

RADIOLOGICAL AND ELEMENTAL ANALYSIS KAOLIN IN
KANKARAKATSINA STATE, NIGERIA

BY

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Declaration

I declare that the work in this dissertation entitled “RADIOLOGICAL AND ELEMENTAL ANALYSIS OF KAOLIN IN KANKARA KATSINA STATE NIGERIA” has been carried out by me in the Department of Physics. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

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Date

Certification

This dissertation entitled RADIOLICAL AND ELEMENTAL CHARACTERIZATION OF KANKARA KAOLIN KATSINA STATE NIGERIA, by PIUS EDISE JOHNSON meets the regulations governing the award of the degree of M.Sc Nuclear Physics of the Ahmadu Bello University, and is approved for its contribution to knowledge and literacy presentation.

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Acknowledgement

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Thank you all and God Almighty blesses you.

Dedication

This research is dedicated to my aunty, Mrs. Esther Ogbevire.

Abstract

This study assesses the concentration of ^{238}U , ^{232}Th and ^{40}K , in-site background radiation, radiological implications and elemental constituents of Kaolin mined from KankaraKatsina State. Ten (10) samples were collected randomly from the kankara kaolin mining sites and the background radiation dose was measured using a portable radiation survey meter. The samples were divided into two for gamma spectrometry analyses and elemental analyses. The samples for gamma spectrometry analysis were prepared and analyzed using NaI(Tl) detector at Centre for Energy Research and Training, Ahmadu Bello University. The samples for elemental analysis were prepared and analyzed using Atomic Absorption Spectrometry (AAS) at Multi-Purpose Laboratory, Ahmadu Bello University. The range of activity concentration of U, Th and ^{40}K in Kaolin samples from the study areas varies from 12.11 – 76.96 Bq/kg, 24.02 – 96.72 Bq/kg and 126.13 – 1038.93 Bq/kg with mean values of 31.63 Bq/kg, 58.06 Bq/kg and 388.64 Bq/kg respectively. The mean value of gamma radiation dose rate measured in Kankara is 66.97 nGy/h which is 7.97 nGy/h more than the world average, 59 nGy/h as stated by UNSCEAR. The average annual dose from such gamma radiation dose rate is 110.07 $\mu\text{Sv}/\text{y}$; the excess lifetime cancer risk was determined to be 0.39×10^{-3} which is more than the world average value of 0.29×10^{-3} . The heavy metals composition detected were below the world average. In view of these, it is concluded that the workers (miners) at the samples mining sites are not safe.

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CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Kaolin (Hydrated aluminum silicate, $[Al_2Si_2O_5(OH)_4]$), is an important industrial clay of economic benefit. Its properties such as fine particle size, platy shape, inertness, non-toxicity, non-abrasiveness, high brightness, whiteness and chemical stability make it a more versatile mineral, with applications in a wide variety of industries (Murray, 1994). Commercial kaolin resources are found as sedimentary deposits and as a product of weathered rocks containing a high proportion of aluminosilicate minerals (Murray, 1994). The name Kaolin is derived from the mineral name Kaolinite.

The industrial mineral kaolin has many uses which includes production of paper, as a substance to accelerate blood clotting, smoothening substance in the production of cosmetics, for the purification of transformer oil and for production of ceramics, to mention but a few (Rowe and Aaron, 2008).

Human beings are exposed to background radiation that stems both from natural and man-made sources. In general, approximately 85% of the annual total radiation dose of any person comes from natural radionuclides of both terrestrial and cosmogenic origin, UNSCEAR (2000). Natural radioactive elements are present in very low concentrations in earth's crust, and are brought to the surface through human activities such as minerals exploration or mining, and through natural processes like leakage of radon gas to the atmosphere or through dissolution in ground water (NORM, 2016). All these

activities are known as Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) (NORM, 2016).

There are two types of TENORM namely Type 1 which is the production and use of thorium and Uranium and Type 2 which involve the mining and processing of ores other than uranium ore, the removal and management of radiation scales and precipitates from equipment associated with industrial activities, China clay extraction which is also known as kaolin mining etc., (EPR, 2010).

The hazardous elements found in TENORM are radium 226, 228 and radon (Rn) 222 and also daughter products from these radionuclides (UNSCEAR, 2010). The elements are referred to as “bone seekers” which when inside the body migrate to the bone tissues and concentrate (James, 2015). This exposure can cause bone cancers and other bone abnormalities (James, 2015).

Soil radionuclide activity concentration is one of the main determinants of the natural background radiation. A number of decay products of ^{232}Th , ^{238}U and ^{40}K series are the main components of external gamma radiation originating from soil. About two thirds of natural radioactivity which exposes public is attributed to progeny of ^{238}U series and Rn. The worldwide annual effective dose from natural sources is estimated to be 2.4mSv (UNSCEAR, 2000).

Natural radionuclides of the uranium to radium and the thorium series as well as potassium 40 are distributed in soil almost homogeneously, regardless of the depth. Their concentration depends on local geological conditions. Each year there are seasonal changes in the gamma radiation dose rate value. Additionally, daily changes and

changes caused by precipitation are observed (Biernacka et al, 2004). These changes are due to differences in exhalation of radon from soil and in the case of precipitation and washing out radon isotopes from the air and their deposition on the soil surface(Biernacka et al, 2004).

1.2 Problem Statement

Although, kaolin has versatile industrial usage, it is also known to consist of significant amount of natural radionuclides which are sources of radiation and affect human during mining, refining and use in manufacturing of products. Many case reports and case series have suggested that exposure to kaolin causes pneumoconiosis(Lemaistre, 1999). In several cases, however, it was not clear whether kaolinite and quartz or quartz alone was responsible for the resulting pneumoconiosis(Gudjonsson and Jacobsen, 1934).

Long term exposure to Kaolin causes the development of radiological diagnosed pneumoconiosis in an exposure-related fashion (Lemaistre, 1999). Clear-cut deterioration of respiratory function and related symptoms has been reported only in cases with prominent radiological findings (Lemaistre, 1999). The composition of the clay – i.e. quantity of minerals other than Kaolinite – is an important determinant of the effects(Middleton, 1996).

Therefore, from a liability standpoint, an employee that has not had respiratory protection over several years could develop bone or other cancer from NORM exposure and decide to seek compensation such as medical expenses and lost wages from the companies which generated the TENORM

1.3 Justification of the Study

Kaolin and other clays are natural components of the soil and occur widely in ambient air as floating dust. Accordingly, exposure of the general population to them must be universal, albeit at low concentrations. In the vicinity of mines and industrial projects, kaolinite is likely to be present at high concentrations in air; as reported by a group of experts under World Health Organization Geneva in 2005 (W.H.O., 2005).

People can be exposed to kaolin in the workplace by inhaling the powder, skin contact, and eye contact. This has great effect to human lungs due to the absorption of the radiation from the radionuclides present in it. In kaolin, the radionuclides suspected to be present are the ^{40}K , ^{238}U and ^{232}Th (UNSCEAR, 2010).

The Occupational Safety and Health Administration (OSHA) has set the legal limit (permissible exposure limit) for typical background radiation experienced by everyone as 2.4mSv/yr., average dose to uranium, minerals miners and nuclear industries workers as 1.5 to 2.5mSv/yr., allowable short term dose for emergency workers as 50mSv/yr.(IAEA, 2009). Thus, the need to undertake this study in order to establish if these limits are exceeded.

1.4 Aim and Objectives

The aim of the present study is to assess the radiological and elemental constituent of Kaolin in Kankara, Nigeria.

The objectives of this research are

- i. To determine the elemental composition of kaolin.
- ii. To measure in-situ background radiation of the study area.

- iii. To estimate the activity concentration of radionuclide (Th, U and K) in kaolin and their radiological implications.
- iv. To estimate the exposure dose of the workers due to mining of kaolin.
- v. To compare the result obtained with the world standard set.

1.5 Scope and Limitation

The scope of this research covers the determination of elemental composition of kaolin in Kankara by employing Atomic Absorption Spectroscopy (AAS), assessing the radiological impacts due to its exploitation to the environment by employing the gamma spectrometry set-up and mapping of background radiation of the entire area.

CHAPTER TWO

LITERATURE REVIEW

2.1 Radioactivity

Radioactivity (also known as nuclear decay or radioactive decay) is the spontaneous disintegration of an unstable nucleus of an atom with the emission of large amount of energy and particles such as alpha, beta, gamma and neutrons. A material containing such unstable nuclei is considered radioactive. Certain highly excited short-lived nuclear state can decay through neutron emission, or more rarely, proton emission (Mohammed *et al.*, 2015)

When an unstable (radioactive) atom emits radiation to become more stable, it is said to disintegrate or decay. Radioactive decay is an interesting process in that it has regular and predictable aspects as well as totally random aspects. The moment at which any one particular atom decays is random and cannot be predicted. However, the time in which, on average, half of a certain (large) number of atoms of a particular isotope will decay is regular, known and entirely predictable. Each kind of radioactive isotope has a specific known time period in which half of the atoms will decay. This is called the half-life and is expressed as (UNSCEAR, 2010).

$$T_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \quad \dots (2.1)$$

where $T_{1/2}$ is the half life of a given radionuclide and λ stands for decay probability constant of a given radionuclide.

In some cases, the half-life of a radionuclide is extremely long. Examples are ^{40}K , ^{238}U and ^{232}Th , with half-lives of 1.3×10^9 , 4.5×10^9 , and 1.4×10^{10} years, respectively.

The activity of a radioactive material gives the number of decays per unit of time. Or in other words activity (A_t) is defined as the number of decays (N_t) per unit time interval.

$$A_t = \lambda N_t \quad \dots(2.2)$$

The S.I. unit of activity is the becquerel (Bq). One becquerel is equivalent to one atom decaying (or disintegrating) per second.

Due to the fact that some radioisotopes decay more rapidly than others, i.e. they have a shorter half-life; equal masses of different radioisotopes can have widely differing activities.

The activity (λN) per unit mass (M) or Volume (V) of a certain radionuclide is called the **specific activity** (SA) of that radionuclide, and is a constant (Mohammad, *et al*, 2015).

$$SA = \frac{\lambda N}{M} \dots(2.3)$$

The corresponding unit that is most commonly used is becquerels per kilogram (Bq/kg) or (Bq/m³) (Cember, 1996).

2.1.1 Radiation sources and doses

Sources of radiation are all around us all the time. Some are natural and some are man-made. The amount of radiation absorbed by a person is measured in dose.

Radiation occurs when energy is emitted by a source and then travels through a medium, such as air, until it is absorbed by matter. Radiation can be described as two basic types, ionizing and non-ionizing radiation (Tomislav, *et al*, 2008).

2.1.2 Non-ionizing radiation

People are exposed to non-ionizing radiation sources every day. This form of radiation does not carry enough energy to ionize atoms or molecules. Microwave ovens, global positioning systems, cellular telephones, television stations, FM and AM radio, baby monitors, cordless phones and garage-door openers all make use of non-ionizing radiation.

Other forms include the earth's magnetic field, as well as magnetic field exposure from proximity to transmission lines, household wiring and electric appliances. These are defined as extremely low- frequency (ELF) waves (Mohammad, *et al.*, 2015).

2.1.3 Ionizing radiation

Some types of radiation have enough energy that they can knock electrons out of their orbits around atoms, upsetting the electron/ proton balance and giving the atom a positive charge. Electrically charged molecules and atoms are called ions. The radiation that can produce ions is called ionizing radiation, (Mohammad, *et al.*, 2015).

This type of radiation is of two types: natural background radiation and artificial or man-made radiation.

2.1.3.1 Natural background radiation

i. Exposure from cosmic radiation

The earth's outer atmosphere is continually bombarded by cosmic radiation. Usually, cosmic radiation consists of fast moving particles that exist in space and originate from a

variety of sources, including the sun and other celestial events in the universe. Cosmic rays are mostly protons but can be other particles or wave energy. Some ionizing radiation will penetrate the Earth's atmosphere and become absorbed by humans, which results in natural radiation exposure.

The doses due to natural sources of radiation vary depending on location and habits. Regions at higher altitudes receive more cosmic radiation(Mohammad,*et al.*, 2015).

ii. Exposure from terrestrial radiation

The composition of the earth's crust is a major source of natural radiation. The main contributors are natural deposits of uranium, potassium and thorium which, in the process of natural decay, will release small amounts of ionizing radiation. Uranium and thorium are “ubiquitous”, meaning they are found essentially everywhere. Traces of these minerals are also found in building materials as much, exposure to natural radiation can occur from indoors as well as outdoors(Mohammad,*et al.*, 2015).

iii. Exposure through inhalation

Most of the variation in exposure to natural radiation results from inhalation of radioactive gases that are produced by radioactive minerals found in soil and bedrock. Radon is an odourless and colourless radioactive gas that is produced by the decay of uranium. Thoron is a radioactive gas produced by the thorium. Radon and thoron levels vary considerably by location depending on the composition of soil and bedrock. Once released into the air, these gases will normally dilute to harmless levels in the atmosphere but sometimes they become trapped and accumulate inside buildings and are

inhaled by occupants. Radon gas poses a health risk not only to uranium miners, but also to homeowners if it is left to collect in the home.

On average, it is the largest source of natural radiation exposure. More information on radon gas and the means to control it can be found on Health Canada's website, (Mohammad,*et al.*, 2015).

iv. Exposure through ingestion

Trace amounts of radioactive minerals are naturally found in the contents of food and drinking water. For instance, vegetables are typically cultivated in soil and ground water which contains radioactive minerals.

Once ingested, these minerals result in internal exposure to natural radiation.

Naturally occurring radioactive isotopes, such as potassium-40 and carbon-14, have the same chemical and biological properties as their non-radioactive isotopes. These radioactive and non-radioactive elements are used in building and maintaining our bodies. Natural radioisotopes continually expose us to radiation.

