ELEMENTAL ANALYSIS OF GEOLOGICAL, HERBAL AND FOOD SAMPLES USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

By

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SUBMITTED IN PATRIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS.

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2. W. Tsegaye Birhanu, A.K Chaubey, T. Tessema Teklemariam, Y.A. Ahmed, B. Ibrahim. Determination of Natural Radioactivity Levels of ^{238}U, ^{232}Th and ^{40}K in rocks around Gondar city, Northwest Ethiopia. **International Journal of Engineering, Science and Mathematics (IJESM), volume 5, issue 3, pp.45-59 March 2015**

3. W. Tsegaye Birhanu, A.K Chaubey, T. Tessema Teklemariam, B.B. Mohammed Dewu and I.I Funtua. Application of Instrumental Neutron Activation Analysis (INAA) in the Analysis of Essential elements in Six Endemic Ethiopian Medicinal plants. **International Journal of Sciences: Basic and Applied Research (IJSBAR), Volume 19, No 1, pp. 223-227, January, 2015**.

4. W. Tsegaye Birhanu, A.K Chaubey, T. Tessema Teklemariam, B.B. Mohammed Dewu, Y.A. Ahmed and N. Abubaker. Analysis of Essential elements in Ethiopian finger millet (Eleusine coracanda) by Instrumental Neutron Activation Analysis (INAA). **International Journal of Basic and Applied Sciences (IJBAS), Volume 4, No 1, pp.82-88, January, 2015**.

5. T. Tessema Teklemariam, A.K Chaubey, W. Tsegaye Birhanu, B.B. Mohammed Dewu and I.I Funtua. Multi Elemental analysis of Medicinal Plant Flower Hygenya Abyssinia "Locally called Chima" Used in Rural of Ethiopia (Gurage Zone, Shamene) as a Medicine to Cure from Tapeworm. **International Journal of Science and Technology. Volume 2, issue12, November, 2014**.

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Abstract

Instrumental neutron activation analysis (INAA) is a nondestructive multi-elemental nuclear technique for determination of elemental and isotopic compositions. In this study, the Nigerian research reactor (NRR-1) based NAA was carried out with the the objective to find out scientific evidences on what essential and toxic isotopic compositions are available in Chilga Woreda soil, six endemic herbal plants and three finger millets.

The results of soil analysis showed that the soil of Chilaga woreda is rich in soil nutrients. The richness of the soil in nutrients, however; has been affected due to the existence of high concentration contents of Al, Mn, Fe and H which cause the soil acidic. Similarly, the results obtained from the six different endemic medicinal plants showed that a total of 20 elements were quantified. Among which Mg, K, Ca, Cl, Al, Fe, Na, V, Mn and Zn are the most essential elements for the prevention and treatment of various human ailments such as asthma, headache, stomach ache, malaria, diabetes Mellituses, blood pressure, stroke, etc. Thus, this study supports the claims made by the traditional healers and the medicinal plants are potential candidates for developing new drugs except Artemisia Abyssinica that contains in excess concentration of Al, Fe and Na .

It is also evidenced from results of finger millet analysis that white, black and mixed finger millets are rich in essential elements that have significant nutritional quality and medicinal properties as compared to Teff and other cereal crops. For instance, essential elements Cl, V and Rb which are present in finger millet are not present in Tef.

The other problem that was assessed in this work is about the natural radioactivity of ^{238}U, ^{232}Th and ^{40}K in rocks around Gondar city using the technique of NaI(Tl) gamma-ray spectrometry. The results obtained indicate the radiation hazards emanating from the natural radionuclides in the rocks, which are commonly used for house construction in the city, do have insignificant harm to the public except the rock from Debecha Rufauel.

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Chapter 1

General Introduction

1.1 Introduction

Instrumental neutron activation analysis (INAA) is a nondestructive analytical nuclear technique involving the use of neutrons gained from accelerator, reactor and isotopic neutron sources to the analysis of chemical composition of geological and biological matters. INNA is believed to be a versatile technique and widely applicable tool in every field of science. Cases in point, recent technological development in high resolution detection using High-Purity Germanium detector (HPGe) gamma-ray spectrometer and computerized data processing software packages in neutron activation analysis (NAA) has opened up new eyes for researchers to examine the geochemical composition of matters, environmental pollution, nuclear structure investigation, astrophysical investigation, criminal investigation, medical examination, nutritional trace elemental analysis, etc further. Neutron activation analysis is a nuclear analytical technique that provides a wealth of information about the world around us.

The superiority of the NAA technique over other techniques such as Atomic Absorption (AA), Mass spectroscopy (MS), X-ray Resonance Fluorescence (XRF) and laser induced breakdown Spectroscopy (LIBS) is its non-destructiveness, high selectivity and sensitivity, and multi-elemental analysis. Moreover, the usefulness and vitality of NAA to the precise

determination of elemental mass and concentration in the sample drawn from the natural environment has made it the top most all of techniques.

Hence, the method is based on the capture of gamma-rays emitted from the irradiated and activated sample. In other words, the samples of which the research considers are irradiated in a nuclear reactor, in which high neutron fluxes are produced. Except light elements such as ^{1}H, ^{7}B, ^{16}O, ^{12}C, ^{14}N and ^{31}P having very much low cross-sections, the majority of other elements in the sample are activated just after neutron capture. Accordingly, by capturing the gamma-rays emitted from the activated sample, qualitative and quantitative based analyses are used to identify the types of elements and their corresponding concentration amounts in the sample of interest. The amount of radioactive isotopes formed during irradiation is directly proportional to the amount of the isotope from which it is formed. Radioactive elements formed can be determine from their characteristic half lives and gamma rays energies

1.2 Rationale/ Justification of the study

All living things including human beings require a number of essential organic and inorganic compounds for their health and normal growth of their bodies. These compounds are used as sources of energy for their day to day activities. Equally, metallic and non-metallic elements which are very essential for the metabolic process of humans, animals and plants bodies are required within certain permissible limits. If, the intake of these chemical elements by living things is either beyond or below the permissible limits,it results in metabolic disturbances. From this context, it is possible to deduce that by employing nuclear or atomic analytical techniques nowadays it has become a subject of scientific interest on multi-elemental analysis. Such area of concern is growing with the aim to find out the the essential chemical elements available and to determine the amount of those elements in soils, cereal crops, food items, air, water, rocks, blood, hair, etc; and

the levels of toxicity prevalent in solid crystals, metals and liquids, etc. To recast a case, analyzing the essential composition of cereal crops, medicinal plants and the soil in which the plant grow seems to be the gap that requires much scientific attention, in relation to their substantial mineral, nutritional and medicinal values.

