in XRF but not in AAS (Brundle *et al.*, 1992). EDTA titration analyses were only done for Fe^{3+} and Al^{3+}. The percentage compositions from EDTA analysis were slightly above measurements from AAS but slightly below the measurements from XRF as shown in table 4.3.

4.3 Mineral Analysis of Raw Clays

4.3.1 XRD Analysis of Raw clays

Two samples were prepared and analyzed. One sample was from a single sampling site (3076) while the other was from a composite sample obtained by uniform mixing of clays from the eight sampling sites. The analysis of raw samples identified Quartz (SiO_2), Albite $Na(AlSi_3O_8)$, Kaolinite $Al_2Si_2O_5(OH)_4$, Muscovite $KAl(Si_3Al)O_{10}(O,F)_2$, Orthoclase $KAlSi_3O_8$, Montmorillonite $(Ca,Na)_{0.3}Al_2(Si, Al)_4O_{10}(OH)_2.xH_2O$ and Dickite $Al_2(Si_2O_5)(OH)_4$. The spectral peaks, names and formulae of minerals and percentage composition in the clays are shown in figures 4.1 (a) and (b). The results on formulae of the minerals establish that iron is not a structural component of the clay minerals though it was detected from elemental analysis. The iron detected from elemental analysis consequently exists as an accessory component of the clays from Kano Plains.
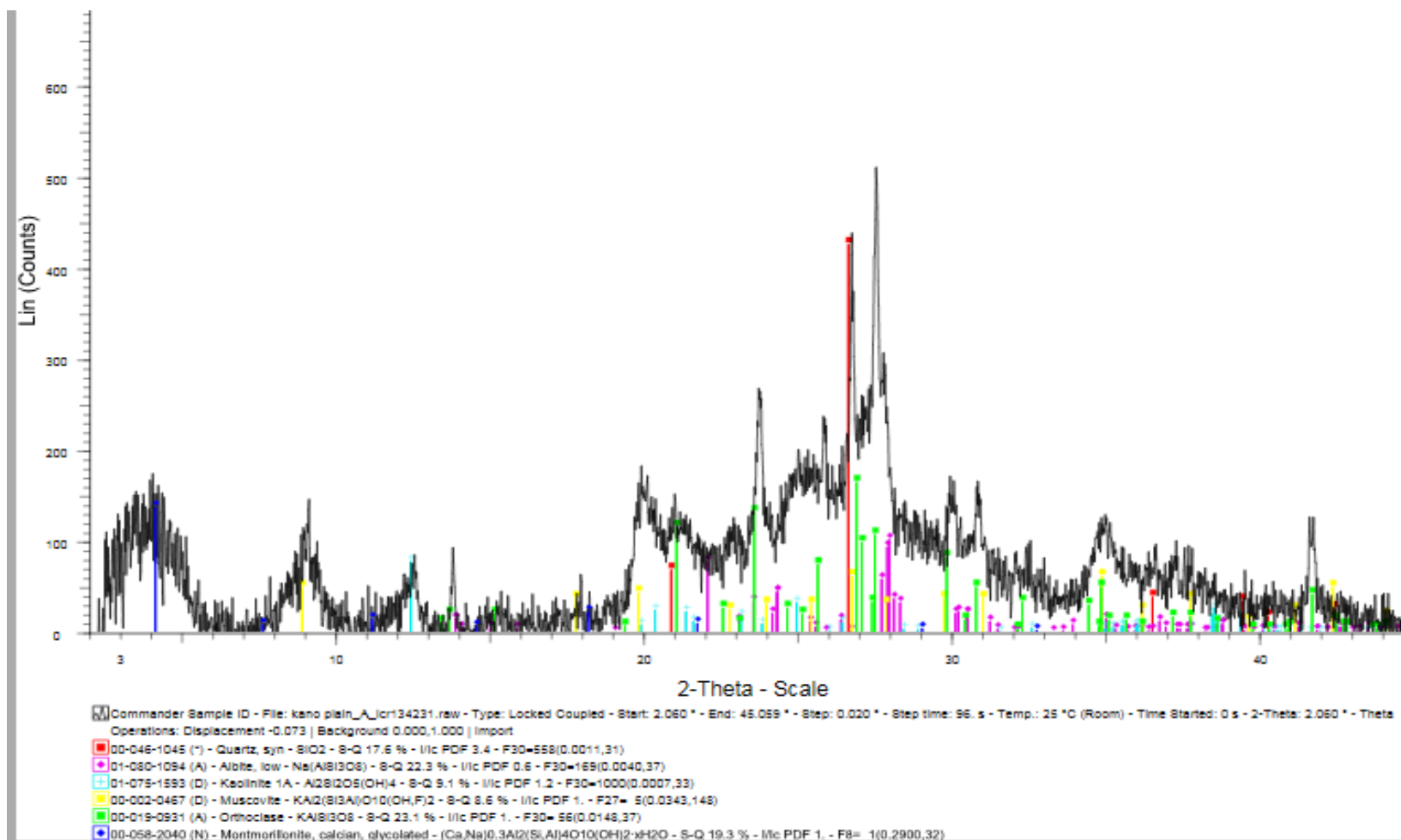
Figure 4.1(a): XRD analysis of raw clay sample from sample 3076, Oren from Kano plains, Kenya
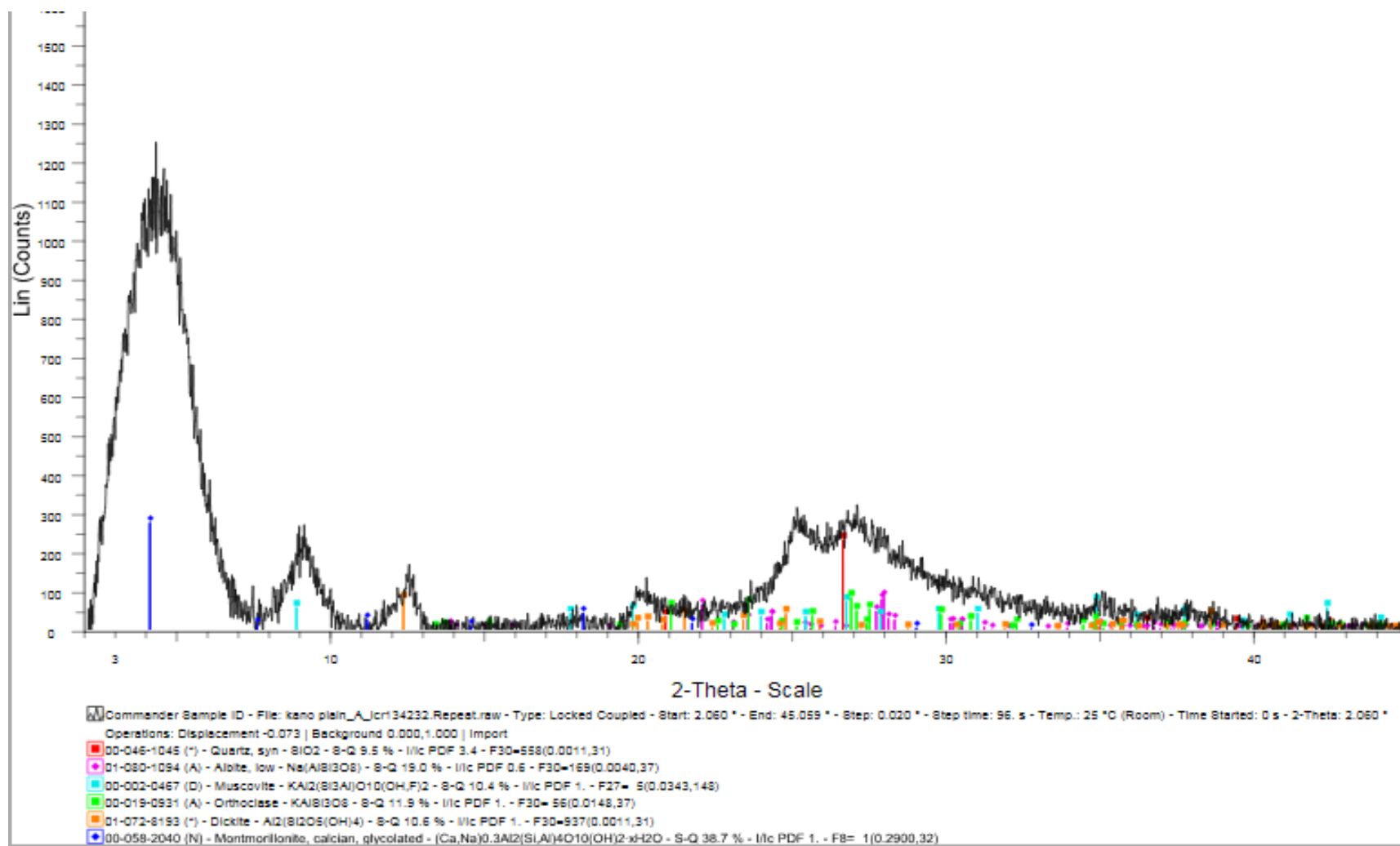
Figure 4.1(b): XRD analysis of raw clay sample from composite sample from Kano plains, Kenya

4.3.2 IR Analysis of Raw Clays

The IR bands found in the clay minerals from Kano plains range from about 3700cm^{-1} to 470cm^{-1}. The peaks at 3695, 3668, 3652, 3620 cm^{-1} are stretching inner bands of -OH groups characteristic of kaolinite. Other peaks that support presence of kaolinite are found at 1635.5 cm^{-1} which is deformation band of water for kaolinite, illite and montmorillonite, and 1100 cm^{-1}, Si-O stretching and 528.5 cm^{-1}, Al-O-Si deformation band of kaolinite. The IRS also indicate presence of montmorillonite evidenced by peaks at 1010-1030 cm^{-1}, In-plane Si-O stretching band, 935cm^{-1}, deformation Al-Al-O vibrational band, 820 and 757 cm^{-1} tetrahedral Al–O out-of-plane and Al–O–Si in-plane vibrations respectively, and 625 cm^{-1} , coupled out-of-plane vibrational band of Al-O and Si-O. Other minerals found in the clays are illite and biotite. Illite is identified by the peaks at 3606.6 cm^{-1}, stretching band of structural hydroxyl groups (both illite and biotite), 3436.9 cm^{-1} , stretching bond of water, and 1635.5 cm^{-1}, deformation band of water (Illite, kaolinite, montmorillonite).

The IR peaks observed, deformation assignment and characteristic minerals are summarized in Table 4.4. In general, the constituent units of clay minerals include hydroxyl groups, tetrahedral silicate/aluminate anions, octahedral metal cations, and interlayer cations. In IR-spectra OH-stretching modes lie in the spectral region of 3400-3750 cm^{-1}. Metal-O-H bending modes occur in the 600-950 cm^{-1} region. Si-O and Al-O stretching modes are found in the 700-1200 cm^{-1} range. Si-O and Al-O bending modes

dominate the 150-600 cm^{-1} region. Lattice vibrational modes in the far-IR range (33 - 333

cm^{-1}) are related to the interlayer cations (Schroeder, 2002). Some peaks observed during

IR analysis of clays from Kano plains are shown in figures 4.2(a) and (b).