2.1.3.2 Artificial sources of radiation

i. Atmospheric testing: The atmospheric testing of atomic weapons from the end of the Second World War until as late as 1980 released radioactive material, called fallout, into the air. As the fallout settled to the ground, it was incorporated into the environment. Much of the fallout had short half-lives and no longer exists, but some continues to decay to this day. People and the environment receive smaller and smaller doses from the fallout every year(UNSCEAR, 2010).

ii. Medical sources: Radiation has many uses in medicine. The most well-known use is X-ray machines, which use radiation to find broken bones and diagnose disease. X-Ray machines are regulated by provincial authorities. Another example is nuclear medicine, which uses radioactive isotopes to diagnose and treat diseases such as cancer. These applications of nuclear medicine, as well as the related equipment, are regulated by the Certified Nuclear Security Commission (CNSC). The CNSC also licenses those reactors and particle accelerators that produce isotopes destined for medical and industrial applications(UNSCEAR, 2010).

iii. Industrial sources: Radiation has a variety of industrial uses that range from nuclear gauges used to build roads to density gauges that measure the flow of material through pipes in factories. It is also used for smoke detectors, some glow -in- the dark exit signs, and to estimate reserves in oil fields. Radiation is also used for sterilization which is done by using large, heavily shielded irradiators. All these uses are licensed by the CNSC(UNSCEAR, 2010).

iv. Nuclear Fuel Cycle: Nuclear power plants (NPPs) use uranium to drive a chain reaction that produces steam, which in turn drives turbines to produce electricity. As part of their normal activities, NPPs release regulated levels of radioactive material which can expose people to low doses of radiation. Similarly, uranium mines, fuel fabrication plants and radioactive waste facilities release some radioactivities that contaminate the soil(UNSCEAR, 2010).

2.2 Health Impacts to Animals, Human and Plants

The presence of radioactive elements i.e. K, U, Th and Ra, as well as heavy metals i.e. Cd, Pb, Ni and As in agricultural soil is associated with negative impacts to the ecosystem (Abdel-Haleem, *et al.*, 2001). Danger may be posed to both, animals, human beings and plant (Ayeni, 2010). Detrimental effects may be caused either directly or indirectly, through different pathways i.e. direct ingestion/inhalation, drinking of contaminated water, contact with contaminated soil and the food chain (Abdel-Haleem, *et al.*, 2001).

The transfer of radionuclides from farm soils to human bodies may be harmful if the maximum dose is exceeded (ICRP, 1990), a situation which may cause serious health problems to human beings. For example, once radionuclides accumulate in human body tissues at higher levels than the standard limit, they may cause severe health problems such as cancer (Lambert, 2007). Also, when ^{226}Ra is deposited in bone tissue, it has a high potential for causing biological damage through continuous irradiation of human skeleton over many years and may induce bone sarcoma (Tomislav, *et al.*, 2008).

2.3 Gamma-ray spectroscopy

Gamma-ray spectroscopy is the quantitative study of the energy spectra of gamma ray sources, such as in the nuclear industry, geochemical investigation and astrophysics.

Most radioactive sources produce gamma rays, which are of various energies and intensities. When these emissions are detected and analyzed with a spectroscopy system, a gamma-ray energy spectrum can be produced.

A detailed analysis of this spectrum is typically used to determine the identity and quantity of gamma emitters present in a gamma source, and is a vital tool in radiometric assay. The gamma spectrum is characteristic of the gamma-emitting nuclides contained in the source, just as in optical spectroscopy, the optical spectrum is characteristic of the material contained in a sample.

Gamma rays are the highest-energy form of electromagnetic radiation, being physically the same as all other forms (e.g., X rays, visible light, infrared, radio) but having (in general) higher photon energy due to their shorter wavelength. Because of this, the energy of gamma-ray photons can be resolved individually, and a gamma-ray spectrometer can measure and display the energies of the gamma-ray photons detected.

Radioactive nuclei (radionuclides) commonly emit gamma rays in the energy range from a few keV to ~ 10 MeV, corresponding to the typical energy levels in nuclei with reasonably long lifetimes. Such sources typically produce gamma-ray "line spectra" (i.e., many photons emitted at discrete energies), whereas much higher energies (upwards of 1 TeV) may occur in the continuum spectra observed in astrophysics and elementary particle physics. The boundary between gamma rays and X-rays is somewhat blurred, as X-rays typically refer to the high energy electronic emission of atoms, which may extend to over 100 keV, whereas the lowest energy emissions of nuclei are typically termed gamma rays, even though their energies may be below 20 keV (Shultis, 2007).

2.3.1 System components and principle of operation

The equipment used in gamma spectroscopy includes an energy-sensitive radiation detector, electronics to process detector signals produced by the detector, such as a pulse sorter (i.e., multichannel analyzer), and associated amplifiers and data readout devices to generate, display, and store the spectrum, (Figure 2.1). Other components, such as rate meters and peak position stabilizers, may also be included.

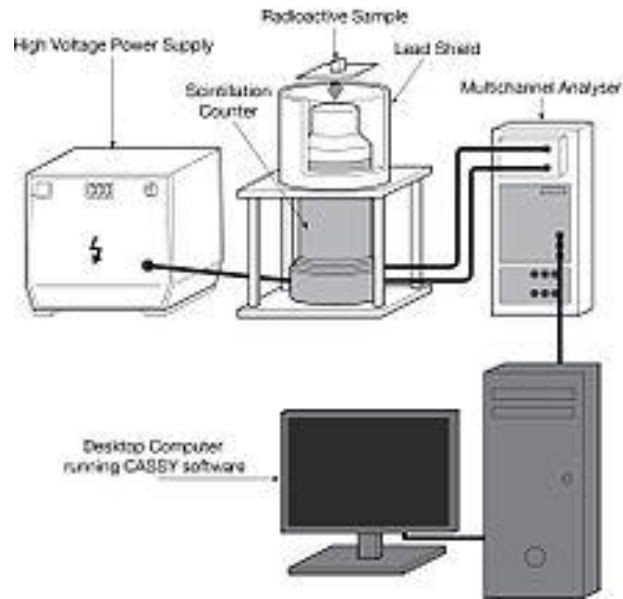


Figure 2.1 Gamma Radiation Laboratory set-up(Brindley, 1951).

The most common detectors include sodium iodide (NaI) scintillation counters and high-purity germanium detectors.

Gamma spectroscopy detectors are active materials that wait for a gamma interaction to occur in the detector volume. The most important interaction mechanisms are the photoelectric effect, the Compton Effect, and pair production. The photoelectric effect is preferred, as it absorbs all of the energy of the incident gamma ray. Full energy absorption is also possible when a series of these interaction mechanisms take place within the detector volume. When a gamma ray undergoes a Compton interaction or pair production, and a portion of the energy escapes from the detector volume without being absorbed, the background rate in the spectrum is increased by one count. This count will appear in a channel below the channel that corresponds to the full energy of the gamma ray. Larger detector volumes reduce this effect.

The voltage pulse produced by the detector (or by the photomultiplier in a scintillation counter) is shaped by a Multi-Channel Analyzer (MCA). The Multi-Channel Analyzer takes the very small voltage signal produced by the detector, reshapes it into a Gaussian or trapezoidal shape, and converts that signal into a digital signal. In some systems, the Analog-to-Digital Conversion is performed before the peak is reshaped. The analog-to-digital converter (ADC) also sorts the pulses by their height. ADCs have specific numbers of "bins" into which the pulses can be sorted; these bins represent the channels in the spectrum. The number of channels can be changed in most modern gamma spectroscopy systems by modifying software or hardware settings. The number of channels is typically a power of two; common values include 512, 1024, 2048, 4096, 8192, or 16384 channels. The choice of number of channels depends on the resolution of the system and the energy range being studied. Pulse-Height Analyzer Principal The multichannel analyzer output is sent to a computer, which stores, displays, and analyzes the data. A variety of software packages are available from several manufacturers, and generally include spectrum analysis tools such as energy calibration, peak area and net area calculation, and resolution calculation(Glenn,2010).

2.3.2 Detector performance

Gamma spectroscopy systems are selected to take advantage of several performance characteristics. Two of the most important include detector resolution and detector efficiency (Glenn, 2010).

2.3.2.1 Detector resolution

Gamma rays detected in a spectroscopic system produce peaks in the spectrum. These peaks can also be called lines by analogy to optical spectroscopy. The width of the peaks is determined by the resolution of the detector, a very important characteristic of gamma spectroscopic detectors, and high resolution enables the spectroscopist to separate two gamma lines that are close to each other. Gamma spectroscopy systems are designed and adjusted to produce symmetrical peaks of the best possible resolution. The peak shape is usually a Gaussian distribution. In most spectra the horizontal position of the peak is determined by the gamma ray's energy, and the area of the peak is determined by the intensity of the gamma ray and the efficiency of the detector (Glenn, 2010).

The most common figure used to express detector resolution is Full Width at Half Maximum (FWHM). This is the width of the gamma ray peak at half of the highest point on the peak distribution. Resolution figures are given with reference to specified gamma ray energies. Resolution can be expressed in absolute (i.e., eV or MeV) or relative terms. For example, a sodium iodide (NaI) detector may have a FWHM of 9.15 keV at 122 keV energy, and 82.75 keV at 662 keV energy. These resolution values are expressed in relative terms. To express the resolution in absolute terms, the FWHM in eV or MeV is divided by the energy of the gamma ray and usually shown as percentage. Using the preceding example, the resolution of the detector is 7.5% at 122 keV, and 12.5% at 662 keV. A germanium detector may give resolution of 560 eV at 122 keV, yielding a relative resolution of 0.46% (Glenn, 2010).

2.3.2.2 Detector efficiency

Not all gamma rays emitted by the source that pass through the detector will produce a count in the system. The probability that an emitted gamma ray will interact with the detector and produce a count is the efficiency of the detector. High-efficiency detectors produce spectra in less time than low- efficiency detectors. In general, larger detectors have higher efficiency than smaller detectors, although the shielding properties of the detector material are also important factors. Detector efficiency is measured by comparing a spectrum from a source of known activity to the count rates in each peak to the count rates expected from the known intensities of each gamma ray(NNRA, 2003).

Efficiency, like resolution, can be expressed in absolute or intrinsic terms. The same units are used (i.e., percentages); therefore, the spectroscopist must take care to determine which kind of efficiency is being given for the detector. Absolute efficiency is the ratio of the number of counts recorded by the detector to the number of gamma rays emitted by the source in all directions (Abbas, 2001). Absolute efficiency of the detector depends not only on the detector properties of the counting geometry (Abbas, 2001). Intrinsic efficiency is the ratio of the number of pulses recorded by the detector to the number of gamma rays hitting the detector (NNRA, 2003).

The energy of the gamma rays being detected is an important factor in the efficiency of the detector. An efficiency curve can be obtained by plotting the efficiency at various energies. This curve can then be used to determine the efficiency of the detector at energies different from those used to obtain the curve. High-purity germanium (HPGe) detectors typically have higher sensitivity(Glenn, 2010).

2.3.3 A scintillation counter

A scintillation counter is an instrument for detecting and measuring ionizing radiation by using the excitation effect of incident radiation on a scintillator material, and detecting the resultant light pulses.

It consists of a scintillator which generates photons in response to incident radiation, a sensitive photomultiplier tube (PMT) which converts the light to an electrical signal and electronics to process this signal.

Scintillation counters are widely used in radiation protection, assay of radioactive materials and physics research because they can be made inexpensively yet with good quantum efficiency, and can measure both the intensity and the energy of incident radiation(Curran, 2009).

2.3.3.1 Principle of operation

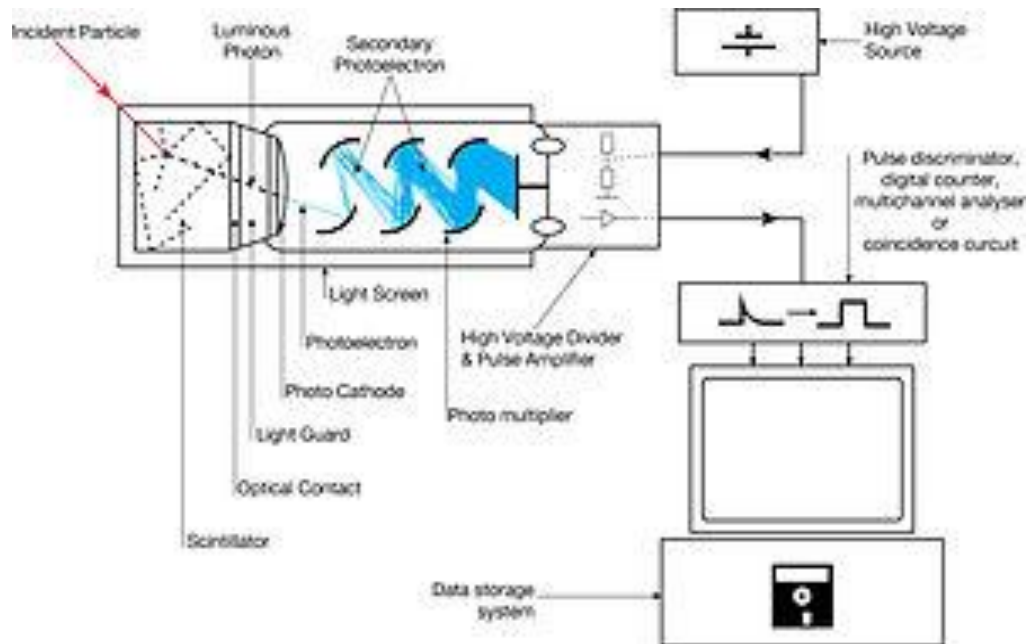


Figure 2.2: Apparatus with a scintillating crystal, photomultiplier, and data acquisition components(Curran, 2009).