On the other hand, nowadays, environmental pollution has become a global subject and area of concern, caused by many factors such as fast growing population, unwise human land use, erosion of fertile land, expansion of industrialization, dissertation, deforestation, medical and industrial waste disposals, etc. Thus, the health and food welfare of human beings will adversely be threatened in the course of time if the environment is getting more and more polluted unless otherwise controlled wisely. In order to make such environmental pollution put under control and monitor it, employing scientific methods is the only viable option to determine the levels of pollutants.

Apparently, there are various contaminants in the environment where human beings live. For instance, heavy metal pollution (Pb, Cd, As, Cr, Hg, Cs, Co, etc) are associated with areas of intensive industrial expansion, addition of fertilizers and pesticides for better agricultural yields, waste disposal of radioactive materials from medical and industrial centers, and the depositions of heavy metals from the atmospheric particles on soil environment are a few to be mentioned. In particular, heavy metals Pb and Cd which have not yet been known for biological function are toxic elements if they are taken in excess amounts.

Similarly, radiation is also the other component of environmental pollution under the condition that the existence of excess amount of radioactive materials. Radiation is a natural part of our environment. The sources of radiations are both natural and manmade (or anthropogenic) radioactive isotopes. About 87% of the background radiation comes from terrestrial and cosmogenic radionuclides. So, human beings are exposed to natural background radiation every day from the ground, soil, building materials, air, food, outer space, and even elements in their own bodies. In particular, potassium, uranium, thorium

and the progenies of uranium and thorium are the major causes of terrestrial background radiation and are found widely distributed through the world in varying amounts.
In light of the above points, in this research work, Instrumental Neutron Activation Analysis using coaxial HPGe detector gamma ray spectrometer was applied to three geological and biological samples. In addition, radiation analysis using NaI(Tl) scintillation detector gamma ray spectrometer was applied to one geological sample. In general, the problems addressed in this research were

- Multi-elemental analysis of soil
- Determination of the activity concentrations and radiation doses of primordial nuclides (^{238}U, ^{232}Th and ^{40}K) in rocks
- The Analysis of essential elements and their curative properties in medicinal plants
- Analysis of essential elements and their nutritional quality in black, white and mixed finger millets

1.3 Statement of the Problem

Soil is an important part of the ecosystem. It consists of a complex mixture organic solids and inorganic solids resulting from geophysical and pedochemical weathering process of parent rocks (Lae & Manoj, 2004), water and air. The content of soils varies from place to place across the landscape. Therefore, soil from such different locations can have different amounts of soil nutrients. A fertile soil is expected to consist of essential elements such as P, K and N in large proportions as primary nutrients and elements like Mg, Ca and S in moderate proportions as secondary nutrients with elements Cu, Mn, Mo and Zn as trace elements and some other elements at the trace levels for the normal growth of plants.
However, soil can be affected by high concentrations of essential/nonessential elements, low concentrations of essential elements, deposition of heavy metals (Pb, Cd, As, Cr, Hg),

high level of acidity, and high cation exchange capacity (CEC). For instance, trace elements like Cu, Mn, Mo, and Zn can be toxic for both plants and soils if their concentration amounts are more than necessary in the soil environment. Similarly, elements such as As, Ba, Cd, Cr, Pb, Ni, and Se which have not yet been known as essential elements in plants can be toxic at high concentrations or under certain environmental conditions in the soil (Slagle et al., 2004). Thus, soil contamination ultimately can end up in plants growing in the soil; animals that eat the plants growing in the soil. Similarly, when humans eat plants grown in the soil, they indirectly absorb contaminants which were present in the soil.

Even though many studies have been done worldwide to investigate soil fertility and composition, scarcity and availability of essential chemical elements, deposition of heavy metals and natural radioactivity in the soil, in Ethiopia researches on soils have not been conducted nationwide very well by employing nuclear and atomic analytical techniques or by any other means in the reminiscent Ethiopian research studies.

Chilaga Woreda, which is found in North Gonadr zonal adminstration, Amhara regional state of Northwest Ethiopia is known for its low production of cereal crops. It is a customary agricultural practice for farmers in the area to support the soil with Urea and Daf fertilizers to heal the soil from high toxicity. Even the production of cereal crops from these soils by supporting them with fertilizers is farfetched. Apart from testing the N, P, and K contents and soil pH meter, the problem that has been observed in soil assessment studies- what is essential and/ or what toxic elements are available in the soil of Chilga Woreda has not been done.

Thus, to address the real problem of the soil of Chilga woreda this study was needed to address the objectives and to find out evidences about the real mineral and chemical compositions of the soil, toxicity and the cause for soil toxicity, the mineral deficiency of the soil using nuclear reactor based neutron activation analysis.

Apart from mineralization, soils are also the source of terrestrial radioactivity. The radioactivity of various soils are related to the nature of parent rocks from which the soils are derived (NCRP, 2003). This implies that all soils and rocks are radioactive at different levels. According to IAEA (2010); Fasae (2013) rocks and some building materials such as soil, bricks and cements can be substantially the cause of external radiation exposure if such materials contain elevated levels of natural radionuclides such as ^{40}K, ^{238}U, and ^{232}Th and the decay series of ^{238}U, and ^{232}Th. In particular, rocks which are commonly used for house building in the form of stones and gravels of different sizes contribute to the external gamma dose rate more than humans receive from the environment (EL-Taher, 2011).

Therefore; measurement of the radioactivity of rocks and understanding the dynamic activities of the natural radioactive radionuclides in the natural environment is very important before using for house buildings as well for other industrial purposes so as to protect the public from radiological hazards (IAEA, 2010).