Table 4. 4 The IR peaks identified, deformation assignments and corresponding minerals in clays of Kano planes

Peaks/Bands (cm^{-1})	Deformation assignment	Characteristic mineral
3695,3668,3652,3620	Stretching bands of inner OH groups	Kaolinite
3606.6	Stretching band of structural hydroxyl groups	Illite, Biotite
3436.9 (Sample 3077, 3079)	Stretching bond of water	Illite
1635.5 (All samples)	Deformation band of water	Kaolininte, illite montmorillonite
	Si-O stretching band	Kaolinite
1100 (3078)	In-plane Si-O stretching band	Montmorillonite, Biotite
1010-1030 cm $^{-1}$ (3079, 3098 3078)	Deformation Al-Al-O vib. band	Illite, Montmorillonite
935 (3076,	Stretching Si-O band	
902.6 (Samples 3076, 3077)	Coupled out-of-plane vib. band of Al-O and Si-O	
625 (3076,	Tetrahedral Al–O out of plane and Al–O–Si in plane vibrations respectively	Montmorillonite
820 and 757 cm $^{-1}$ (3100 3078,3076)	Deformation band of Al-O-Si	Kaolinite
528.5 (Sample 3076, 3079, 3100)		
466.7 (Sample 3076, 3078, 3100)	Deformation band of Si-O-Si	
		Kaolinite
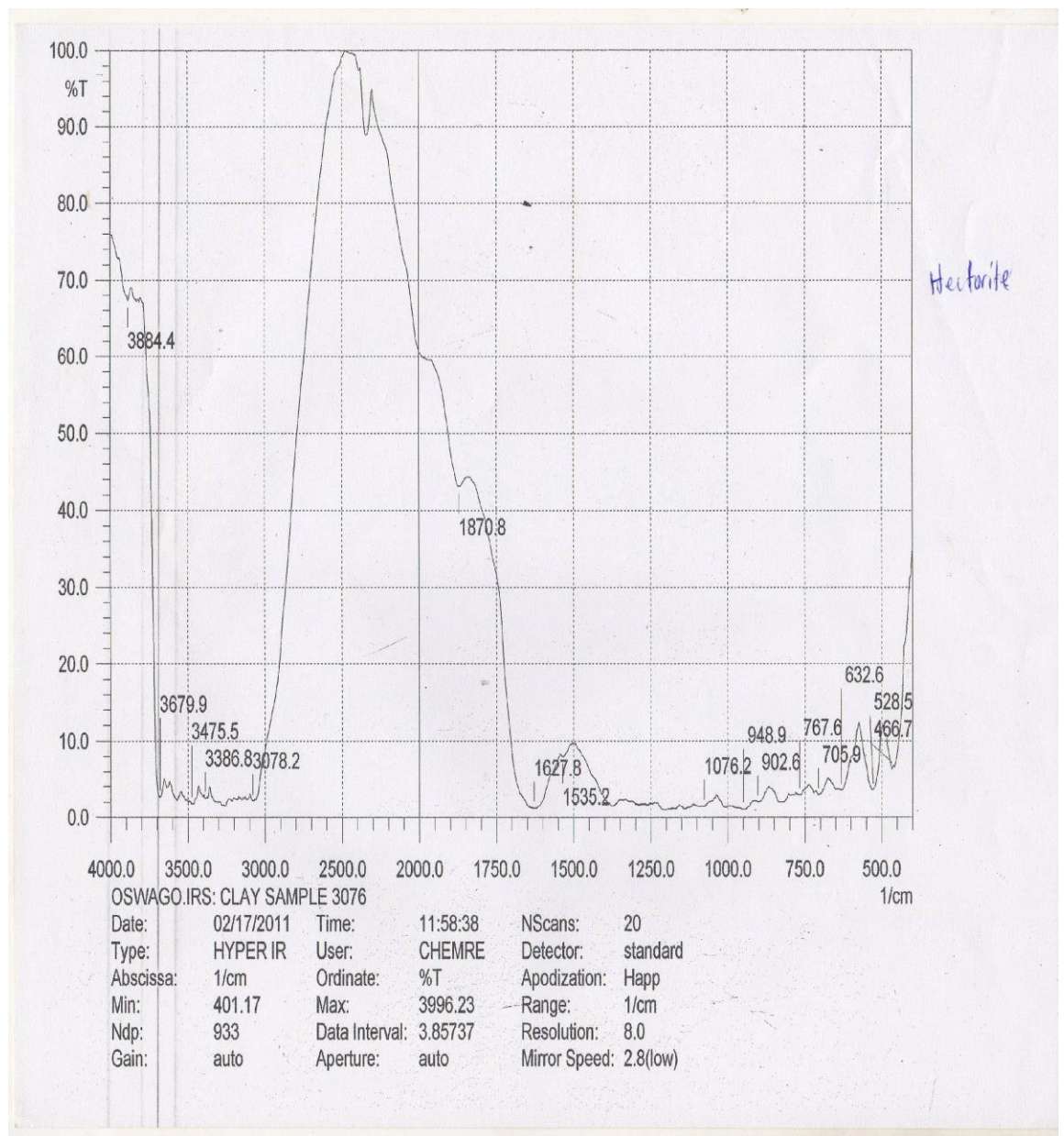
Figure 4.2(a) IR spectrum of clay sample from sample 3076 (Oren from Kano plains, Kenya
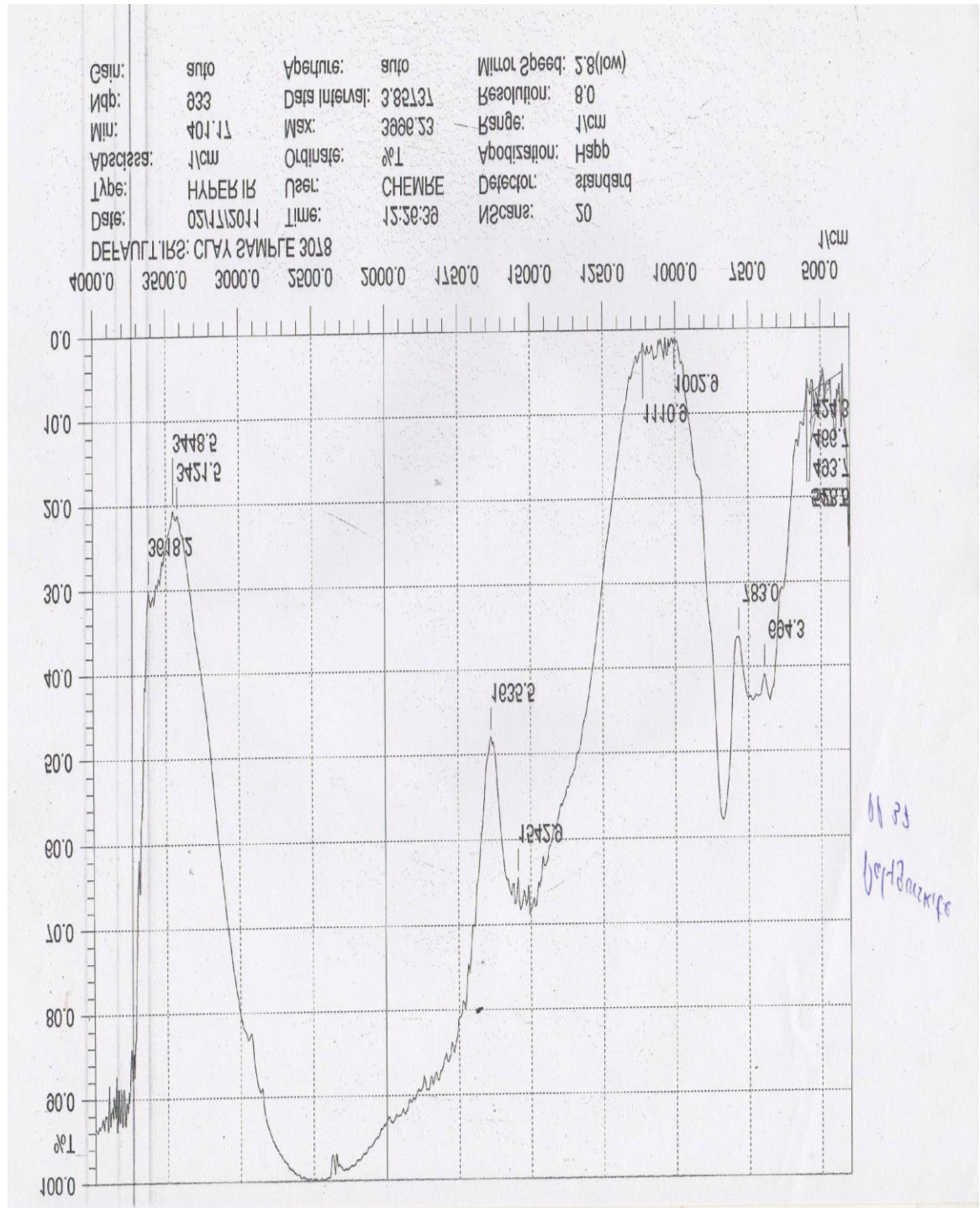
Figure 4.2(b) IR spectrum of clay sample from sample 3078 (Thurgem from Kano plains, Kenya

4.4 Chemical Analysis of Acid-Treated Clays

Acid treatment causes a reduction in composition of most elements with a higher reduction being achieved at higher concentrations and temperatures. The boiling temperature of acid-clay mixture varied differently with concentrations for HCl and H_2SO_4 (Table 4.5). The acid-clay mixture boiling temperature for HCl increases from 97^oC at 2M acid concentration to a maximum of 105^oC at 8M concentration and then reduces to about 76^oC at 11 M acid concentration due to higher volatility of the acid in the mixture at higher concentrations. For the less volatile H_2SO_4 the acid-clay mixture boiling temperature increases steadily from 99^oC at 2 M to about 310^oC at 18 M acid concentration.

Table 4.5 Boiling temperature of Acid-clay mixtures for HCl and H_2SO_4 at different acid concentrations

Acid concentration (Mol/L)	2	4	6	8	10	11	18
Boiling temperature of HCl-clay mixture (^oC)	97	100	104	105	98	76	■
Boiling temperature of H_2SO_4-clay mixture (^oC)	99	103	112	125	165	■	310

4.4.1 Treatment with Different Concentrations of HCl and H_2SO_4 at Room Temperature (25^oC)

Of the three major elements in the clays (SiO_2, Al_2O_3 and Fe_2O_3), there was general decrease in percentage composition of Fe with increase in acid concentration for the two inorganic acids. This is because the dissolution is both concentration and temperature

dependent. This is likely due to absence of iron in the mineral structure as evidenced from mineral analysis.

There was however no appreciable change in percentage composition of Al and Si and this was likely due to the presence of the elements in the mineral structure of the clays. The non-effect of composition of Si is due to both its being a structural component of the minerals and insolubility in mineral acids which cause increase in its percentage as the other elements dissolve (Table 4.6).

Table 4.6 Percentage SiO_2, Al_2O_3 and Fe_2O_3 in HCl-treated clays at room and boiling temperatures

Element (In oxide form)	Leaching Temperature	Raw	2M	4M	6M	8M	10M	11M
Fe_2O_3	% at 25°C	8.25	6.76	6.13	5.78	4.63	4.19	3.12
	% at Boiling Temperature	8.25	5.33	3.11	1.74	1.45	2.01	1.58
Al_2O_3	% at 25°C	15.90	14.20	15.51	14.59	14.42	13.70	15.37
	% at Boiling Temperature	15.90	13.68	12.47	12.24	14.24	13.22	12.52
SiO_2	% at 25°C	55.15	55.27	55.31	56.38	57.54	55.56	55.20
	% at Boiling Temperature	55.15	55.31	55.42	61.25	63.40	62.20	63.80

4.4.2 Treatment with Different Concentrations of HCl and H$_2$SO$_4$ at Boiling Temperatures

There is more enhanced dissolution of Fe and Al in the clays at boiling temperatures for the two acids than at room temperature. More Fe than Al is dissolved and washed out because of its existence as non-mineral constituent. The more enhanced acid dissolution is because acid concentration enhances removal of Fe and Al at temperatures above 30°C. The extraction of Al is both concentration and temperature dependent and is enhanced at higher temperature and concentration. This is why the percentage iron and aluminium decreases as the concentration increases (Myriam *et al*.,1998). For HCl, a steady decrease in percentage of minerals is observed for acid concentrations of 2M to 8M and then decreases from 10M and 11M due to lower boiling temperature for acid-clay mixture at the higher concentrations. The dissolution of Al in particular increases appreciably with increase in acid concentration to 4M HCl and then decreases with further increase in acid concentration. This may be due to increase in rate of diffusion of Al $^{3+}$ ions from solid to the solution with increase in acid concentration and diffusion of hydronium ions to a maximum of 4M. The decrease in extraction rate at higher concentrations may be due to collapse of the clay structure or blockage of H$^+$ ion diffusion by Al^{3+} ions, (Poppleton and Sawywer, 1977; Eisele, 1980; Eisele *et al*., 1983; Shanks *et al*., 1986). There is however a steady decrease in percentage Fe and, to a lesser extent, Al in the clays with increase in acid concentration for H$_2$SO$_4$ due to steady increase in boiling temperature of acid-clay mixture with increase in acid concentration.

The enrichment of SiO_2 as the other elements are dissolved is due to the mobilisation of the octahedral cations which pass into the solution as insoluble silica remain in solid state(Sabu *et al*.,1999; Pushpletha *et al*.,2005). The percentage elemental removal by H_2SO_4 is comparatively higher than that of HCl for any given concentration and temperature Tables 4.7(a) and (b). This may be attributed to more severity of sulphuric acid over hydrochloric acid which enables it to avail more H+ for exchange of cations during dissolution of clay minerals.