When an ionizing particle passes into the scintillator material, atoms are ionized along a track. For charged particles, the track is the path of the particle itself. For gamma rays (uncharged), their energy is converted to an energetic electron via either the photoelectric effect, Compton scattering or pair production. The chemistry of atomic de-excitation in the scintillator produces a multitude of low-energy photons, typically near the blue end of the visible spectrum. The number of such photons is in proportion to the amount of energy deposited by the ionizing particle. Some portion of these low-energy photons arrive at the photocathode of an attached photomultiplier tube. The photocathode emits at most one electron for each arriving photon by the photoelectric effect. This group of primary electrons are electrostatically accelerated and focused by an electrical potential so that they strike the first dynode of the tube. The impact of a

single electron on the dynode releases a number of secondary electrons which are in turn accelerated to strike the second dynode. Each subsequent dynode impact releases further electrons, and so there is a current amplifying effect at each dynode stage. Each stage is at a higher potential than the previous to provide the accelerating field. The resultant output signal at the anode is in the form of a measurable pulse for each group of photons that arrived at the photocathode, and is passed to the processing electronics. The pulse carries information about the energy of the original incident radiation on the scintillator. The number of such pulses per unit time gives information about the intensity of the radiation. In some applications individual pulses are not counted, but rather only the average current at the anode is used as a measure of radiation intensity.

The scintillator must be shielded from all ambient light so that external photons do not swamp the ionization events caused by incident radiation. To achieve this a thin opaque foil, such as aluminized mylar, is often used, though it must have a low enough mass to minimize undue attenuation of the incident radiation being measured (Curran, 2009).

2.3.3.2 Detection materials

The scintillator consists of a transparent crystal, usually a phosphor, plastic (usually containing anthracene) or organic liquid that fluoresces when struck by ionizing radiation. Cesium iodide (CsI) in crystalline form is used as the scintillator for the detection of protons and alpha particles. Sodium iodide (NaI) containing a small amount of thallium is used as a scintillator for the detection of gamma waves and zinc sulfide (ZnS) is widely used as a detector of alpha particles. Zinc sulfide is the material

Rutherford used to perform his scattering experiment. Lithium iodide (LiI) is used in neutron detectors(L'Annunziata, 2012).

2.3.3.3. Sodium iodide detector advantages

Scintillation detectors use crystals that emit light when gamma rays interact with the atoms in the crystals. The intensity of the light produced is proportional to the energy deposited in the crystal by the gamma ray. The mechanism is similar to that of a thermoluminescent dosimeter. The detectors are joined to photomultipliers that convert the light into electrons and then amplify the electrical signal provided by those electrons. Common scintillators include thallium- doped sodium iodide (NaI(Tl)) often simplified to sodium iodide (NaI) detectors and bismuth germanate (BGO). Because photomultipliers are also sensitive to ambient light, scintillators are encased in light-tight coverings. Scintillation detectors can also be used to detect alpha - and beta-radiation. Thallium-doped sodium iodide (NaI(Tl)) has two principal advantages:

1. It can be produced in large crystals, yielding good efficiency, and
2. It produces intense bursts of light compared to other spectroscopic scintillators.

NaI(Tl) is also convenient to use, making it popular for field applications such as the identification of unknown materials for law enforcement purposes(L'Annunziata, 2012).

2.4. Kaolin

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is a layered silicate mineral, with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6) octahedral, Howie, *et al.*,(1992). Rocks that are rich in kaolinite are known as kaolin or china clay(Walter, 2011).

The name is derived from Chinese Gao Ling literally "High Ridge", a village near Jingdezhen, Jiangxi Province, China (Schroeder and Paul, 2003). The name entered English in 1727 from the French version of the word: kaolin, following Francois Xavier d'Entrecolles's reports from Jingdezhen. Kaolinite has a low shrink–swell capacity and a low cation-exchange capacity (1–15 meq/100g)(Kuzvert, 1984). It is a soft, earthy, usually white mineral (dioctahedral phyllosilicate clay), produced by the chemical weathering of aluminum silicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors. Alternating layers are sometimes found, as at Providence Canyon State Park in Georgia, United States. Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or as liquid slurry.

2.4.1 Natural occurrence of kaolin

Kaolin as a clay contains 10 - 95% of the minerals kaolinite and usually consists mainly of kaolinite (85 - 95%)(Kuzvert, 1984). Kaolin and the clay mineral kaolinite are natural components of the soil and occur widely in ambient air as floating dust. Kaolinite is formed mainly by decomposition of feldspars (potassium feldspars), granite, and

aluminum silicates. It is also not uncommon to find kaolin deposited together with other minerals (illite, bentonite). The process of kaolin formation is called Kaolinization, Grim(1968). Kaolinite formation occurs in three ways:

- Crumbling and transformation of rocks due to the effects of climatic factors (Zettlitz type);
- Transformation of rocks due to hydrothermal effects (Cornwall type); and
- Formation by climatic and hydrothermal effects (mixed type).

Plate I below is an example of a pure mined kaolin as it is whitish in colour, Plate II is an example of impure mined kaolin, and reddish brown due to present of impurities such as quartz, feldspar etc., and Plate III is a site of kaolin deposit where it is mined, the center is white which is composed with the pure kaolin and the banks are reddish brown due to the present of impurities with kaolin.



Plate I: A pure Kaolin



Plate II: impure Kaolin



Plate III: Mining Site of Kaolinite

2.4.2 Properties and chemical constituents of kaolin

Kaolin belongs to the group of clay minerals that contains atoms of silicon, aluminum, oxygen, ferrous and ferric iron, and hydroxyl groups as the main constituents, Ajayi(1981). It also has other elements such as phosphorus, potassium, calcium, sodium, magnesium, etc., in minutest quantities. Members of the kaolin family include dickite, nacrite, allophone, and hallosite (Brindley, 1951). The iron content in each type of kaolin clay determines its colour. It is usually white to near white in colour. Other colours such as purple, bleach brown, etc., are due to the impurities in the material.

The chemical formula of kaolin is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ which is a non-magnetic and relatively good electrical conductor, having a mean relative density of $2.58 \times 10^3 \text{ kg/m}^3$

and a fusion point of about $1,785^{\circ}\text{C}$ (Johnstone and Johnstone, 1961). Nkuesenam (1976) has shown a density range of $1.54\text{-}1.93 \times 10^3 \text{Kg/m}^3$ for impure kaolin.

2.5 Uses of Kaolin

The industrial mineral kaolin has many uses. It has favorable properties such as natural whiteness, fine particle size, non-abrasiveness, and chemical stability.

Two basically different processes are used to refine kaolin and remove the major impurities. The simplest process is called air floatation or the dry process, Murray (1960). The property of the finish product depends on a large extent on those properties inherent in the crude kaolin.

The main use of the mineral kaolinite is the production of paper; its use ensures the gloss on some grades of coated paper. Kaolin is also known for its capabilities to induce and accelerate blood clotting. In April 2008 the US Naval Medical Research Institute announced the successful use of a kaolinite-derived aluminosilicate infusion in traditional gauze, known commercially as QuikClot Combat Gauze (Rowe and Aaron, 2008).

Kaolin is used (or was used in the past): in ceramics (it is the main component of porcelain), it is as a light diffusing material in white incandescent light bulbs, also used in cosmetics as 'pre-work' skin protection and barrier creams (Stokoderm, 2016), it is used in paint to extend the titanium dioxide (TiO_2) white pigment and modify gloss levels for modifying the properties of rubber upon vulcanization, it is also used in adhesives to modify rheology (Physics of the formation and flow of matter) (Ciullo and Peter, 1996), it is used in organic farming as a spray applied to crops to deter insect damage, and in

the case of apples, to prevent sun scald, also used as whitewash in traditional stone masonry homes in Nepal (the most common method is to paint the upper part with white kaolin clay and the middle with red clay; the red clay may extend to the bottom, or the bottom may be painted black), it is used as a filler in Edison Diamond Discs which is used as an indicator in radiological dating(Diamond and Jared, 1999), more recently, industrially- produced kaolinite preparations were common for treatment of diarrhea(Chen 2014).In its altered metakaolin form, as a base component for geopolymer compounds, it is a component of Quikclot Combat Gauze, a special gauze preparation designed to stop bleeding from extensive wounds.

2.6 Deposit of Kaolin in Nigeria

Many of the non- metallic minerals, which are vital to the industrial take off of the country, have been found in commercial quantities within the country. They include limestone, dolomite, marble, **kaolin**, barite, diatomite, feldspar, quartz and silica sands, gypsum, talc, silimanite, kyanite, phosphate, salt and bentonite(Brindley, 1951).

Prior to 1975, the production of kaolin in Nigeria had been very irregular, insignificant and production data were not properly documented. Only in 1970 did the total production of Kaolin got to as much as 400 tones. In 1975, 560 tones alone were produced. A peak production of 3.4 thousand tones was explored in 1976 as reported in 1985 by Federal Ministry of Mines, Power and Steel, Nigeria. Nigeria is endowed with extensive kaolin deposits and potential consumer industries abound in the country.

Kaolin deposits are wide spread throughout Nigeria. Almost every state in Nigeria has at least one known deposits of kaolin. In Anambra state, there is the Ozubulu deposit,

Darazo deposit in Bauchi, Akpene-Obom deposit in Cross-River state, Kankara deposit in Katsina state, just to mention a few(Badmus, 2009).

2.6.1 The kaolin deposit in kankara

Katsina state has large deposit of kaolin and asbestos and other needed minerals for good industrial take off. Kaolin is one of the major natural resources that abound in Katsina state. It is hugely deposited in thousands square metres scattered in many local government areas of the state. It is known to be deposited in huge commercial quantity at Kankara local government area and its environs(Macleod, 1996).

The map (figure 2.6) is the map of Katsina state with its 34 local government area showing Kankara local government bordered by Faskari, Bakori, Malumfashi, Musawa and Dan Musa. This huge deposit of kaolin lies in Kankara within the area close to Dan Musa and Musawa local government(Ebipa, 1977).



Figure 2.3: Map of Katsina State local Government showing Kankara L.G.A.(Oyeka, 1976).

Several exploratory trips to the sites have been undertaken by geologists. The first geological work on the first deposit (Kankara 1) was carried out on behalf of an insecticide manufacturing company based in Jos. Several pits were sunk and some opencast paddocks around the old workings were opened. The resulting shafts were later examined by members of the geological survey(Nkuesenam, 1976). The work was

followed by a more detailed investigations conducted by economic geologists of the same unit. From their investigation, they proved that there are reserves of lenses of pure and contaminated kaolin in Kankara I and II and are of the order of 1.15×10^6 and 2.28×10^6 metric tons respectively (Nkuesenam, 1976).

2.7 Review of Previous Works

Haydn H. Murray worked on the industrial application of Kaolin in collaboration with Georgia Kaolin Company, Elizabeth, New Jersey; he listed the chemical constituent of both literature values and Georgia Kaolin. Furthermore, listed the industrial uses of Kaolin, where he stated its quality in application in Rubber, Ceramics, Paints, and Plastics and listed 25 other applications.

Ebipa from Ahmadu Bello University Zaria conducted a research on Geophysical exploration for buried Kaolin minerals near Kankara Katsina province, Kaduna state, Nigeria. He concluded that the Kankara 1 deposit is a valuable asset disseminated over an area of approximately 2 square kilometer and the deposit occurs in sporadic lenses and the proved reserves on the basis of the gravity result is of the order of $(1.72 \pm 0.40) \times 10^6$ metric tons.

William J. Corbett, John Burson and R. A. Young worked on Gamma-Irradiation of Kaolinite at Georgia Institute of Technology, Atlanta, Georgia (William, *et al.*, 2011). In their work, they concluded that there were changes in the physical and colloidal properties of Kaolin as a result of exposure to large doses of gamma-radiation.

A group of experts under the sponsorship of World Health Organization (W.H.O) Geneva in 2005 carried out a research on Environmental Health Criteria of Bentonite,

Kaolin, and selected clay minerals; they studied the effects on both animals and humans exposed to these clays. The experts concluded that Kaolin produces a specific pneumoconiosis, known as Kaolinosis due to the presence of radionuclides. Its fibrogenic potential is considered to be at least an order of magnitude less than that of quartz, and concluded that Kaolin should not be considered as ordinary dust (W.H.O., 2005).

In view of these, this work is undertaken to determine the radiological implications around mining sites of Kaolin in Kankara.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials and Equipment

Below is the list of the materials used in this study:

- Mortar and pestle
- Hand trowel
- Measuring tape
- Oven
- Cylindrical plastic containers
- Disposable hand glove
- Polythene bags
- Electronic analytical balance
- Candle wax
- Radiation Survey Meter(Canberra InSpector1000)
- Global Positioning System (G.P.S)
- Marker
- Vaseline
- Masking adhesive tape
- Gamma Spectrometry Set up (Canberra Model: 727, SN. 11914167)
- Atomic Absorption Spectrometer Setup (Agilent Technologies 200 series SpectrAA Model Number 280FS)

3.2 Study Area

The Kankara kaolin deposits lie within an area bounded by latitude $11^{\circ}53'N$ and $11^{\circ}54'N$ and longitudes $7^{\circ}26'E$ and $7^{\circ}28'E$, and extend over an area bordering Elgoje, Danmarke, Ungwarliman and Yargoje villages. The deposits are completely buried under variable thicknesses of overburden and occur in sporadic lenses of varying sizes and geometry(Oyeka, 1976).

Figure 3.1 shows the mining pits dug by miners for industrial take off. From the map, it is obvious that kaolin is sporadically deposited.