Although the construction industry in Ethiopia is growing in an alarming rates, there is no governing law and regulation that is forced to measure the radioactivity levels of building materials before they are used for construction purpose. On top of that in Ethiopia, since research on environmental radioactivity has not yet been conducted satisfactorily, the radioactivity map of the country has not yet been addressed and thus areas with high or low background radiation have not yet been identified clearly. For instance, radioactivity assessments done in other parts of the world like Ramsar (Iran), Guar pain (Brazil), Southwest France, Kerala (India), Yangijang (China) and Hong Kong (China) showed that these areas were found with highest natural background radiation (UNSCEAR, 1993; Soharabi, 1997; Ghiassi-nejad et al., 2002) due to the existence of elevated contents of radioactive elements such as ^{40}K, ^{238}U, and ^{232}Th.

Therefore; the this study was considered necessary to investigate the radioactivity levels

of rocks around Gondar city in Northwest Ethiopia where heavy constructions are underway using rocks collected from the local areas around the city. The specific activities of ^{40}K, ^{238}U, and ^{232}Th radionuclides and their possible radiological hazards have been determined based on radium equivalent activity, dose rates, internal and external radiation indices.

On the other hand, soil radioactivity, fertility or contamination has direct impact on cereal crops and plants that grow on soil, and then ultimately on animals and plants that eat both plants and cereal crops. It is obvious that, for many centuries plants provided man with all his basic needs such as food, clothing, shelter, flavor and fragrances (Gurib-Fakima, 2006). Equally on medicinal aspect, medicinal plants have been in use traditionally for centuries as curative properties for various types of human diseases and infections even before and after modern conventional medicines were put in use. It is for the very reason that many of the plant species used for this purpose have been found to contain essential therapeutic substances that are useful for medication. Even in today's world, medicinal plants have become important for the preparation of various drugs singly or in combination as they are the principal source of raw material for the other medicines. However, as studies indicate the effectiveness of medicinal plants for therapeutic reason is often accounted for their organic constitutes like flavonoids, alkaloids, essential oils, vitamins, etc (Folashade & Omoregie, 2013; Salihu & Ado, 2013; Suchita et al., 2014; Adachukwu & Yusuf, 2014) but little attention has been given to the role of their inorganic constituents (Niamat et al., 2012; Pednekar & Raman, 2013).

In the same way, 80% of the Ethiopian population commonly use traditional medicinal plants as curative properties. But according to the report of Hawaze et al. (2012) recent research made on Ethiopian medicinal plants has been focused mainly on inventories and checklists. Although some of them have been touched, the majority of them are still awaiting scientific studies (Endashaw, 2007; Belayneh et al., 2012).

It is based on such research gap that the present study was basically concerned with the

invetigation of the essential and toxic inorganic elemental compositions of six Ethiopian endemic medicinal plants known as Thymus Schimperi (or Tossign), Echinops Kebericho (Keberichio), Artemisia Abyssinical (Chikugn), Lippia Adolensis (Kesse), Celematics Longicanda (Nechyeazo harge) and Millettia ferruginea (Birbra) as these medicinal plants are widely used in Ethiopia as traditional medicines to cure various ailments as spice of food and even in some places as food supplements. Moreover, the study could address that if excess doses or prolonged intake of medicinal plants can lead to accumulation of trace elements which can be toxic and cause various health related problem.

Apart from herbal plants, cereal crops like finger millet and tef can also be used as medicines for preventing diabetes in human body. Finger millet (Eleusine coracanda) is an indigenous crop to the Ethiopian highland and has been cultivated for centuries before it spread to African and Asian countries (Rajalakshmi et al., 2014). As studies suggest finger millet is a stable food with rich constituents of carbohydrate, protein, fat, vitamins and essential inorganic nutrients (Shimelis et al., 2009; Khouloud et al., 2013; Amadou et al., 2013). It is considered as wonderful cereal crop because of its good storage of quality, high nutritive value and therapeutic value. Finger millet is grown almost exclusively once a year.

In Ethiopia, finger millet is known in Amharic by "Dagussa". It is known as a good source of energy and is usually used to make liquor (a local alcoholic drink known as Araki and local beer namely, "Tella"). Even though finger millet has been grown as a subsistence crop for centuries in Ethiopia, it has still remained an orphaned cereal crop with little scientific evidences about its chemical composition. Therefore, this study was needed to evaluate the nutritional value and to determine the chemical composition of three finger millets: white, black and mixed species. Hopefully, this will aid promotion the use of finger millet in the management of the nutrition-related problems in Ethiopia.

In general, the research problems that are discussed so far have not yet been addressed for investigated seems to be the gap. Thus, in this study the essential chemical elements,

levels of radioactive or toxic elements in the samples that are drawn from the natural environment of the study areas were analyzed qualitatively and quantitatively based on instrumental neutron activation analysis using HPGe and NaI (Tl) detector gamma ray spectrometry.

1.4 Purpose and Objective of the Research

1.4.1 Purpose of the Research

The aim of this thesis is to investigate and provide first hand scientific information about the soil related problem in Chilga Woreda, about the essential chemical elements in endemic Ethiopian medicinal plants and nutritional quality of finger millet. It is for the very reason that knowledge based manipulation of natural environment is an indisputable practice of the 21^{st} century academics. In so doing, this experimental based research was obtained as an appropriate tool for this study for it is helpful in developing basic understandings about the chemical composition and natural radioactivity in geological and biological samples to be drawn from such as soils, rocks, finger millet and medicinal plants. Information gained from this study would also be helpful for agricultural experts, nutritionists, health and radiation works, and the public at large to redesign their mode of operations how to manipulate natural resources easily in such a way that would be very suitable and convenient to human beings.

1.5 Objective of the Research

The general objective of this research is to determine the essential and toxic chemical elements in soils, finger millets and medicinal plants on qualitative and quantitative using an accurate, sensitive and reliable nuclear analytical technique known as instrumental neutron activation analysis regardless of which the physical and chemical compositions of

the samples under investigation.