Table 4.7(a) Summary of average percentage Fe_2O_3 in raw and acid-treated clays at room and boiling temperatures

% Fe_2O_3 in:	Raw Clay	2 M	4 M	6 M	8 M	10 M	11 M	18 M
HCl RT	7.00 ±0.53	6.76 ±0.28e	6.13 ±0.25d	5.09 ±0.20c	4.63 ±0.18bc	4.19 ±0.19	1.90 ±0.10	
H_2SO_4 RT	7.00 ±0.53	6.38 ±0.27[d]	4.03 ±0.21[c]	4.00 ±0.19[c]	3.46 ±0.14[b]	3.3 ±0.14		2.05 ±0.08[a]
HCl BT	7.00 ±0.53	5.33 ±0.22	3.11 ±0.14	1.74 ±0.11	1.45 ±0.09	2.01 ±0.11	1.58 ±0.05	
H_2SO_4 BT	7.00 ±0.53	3.02 ±0.15[d]	2.21 ±0.13[c]	1.19 ±0.07[b]	1.02 ±0.06[ab]	0.93 ±0.04		0.76 ±0.03[a]

RT in all tables implies Room Temperature of 25ºC
BT implies Boiling Temperature which varies for different acids with different concentrations

Table 4.7(b) Summary of average percentage Al_2O_3 in raw and acid-treated clays at room and boiling temperatures

% Al_2O_3 in	Raw Clay	2 M	4 M	6 M	8 M	10 M	11M	18 M
HCl RT	15.30 ±0.37	14.20 ±0.21	15.51 ±0.15	14.59 ±0.19	14.42 ±0.19	13.70 ±0.22	15.37 ±0.20	
H_2SO_4 RT	15.30 ±0.37	12.72 ±0.17	12.58 ±0.12	12.10 ±0.08	11.21 ±0.17	12.14 ±0.14		12.15 ±0.14
HCl BT	15.30 ±0.37	13.68 ±0.16	13.75 ±0.15	12.40 ±0.21	14.24 ±0.26	11.87 ±0.22	12.52 ±0.20	
H_2SO_4 BT	15.30 ±0.37	12.54 ±0.13	12.28 ±0.11	26.47 ±15.57	10.89 ±0.24	9.93 ±0.29		9.47 ±0.24

The results obtained show that treating the clays with cold sulphuric, cold hydrochloric, hot hydrochloric and hot sulfuric lowered the iron levels to 2.05. 1.90, 1.45 and 0.76 respectively. Similar results had been obtained from treatment of clays from Mwea in Kirinyaga, Kenya with mineral acids (Muriithi *et al*., 2012). The best results obtained with boiled mineral acids at concentrations of 4- 6 molar. Reduction of iron content in the clays to about 1 % removes the undesirable fluxing and staining characteristics of the element from the clays and renders them suitable for use in production of high quality ceramic products.

The percentage alumina of 12- 18% in the clays is within the range recommended for extraction of the metal but is below the recommended range of above 40% percentage.
 Percentage silica is not affected by the mineral acids and increases as iron and aluminium are washed away. Percentage alumina is reduced to a very small extent by the mineral acids.

The increase in percentage silica however reduces plasticity of the clays hence lower the desired moulding property of clays.

During acid attack on clays, protons penetrate into the clay mineral layers and attack the structural OH groups. The resulting dehydroxylation is connected with successive release of the central atoms from the octahedra as well as with removal of Al from the tetrahedral

sheets. This causes gradual transformation of layered tetrahedral sheets to three-dimensional framework leading to formation of an amorphous partly protonated silica phase and destroys the parent mineral structure (Komadel *et al*., 1998; Komadel and Misaelides, 1999).

Percentage silica is not affected by the mineral acids and increases as iron and aluminium are washed away. Percentage alumina is reduced to a very small extent by the mineral acids. The increase in percentage silica however reduces plasticity of the clays hence lower the desired

4.5 Mineral Analysis of Acid-Treated Clays

4.5.1 XRD Analysis

Treatment of clays with 6M H_2SO_4 gave different results with respect to compositions and identifications of minerals from the raw samples. Montmorillonite, dickite, kaolinite and quartz that were detected in raw clays were not detected completely after acid treatment, while Ilmenite $(Ni_{0.5},Mn_{0.5})TiO_3$ and $(Ni_{.25}Mn_{.25}Zn_{.25}Mg_{.25})TiO_3$, microcline $(Ni_{.25}Mn_{.25}Zn_{.25}Mg_{.25})TiO_3$ and calcite $CaCO_3$ that were not detected in raw clays were detected only after boiling the clays with the acid. Percentage composition of Orthoclase and Albite in sample 3076 did not change appreciably after boiling with the acid but increased appreciably in composite sample. These findings are demonstrated by the spectral results from XRD in figures 4.2 (a) and 4.2 (b) and summarised data in tables 4.7 (a)-(b).

Results from sample 3076 and the composite sample gave different percentage compositions of the minerals for both raw and acid-treated clays. Percentage composition of Montmorillonite was 19.3% in sample 3076 and 38.7% in the composite sample. Muscovite had a percentage composition of 8.6% and 10.4% in sample 3076 and composite sample respectively. Orthoclase had a percentage of 23.1% and 23.1% in sample 3076 and composite samples respectively. Percentage kaolinite was 9.1% and only detected in sample 3076. Albite had a percentage composition of 22.3% and 19.0%, while quartz had percentages of 17.6% and 9.5% in sample 3076 and composite samples respectively.

Ilmenite, macrocline and calcite were only detected after boiling the clay samples with the acid. Ilmenite had percentages of 3.6% and 7.0% in sample 3076 and composite samples respectively. Macrocline had a percentage of 45.3% and only detected in boiled sample 3076. The peaks, names, formulae and percentage composition of minerals in acid-treated clays are shown in figures 4.3 (a)-(b) and a summary of percentage mineral composition is given in tables 4.8 (a) and (b).
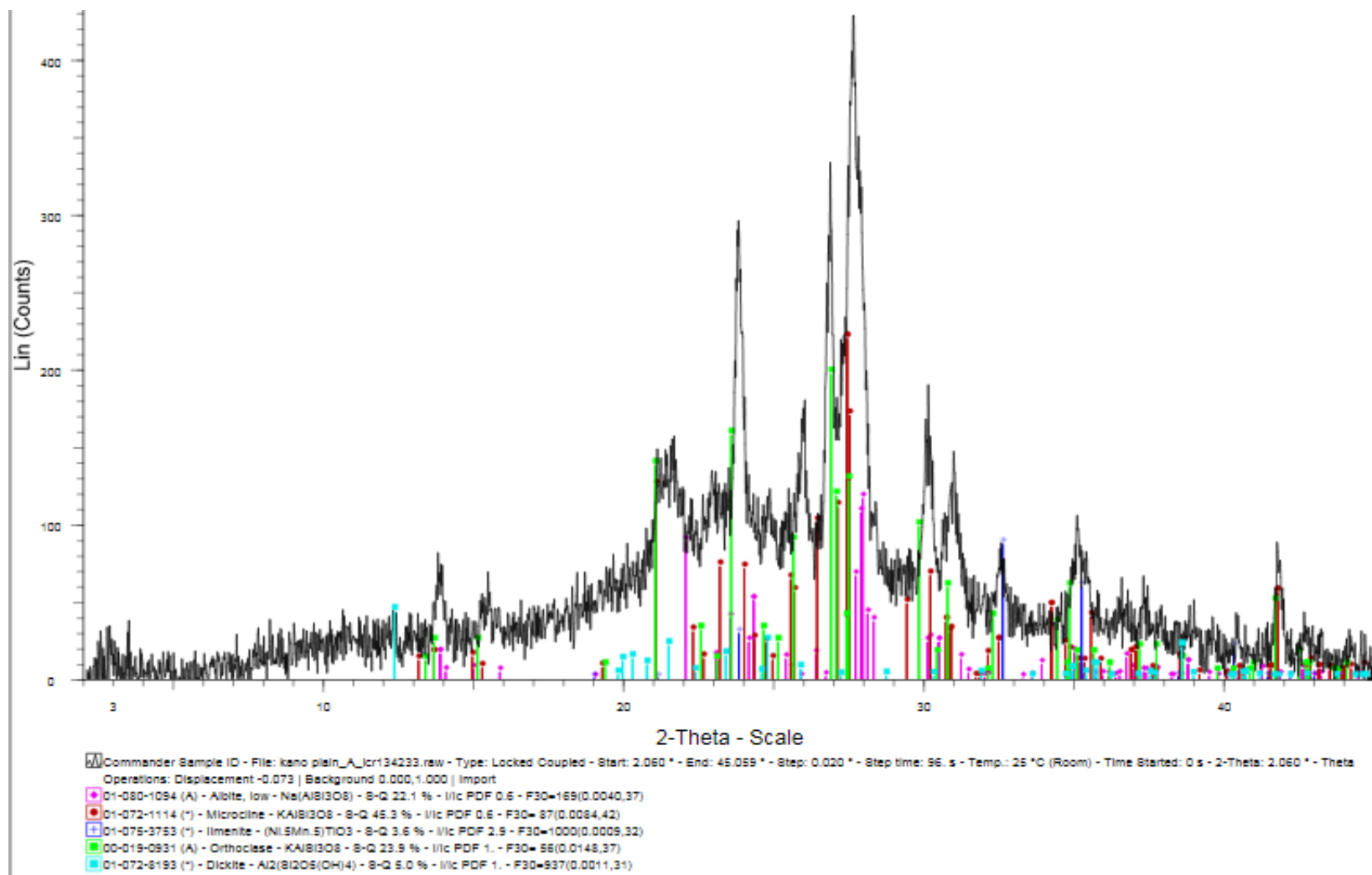
Figure 4.3(a): XRD analysis of acid-boiled clay sample from sample 3076(Oren from Kano plains, Kenya
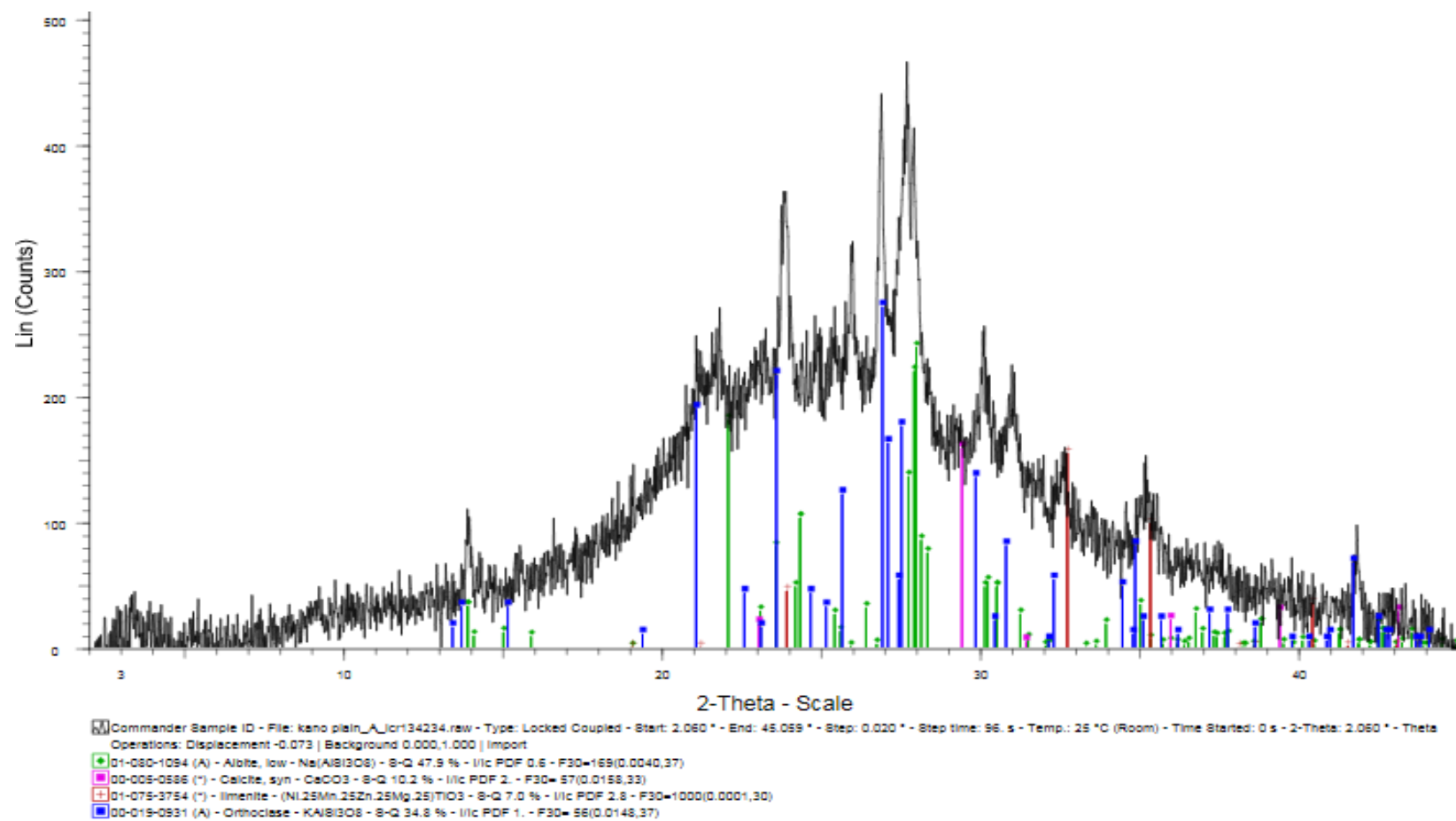
Figure 4.3(b): XRD analysis of acid-boiled clay sample from composite sample from Kano plains, Keny

Table 4.8(a) Minerals and % composition in raw and acid-boiled clay samples from one site sample (Oren-Sample 231) in Kano plains, Kenya