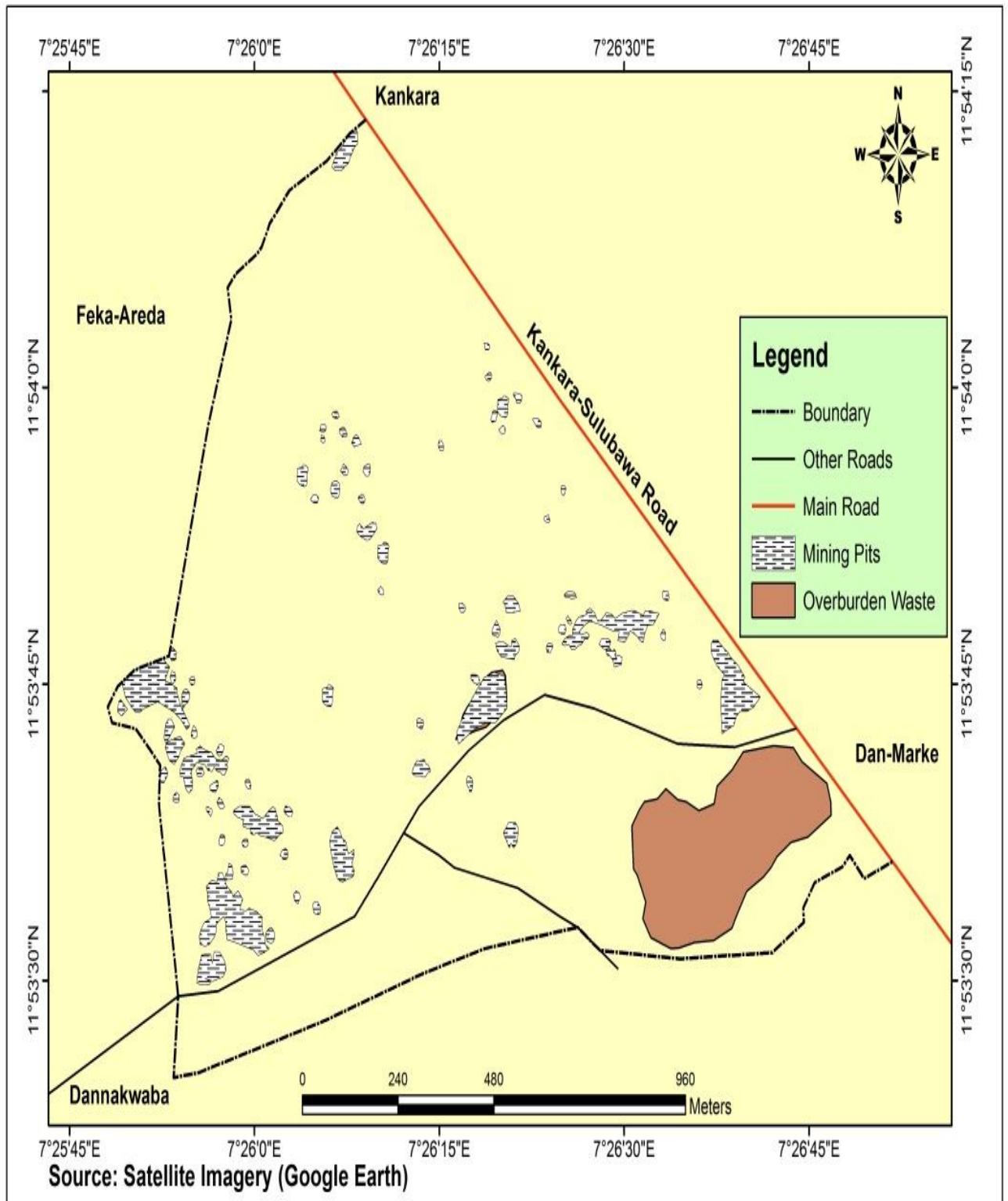


Figure 3.1: Kankara Kaolin mining Pits (Satellite Imagery, Google Earth)

3.3 Methodology

3.3.1 Sample collection

The sampling strategy was based by taking samples from the mining sites chosen randomly from figure 3.1 above.

About 1kg of Kaolin sample was collected at each sampling point (figure 3.2). A total number of ten (10) samples was collected and packed in a well labeled polyethylene bags. At each sampling point, the radiation dose level was measured using a portable survey meter (Canberra InSpector1000). The measurement was carried out by taking five different measurements from each point and the mean value was used in order to reduce error. The location of each sampling point was recorded with the aid of Global Positioning System (GPS).

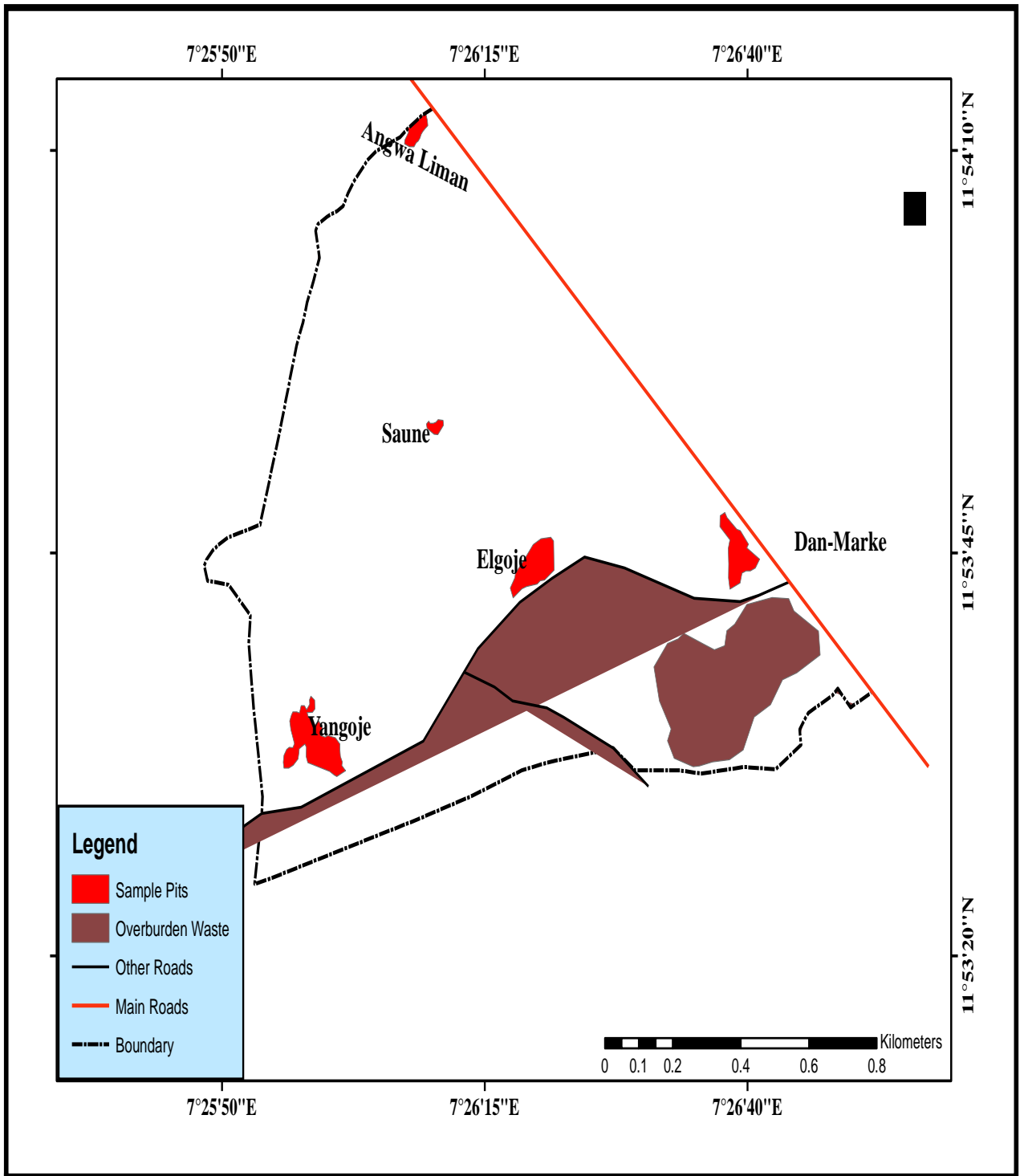


Figure 3.2: Map showing sampling pits

The plates IV and V are photograph of some of the sampling pits found in KankaraKatsina state. The depth of the pits measured from the vent of the pits ranges from 18ft 8 inches to 22ft 7 inches. Plate VI shows the different grades of Kaolin found in Kankara local government; there are about two to three types of the grades in each mining site except at Angwalima that has only one type of the grade.



Plate IV: The Kaolin mining pits at YargojeKankaraKatsina State



Plate V: The vent and path of a pit



Plate VI: The different grades of Kaolin found in Kankara

3.3.2 Sample preparation

All samples that were collected were air dried in the laboratory and further dried at 120⁰C in an electric oven for 24 hours to remove moisture. After drying in oven, mortar and pestle was used to crush the samples to fine powder. Each prepared samples was divided into two and labeled as Sample A and Sample B.

3.3.2.1 Preparation of samples for AAS analysis

The Sample A which was about 5g was taken to Multi-Purpose laboratory, Chemistry Department, Ahmadu Bello University, Zaria for elemental analysis. At the laboratory, about 3g of each of the sample A was weighed, and then digested with a mixture of 10 ml concentrated hydrochloric acid (HCL) and 3.5 ml concentrated nitric acid (HNO₃). The mixtures were left overnight without heating under the switch-on fume cupboard and heated for 2 hours at 104⁰C on the next day. Distilled water was added to the digested samples and then filtered with a whatman filter paper and topped up to 100 ml volumetric flask with distilled water. The solution was transferred into sampling bottles for analysis. Then concentration of these heavy metals in the kaolin samples was analyzed using an Agilent Technologies 200 series SpectrAA AAS (Atomic Absorption Spectrometer), (Plate VII) at Multi-Purpose laboratory, Ahmadu Bello University, Zaria.



Plate VII: Experimental Set up of the Atomic Absorption Spectrometer at Multi-Purpose laboratory, Ahmadu Bello University, Zaria.

3.3.2.2 Preparation of sample for gamma spectrometry measurement

Sample B which was about 500.0g was transferred to cylindrical plastic containers with height and diameter of 6.5cm. Then the containers were sealed tightly with cap, Vaseline was used to smear inner part of the cap, then candle wax was used to fill up gaps between the lid cap and the container, then wrapped with adhesive masking tape and finally, stored for at least four weeks to allow secular equilibrium between the mother element U-238 and daughter element Rn-222.

3.3.3 Experimental set-up

3.3.3.1 Gamma spectrometry measurement

Gamma spectrometry measurement system consists of Sodium Iodide Thallium activated (NaI(Tl)) detector of dimension 7.62cm x 7.62cm housed in 6.0cm thick lead

shield and line with cadmium (Cd) and copper (Cu) sheets (CERT manual, 1999). Computer based Multi- channel Analyzer (MCA) card system MAESTRO programme from ORTEC is used for data acquisition and analyses of gamma spectra. The background count was estimated by placing each of the samples' empty containers on the detector then counted. The chosen configuration was strictly maintained throughout the analyses.



Plate VIII: Experimental Set up of the Gamma Spectrometry at Centre for Energy Research and Training, Ahmadu Bello University, Zaria

The samples were mounted on the detector surface and counted for a period of 29,000secs in reproducible sample detector geometry and the count rate in count per second (cps) was obtained for each radionuclide in every sample analyzed. After the subtraction of background counts, conversion of the cps to activity concentration in Bq/kg was achieved using the conversion factors which are different for each nuclide as shown in Table 3.1 below (Jonah, *et al.*, 2012).

Table 3.1 Calibration Factor and Detection Limit used in the Analysis (Jonah, *et al.*, 2012)

Element	Isotope	Calibration Factor (cps/Bq/kg)	Detection Limit (Bq/kg)
^{226}Ra	^{214}Bi	8.632	3.84
^{232}Th	^{208}Tl	8.768	9.08
^{40}K	^{40}K	6.431	14.54

The activity concentrations of Th-232 and U-238 were calculated on the assumption that secular equilibrium was established with their decay products. For concentrations of Th-232 and U-238, the following gamma transition lines were used: Th series, Ac (911 keV); U series, Pb (351.9 keV) and Bi (609.2 keV). The activity concentration of K-40 was determined from the peak area of 1,460 keV lines, as shown below.

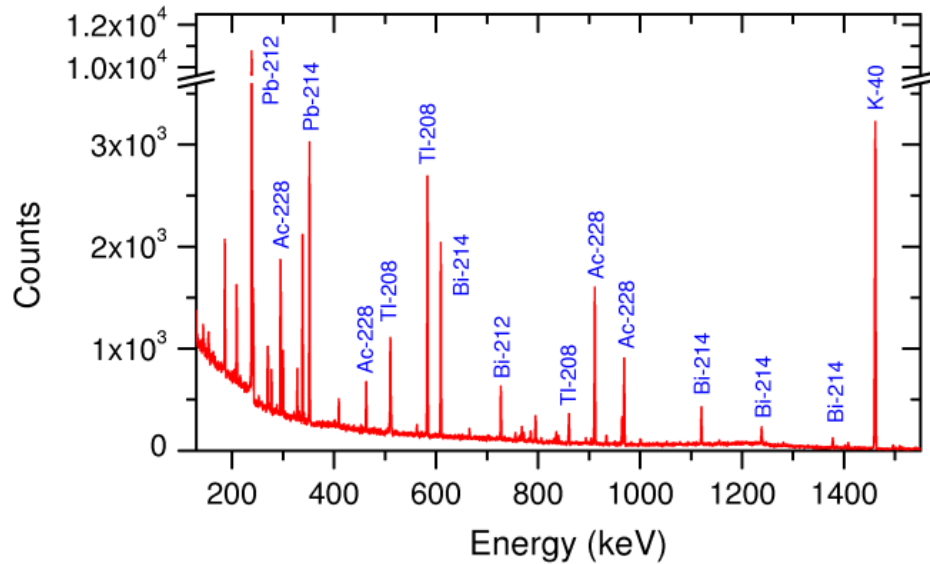


Figure 3.3: Gamma Transition lines (Beretka and Mathew, 2005).