The second objective of the research is to study the activity concentrations, radiation levels and radiological hazards of natural radioactive isotopes (^{238}U, ^{232}Th, and ^{40}K) in rocks around Gondar city using the NaI(Tl) scintillation detector gamma-ray spectrometer.

The specific objectives of the research are

- to determine the concentration ranges, distribution and behavior of major, minor and trace essential nutrients (or minerals) in the soil of Chilga Woreda,
- to determine the activity concentrations, radiation doses of the terrestrial radionuclides (^{238}U, ^{232}Th and ^{40}K) in rocks around Gondar city and compare them with the international recommended radiological limits,
- to investigate the essential and nutritional quality of white, black and mixed species of finger millets and compare them with nutritional quality of white and purple Tef
- to determine and relate the concentration of elements found in medicinal plants relative to their potential to impact on humans health performance.
- to demonstrate the feasibility of Instrumental Neutron Activation Analysis in multi elemental analysis over a wide range of concentration.

1.6 Significance of the study

In this study, element characterization and measurement of natural radioactivity has been carried out with the objective to assess the essential mineral contents, mineral scarcities, heavy metals toxicity and the level of radiation emission in the geological and biological samples drawn from the natural environment of the study areas. Thus, it has been possible to come up with new experimental results, which represent the reality in the actual environment.

On top of the elemental analysis, this study also provides a picture about the existing challenges and investment opportunities of the research areas. It can also shed light on

- how to use knowledge based medicinal plants for treatment of various diseases,
- efforts to enhance soil fertility, production and utilization of cereal crops and plant growth to ensure food security and self-sufficiency in chilga woreda
- creating awareness among the public that white, black and mixed finger millets are substantially enriched in nutritional values as compared to other cereal crops
- providing adequate information about the levels of natural radioactivity or potentially toxic elements in the natural environment.

Finally, the information or knowledge generated from the study will also be helpful for people living in the surrounding areas of the target population of the sites in which the research has been conducted. Furthermore, it also would be beneficial for traditional medicine practitioners, producers and investors in assessing their activities, to redesign and upgrade their traditional practice into scientific ways. Likewise, this study can be used as a scaffold for future research endeavours and the data obtained in this study may be useful for natural radioactivity mapping of the Amhara regional state.

1.7 Limitation of the Study

The limitation that can be seen in this study is **on line elemental analysis**. On line elemental analysis using Prompt Gamma-ray Neutron Activation Analysis (PGNAA) couldn't be carried out for the very reason that the research reactor used in the present experimental research was designed in such a way appropriate for **off line** Delayed Gamma-ray Neutron Activation Analysis (DGNAA). Under such condition, analysis of light nuclides such as H, B, N, C and O whose atomic numbers usuallyare less than 9 ($Z<9$) was not performed as these elements have very low cross sections to make thermal and

epithermal neutron induced reaction. Therefore, the activity of such light elements could not be easily detected.

1.8 Scope/Delimitation of the Study

This study is aimed at identifying and characterizing the concentration amounts of essential elements, levels of radioactivity and potential toxic elements in the geological and biological samples collected from the researchable areas of the Amhara regional state in Northwest Ethiopia. However, due to some constraints such as the need of extended time, inadequate financial and material resources, lack of nuclear analytical instruments, unmanageable sample size and wide range of area coverage, the study is narrowed in scope mainly to only four specific areas known as Bahirdar city, Gondar city and its surrounding areas, Chilga woreda of North Gondar zone and limo kemkem woreda of South Gondar zone, all of which belong to the Amhara regional state.

This is, therefore; in light of such delimitation, the multi-elemental analysis of soils, finger millets and medicinal herbs were confined to Chilga woreda, Bahirdar city and Taragedam areas of south Gonadr respectively whereas the levels of radioactivity in rocks was limited only to Gondar and its surrounding areas known as Gondar Zuria woreda.

Chapter 2

Theoretical background

2.1 Introduction

Atomic nucleus is a quantal many body system consisting of protons and neutrons. These protons and neutrons, also known as nucleons, have discrete energy levels and certain characteristic in the atomic nucleus that they exist in. On top of that, depending on the types of nuclear reactions and the configuration rearrangements of neutrons and protons in the nucleus just after reaction, a nucleus could be in a state of energetically stable or unstable. Usually, unstable nuclides with this feature are called radioactive isotopes, and the process is called nuclear decay or disintegration. Mostly, in nuclear decay, the gamma emission process is accompanied by the emissions of alpha or beta particles.

For instance, if a stable atomic nucleus is bombarded by neutrons or charged particles, compound nucleus excitation with high energy states would be formed and the process is known as nuclear activation. Neutrons, in particular, due to their electrical neutrality can interact with a target nucleus easily at very close distance and at all energies.

Even though the possibility of inducing nuclear transformation by irradiation was introduced in 1934 by F. Joliot and Irene Joliot-Curie, nuclear activation analysis based on neutrons for the first time was discovered and demonstrated practicably by Hevesy & Levi (1936) in a year 1936 that is four years after the discovery of neutron by Chadiwck

in 1932. What Hevesy & Levi (1936) did were that by activating the dysprosium in the alloy of yttrium using neutrons they tried to determine about one percent of dysprosium from yttrium. It was this experimental research that took the lead to the development of Neutron Activation Analysis(NAA).

Neutron Activation Analysis technique has become the best technique starting from the early 1940's with the development of nuclear research reactors followed by the fabrication of best detectors, gamma spectrometry system, advanced computers and software packages in 1950- 1970's. Nowadays, NAA technique is believed to be superior over other analytical techniques like Atomic Absorption(AA), X-ray Resonance Fluorescence(XRF), coupled Plasma Atomic Absorption Spectrometry(CPAAS) and Inductively Couples Plasma Mass Spectrometry (ICPMAS) for the very reason that it has a broad application in various fields of science such as engineering, geology, chemistry, biology, archeology, forensic science, materials science, health and environmental studies.