Sample	Mineral	Formula	% in raw sample	% in acid-boiled sample
3076 (One site sample)	Montmorillonite, Calcian, glycolated	$(Ca,Na)_{0.3}Al_2(Si, Al)_4O_{10}(OH)_2.xH_2O$	19.3	Not detected
	Kaolinite	$Al_2Si_2O_5(OH)_4$	9.1	Not detected
	Muscovite	$KAl(Si_3Al)O_{10}(O,F)_2$	8.6	Not detected
	Albite	$Na(AlSi_3O_8)$	22.3	22.1
	Orthoclase	$KAlSi_3O_8$	23.1	23.9
	Quartz	SiO_2	17.6	Not detected
	Microcline	$KAlSi_3O_8$	Not detected	45.3
	Ilmenite	$(Ni_{0.5},Mn_{0.5})TiO_3$	Not detected	3.6
	Dickite	$Al_2(Si_2O_5(OH)_4$	Not detected	5.0

Table 4.8 (b): Minerals and % composition in raw and acid-boiled clays in a composite sampling site from Kano Plains, Kenya

Sample	Mineral	Formula	% in raw sample	% in acid-boiled sample
Composite Sample	Montmorillonite, Calcian, glycolated	$(Ca,Na)_{0.3}Al_2(Si, Al)_4O_{10}(OH)_2.xH_2O$	38.7	Not detected
	Muscovite	$KAl(Si_3Al)O_{10}(OH,F)_2$	10.4	Not detected
	Albite	$Na(AlSi_3O_8)$	19.0	47.9
	Orthoclase	$KAlSi_3O_8$	11.9	34.8
	Quartz	SiO_2	9.5	Not detected
	Dickite	$Al_2(Si_2O_6(OH)_4$	10.6	Not detected
	Ilmenite	$(Ni_{.25}Mn_{.25}Zn_{.25}Mg_{.25})TiO_3$, $(Ni_{0.5},Mn_{0.5})TiO_3$	Not detected	7.0
	Calcite	$CaCO_3$	Not detected	10.2

There is the possibility that acid treatment and heating cause structural changes in the clays. This could lead to transformation of the clay structure leading to formation of different mineral structures and disappearance of some minerals after heating. This could explain the detection of Ilmenite, macrocline and calcite after combined acid-treatment and boiling, and disappearance of montmorillonite, muscovite and kaolinite after boiling with sulphuric acid.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDIES

5.2 Conclusions

i) Percentage range of elements, in oxide form, of clays of Kano plains are in the ranges of 50-65% SiO_2, 12-18% Al_2O_3, 4-10% Fe_2O_3, 0.4-1.0% MgO, 2.0-3.0% K_2O, 1.0-2.0% Na_2O, 0.02-0.25% MnO, 0.5-2.3% CaO, 1.0-2.5% TiO2 and 10-15% water by AAS with XRF giving percentage ranges of 48-66% SiO_2, 14-20% Al_2O_3, 5-12% Fe_2O_3, 2.6-3.4% K_2O, 0.05-0.19% MnO, 1.2-2.6% CaO and 0.8-2.2% TiO_2. EDTA titrations gave percentage range of Al2O3 and Fe_2O_3 as 13.3-18.6 and 4.2-11%, respectively.

ii) The percentage SiO_2, Al_2O_3 and Fe_2O_3 in acid-treated clays varied with acid type, concentration and temperature. Percentage SiO_2 in HCl-treated varied to a negligible extent and ranged from 55.15-57.54 at room temperature for variation of acid concentration from 2.0-12.0M and from 55.15-63.8% at boiling temperatures with a similar variation in acid concentration.

Percentage Al_2O_3 reduced from 15.9 in raw clay to 13.7% on treatment with HCl at room temperature, and from 15.9 to 12.24% on treatment with different concentrations of HCl at boiling temperatures.

Percentage Fe_2O_3 reduced from 8.25% in raw clay to 3.12% on treatment with HCl at room temperature, and from 8.25% to 1.58% on treatment with different concentrations of HCl at boiling temperatures.

Percentage SiO_2 in H_2SO_4-treated varied to a negligible extent and ranged from 55.15-57.54 at room temperature for variation of acid concentration from 2.0-12.0M and from 55.15-63.8% at boiling temperatures with a similar variation in acid concentration.

Percentage Al_2O_3 reduced from 15.9% in raw clay to 11.21% on treatment with H_2SO_4 at room temperature, and from 15.9% to 9.47% on treatment with different concentrations of H_2SO_4 at boiling temperatures.

Percentage Fe_2O_3 reduced from 8.25% in raw clay to 2.05% on treatment with H_2SO_4 at room temperature, and from 8.25% to 0.76% on treatment with different concentrations of H_2SO_4 at boiling temperatures.

iii)   The minerals present in raw clays of Kano plains includes Quartz (SiO_2), Albite $Na(AlSi_3O_8)$, Kaolinite $Al_2Si_2O_5(OH)_4$, Muscovite $KAl(Si_3Al)O_{10}(O,F)_2$, Orthoclase $KAlSi_3O_8$, Montmorillonite $(Ca,Na)_{0.3}Al_2(Si,Al)_4O_{10}(OH)_2.xH_2O$ and Dickite $Al_2(Si_2O_5(OH)_4$. Ilmenite, $(Ni_{.5}Mn_{.5})TiO_3$, $(Ni_{.25}Zn_{.25}Mg_{.25})TiO_3$ and Microcline, $KAlSi_3O_8$ are only detected after boiling the clays with mineral acid.

5.3 Recommendations

i)   Treatment of clays at high temperatures destroys the natural properties. Further studies should be carried out to establish the extent to which the destruction takes place.

ii)   The interconversion of raw clay minerals to different minerals by acid-treatment and boiling should be further investigated to establish in particular the possibility of obtaining ilmenite from the clays for extraction of titanium.

iii)   Plasticity of clay is reduced or affected by acid-treatment. Further work should be done to establish the extent of loss of plasticity and find methods of restoring plasticity after acid-leaching.

iv)   Further studies should be done to establish cement-manufacturing properties of clays in Kano plains given the possibility of conversion of the composite minerals into calcite.

v)   The effect of acid: sample ratio that is suitable for iron removal from the clay should be investigated.

vi)   Further research should be done on adjacent clays in the expansive Lake Victoria region to establish possibility of improving their ceramic production qualities and identify other technological uses.

vii)   The percentage Al in Kano clays is appreciable and further investigation on possibility of extracting aluminium should be explored.

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APPENDIX

APPENDIX 1

Tables of Detailed Elemental Analysis Results of Raw Clays from Kano Plains

Table 6.1 Full assay results from AAS, XRF and EDTA for raw clays from Kano plains, Kenya

THE ELEMENTAL COMPOSITION (FULL ASSAY) OF RAW CLAYS FROM KANO PLAINS, KENYA.											
SAMPLE	% SiO_2	%Al_2O_3	% Fe_2O_3	% K_2O	% Na_2O	%MgO	%MnO	% TiO_2	% CaO	% LOI	TOTAL
3076AAS	62.37±0.02	14.33±0.45	4.33±0.11	3.11±0.08	1.86±0.01	0.45±0.01	0.20±0.01	1.22±0.01	0.80±0.01	10.03±0.06	98.76±0.47
XRF	63.58±0.13	14.74±0.16	6.27±0.16	3.41±0.06			0.10±0.00	0.83±0.00	1.37±0.00	10.03±0.06	100.12
EDTA		13.62±0.04	5.22±0.10								
3077 AAS	64.70±0.10	13.65±0.30	3.74±0.08	2.40±0.05	1.16±0.02	0.44±0.01	0.02±0.01	0.92±0.02	0.56±0.02	10.99±0.10	98.58±0.31
XRF	65.92±0.04	14.76±0.19	5.18±0.15	3.08±0.03			0.05±0.00	0.77±0.01	1.18±0.00	10.99±0.10	101.93
EDTA		14.15±0.05	4.16±0.06								
3078 AAS	61.44±0.06	12.54±0.37	5.94±0.06	2.84±0.02	1.76±0.01	0.77±0.01	0.24±0.01	1.18±0.01	1.04±0.01	11.00±0.11	98.79±0.43
XRF	63.73±0.06	14.68±0.20	7.70±0.18	2.87±0.01			0.13±0.01	1.22±0.01	2.04±0.01	11.00±0.11	103.37
EDTA		13.30±0.10	6.37±0.04								
3079 AAS	49.85±0.28	17.21±0.27	10.28±0.06	2.43±0.15	1.08±0.02	1.12±0.02	0.23±0.01	2.49±0.01	1.67±0.01	15.40±0.10	101.75±0.73
XRF	51.59±0.16	17.60±0.20	11.54±0.07	2.33±0.02			0.19±0.01	2.23±0.01	2.55±0.01	15.40±0.10	103.43
EDTA		17.53±0.15	10.56±0.08								
3087 AAS	45.47±0.18	14.47±0.36	5.94±0.06	2.31±0.02	1.06±0.03	1.06±0.02	0.21±0.01	2.01±0.01	1.71±0.02	14.17±0.15	88.37±0.36
XRF	47.53±0.23	16.86±0.12	7.70±0.18	2.57±0.01			0.17±0.00	2.04±0.01	1.82±0.02	14.17±0.15	92.86
EDTA		15.30±0.10	6.37±0.04								
3098 AAS	53.37±0.09	16.53±0.30	10.28±0.06	2.07±0.01	0.98±0.01	1.15±0.02	0.21±0.02	2.23±0.01	1.68±0.01	12.67±0.12	101.06±0.23
XRF	55.25±0.11	17.72±0.21	11.54±0.07	2.65±0.02			0.19±0.01	1.91±0.00	2.32±0.02	12.67±0.12	104.25
EDTA		17.17±0.15	10.56±0.08								
3100 AAS	54.24±0.12	17.95±0.19	5.68±0.10	2.50±0.02	1.35±0.02	0.73±0.01	0.13±0.01	1.52±0.01	1.15±0.02	9.77±0.15	95.01±0.13
XRF	56.67±0.30	19.55±0.30	8.66±0.08	2.95±0.05			0.12±0.01	1.18±0.00	1.29±0.02	9.77±0.15	100.19
EDTA		18.57±0.06	6.14±0.11								
3104 AAS	49.76±0.23	15.75±0.15	9.79±0.03	2.78±0.01	1.28±0.01	1.17±0.02	0.25±0.01	2.35±0.01	2.34±0.01	15.11±0.10	100.58±0.22
XRF	52.56±0.10	17.05±0.55	10.43±0.13	3.06±0.06			0.16±0.00	1.85±0.01	2.84±0.02	15.11±0.10	103.06
EDTA		16.57±0.15	10.43±0.13								

Experimental data compiled in October, 2012.

Table 6.2 Full assay AAS analysis of raw clays from Kano plains

Percentage elemental composition (oxides) of clays in Kano Plains.

Sample	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	MnO_2	LOI	Total
3076	62.37 ±0.02	14.33 ±0.45	4.33 ±0.11	3.11 ±0.08	1.86 ±0.01	0.80 ±0.01	0.45 ±0.01	2.49 ±0.01	0.20 ±0.01	10.03± 0.06	98.76 ±0.47
3077	64.70 ±0.10	13.65 ±0.30	3.74 ±0.08	2.40 ±0.05	1.16 ±0.02	0.56 ±0.02	0.44 ±0.01	2.01 ±0.01	0.02 ±0.01	10.99± 0.10	98.58 ±0.31
3078	61.44 ±0.06	12.54 ±0.37	5.94 ±0.06	2.84 ±0.02	1.76 ±0.01	1.04 ±0.01	0.77 ±0.01	2.23 ±0.01	0.24 ±0.01	11.00± 0.11	98.79 ±0.43
3079	49.85 ±0.28	17.21 ±0.27	10.28 ±0.06	2.43 ±0.15	1.08 ±0.02	1.67 ±0.01	1.12 ±0.02	1.52 ±0.01	0.23 ±0.01	15.40± 0.10	101.75 ±0.73
3087	45.47 ±0.18	14.47 ±0.36	5.94 ±0.06	2.31 ±0.02	1.06 ±0.03	1.71 ±0.02	1.06 ±0.02	2.35 ±0.01	0.21 ±0.01	14.17± 0.15	88.37 ±0.36
3100	53.37 ±0.09	16.53 ±0.30	10.28 ±0.06	2.07 ±0.01	0.98 ±0.01	1.68 ±0.01	1.15 ±0.02	1.18 ±0.01	0.21 ±0.02	12.67± 0.12	101.06 ±0.23
3104	54.24 ±0.12	17.95 ±0.19	5.68 ±0.10	2.50 ±0.02	1.35 ±0.02	1.15 ±0.02	0.73 ±0.01	0.92 ±0.02	0.13 ±0.01	9.77±0.15	95.01 ±0.13

Table 6.3 Mean Percentage Composition of Different Minerals from different Instruments/Methods

% Mean composition of different minerals in raw clays by different methods

Parameter	AAS %(Mean±SE)	EDTA %(Mean±SE)	XRF %(Mean±SE)	p-value
SiO_2	55.15±1.36		57.10±1.30	0.303
Al_2O_3	15.30±0.37	15.78±0.38	16.62±0.35	0.042
Fe_2O_3	7.00±0.53	7.48±0.51	8.63±0.46	0.068
K_2O	2.56±0.07		2.86±0.07	0.002
MnO_2	0.19±0.01		0.14±0.01	0.010
TiO_2	1.74±0.12		1.50±0.11	0.150