3.3.3.2 Energy calibration

Calibration of MCA was carried out to relate the energy to the channel numbers. The amplifier voltage was set to 900 Volts at constant coarse gain of 16 while the amplifier fine gain was varied between 4 and 5 to ensure ^{137}Cs single peak rises at channel number 180. The photo peaks of the standard isotopic sources of ^{137}Cs with 661.6 keV and those of ^{60}Co with 1173.2 keV and 1332. keV were obtained after counting for 100 seconds. The table 3.2 below shows the Spectral Energy Windows used in the sample analysis (CERT Manual, 1999).

Table 3.2 Spectral Energy Windows used in the analysis(CERT Manual, 1999)

Element	Gamma Energy (keV)	Energy Window (keV)
Analysis		
Ra-226	1764.0	1620 – 1820
Th-232	2614.5	2480 – 2820
K-40	1460.0	1380 – 1550

3.3.3.3 Procedure for energy calibration of the peaks

- i. From the opened MAESTRO window, ‘calculate’ was clicked, then ‘calibration’ was clicked, a dialog box with inscription calibrate appeared which allow me to type in the calibration energy (e.g. 661.66 keV for ^{137}Cs). Then OK was clicked.

- ii. The two knobs COARSE GAIN and FINE GAIN on ORTEC 485 were used to adjust the peak fittings at channel number 180 for each peak that appear in the spectrum.
- iii. The document was saved at the end of the energy calibration by clicking on ‘Save As’.
- iv. The detector chamber was opened and the two standard sources were removed, then the detector chamber was closed and the system was shut down by following the shutdown procedure.

3.3.4 Data analysis

3.3.4.1 Determination of activity concentration

The net counts for each sample and background were acquired using the Software MAESTRO from ORTEC. Then, the background was subtracted from the net numbers of counts under each and every peak of interest. The net count was converted to activity concentration of natural radionuclides (^{238}U , ^{232}Th and ^{40}K) using the following expression in equation (3.1) below (Jibiri, *et al.*, 2007)

$$Activity(Ra, Th, K) = \frac{cps(Ra,Th,K)}{Calibration\ factor\ (Ra,Th,K)} \text{ Bq/kg} \quad \dots(3.1)$$

cps = Net count per second

Gamma radiation dose rate (H) was determined with Canberra portable scintillation spectrometer InSpector1000. This spectrometer is an easy to use, hand-held, digital and multichannel analyzer ideal for the environment monitoring purposes.

CHAPTER FOUR

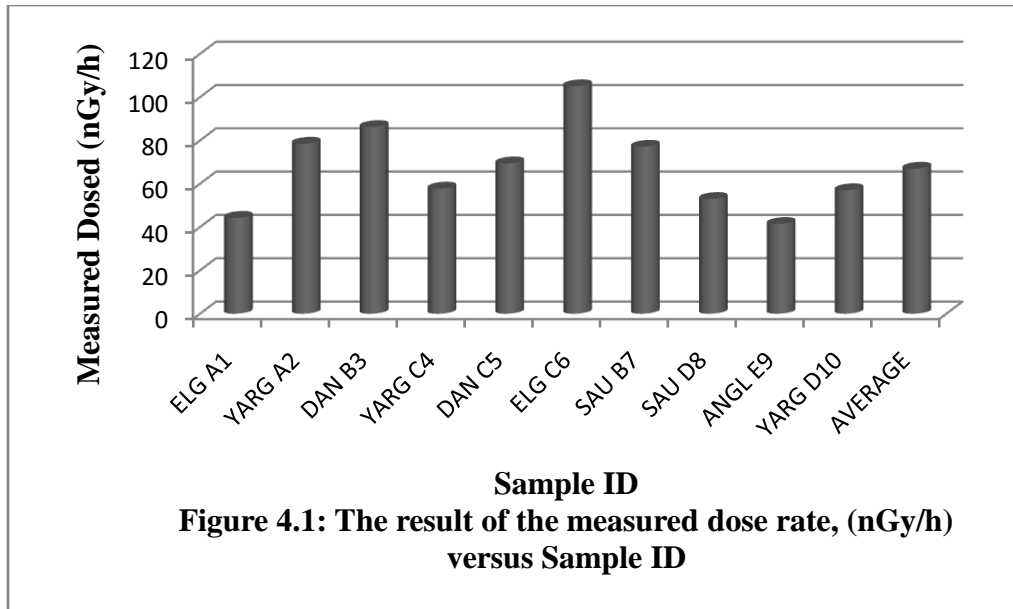
RESULTS AND DISCUSSION

4.1 Introduction

This study was aimed at assessing the radionuclide and elemental composition of Kankara kaolin using NaI(Tl) detector and Atomic Absorption Spectrometer. The samples were obtained from the mining sites and prepared for analysis at Centre for Energy Research and Training laboratory and at Multi-Purpose laboratory, Ahmadu Bello University, Zaria for the Gamma-ray spectroscopy and elemental composition respectively. The measured radiation dose level, the radioactivity concentration, the radiation absorbed dose rate, annual effective dose rate, radium equivalent activity and excess lifetime cancer risk for natural radionuclides (^{226}Ra , ^{232}Th and ^{40}K) and the elemental composition were determined. The results obtained were presented and discussed in this chapter.

4.2 Measured Radiation Dose Level

The average measured radiation dose was found to be 66.97 nGy/h with maximum value of 105.03 nGy/h at sample location (ELG C6) and minimum value of 41.43 nGy/h at sample location (ANGL E9), this may be due to the rock found in site ELG and not in ANGL as shown in Figure 4.1,



4.3 Activity Concentrations of Natural Radionuclides

The average activity concentration for Ra-226 obtained was 31.63 ± 3.07 Bq/kg with maximum activity of 76.96 ± 2.24 Bq/kg and minimum value of 12.11 ± 0.78 Bq/kg, the average activity concentration of Th-232 was found to be 58.08 ± 1.71 Bq/kg with maximum value of 96.72 ± 2.32 Bq/kg and minimum value of 24.02 ± 0.59 Bq/kg and finally, the activity concentration for K-40 was found to be 388.64 ± 3.97 Bq/kg with maximum value of 1038.93 ± 7.24 Bq/kg and minimum value of 126.13 ± 1.34 Bq/kg as shown in Figure 4.2. The figure shows the measured activity concentration for the three natural radionuclides Ra-226, Th-232 and K-40 in all the sampling sites.

Table 4.2 compares the activity concentration of natural radionuclides in the Kaolin measured in this work with activity concentration in soil of some countries, it is obvious from the table that Malaysia has the highest in radium-226 and thorium-232, Lithuania in potassium-40, while the lowest in radium-226 is India, thorium-232 is Egypt and

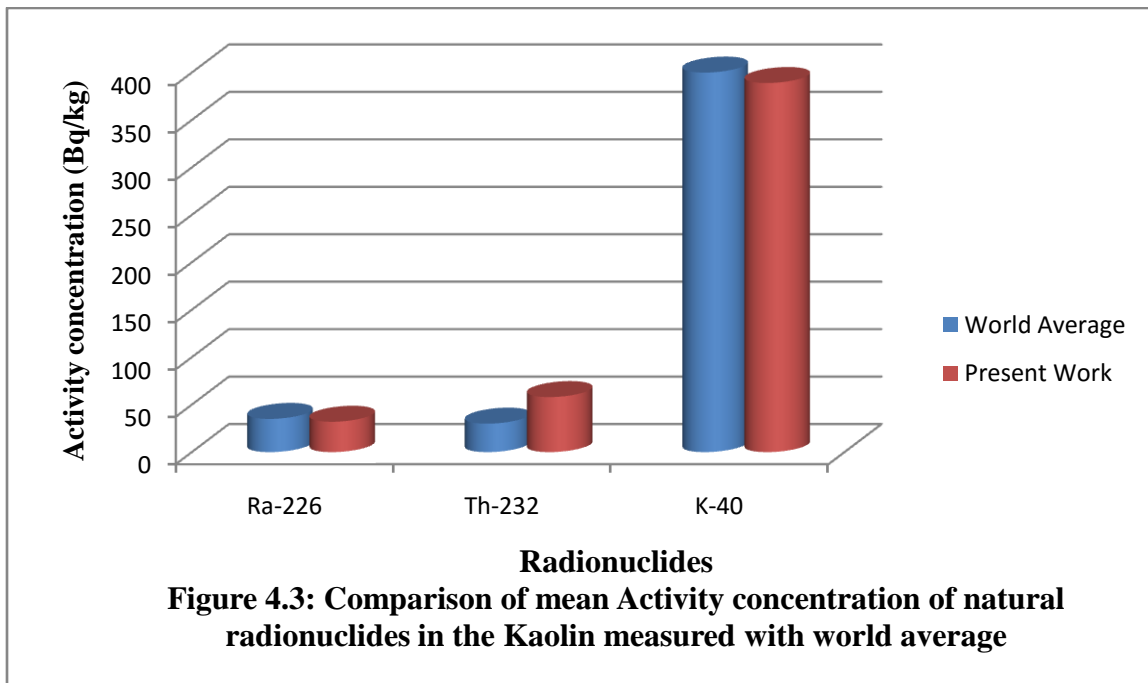
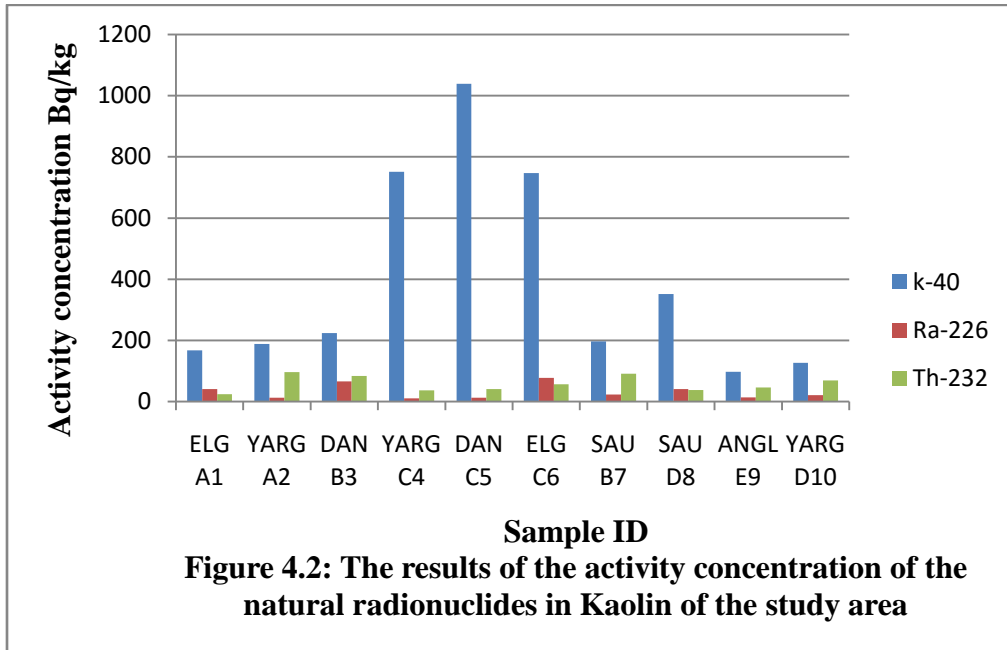
potassium-40 is Malaysia which may due to the geographical location and frequent mining in the countries that have high values.

Table 4.2: Comparison of mean Activity concentration of natural radionuclides in the Kaolin measured in this work with published data (UNSCEAR, 2000).

Country	²²⁶ Ra		²³² Th		⁴⁰ K	
	Range	Mean	Range	Mean	Range	Mean
Algeria	2 - 110	30	2 – 140	25	66 – 1150	370
Egypt	6 - 120	37	2 – 96	18	29 -650	320
Hungary	66 - 12	29	12 – 45	28	79 – 570	370
India	81 - 7	29	14 – 160	64	38 – 760	400
Kenya	92 - 11	37	35 – 74	43	543 -837	708
Lithuania	3 - 30	50	9 – 48	25	350 – 850	600
Malaysia	49 - 86	66	63 – 110	82	170 – 430	310
United State	4 - 140	35	4 – 130	35	100 – 700	370
World Average		33		45		400
Present						
Work	12 - 77	32	24 – 97	58	126 – 1038	389

The measured mean activity concentration of natural radionuclides in Kaolin is higher in Potassium-40 and has a value of 389Bq/kg which is lesser than the world average of 400Bq/kg, but in Thorium-232-40 which has a value of 58Bq/kg is higher than the world average of 45Bq/kg. The uranium progeny, ²²⁶Ra is found to be about 32Bq/kg on average; thus lower than the world average of 33Bq/kg by unity.

Figure 4.3 shows the comparison of mean Activity concentration of natural radionuclides in the Kaolin measured with world average.