Surprisingly, NAA technique has been found an increasingly important method because of the following advantages (Popescu et al., 2009; Cristache et al., 2008):

- a nuclear based technique that measures the intensity of γ-rays of characteristic energy and half-life using automated multichannel analyzer gamma spectrometry,
- intrinsically simultaneous observation of large blocks of elements (about 20-45 or more elements) within a sample of interest,
- non-destructiveness on the sample regardless of which any chemical element is available in the sample,and thus can be used repeatedly if needed
- universal application to nuclear matter including gases, solids, liquids that can be activated just upon neutron capture
- high accuracy and sensitivity (i.e several trace and ultra-trace elements even below 1μg can be detected with a significant accuracy and precision)

- reliability of the technique provides promising results repeatedly,
- virtually no matrix effects (i.e largely free from matrix interference),
- small sample size for irradiation and can vary in the ranges of mg to gm, resulting in a matrix and concentration independent

In neutron activation analysis, the basic essentials required to carry out multi-elemental analysis in the samples of interest are (1) neutron sources (2) a detailed knowledge of neutron induced reactions that occur when neutrons interact with target nuclei, and (3) appropriate instrumentation for detecting the gamma rays which are fingerprint to each radioactive isotope available within irradiated samples.

Since neutrons are electrically neutral, they have the capability to penetrate deeply into the nuclei of a given material easily and then get captured as a result of which neutron induced radioisotopes are formed at high energy excitations. From this point of view, if a researcher wants to conduct NAA based research, undoubtedly she/he needs neutron source that can generate neutron at high flux. Actually, there are a number of ways in which neutrons are produced but the most common neutron sources are discussed in the next section 2.2 in detail.

2.2 Neutron Sources

Neutrons are the major fundamental building blocks of matter. Neutrons are electrically neutral particles having about the same mass as protons and are bounded within the nucleus of an atom. The lifetime of free neutron is about 10.24 minutes and undergoes beta decay into protons (Monlnar, 2004). Neurons are produced in different mechanisms but the most common sources of neutrons are the following.

- Isotopic neutron sources [such as (α, n) and (γ, n) sources]
- Accelerator based spalled neutron sources

- Reactor neutron sources

2.2.1 Isotopic neutron sources

(Alpha, n) neutron sources

Neutrons are produced in isotopic neutron sources that are designed purposely for producing neutrons. There are different types of installed neutron sources among which isotopic neutron source and californium-252 neutron source are the most commonly used neutron sources designed for the purpose of neutron activation analysis. In isotopic neutron sources, a nuclear reaction (α,n) takes place between alpha particles and light elements with low atomic numbers. The (α,n) reaction sources are composed of a mixture of metallic beryllium and alpha emitters compound of Americium-241, Radium-226 or plutonium-239 within which the neutrons are produced via the following reaction immediately after alpha particles are emitted.

$$\begin{aligned} {}^{241}Am &\rightarrow \alpha + {}^{237}Np \\ {}^{9}_{4}Be + {}^{4}_{2}\alpha = ({}^{13}_{6}C)^{*} &\rightarrow {}^{12}_{6}C + {}^{1}_{0}n \end{aligned} \tag{2.2.1}$$

Where, Beryllium is homogenously mixed with Americium-241 or Plutonium-239 and is usually enclosed in a stainless steel capsule. In effect ^{241}Am-^{9}Be and ^{239}Pu-^{9}Be isotopic neutron sources as shown in figure 2.1 can produce a neutron flux about 5×10^{10} n s^{-1} . Neutron flux can be increased possibly with increasing the activity of parent α sources and thickness of beryllium (Kakavand et al., 2007).

Similarly, neutrons can be generated from californium-252 fission neutron source. Californium-252 fission neutron source has the capacity to produce neutrons at the rate of about 2×10^{12} n s^{-1}g^{-1} or more due to the process of spontaneous fissions. Reports suggest that neutrons produced from Californium-252 are more useful than Pu-Be neutron sources.

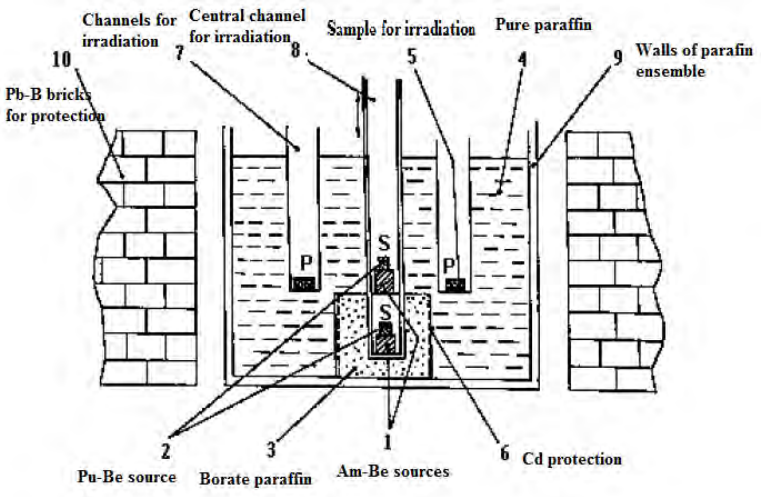

Figure 2.1: The irradiation block containing ^{241}Am-^{9}Be and ^{239}Pu-^{9}Be neutron sources

Photoneutron sources [(γ,n)neutron source]

Photoneutron sources are other mechanism of neutron sources within which neutrons are produced by the interaction of gamma rays with either Beryllium or deuterium (D_2O) target nuclei. The gamma emitter in photoneutron sources is surrounded by Beryllium or deuterium target. Thus, when γ-rays energy emitted from a gamma ray emitter ^{123}Sb is greater than 1.66 MeV that is the binding energy of the last neutron in Beryllium-9, the last neutron which is loosely attached in Beryllium-9 will be ejected out resulting in neutron production. In a similar fashion, neutrons can also be produced by the interaction of gamma rays with a deuterium nucleus. The (γ, n) reactions look like the following

$$ {}^{0}_{0}\gamma + {}^{9}_{4}Be = ({}^{9}_{4}C)^{*} \rightarrow {}^{8}_{4}C + {}^{1}_{0}n \tag{2.2.2} $$

$$ {}^{0}_{0}\gamma + {}^{2}_{1}H = ({}^{2}_{1}H)^{*} \rightarrow {}^{1}_{1}H + {}^{1}_{0}n \tag{2.2.3} $$

Where, ${}^{0}_{0}\gamma$ is the incident gamma ray, ${}^{9}_{4}$Be and ${}^{2}_{1}$H are target nuclei, and ${}^{8}_{4}$C and ${}^{1}_{1}$H are product nuclei, and ${}^{1}_{0}n$ is also product neutron.