Table 6.4 Percentage Fe₂O₃ in raw and H₂SO₄ - treated clay samples from Kano Plains, Kenya

AAS, XRF and EDTA titration results for % Fe₂O₃ in Raw and H₂SO₄-treated clays from Kano plains, Kenya													
Acid/Conc.	Raw	2M H₂SO₄ RT	2M H₂SO₄ BT	4M H₂SO₄ RT	4M H₂SO₄ BT	6M H₂SO₄ RT	6M H₂SO₄ BT	8M H₂SO₄ RT	8M H₂SO₄ BT	10M H₂SO₄ RT	10M H₂SO₄ BT	18M H₂SO₄ RT	18M H₂SO₄ BT
3076 AAS	4.33±0.09	3.09±0.04	1.46±0.01	2.72±0.05	0.68±0.01	2.52±0.06	0.67±0.05	2.66±0.08	0.68±0.06	2.69±0.08	0.61±0.02	2.93±0.06	0.53±0.04
3076EDTA	5.22±0.10	3.54±0.10	1.77±0.10	2.87±0.01	0.87±0.01	2.93±0.04	0.79±0.04	2.88±0.09	0.73±0.01	2.96±0.06	0.69±0.02	2.71±0.04	0.58±0.01
3076 XRF	6.27±0.06	4.41±0.02	2.65±0.24	3.52±0.05	1.58±0.07	3.51±0.07	0.93±0.07	3.22±0.08	0.82±0.06	3.03±0.07	0.81±0.02	2.87±0.09	0.59±0.05
3077 AAS	3.74±0.08	3.19±0.02	1.43±0.06	2.69±0.08	0.65±0.01	2.26±0.07	0.58±0.03	2.22±0.08	0.60±0.06	2.05±0.06	0.58±0.08	2.14±0.05	0.27±0.02
3077EDTA	4.16±0.06	3.46±0.06	1.88±0.02	2.87±0.03	0.87±0.03	2.85±0.05	0.67±0.02	2.41±0.06	0.80±0.09	2.21±0.10	0.82±0.06	2.39±0.03	0.52±0.01
3077 XRF	5.18±0.15	3.61±0.01	2.38±0.08	3.25±0.09	1.34±0.08	3.42±0.07	0.80±0.06	3.20±0.03	0.99±0.03	2.80±0.04	0.94±0.01	2.41±0.06	0.75±0.05
3078 AAS	5.94±0.06	4.80±0.02	1.99±0.22	3.99±0.08	1.26±0.07	3.37±0.09	0.80±0.06	2.80±0.01	0.73±0.03	2.03±0.05	0.79±0.02	1.45±0.01	0.66±0.07
3078EDTA	6.37±0.04	5.01±0.04	2.94±0.09	4.12±0.02	1.89±0.04	3.83±0.06	0.78±0.01	2.89±0.10	0.85±0.03	2.47±0.05	0.96±0.02	1.59±0.06	0.74±0.01
3078 XRF	7.70±0.08	5.80±0.08	3.53±0.11	5.25±0.02	2.58±0.01	4.17±0.02	0.85±0.05	3.50±0.05	0.79±0.07	3.18±0.04	0.80±0.02	1.39±0.07	0.76±0.04
3079 AAS	10.27±0.06	8.34±0.05	2.50±0.07	5.48±0.04	2.17±0.04	4.77±0.02	1.28±0.05	4.34±0.06	0.76±0.04	3.78±0.01	0.91±0.07	1.63±0.07	0.66±0.02
3079EDTA	10.57±0.07	8.66±0.03	2.87±0.12	5.78±0.09	2.87±0.02	4.89±0.08	1.53±02	4.69±0.05	0.80±0.03	3.94±0.05	1.00±0.03	1.71±0.02	0.72±0.02
3079 XRF	11.57±0.06	9.19±0.07	5.57±0.09	7.66±0.06	2.84±0.05	4.92±0.07	1.68±0.05	4.76±0.06	1.48±0.03	4.55±0.03	0.98±0.01	2.94±0.02	0.77±0.02
3087 AAS	9.67±0.07	7.70±0.01	2.58±0.11	6.86±0.08	1.46±0.01	5.84±0.10	1.34±0.04	4.40±0.07	0.76±0.04	3.88±0.04	0.76±0.01	1.05±0.01	0.58±0.03
3087EDTA	10.27±0.06	8.38±0.04	3.32±0.10	2.15±0.08	2.33±0.01	6.06±0.07	1.63±0.03	4.66±0.03	1.04±0.06	4.45±0.03	0.94±0.06	1.22±0.03	0.68±0.01
3087 XRF	11.27±0.05	9.18±0.07	5.57±0.10	6.46±0.07	3.84±0.04	6.60±0.05	2.38±0.03	5.34±0.08	1.37±0.10	5.21±0.05	1.28±0.07	2.84±0.07	0.97±0.01
3098 AAS	10.53±0.06	8.04±0.04	2.72±0.05	2.98±08	1.83±0.21	6.46±0.04	0.94±0.08	5.30±0.09	0.77±0.05	3.45±0.01	0.72±0.03	2.76±0.05	0.68±0.03
3098EDTA	11.13±0.05	8.44±0.07	2.98±0.02	1.83±0.04	2.70±0.06	6.58±0.09	1.25±0.06	4.86±0.60	1.06±0.03	5.04±0.08	0.78±0.01	2.86±0.02	0.88±0.02
3098 XRF	11.63±0.06	9.16±0.07	5.39±0.16	7.18±0.04	3.27±0.03	6.51±0.02	1.73±0.06	5.44±0.05	1.86±0.09	5.57±0.02	1.35±0.04	2.56±0.02	0.85±0.09
3100 AAS	5.97±0.08	3.48±0.01	1.90±0.09	1.54±1.08	1.90±0.10	2.74±0.05	0.60±0.09	2.46±0.09	0.55±0.07	2.10±0.07	0.58±0.05	1.42±0.06	0.47±0.04
3100EDTA	6.14±0.07	4.47±0.09	2.25±0.05	2.30±0.09	2.25±0.05	2.88±0.02	0.74±0.08	2.69±0.02	0.81±0.06	2.37±0.04	0.71±0.02	1.54±0.06	0.62±0.02
3100 XRF	8.66±0.08	5.21±0.07	2.61±0.15	4.27±0.11	2.45±0.02	3.21±0.01	0.93±0.06	2.92±0.04	1.03±0.01	2.48±0.07	0.79±0.05	1.66±0.01	0.72±0.02
3104 AAS	9.79±0.03	7.61±0.04	2.98±0.51	2.54±0.09	2.13±0.04	1.15±0.08	1.06±0.06	1.12±0.01	1.03±0.05	2.16±0.06	1.10±0.07	1.30±0.03	1.09±0.07
3104EDTA	10.43±0.05	8.35±0.02	3.74±0.06	3.42±0.05	3.74±0.06	1.89±0.01	1.73±0.05	1.67±0.01	1.41±0.06	3.10±0.02	1.38±0.07	1.56±0.01	1.37±0.04

Table 6.5 Percentage Fe$_2$O$_3$ in different concentrations of HCl and H$_2$SO$_4$

Sample	3076	3077	3078	3079	3087	3098	3100	3104
Raw	4.33 ±0.11	3.74 ±0.08	5.94 ±0.04	10.28 ±0.06	5.97 ±0.06	10.28 ±0.06	5.68 ±0.10	9.79 ±0.03
2M HCl	2.44 ±0.02	2.57 ±0.03	3.82 ±0.08	5.81 ±0.06	5.71 ±0.04	5.44 ±0.09	3.82 ±0.06	6.43 ±0.10
2M H$_2$SO$_4$	1.46 ±0.01	1.43 ±0.06	1.99 ±0.22	2.50 ±0.07	2.58 ±0.11	2.72 ±0.05	1.90 ±0.09	2.98 ±0.51
4M HCl	1.44 ±0.09	1.72 ±0.02	1.94 ±0.06	3.00 ±0.05	2.76 ±0.06	2.49 ±0.05	1.81 ±0.02	3.57 ±0.09
4M H$_2$SO$_4$	0.68 ±0.1	0.65 ±0.06	1.26 ±0.07	2.17 ±0.04	1.46 ±0.01	1.83 ±0.21	1.90 ±0.01	2.13 ±0.04
6M HCl	**0.78 ±0.04**	**0.89 ±0.08**	**0.79 ±0.02**	**0.88 ±0.05**	**1.89 ±0.02**	**1.04 ±0.02**	**0.53 ±0.03**	**1.83 ±0.08**
6M H$_2$SO$_4$	**0.67 ±0.05**	**0.58 ±0.03**	**0.80 ±0.06**	**1.28 ±0.05**	**1.34 ±0.04**	**0.94 ±0.08**	**0.06 ±0.09**	**1.06 ±0.06**
8M HCl	**0.89 ±0.05**	**0.94 ±0.08**	**0.88 ±0.02**	**0.80 ±0.01**	**1.72 ±0.04**	**0.56 ±0.05**	**0.71 ±0.08**	**1.02 ±0.01**
8M H$_2$SO$_4$	**0.68 ±0.06**	**0.60 ±0.06**	**0.73 ±0.03**	**0.76 ±0.04**	**0.76 ±0.04**	**0.77 ±0.05**	**0.55 ±0.07**	**1.03 ±0.05**
10 M HCl	0.68 ±0.01	0.96 ±0.07	1.58 ±0.05	1.72 ±0.02	1.04 ±0.06	2.76 ±0.06	1.05 ±05	1.01 ±0.03
10 M H$_2$SO$_4$	0.61 ±0.02	0.58 ±0.08	0.79 ±0.02	0.91 ±0.07	0.76 ±0.01	0.72 ±0.03	0.58 ±0.05	1.10 ±0.07
11M HCl	1.015 ±0.07	1.12 ±0.04	1.08 ±0.08	1.05 ±0.09	1.83 ±0.03	1.88 ±0.09	1.22 ±0.03	1.42 ±0.05
18M H$_2$SO$_4$	0.53 ±0.04	0.27 ±0.02	0.66 ±0.07	0.66 ±0.02	0.58 ±0.03	0.68 ±0.03	0.47 ±0.04	1.09 ±0.07

Table 6.6 Percentage Fe₂O₃ in raw and HCl - treated clay samples from Kano Plains, Kenya