4.4 Absorbed Dose Rate

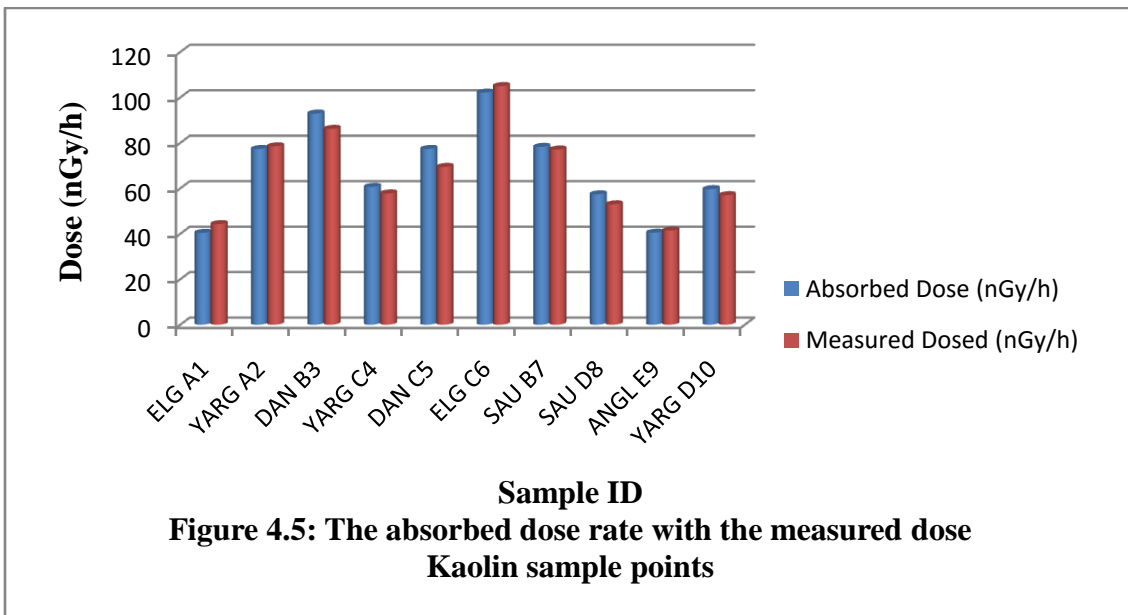
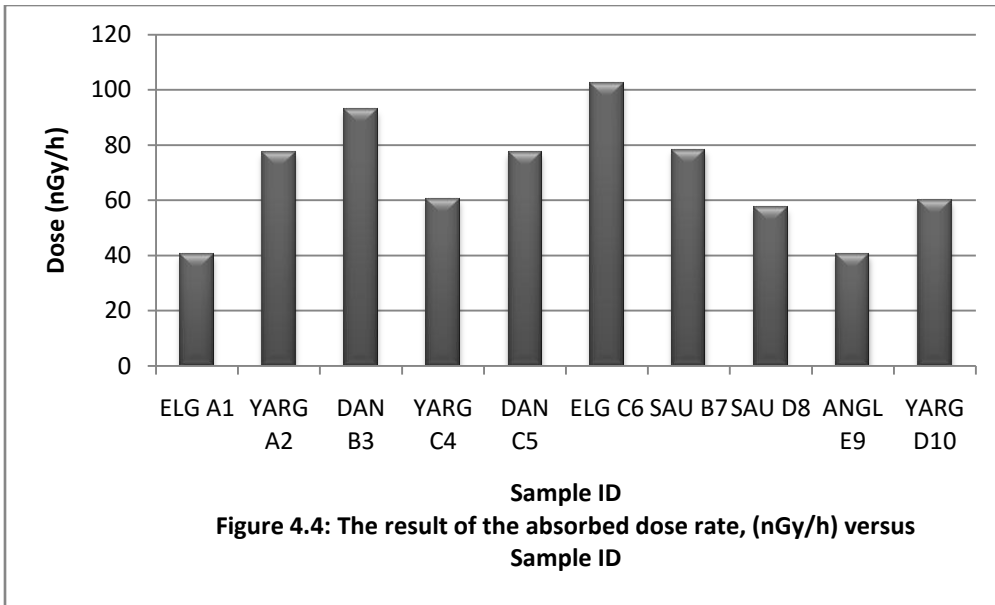
The absorbed dose rates (D) was calculated through the following relation:(UNSCEAR, 2000).

$$D = 0.427C_{Ra} + 0.662 C_{Th} + 0.043 C_K \text{ (nGyh-1)} \quad \dots (4.1)$$

Where C_{Ra} , C_{Th} and C_K are the activity concentrations in $Bqkg^{-1}$ of radium, thorium and potassium, respectively.

The results of the calculated absorbed dose rate in kaolin samples range from 40.44 to 102.13 nGy/h with a mean value of 68.66 (Table 4.4, (Figure 4.4). The average absorbed dose rate in this study is higher than the worldwide average value 57 nGy/h reported by UNSCEAR(2000). Figure 4.4 shows the absorbed dose rate calculated as a result of activity concentration.

Figure 4.5 compares the calculated absorbed dose rate with the measured absorbed dose after conversion to nGy/h. the measured dose is higher than the calculated dose rate in these sample location ELGA1, YARGA2, ELGC6 and ANGE9 (Figure 4.5), which may be due to the presence of mountain at the areas. The average measured absorbed dose is 66.98 nGy/h and is higher than the worldwide average of 59 nGy/h(UNSCEAR, 2000).



4.5 Annual Effective Dose Rate, Hazard Index, Radium Equivalent and Excess Lifetime Cancer Risk

To estimate the annual effective doses (AEDR), we took into account the conversion coefficient from absorbed dose rate in air to effective dose and the outdoor occupancy factor. In the UNSCEAR recent report (UNSCEAR, 2010), the committee used 0.7 Sv/Gy for the conversion coefficient from absorbed dose in air to effective dose received by adults, and 0.8 for the indoor occupancy factor, implying that 20% of the time is spent outdoors, on average, around world. The annual effective dose equivalent rate, in units of millisievert/year, is calculated from the following formula (UNSCEAR, 2010).

$$\text{AEDR} = D(\text{nGyh}^{-1}) \times 24(\text{h}) \times 365(\text{day}) \times 0.2(\text{outdoors occupancy factor}) \times 0.7(\text{conversion coefficient}) \times 10^{-6} \quad \dots (4.2)$$

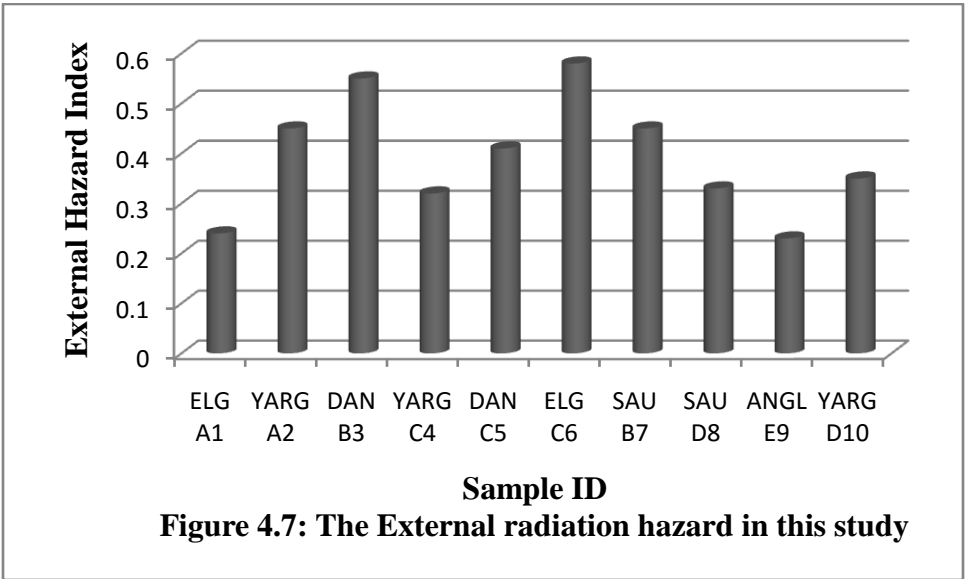
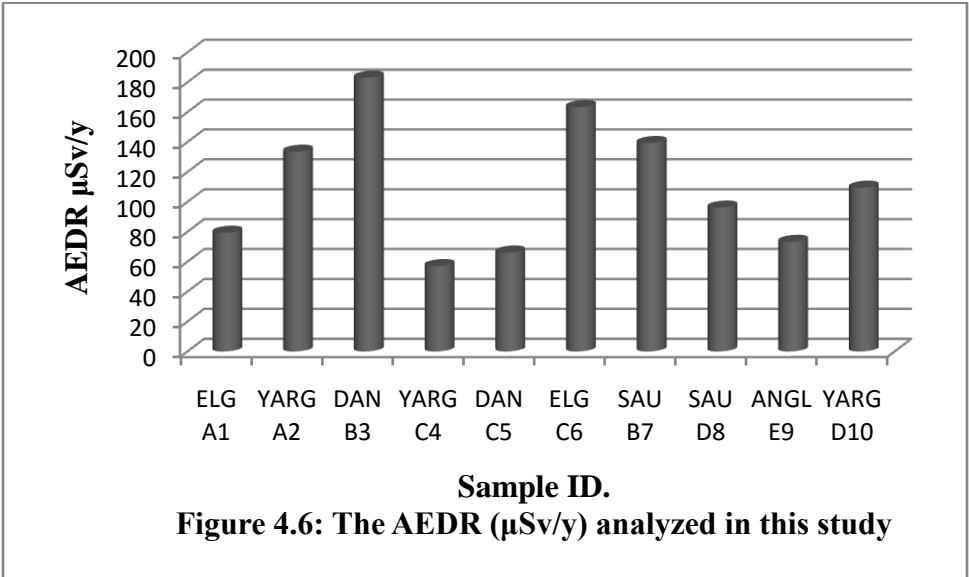
The mean annual effective dose rate was found to be 0.11 mSv/y with a maximum value of 0.18 mSv/y at the sampling location DAN B3 and minimum value of 0.06 mSv/y at the sampling location YARG C4 (Figure 4.6).

The external hazard index H_{ex} was calculated by the following equation:(UNSCEAR, 2000).

$$H_{\text{ex}} = C_{\text{Ra}}/370 + C_{\text{Th}}/259 + C_{\text{K}}/4810 \quad \dots (4.3)$$

Where C_{Ra} , C_{Th} and C_{K} are activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in Bqkg^{-1} , respectively.

The mean value was found to be 0.39 nGy/y while maximum value is 0.58 nGy/y at sample location ELG C6 and minimum value of 0.23 nGy/y at sample location ANGL E9 (Figure 4.7) was also obtained.



The Radium equivalent activity and its index were calculated from the relation(UNSCEAR, 2000).

$$(Ra_{eq}) = A_U + 1.43A_{Th} + 0.077A_K \quad \dots (4.4)$$

$$(I_{yr}) = 0.0067A_U + 0.01A_{Th} + 0.000067A_K \quad \dots (4.5)$$

Where, A_U , A_{Th} , and A_K are the average activity concentrations of ^{238}U , ^{232}Th and ^{40}K , respectively in kaolin in units of Bq/kg.

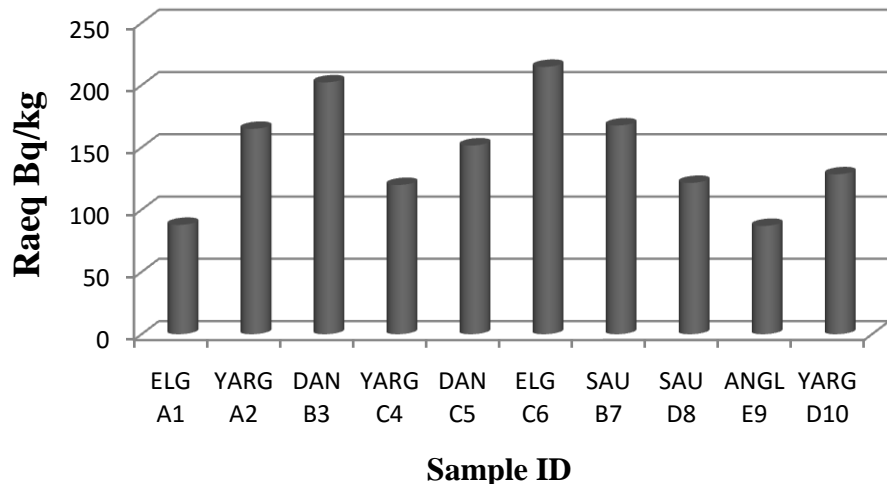
The mean value of the radium equivalent activity was found to be 144.59Bq/kg with maximum value of 214.74 Bq/kg at sample location (ELG C6) and minimum value of 86.98 Bq/kg at sample location (ANGL E9), (Figure 4.8).

And the excess lifetime cancer risk (ELCR) was calculated for kaolin samples from equation 4.6 and presented in figure 4.9

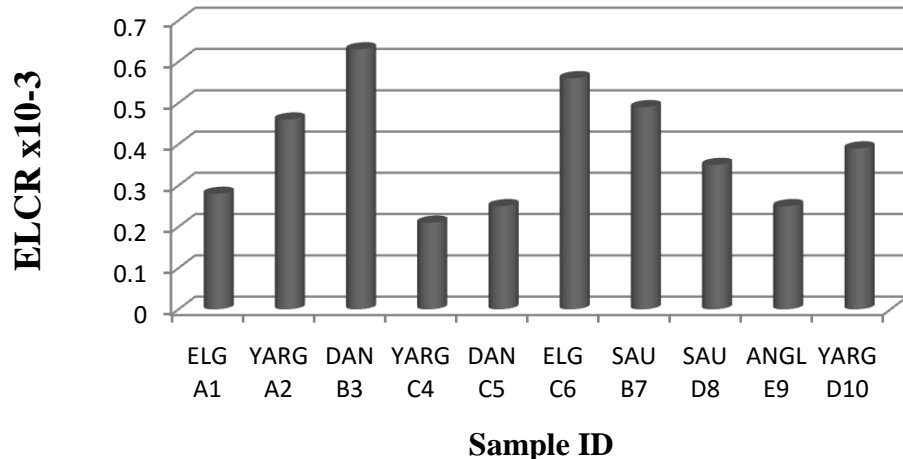
$$ELCR = AEDR \times DL \times RF \quad \dots (4.6)$$

Where AEDR is the annual effective dose rate, DL is duration of life (70 years) and RF is the risk factor (Sv^{-1}), (fatal cancer risk per Sievert) which is 0.05 (ICRP,1990).

The mean value of excess lifetime cancer risk was found to be 0.39×10^{-3} with maximum value of 0.64×10^{-3} at sample location DAN B3 and minimum value of 0.21×10^{-3} at sample location YARG C4 (Figure 4.9).