In photoneutron source, neutron flux per 1 curie of γ-activity ia about (10^6)n s^{-1}.

2.2.2 Accelerator based spalled neutron sources

Spallation neutron sources are accelerated-driven neutron sources that produce pulsed neutron beams based on the continuous bombardments of high energy protons on a target made of carbon or heavy metals as shown in figure 2.2. In neutron spallation process, the energetic incident particles or protons collide continuously with the target and excite the nuclei of the target into high energy excitation. Just upon the de-excitation of the nuclei, they give off product particles predominantly prompt neutrons and most of these neutrons are evaporation neutrons with average energies of about 2.0 MeV. These neutrons are produced at a rate roughly proportional to the power deposited on the target by the bombarding particles. For instance, as experimental studies reported a 1 Gev proton can produce around 20 -30 neutrons. Since the energy of the spalled neutrons is on average

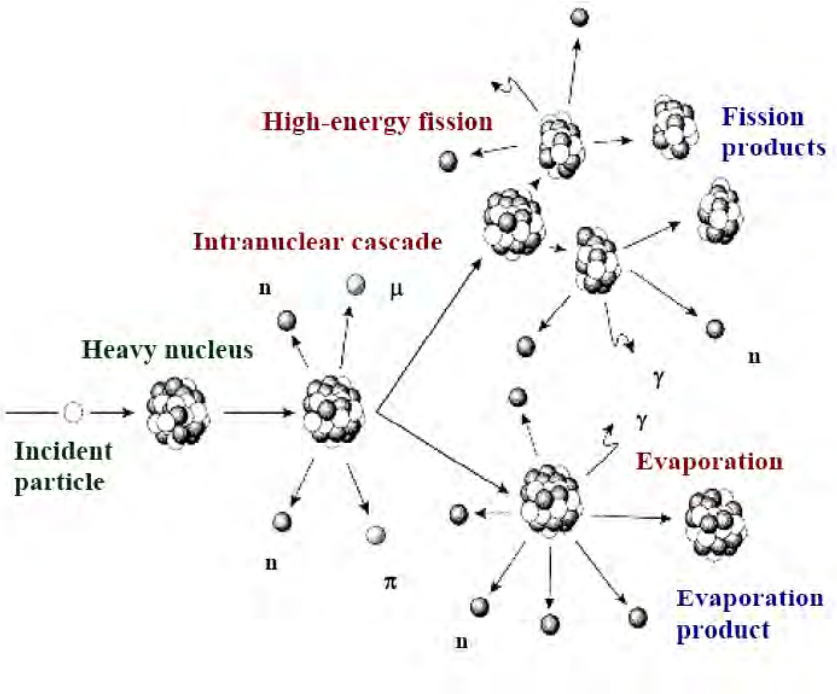

Figure 2.2: Schematics of a Spallation reaction of neutron source

2.0Mev, this energy is expected to be reduced to thermal energies using moderators like those neutrons moderated in the case of reactor based neutron sources. Just after sufficient neutron fluxes has been produced, the neutron fluxes must be guided using beam guide

to irradiate the sample of interest for the purpose of neutron activation.

$$ {}^{0}_{0}\gamma + {}^{9}_{4}Be = ({}^{9}_{4}C)^{*} \rightarrow {}^{8}_{4}C + {}^{1}_{0}n \tag{2.2.4} $$

2.2.3 Reactor neutron sources

Neutron flux produced by nuclear reactor is the most effective and offers the highest available sensitivities for most elements. In nuclear reactor, neutrons are produced when heavy fissile nuclei such as ^{233}U, ^{235}U, ^{238}U, ^{239}Pu and ^{241}Pu undergo spontaneous fission into daughter fragments (also known fission products) with the simultaneous emissions of neutrons following the capture of slow neutrons as shown in figure 2.3. In many research reactors, the most commonly used fissile nucleus as a fuel is ^{325}U and the following reaction takes place within the reactor:

$$ \begin{aligned} {}^{1}_{0}n + {}^{235}U &= {}^{90}_{38}Sr + {}^{143}_{54}Xe + 3{}^{1}_{0}n + Q_0 \\ {}^{1}_{0}n + {}^{235}U &= {}^{91}_{36}Kr + {}^{142}_{56}Ba + 3{}^{1}_{0}n + Q_0 \end{aligned} \tag{2.2.5} $$

Where, ${}^{90}_{38}Sr$, ${}^{143}_{54}Xe$, ${}^{91}_{36}Kr$ and ${}^{142}_{56}Ba$ are the fission products, $3{}^{1}_{0}n$ represent product neutrons during each fission having an average energy 2 Mev and $Q_0 \simeq$ the total kinetic energy of the fission fragments, gamma rays and several fast neutrons.

As can be seen in figure 2.3, one neutron of the 3 product neutrons goes on again to

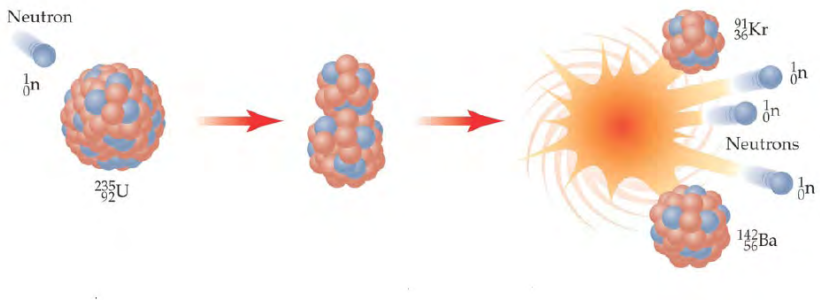

Figure 2.3: Illustrative diagram showing how neutrons are produced in nuclear reactor via fission

cause another fission process and such chains of reactions will continue until a steady