Acid/Conc.	Raw	2M HCl$_{RT}$	2M HCl$_{BT}$	4M HCl$_{RT}$	4M HCl$_{BT}$	6M HCl$_{RT}$	6M HCl$_{BT}$	8M HCl$_{RT}$	8M HCl$_{BT}$	10M HCl$_{RT}$	10M HCl$_{BT}$	11M HCl$_{RT}$	12M HCl$_{BT}$
3076 AAS	4.340±0.05	3.640±0.08	2.440±0.02	3.625±0.04	1.440±0.09	3.245±0.04	0.785±0.04	3.305±0.09	0.885±0.05	3.210±0.04	0.680±0.01	0.730±0.02	1.015±0.07
3076 EDTA	5.220±0.06	3.900±0.03	3.053±0.06	3.907±0.06	2.303±0.05	3.467±0.05	1.210±0.01	3.707±0.03	1.137±0.03	3.300±0.01	1.027±0.08	0.997±0.03	1.183±0.03
3076 XRF	6.270±0.05	4.380±0.06	4.490±0.03	4.397±0.03	2.907±0.04	4.230±0.02	1.399±0.02	3.940±0.07	1.323±0.05	3.427±0.06	1.843±0.08	1.153±0.06	1.097±0.06
3077 AAS	3.737±0.08	3.253±0.07	2.577±0.03	2.797±0.03	1.720±0.02	2.413±0.07	0.887±0.08	2.247±0.08	0.937±0.07	2.167±0.08	0.963±0.07	1.123±0.04	1.430±0.09
3077 EDTA	4.163±0.06	3.590±0.07	2.793±0.02	3.183±0.06	1.907±0.04	3.137±0.06	1.363±0.06	2.773±0.01	1.200±0.01	2.560±0.04	1.053±0.06	1.347±0.03	1.443±0.01
3077 XRF	5.177±0.05	3.740±0.10	3.530±0.06	3.493±0.03	2.823±0.01	3.863±0.07	1.863±0.08	3.660±0.06	1.780±0.02	3.563±0.04	1.123±0.05	1.427±0.06	1.463±0.04
3078 AAS	5.940±0.06	4.927±0.03	3.823±0.08	4.443±0.07	1.943±0.06	3.857±0.06	0.787±0.02	3.370±0.04	0.880±0.02	2.153±0.05	1.577±0.05	1.503±0.01	1.080±0.01
3078 EDTA	6.370±0.04	5.300±0.08	4.493±0.02	4.887±0.03	2.387±0.06	4.123±0.09	0.920±0.03	3.693±0.06	1.053±0.04	2.460±0.06	1.830±0.03	1.713±0.03	1.267±0.04
3078 XRF	7.703±0.08	6.183±0.08	5.330±0.04	5.740±0.02	2.857±0.03	4.750±0.05	2.013±0.05	4.680±0.03	1.367±0.02	3.953±0.07	2.480±0.05	1.693±0.03	1.463±0.08
3079 AAS	10.267±0.08	8.460±0.06	5.813±0.06	7.000±0.02	3.000±0.05	5.633±0.03	0.881±0.05	4.567±0.02	0.803±0.01	4.067±0.05	2.200±0.04	1.720±0.02	1.050±0.09
3079 EDTA	10.567±0.01	8.897±0.04	6.310±0.06	8.220±0.07	3.560±0.03	6.263±0.07	1.265±0.06	4.923±0.02	0.973±0.02	4.730±0.01	2.620±0.05	1.787±0.02	1.110±0.02
3079 XRF	11.567±0.05	9.720±0.06	8.193±0.04	8.490±0.06	5.777±1.06	7.627±0.07	3.657±0.01	7.120±0.05	2.777±0.03	7.057±0.04	3.620±0.05	3.293±0.08	1.457±0.08
3087 AAS	9.667±0.03	8.240±0.05	5.713±0.04	7.320±0.09	2.760±0.06	6.643±0.06	1.887±0.02	6.433±0.07	1.717±0.04	6.093±0.09	2.220±0.03	1.043±0.06	1.833±0.03
3087 EDTA	10.267±0.05	8.633±0.04	5.943±0.04	7.830±0.07	3.403±0.06	7.517±0.05	2.200±0.05	6.773±0.07	1.920±0.04	6.727±0.07	2.800±0.02	1.237±0.02	1.980±0.01
3087 XRF	11.267±0.05	9.880±0.08	7.937±0.08	9.457±0.07	5.643±0.05	8.177±0.04	3.833±0.06	7.203±0.06	2.920±0.02	7.130±0.05	3.073±0.07	3.897±0.03	2.317±0.08
3098 AAS	10.533±0.05	8.137±0.10	5.443±0.09	7.930±0.09	2.487±0.05	6.237±0.05	1.040±0.02	5.653±0.05	0.563±0.05	4.763±0.05	2.863±0.05	2.757±0.06	1.877±0.09
3098 EDTA	11.133±0.03	8.837±0.08	6.363±0.07	8.387±0.05	2.880±0.02	6.747±0.06	1.427±0.09	6.180±0.05	0.877±0.04	5.333±0.09	2.937±0.06	2.980±0.09	2.087±0.05
3098 XRF	11.633±0.058	10.307±0.081	9.433±0.230	9.560±0.193	4.213±0.191	7.393±0.055	3.093±0.139	7.070±0.128	2.677±0.05	6.837±0.09	2.957±0.05	3.417±0.03	2.457±0.07
3100 AAS	5.680±0.098	4.480±0.061	3.817±0.067	3.790±0.175	1.810±0.026	3.100±0.056	0.533±0.031	2.767±0.110	0.710±0.08	2.860±0.05	1.053±0.05	1.950±0.07	1.217±0.03
3100 EDTA	6.140±0.108	4.797±0.050	4.157±0.167	4.197±0.192	2.250±0.131	3.557±0.076	0.830±0.066	3.623±0.188	0.910±0.02	2.623±0.07	1.190±0.04	1.803±0.01	1.497±0.02
3100 XRF	8.663±0.080	6.293±0.061	5.783±0.142	5.817±0.093	3.217±0.097	4.517±0.038	2.073±0.115	4.187±0.051	1.937±0.03	4.020±0.06	2.157±0.09	2.367±0.04	2.320±0.09

Table 6.7. Percentage Al$_2$O$_3$ in Raw and HCl-treated clay samples from Kano plains

AAS, XRF and EDTA titration results for % Al$_2$O$_3$ in Raw and HCl-treated clays from Kano plains, Kenya

| Acid/Conc.	Raw	2M HCl$_{RT}$	2M HCl$_{BT}$	4M HCl$_{RT}$	4M HCl$_{BT}$	6M HCl$_{RT}$	6M HCl$_{BT}$	8M HCl$_{RT}$	8M HCl$_{BT}$	10M HCl$_{RT}$	10M HCl$_{BT}$	11M HCl$_{RT}$	12M HCl$_{BT}$
3076 AAS	14.33±0.45	13.30±0.24	11.87±0.01	13.45±0.26	13.16±0.31	12.66±0.31	10.46±0.23	12.60±0.34	10.53±0.36	12.47±0.22	9.52±0.28	12.57±0.30	10.67±0.32
3076 EDTA	13.62+0.04	13.75+0.02	11.87+0.06	13.80+0.10	13.80+0.12	13.21+0.10	11.54+0.10	13.47+0.11	12.38+0.06	12.80+0.06	10.31+0.07	13.78+0.11	11.30±0.06
3076 XRF	14.74+0.16	14.04+0.25	12.17+0.06	14.26+0.64	14.56+0.31	13.68+0.19	14.70+0.17	14.38+0.35	13.82+0.15	14.19+0.56	13.44+0.35	15.62+0.34	13.55±0.34
3077 AAS	13.65+0.30	11.08+0.42	12.69+0.26	15.57+0.14	12.49+0.32	14.69+0.37	11.56+0.38	14.33+0.24	12.43+0.28	11.54+0.33	9.39+0.42	14.71+0.38	10.51±0.38
3077 EDTA	14.15+0.05	11.14+0.06	13.20+0.06	16.25+0.05	13.36+0.07	15.59+0.06	11.85+0.06	15.01+0.03	12.98+0.03	12.50+0.07	10.43+0.10	15.44+0.32	11.57±0.36
3077 XRF	14.76+0.19	12.91+0.14	13.79+0.18	16.83+0.14	14.77+0.13	15.82+0.11	12.32+0.85	16.47+0.31	14.62+0.24	14.28+0.36	12.59+0.36	15.71+0.38	12.66±0.25
3078 AAS	12.54+0.37	11.41+0.31	11.64+0.28	13.41+0.48	11.52+0.18	12.56+0.20	10.67+0.28	13.44+0.30	9.50+0.20	11.38+0.24	8.58+0.34	12.50+0.44	9.11±0.44
3078 EDTA	13.30+0.10	12.23+0.71	12.09+0.07	14.07+0.50	12.46+0.08	13.51+0.06	11.76+0.02	14.11+0.11	10.48+0.05	11.64+0.27	9.70+0.06	13.64+0.25	10.65±0.30
3078 XRF	14.68+0.20	13.19+0.91	12.53+0.26	14.68+0.25	13.68+0.17	13.54+0.42	13.71+0.20	14.43+0.36	11.72+0.18	12.47+0.40	10.52+0.33	14.68+0.24	12.03±0.41
3079 AAS	17.21+0.27	16.43+0.32	14.19+0.34	15.41+0.36	14.28+0.39	15.10+0.34	14.54+0.32	14.70+0.05	16.53+0.30	10.45+0.11	11.47+0.40	15.15+0.18	12.54±0.41
3079 EDTA	17.53+0.15	16.66+0.01	15.39+0.05	15.91+0.08	14.89+0.01	15.83+0.07	15.50+0.05	14.98+0.03	17.11+0.10	15.58+0.08	12.09+0.03	16.26+0.31	13.65±0.30
3079 XRF	17.60+0.20	16.85+0.07	16.15+0.09	16.71+0.23	15.49+0.33	16.09+0.35	16.46+0.26	15.65+0.28	18.53+0.22	16.27+0.28	13.72+0.26	16.68+0.38	14.13±0.26
3087 AAS	14.47+0.36	12.47+0.19	12.66+0.19	13.73+0.27	12.65+0.33	13.60+0.23	11.17+0.38	12.56+0.10	14.47+0.42	12.29+0.18	9.60+0.20	12.09+0.51	10.49±0.46
3087 EDTA	15.30+0.10	12.83+0.06	13.44+0.11	14.73+0.05	12.78+1.12	14.40+0.06	11.39+0.05	13.16+0.05	15.74+0.05	13.85+0.06	10.60+0.03	13.73+0.25	11.61±0.25
3087 XRF	16.86+0.12	14.49+0.19	14.73+0.26	16.67+0.22	13.64+0.33	16.33+0.40	13.07+0.26	15.56+0.22	16.73+0.17	17.04+0.61	12.53+0.40	16.36+0.43	12.75±0.19
3098 AAS	16.53+0.30	14.82+0.13	13.72+0.16	16.45+0.42	12.46+0.44	16.59+0.04	12.47+0.18	15.14+0.24	13.54+0.21	15.04+0.17	11.38+0.39	17.69+0.30	11.50±0.39
3098 EDTA	17.17±0.15	15.48±0.02	14.37±0.06	16.84±0.06	13.32±0.11	16.88±0.10	12.62±0.06	16.03±0.08	14.04±0.05	15.47±0.07	12.18±0.14	18.41±0.13	12.46±0.43
3098 XRF	17.72±0.21	16.69±0.09	15.49±0.42	17.44±0.43	14.63±0.44	18.39±0.46	13.69±0.20	17.73±0.09	14.94±0.39	16.82±0.14	13.64±0.31	18.72±0.24	13.67±0.33
3100 AAS	17.95±0.19	13.83±0.23	12.89±0.78	15.75±0.12	12.62±0.27	12.58±0.31	11.89±0.12	11.26±0.12	13.76±0.12	12.03±0.23	12.55±0.28	15.29±0.29	13.77±0.12
3100 EDTA	18.57±0.06	14.36±0.06	12.66±0.27	16.46±0.06	13.07±0.06	13.17±0.05	12.50±0.13	11.94±0.05	14.77±0.01	12.74±0.08	13.77±0.10	16.22±0.23	14.65±0.25
3100 XRF	19.55±0.30	15.30±0.32	15.62±0.24	17.61±0.35	17.60±0.29	14.79±0.25	13.52±0.28	12.51±0.44	15.54±0.31	13.59±0.40	13.74±0.26	16.67±0.39	17.09±0.44
3104 AAS	15.75±0.15	15.30±0.47	14.55±0.13	14.54±0.44	13.61±0.27	12.48±0.23	8.58±0.18	14.60±0.39	15.16±0.12	13.82±0.08	14.11±0.10	14.68±0.13	12.49±0.37