Sample ID
Figure 4.8: The Radium equivalent activity, Bq/Kg analyzed in this study



Sample ID
Figure 4.9: The Excess Lifetime Cancer Risk analysed in this study

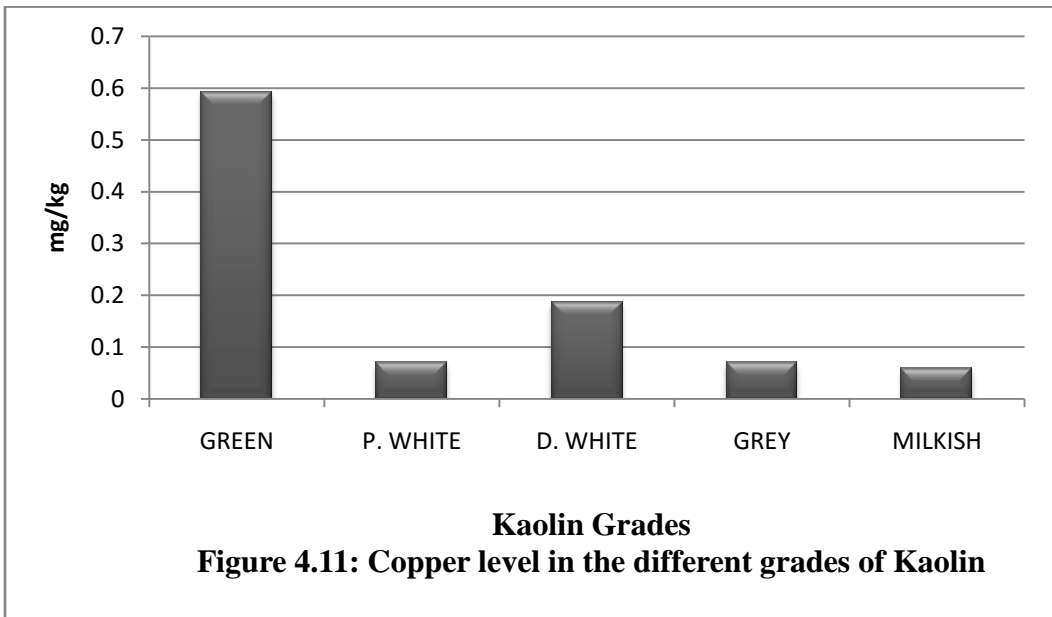
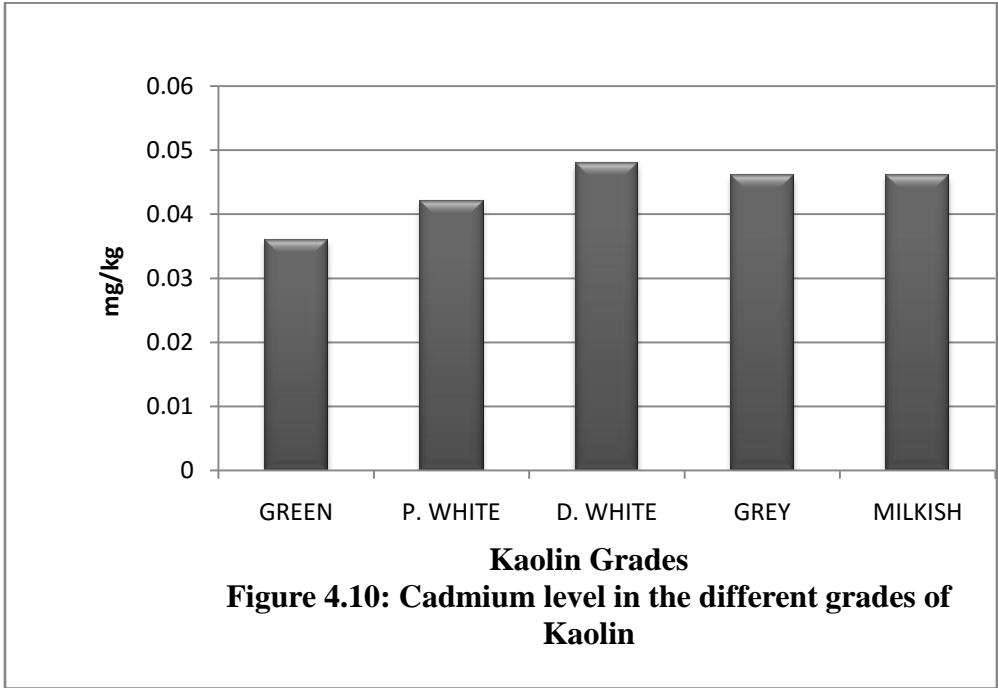
4.5 Elemental Constituents of Kankara Kaolin

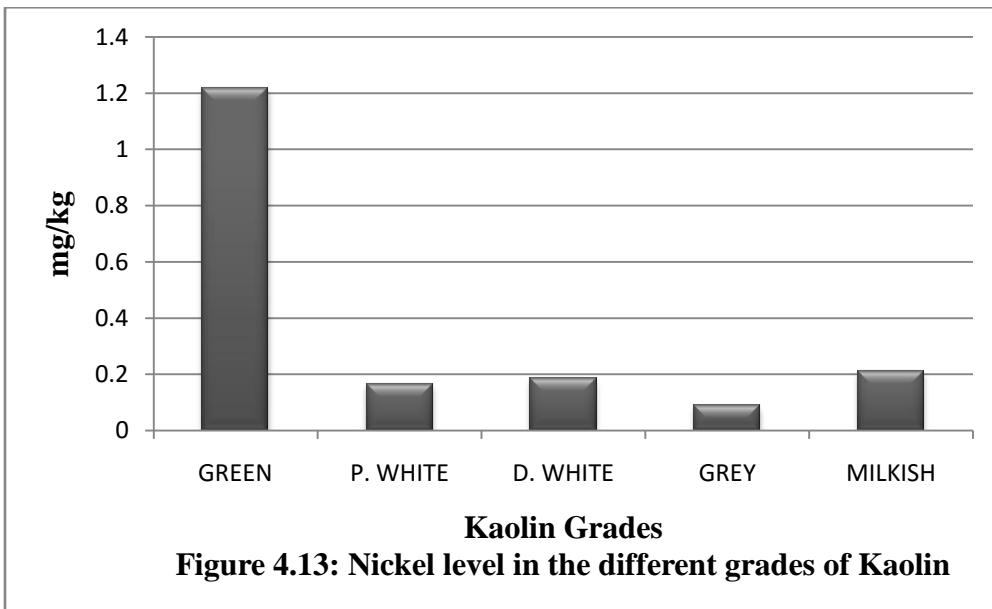
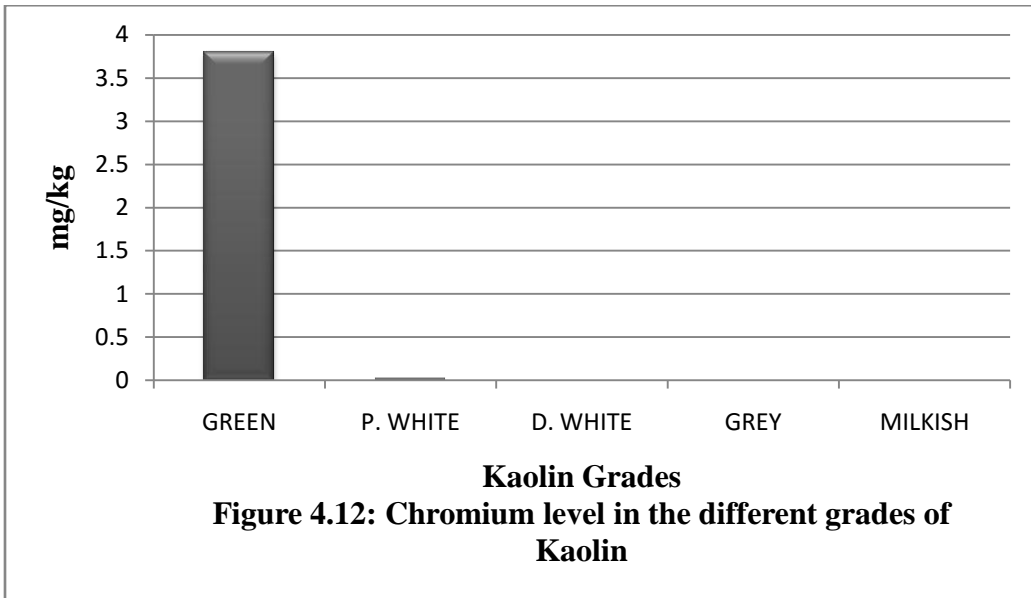
The concentration of Cadmium in the various grades of Kaolin was found in low range of 0.222 to 0.499 mg/kg (Figure 4.10). The maximum level of Cd in the soil according to Dutch standard is 0.8 mg/kg (W.H.O., 1996). Several compounds of Cadmium are used in chemical industries and in the manufacture of pesticide and herbicides (Alloway and Ayres, 1998). Cadmium is extremely toxic to human when the standard level is exceeded.

The concentration of copper in the Kaolin grades was between 0.058 - 0.592 mg/kg, the permissible limit recommended by Dutch standard is 36 mg/kg. The value of copper in the green Kaolin is very high which is 0.592 mg/kg compare to the other grades. Copper is a micro element which is essential in plant growth and occurs generally in soil, sediment and air. Cu content has been reported to differ according to the soil type and pollution source (Ouder, *et. al.*, 2007).

The concentration of chromium in the Kaolin grades was not found in some of the samples (dirty white, grey and milkish Kaolin), but has a value of 3.805 mg/kg in the greenish sample. Permissible limit recommended by World Health Organization (W.H.O) is 100 mg/kg (W.H.O., 1996).

The concentration of nickel in Kaolin samples was between 0.090 – 1.215 mg/kg, it is very high in the green Kaolin and very low in the grey Kaolin, this may be due to the presence of rock at the site of the green kaolin and absent at the site of the grey kaolin. Recommended limit of Ni by W.H.O.(1996) is 35 mg/kg, the samples were below the recommended limit. Nickel has been considered to be an essential trace element for human and animal health (Hjortenkrans, 2005).





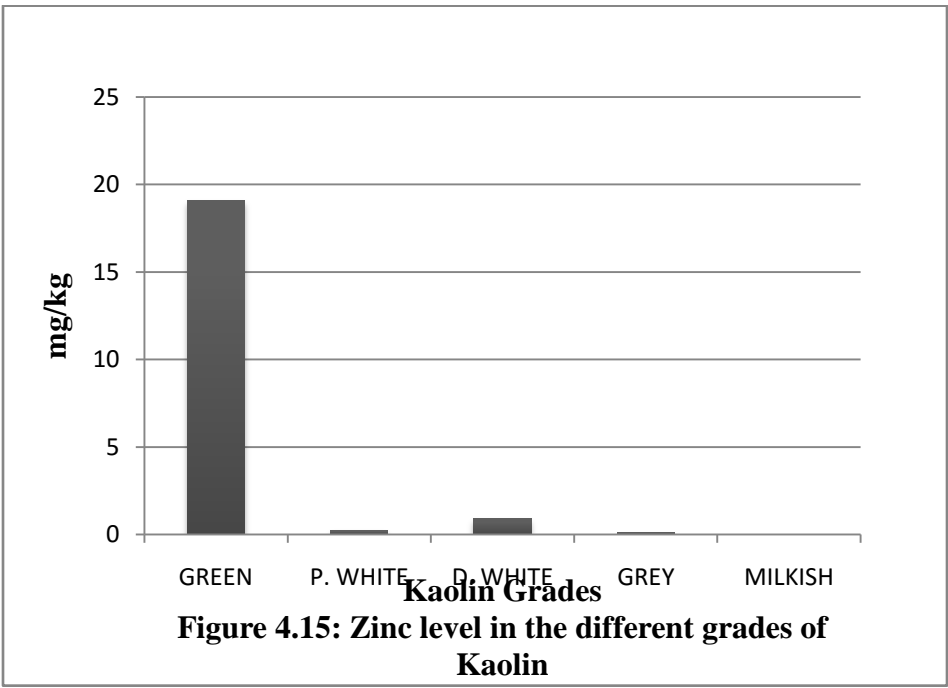
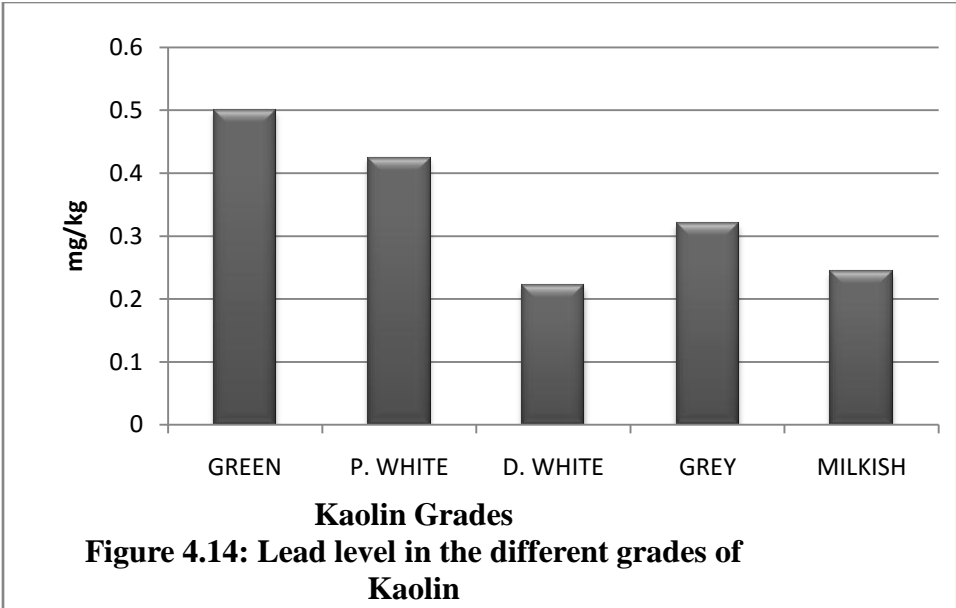
The concentration of lead in Kaolin samples varies from 0.222 – 0.499 mg/kg. The Dutch limit of lead is 85 mg/kg. All the samples are below the limit which means the environments is not polluted. Lead has toxic properties and is found in large amounts in many electronic devices, Nordic council of ministers(1995).