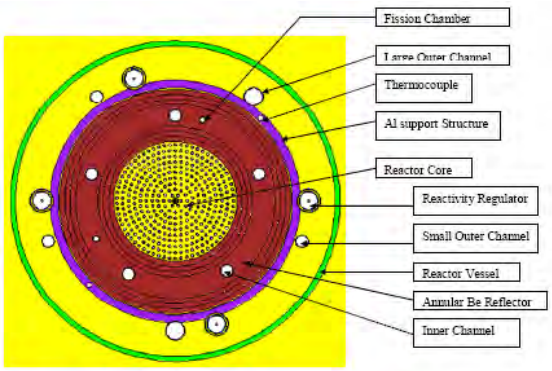

Figure 2.4: Diagram of a core reactor

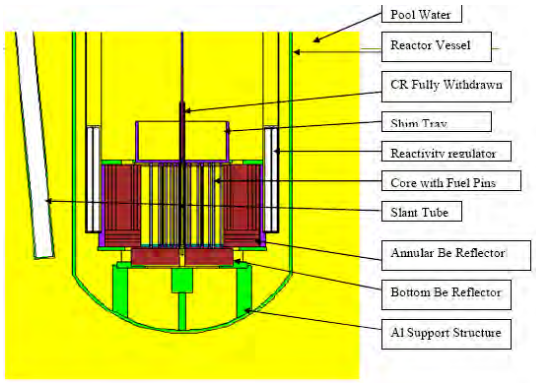

Figure 2.5: different parts of the Nuclear Reactor Swimming pool-type

higher neutron beams in the range of 10^{11} -10^{18} n $cm^{-2}s^{-1}$ are produced depending on the enrichment level of the uranium used, power and the design of the reactor. Since neutrons produced in a reactor are very fast having high energies in Mev range, they must be reduced by many orders of magnitude using neutron moderators such as light water (H_2O), heavy water (D_2O) and graphite until 95% of the neutrons attain in thermal equilibrium with moderator themselves (De Bruin, 1983). Such moderation is performed through a large number of successive collisions of neutrons with hydrogen and oxygen nuclei of the water molecules due to the fact that these nuclei in light and heavy waters have low cross-sections for thermal neutrons. Hydrogen, in particular, is known as the most perfect neutron scatter due to its low mass number and low cross section. It also absorbs a large fraction of the neutron energy in each collision.

However, it is observed practically that neutrons produced in different reactors and even within the different positions of the same reactor can have various components of neutron energy distributions and fluxes. For instance, most neutron energy distributions are quite broad and consist of three principal components known as Thermal, Epithermal, and Fast neutrons.

With regard to the structural set up of the nuclear reactor, the core of the reactor and its surrounding components are presented in the diagrams as shown in figures 4 and 5 .

2.3 Principles of Neutron Activation Analysis(NAA)

Neutron activation analysis is an isotopic or elemental method of analysis, in which the majority of the atoms in the sample to be analyzed become induced radioactive isotopes resulting from nuclear reactions between the targeted sample containing atomic nuclei and the projectile neutrons bombarded on the sample. Just upon the neutron capture a neutron fused compound nucleus in excited state with energy equal to the binding energy of the added neutron is formed. This excited new compound nucleus will very quickly de-excite within $\sim 10^{-14}$ sec into lower configuration states of relatively stable radioactive nucleus through the emission of one or more γ-rays known as prompt gamma-rays (Baechler, 2002) as depicted in figure 2.6. This radioactive nucleus in the lower configuration in turn de-excites directly to the ground state of stable daughter isotope through the emission of beta particle accompanied by γ-rays known as delayed gamma-rays. The nuclear reaction that undergoes as shown in figure 2.6 can be represented in

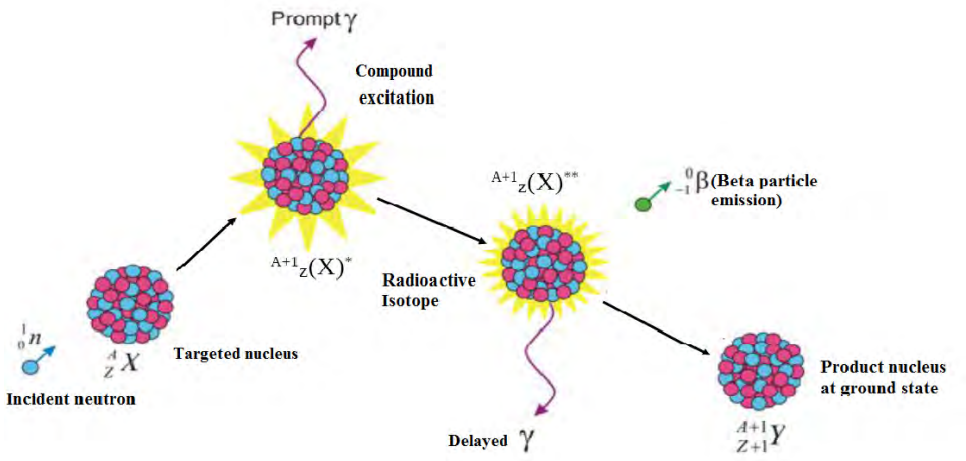

Figure 2.6: Illustrative diagram showing how neutron is captured by a target following by beta particle and gamma-rays emissions

the following expressions:

$$^{1}_{0}n + ^{A}_{Z}(X) \rightarrow ^{A+1}_{Z}(X)^{*} \ (compound\ nucleus\ excitation)$$

$$^{A+1}_{Z}(X)^{*} \rightarrow ^{A+1}_{Z}(X)^{**} + \gamma \ (prompt\ gamma\ ray\ emission)$$