APPENDIX 2

Graphs of Additional Data

Graph 6.1 Percentage Fe$_2$O$_3$ in each raw clay sample from different analytical methods
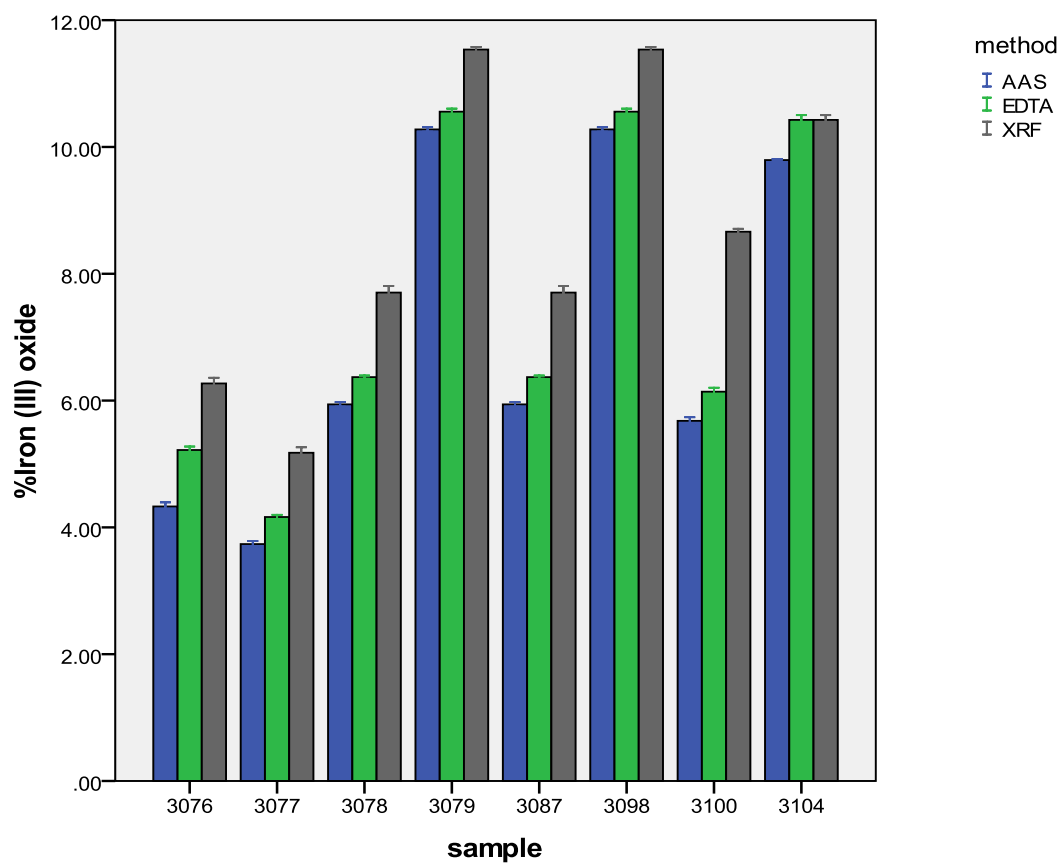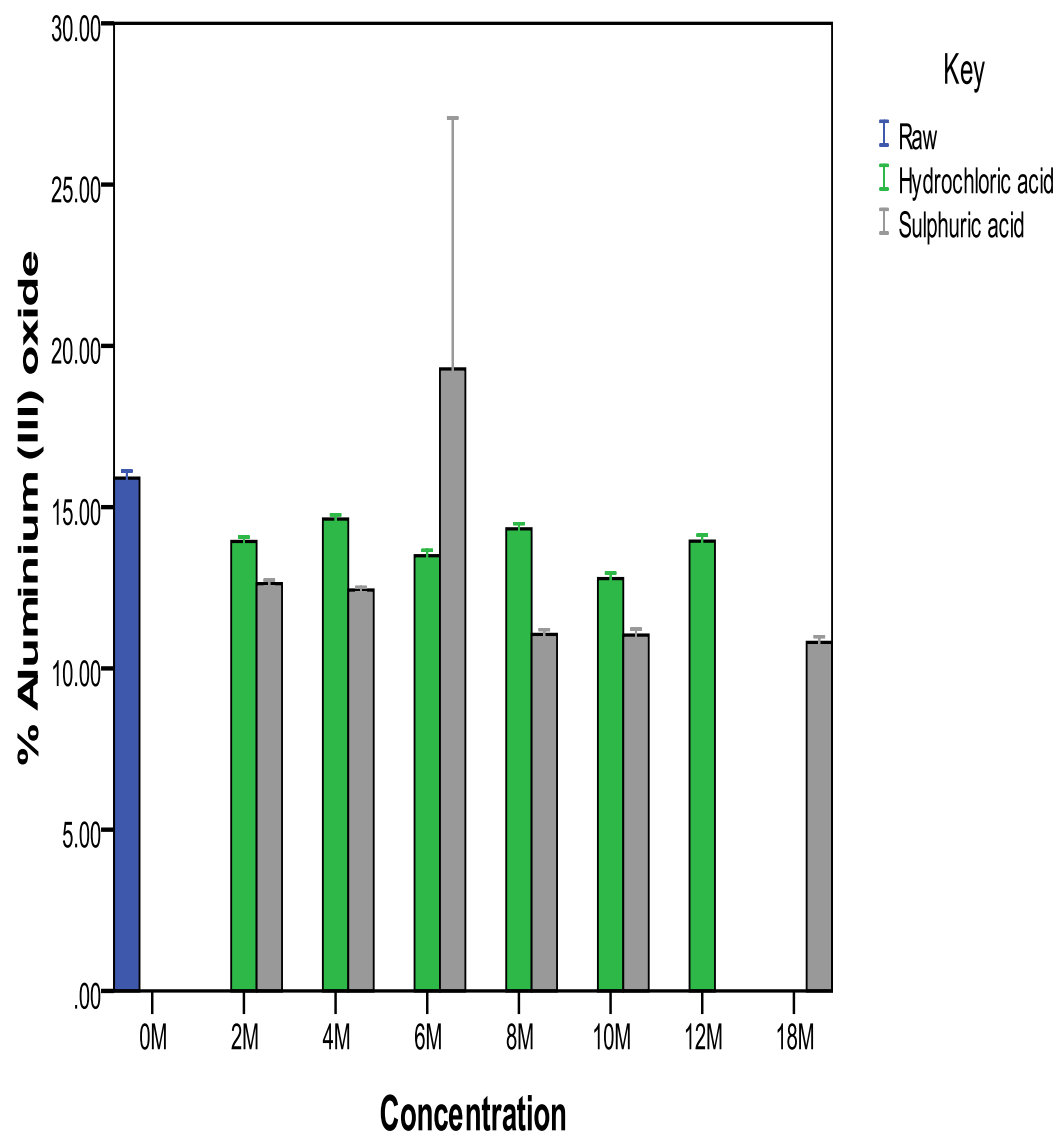
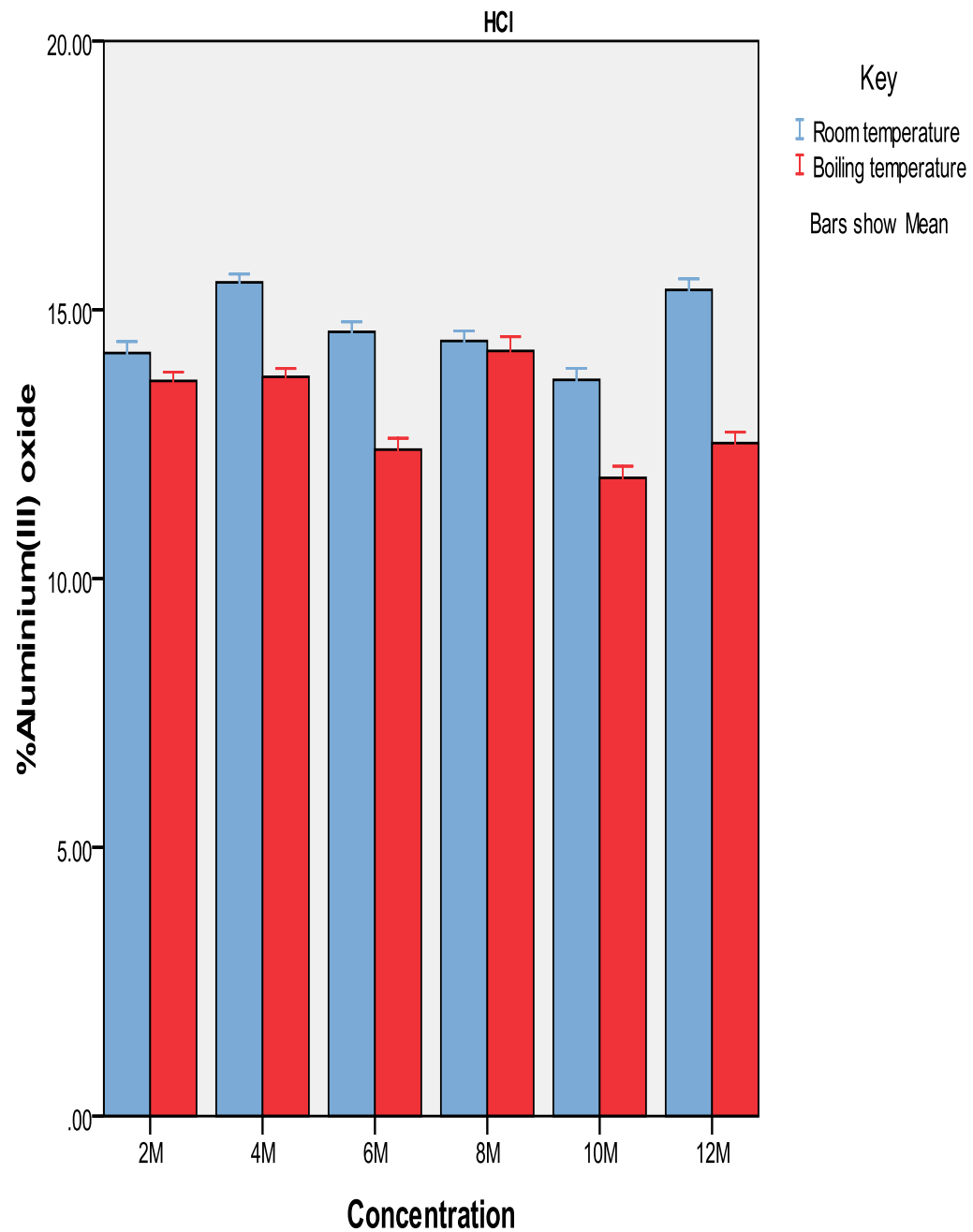**Graph 6.2 Percentage Fe$_2$O$_3$ in Raw and HCl-treated Clays at room and boiling temperatures**
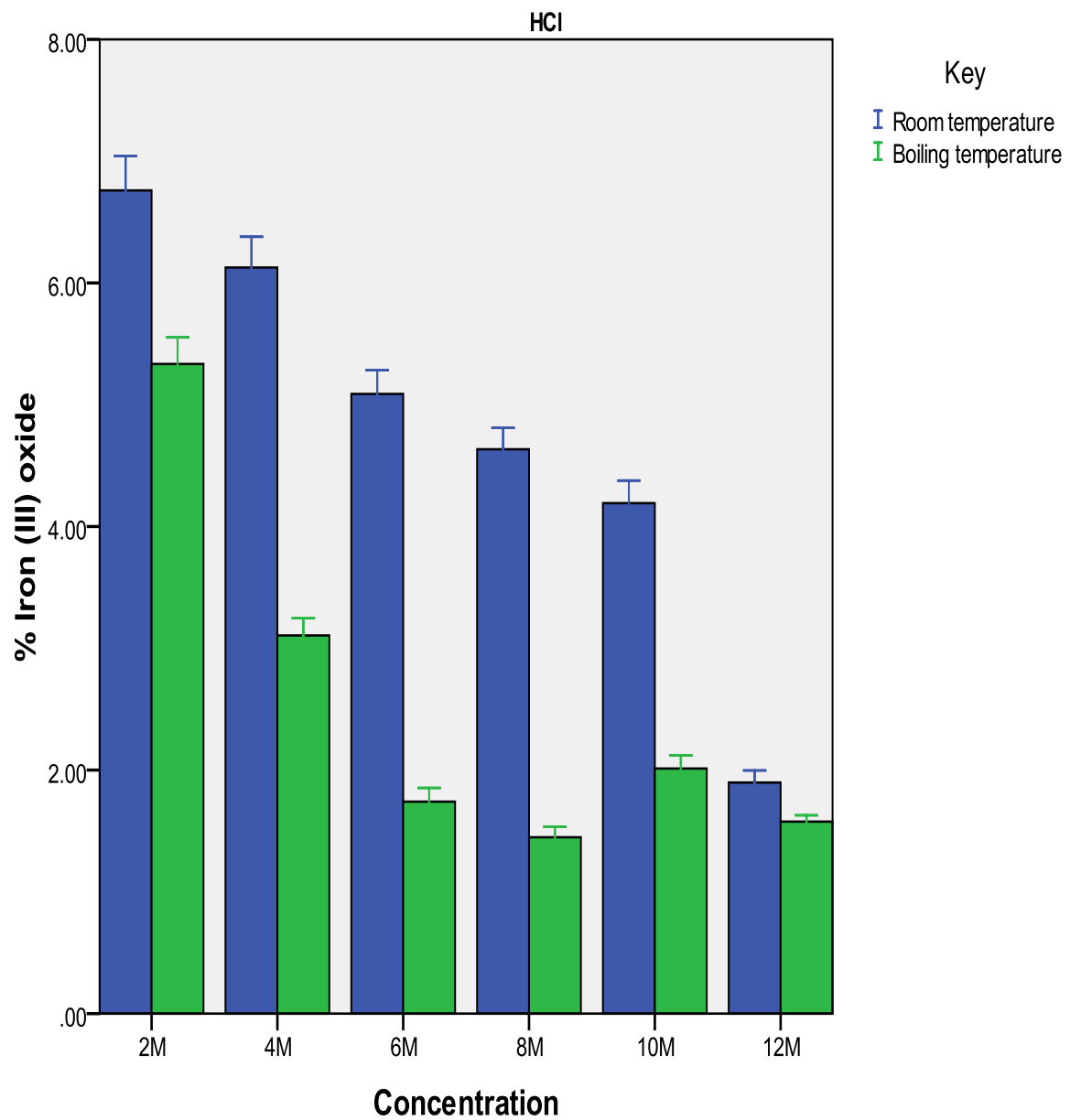
Graph 6.3: Percentage Alumina in raw clays by different analytical methods
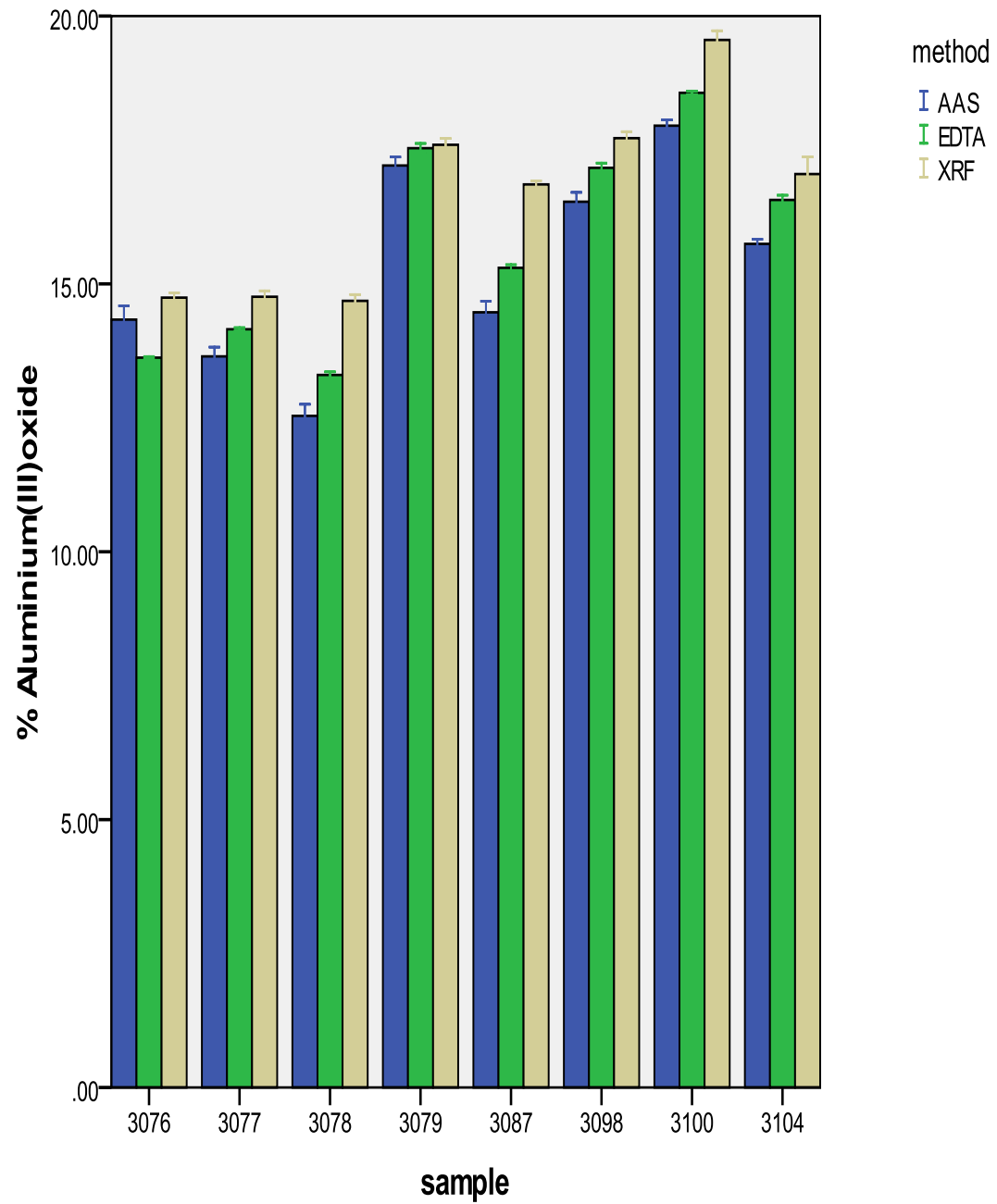
Graph 6.4: Comparison of average % Al$_2$O$_3$ in HCl and H$_2$SO$_4$-treated clays at room temperature (Mean±SE)