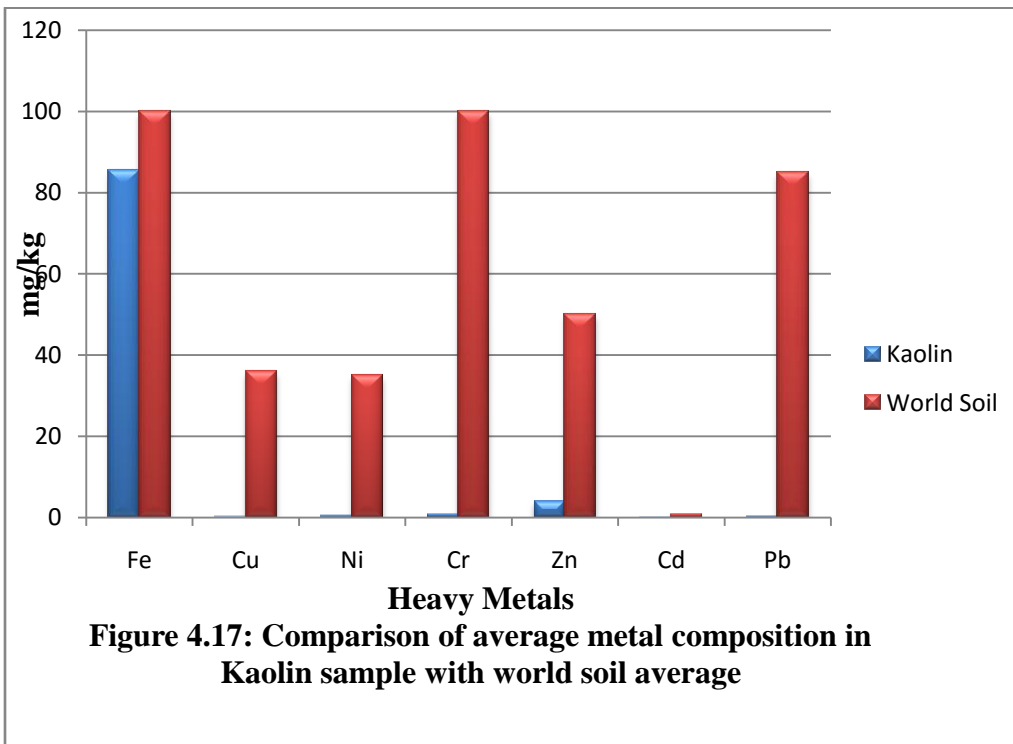
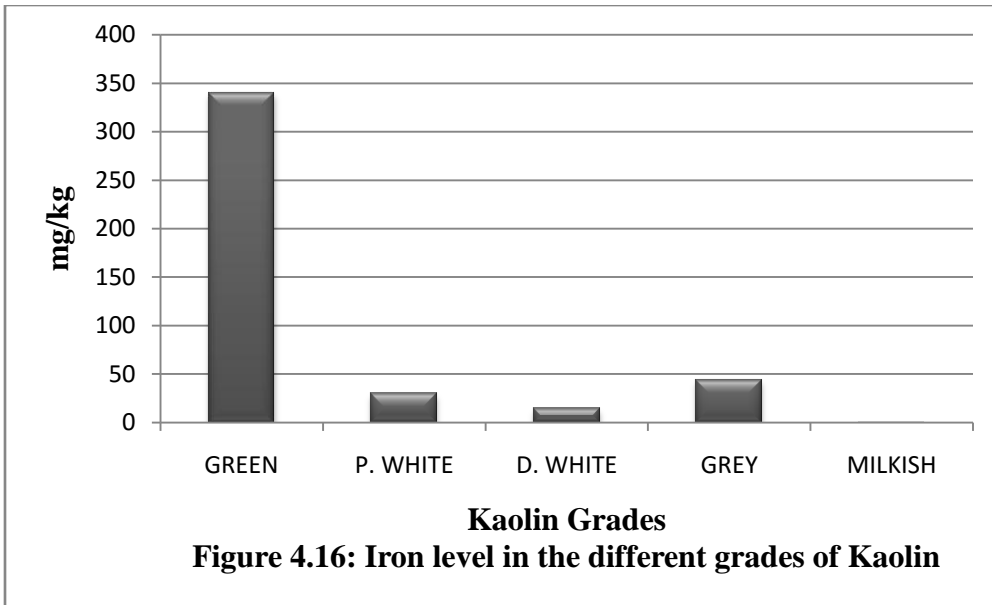
The concentration of zinc was not detected in the milkfish Kaolin. However, it was found to be 19.089 mg/kg and low in the grey kaolin. The recommended limit by W.H.O.(1996) is 50 mg/kg.

The concentration of iron in the Kaolin samples varies between 0.065 – 339.756 mg/kg, It is very high in the green Kaolin and very low in the milkish Kaolin. Recommended limit by W.H.O. is 10 -300 mg/kg based on the type and location of soil. The presence of iron in kaolin determines its colour, and iron is associated with rocky environments.

Table 4.6 in appendix I shows the elemental concentration detected in the various grades of Kaolin and Table 4.7 in appendix I shows their average values compared with the world average. The average values of all the elements are below the world average.

Figure 4.17 shows the average of the elemental composition in Kaolin samples with the worldwide average elemental composition in soil samples.





CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, data on the activity concentrations of natural radionuclides (^{226}Ra , ^{232}Th and ^{40}K) as well as absorbed dose, the annual effective dose rates, radium equivalent activity, external hazard index, excess lifetime cancer risk and heavy metal composition in Kaolin samples of KankaraKatsina state, Nigeria were quantified using a well calibrated gamma ray spectrometry detector and Atomic Absorption Spectrometry.

The mean activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Kaolin samples were estimated to be 32.43Bq/kg, 58.16Bq/kg and 389.09Bq/kg respectively. This result compare quite well with the worldwide average value of activity concentrations for natural radionuclides reported by UNSCEAR(2000), except for ^{232}Th which is higher than the worldwide average and ^{226}Ra is a unit less than the worldwide average.

The calculated and direct measured values of gamma radiation dose are higher than the dose limits set out by the Council of Ministers Ordinance of 18 January 2005. (Regulations of the Council of Ministers, (Poland); (Anonymous, 2005). This implies that the living organisms in the area might have absorbed much radiation

The mean value of the annual effective dose rate was 0.11mSv/y (110 μ Sv/y) which is higher than the world limit 0.07mSv/y (70 μ Sv/y) as reported by Orgun, *et al.*, (2007).

The radiological hazards to the public in the study area were assessed based on calculation of radium equivalent activity (Ra_{eq}), the external hazard and internal hazard index, the average Ra_{eq} was found to be 144.59 Bq/kg which is less than the recommended maximum accepted safety value of 370 Bq/kg(Lu and Zhang, 2006). The

external hazard and its index were all less than unity, except at the sample location YARG A2, DAN B3, ELG C6 and SAU B7 which have values higher than that recommended by ICRP.

The value calculated for the Excess lifetime cancer risk which is 0.39×10^{-3} is higher than the recommended value 0.29×10^{-3} (UNSCEAR, 2000).

The value of the metals Fe, Cu, Ni, Cr, Zn, Cd and Pb are below the worldwide recommended limits, but they are far higher in the green Kaolin compare to others.

Based on the result obtained, it's indicated that the people living in the study areas may be safe but the workers (miners) in the study areas may not be safe because they are directly exposed to the Kaolin.

5.2 Recommendations

Based on this research, the following recommendations are made

- i. Similar research should be carried out using different analytical technique to verify the result.
- ii. Assessment of radiological concentrations in plants grown in the study areas should be carried out.
- iii. The public should be constantly enlightened of the danger of exposure to ionizing radiation.

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APPENDIX I

Table 4.1: Activity concentrations of natural radionuclides Ra-226, Th-232 and K-40 in Kaolin samples measured.

Sample ID	k-40	Ra-226	Th-232
ELG A1	166.99 ± 1.23	40.64 ± 3.32	24.02 ± 0.59
YARG A2	188.77 ± 8.26	12.11 ± 3.28	96.72 ± 2.32
DAN B3	223.79 ± 6.76	65.73 ± 3.92	83.43 ± 3.46
YARG C4	750.68 ± 5.09	10.19 ± 2.08	36.29 ± 0.31
DAN C5	1038.93 ± 7.24	12.75 ± 1.68	41.13 ± 2.16
ELG C6	746.50 ± 5.85	76.96 ± 2.24	56.15 ± 1.65
SAU B7	196.39 ± 1.88	22.90 ± 4.87	90.67 ± 2.44
SAU D8	351.05 ± 1.50	40.88 ± 2.96	37.51 ± 1.06
ANGL E9	97.12 ± 0.38	13.55 ± 3.48	46.12 ± 1.85
YARG D10	126.13 ± 1.4	20.58 ± 2.88	68.65 ± 1.22
Average	388.64	31.63	58.06
Range	126.13 – 1038.93	12.11 – 76.96	24.02 – 96.72

Table 4.3: Measured Dose rate of Kankara Kaolin mining sites

Sample ID	Measured Dosed (nGy/h)
ELG A1	44.26
YARG A2	78.50
DAN B3	86.19
YARG C4	57.76
DAN C5	69.43
ELG C6	105.03
SAU B7	77.09
SAU D8	52.98
ANGL E9	41.43
YARG D10	57.01
AVERAGE	66.968

Table 4.4: Comparison of the calculated absorbed dose rate and measured dose rate

Sample ID	Calculated Dose (nGy/h)	Measured Dose (nGy/h)
ELG A1	40.44	44.26
YARG A2	77.32	78.50
DAN B3	92.92	86.19
YARG C4	60.65	57.76
DAN C5	77.35	69.43
ELG C6	102.13	105.03
SAU B7	78.25	77.09
SAU D8	57.38	52.98
ANGL E9	40.49	41.43
YARG D10	59.66	57.01
AVERAGE	68.66	66.97

Table 4.5: Annual effective dose (AEDR), External hazard and index (H_{ex} , I_{yr}), Radium equivalent (Ra_{eq}) and Excess lifetime cancer risk (ELCR) of Kaolin measured in this work

	AEDR	H_{ex}	I_{yr}	Ra_{eq}	ELCR
Sample ID	$\mu\text{Sv/y}$	nGy/y	nGy/y	Bq/Kg	$\times 10^{-3}$
ELG A1	79.34	0.24	0.52	87.85	0.28
YARG A2	133.55	0.45	1.06	164.95	0.46
DAN B3	183.03	0.55	1.29	202.27	0.64
YARG C4	57.04	0.32	0.48	119.89	0.21
DAN C5	66.12	0.41	0.57	151.56	0.23
ELG C6	163.34	0.58	1.13	214.74	0.57
SAU B7	139.36	0.45	1.07	167.68	0.49
SAU D8	96.19	0.33	0.67	121.55	0.34
ANGL E9	73.22	0.23	0.56	86.98	0.26
YARG D10	109.49	0.35	0.83	128.46	0.39
AVERAGE	110.07	0.39	0.82	144.59	0.39

Table 4.6: The elemental concentration in the grades of Kaolin

Elemental Concentration in Kaolin Sample in mg/Kg							
SAMPLE							
ID	Fe	Cu	Ni	Cr	Zn	Cd	Pb
GREEN	339.756	0.592	1.215	3.805	19.089	0.036	0.499
P. WHITE	29.232	0.069	0.165	0.021	0.254	0.042	0.424
D. WHITE	14.491	0.186	0.185	0	0.907	0.048	0.222
GREY	43.932	0.069	0.09	0	0.132	0.046	0.319
MILKISH	0.065	0.058	0.211	0	0	0.046	0.244
AVERAGE	85.4952	0.1948	0.3732	0.7652	4.0764	0.0436	0.3416

Table 4.7: The average elemental concentration compared with the world average

ELEMENTS	World	
	Kaolin	Soil
Fe	85.5	100
Cu	0.19	36
Ni	0.37	35
Cr	0.77	100
Zn	4.08	50
Cd	0.04	0.8
Pb	0.34	85

APPENDIX II

Kaolin sampling points within the mines and its surrounding communities and Depth

SAMPLE COORDINATE				
Name of Sample				
location	Sample ID	North (N)	East (E)	Depth
ELGOJE	ELG A1	7 ⁰ 26 ¹ 18.6 ¹¹	11 ⁰ 53 ¹ 44.7 ¹¹	20ft 2inch
YARGOJE	YARG A2	7 ⁰ 25 ¹ 58.3 ¹¹	11 ⁰ 53 ¹ 34.2 ¹¹	22ft 7inch
DAN MARKE	DAN B3	7 ⁰ 26 ¹ 36.2 ¹¹	11 ⁰ 53 ¹ 42.2 ¹¹	21ft 7inch
YARGOJE	YARG C4	7 ⁰ 25 ¹ 52.6 ¹¹	11 ⁰ 53 ¹ 31.7 ¹¹	22ft 3inch
DAN MARKE	DAN C5	7 ⁰ 26 ¹ 38.4 ¹¹	11 ⁰ 53 ¹ 44.7 ¹¹	21ft 5inch
ELGOJE	ELG C6	7 ⁰ 26 ¹ 21.5 ¹¹	11 ⁰ 53 ¹ 39.4 ¹¹	20ft 8inch
SAUNE	SAU B7	7 ⁰ 26 ¹ 10.2 ¹¹	11 ⁰ 53 ¹ 52.8 ¹¹	19ft 6inch
SAUNE	SAU D8	7 ⁰ 26 ¹ 11.4 ¹¹	11 ⁰ 53 ¹ 50.3 ¹¹	19ft 10inch
ANGWALIMAN	ANGL E9	7 ⁰ 26 ¹ 8.3 ¹¹	11 ⁰ 54 ¹ 11.7 ¹¹	18ft 8inch
YARGOJE	YARG D10	7 ⁰ 25 ¹ 59.6 ¹¹	11 ⁰ 53 ¹ 29.1 ¹¹	21ft 4inch