Graph 6.5: Percentage aluminium oxide in HCl-treated clays at room and boiling temperatures

APPENDIX 3

Summary of Minerals Detected In Raw and Acid-Treated Clays

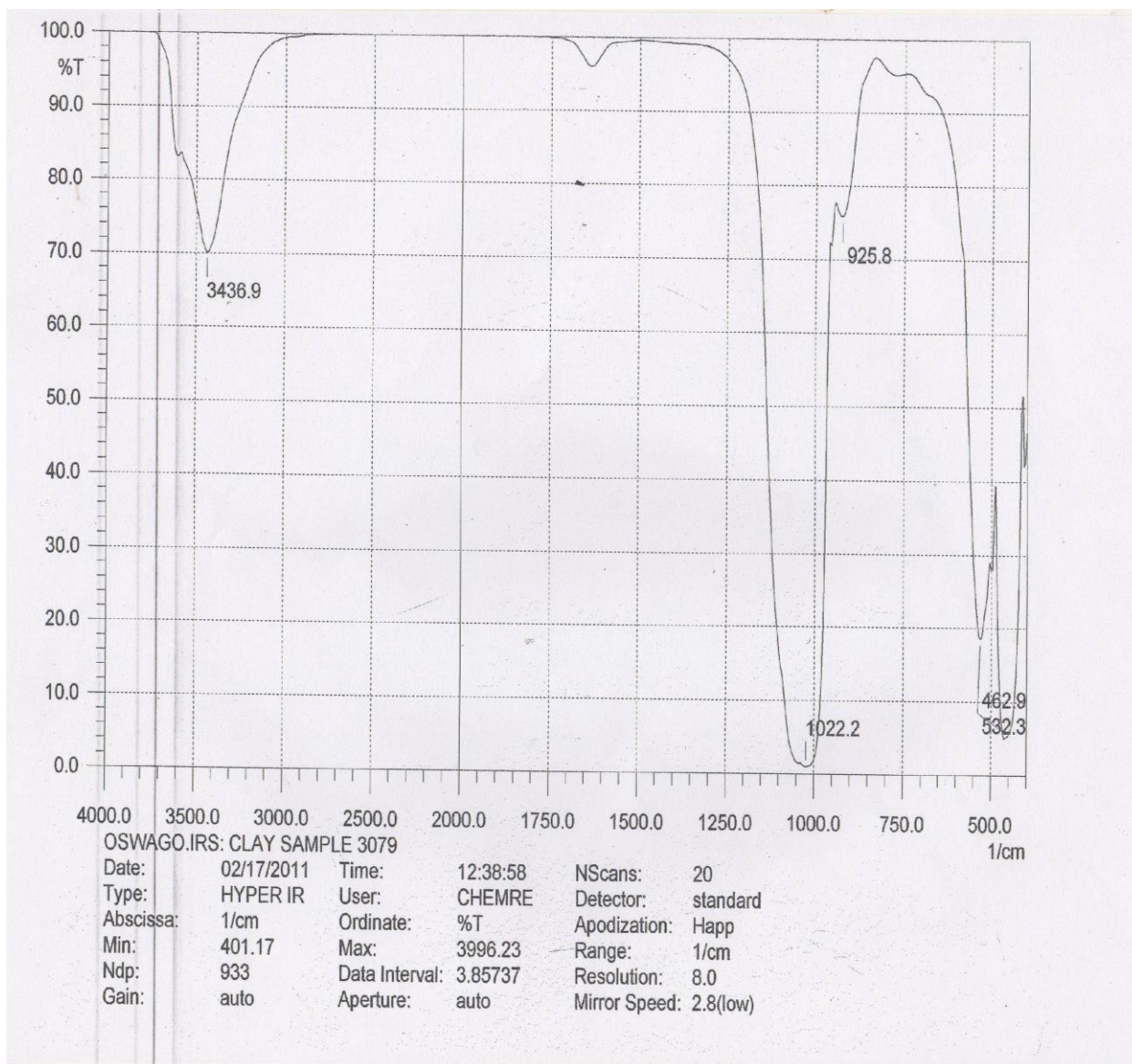**Table 6.8 Percentage composition of clay minerals raw clays in one site and composite sample from Kano planes.**

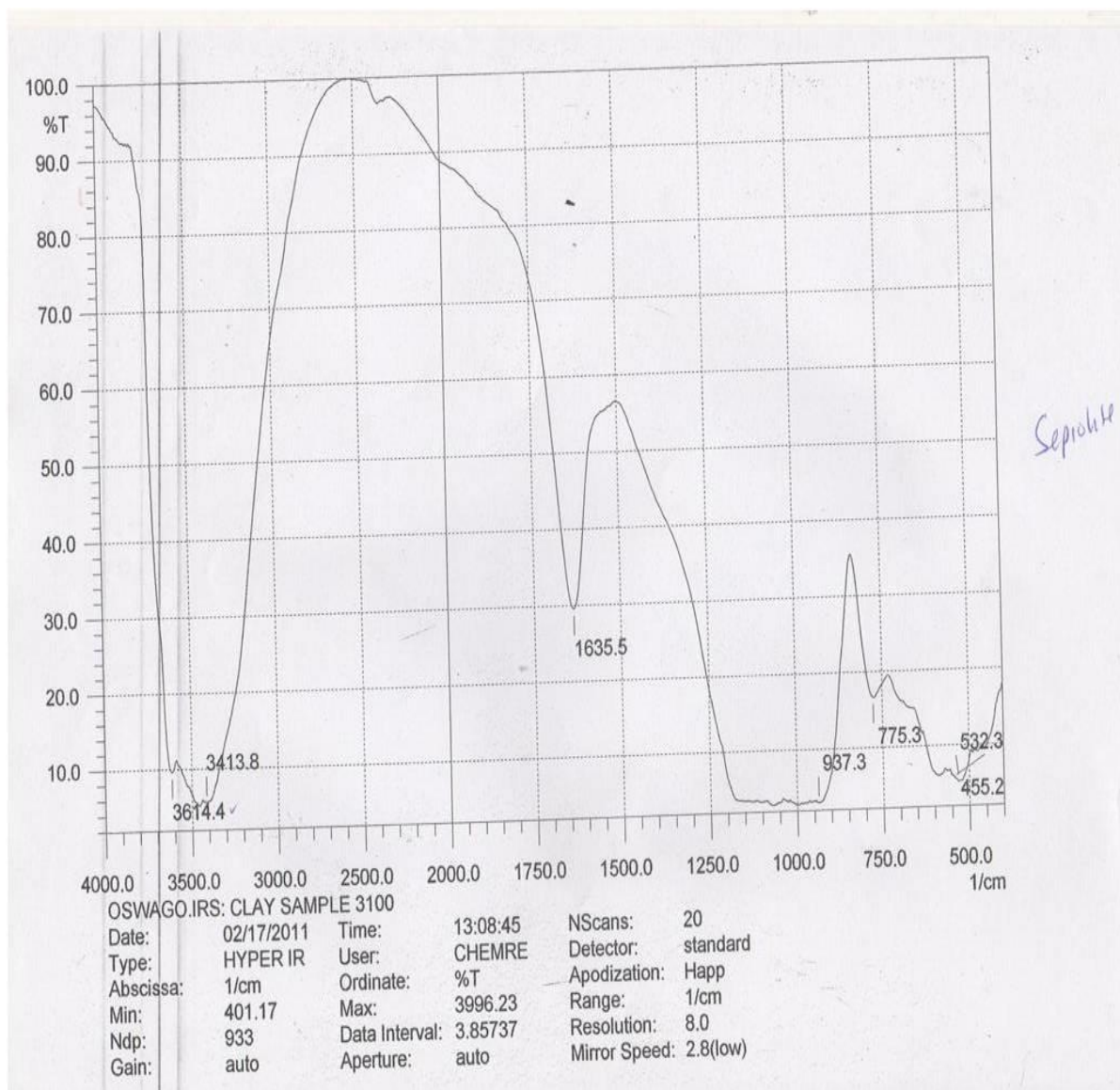| Mineral	Formula	Sample site	Percentage composition
Montmorillonite, Calcian, glycolated	$(Ca,Na)_{.3}Al_2(Si, Al)_4O_{10}(OH)_2.xH_2O$	Oren Composite sample	19.3% 38.7%
Kaolinite	$Al_2Si_2O_5(OH)_4$	Oren Composite sample	9.1% Not detected
Muscovite	$KAl(Si_3Al)O_{10}(OH,F)_2$	Oren Composite sample	8.6% 10.4%
Albite	$Na(AlSi_3O_8)$	Oren Composite sample	22.3% 19.0%
Orthoclase	$KAlSi_3O_8$	Oren Composite sample	23.1% 11.9%
Quartz	SiO_2	Oren Composite sample	17.6% 9.5%
Dickite	$Al_2(Si_2O_6(OH)_4$	Oren Composite sample	Not detected 10.6%

APPENDIX 4

IR ANALYSIS SPECTRA
Spectrum 6.1 IRS spectrum for clay sample from Riat Market, Kano Plains, Kenya.

OSWAGO.IRS: CLAY SAMPLE 3079

Date:	02/17/2011	Time:	12:38:58	NScans:	20	
Type:	HYPER IR	User:	CHEMRE	Detector:	standard	
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ	
Min:	401.17	Max:	3996.23	Range:	1/cm	
Ndp:	933	Data Interval:	3.85737	Resolution:	8.0	
Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)	

Spectrum 6.2 IR spectrum for clay sample from Anywang' River bank,Kano Plains, Kenya.

APPENDIX 5

KENYA CLAY IMPORTS DATA

Table 6.9: Kenya Clay Imports From 2007-2011

The following is the information about clay imports in Kenya for the years 2007-2011

Year	Total Quantity of clay imports(Kgs)	Total Value of clay imports (Kshs)	Cummulative value (Kshs)
2007	2,840,127.00	40,772,933.73	40,772,933.73
2008	3,262,849.00	58,762,185.05	99,535,118.78
2009	3,184684.00	77,276,073.89	176,811,192.70
2010	4,130,286.00	89,968,766.38	266,779,959.10
2011	1,675,472.00	73,375,773.62	340,155,732.70

Source: Kenya National Bureau of Statistics, 2012.