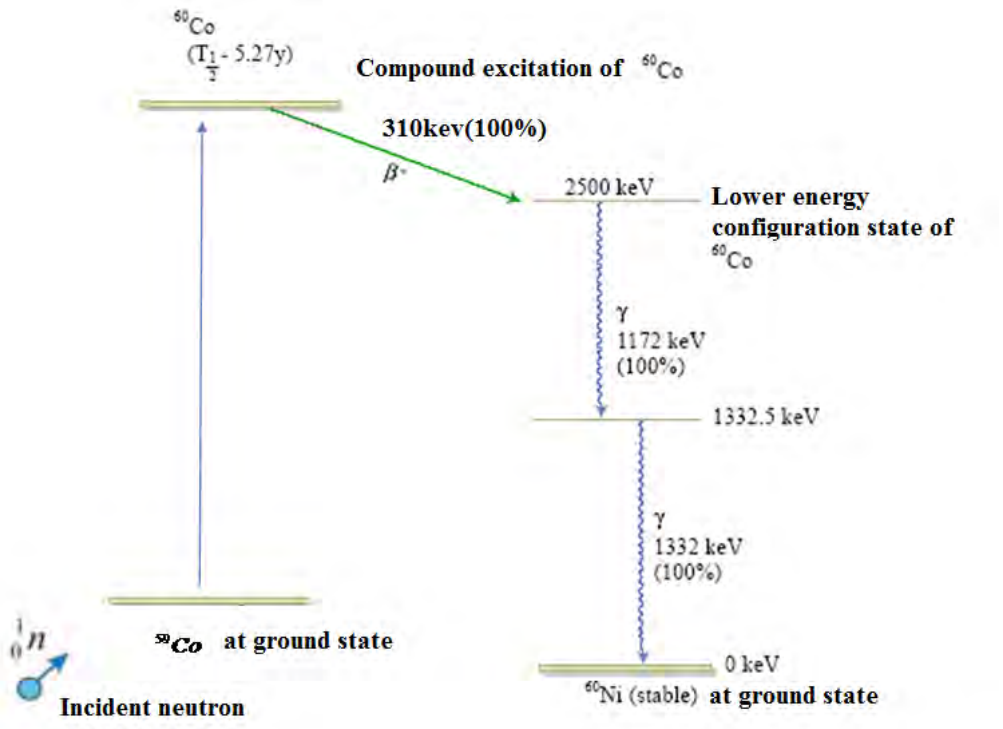

Figure 2.7: The decay of delayed gamma-ray from cobalt-60

$$^{A+1}_{Z}(X)^{**} \rightarrow {}^{A+1}{}_{Z+1}(Y) + {}^{0}_{-1}\beta + \gamma \ (delayed\ gamma\ ray\ emission)$$

Where, X is the target nucleus and Y is the product daughter isotope, ${}^{1}_{0}$n is the projectile neutron, γ is emitted gamma ray, ${}^{A}_{Z}$(X) is the target nucleus, ${}^{A+1}$(X)* is the compound nucleus excitation after neutron capture, ${}^{A+1}$(X)** is the radioactive nucleus is in the lower configuration state after prompt gamma-ray emission, ${}^{A+1}_{Z+1}$(Y) is final product daughter nucleus at ground state and ${}^{1}_{0}\beta$ is the positron particle emission.

The energy levels of a nucleus are different for every isotope. Therefore, gamma rays emitted from one isotope will not have the same properties (such as energy and intensity) as gamma rays emitted from any other isotope. In other words, gamma rays are characteristic for each isotope. In addition, the decay of each nucleus is characterized by its half-life, which can be on a wide scale from the fraction of nanosecond to billions of years(Hassan, 2007). Most unstable radioactive nuclides stabilize by beta-decay but the emission of beta-particles is often accompanied by discrete gamma radiation similar to

the illustrative decaying energy diagram as shown in figure 2.7 for cobalt-59. Cobalt-59 is an atom which excites by capturing a neutron in to high excitation energy and decays into stable nickel-60 by emitting beta particle accompanied by two discrete gamma ray energies 1172 and 1332.5 keV with a half-life of 5.27 years. Therefore, this implies gamma rays emitted from energy levels one isotope will not have the same energy and intensity as gamma rays emitted from any other isotope.

2.3.1 Prompt and Delayed Gamma-rays NAA

In neutron activation analysis, measurement of gamma-rays radiation during the process of sample irradiation in a reactor is possible and this form of analysis is referred to as prompt gamma ray neutron activation analysis (PGNAA). It is an online analytical technique with the neutron beam guide and the gamma-rays detector assembled together. It has been shown to be an effective method for simultaneous determination of many elements including light elements such as ^{1}H, ^{5}B, ^{14}N and ^{12}C and some other elements such as S, P, Cd, Pb, Sm and Gd in a sample matrix (Baechler, 2002; Hassan, 2007). The prompt gamma ray NAA technique is superior over other analytical techniques due to its unique, non-destructive nuclear analytical method and provides results that are representative for the entire volume of the sample under investigation (Andreson et al., 2004). However, the application of PGNAA technique is limited only to a few research laboratories due to radiological effects on the workers and analysts involved and due to the gamma-rays self absorption by the sample itself which lead to significant errors.

On the other hand, measurement of the characteristic discreet gamma-rays after the sample irradiation has been completely irradiated and cooled for some time is also possible and such form of activation analysis is known as Delayed Gamma-ray Neutron Activation Analysis (DGNAA). It is an off-line analysis. The delayed gamma-ray NAA method is a safe and non-destructive multi-elemental analysis that is widely used in many research laboratories. The limitation of DGNAA is it cannot detect light elements whose atomic

numbers (Z) are less than 9 and even some other heavy elements like P, S, Pd and Gd whose cross-sections are very much smaller. In DGNAA technique, the emission of the neutron induced delayed γ-rays is a function of the half-life time of the radionuclide which could be varied from fractions of a second to several years.

2.3.2 Instrumental and Radiochemical NAA

Neutron activation analysis can also be classified into two major categories of different types known as Radiochemical Neutron Activation analysis (RNAA) and Instrumental Neutron Activation Analysis (INAA) techniques based on their difference in sensitivities and chemical treatment of the sample under investigation (Moon et al., 2002).

Radiochemical neutron activation analysis (RNAA) is a technique that is used when a desired element or elements cannot be detected or determined accurately by instrumental neutron activation analysis (INAA) or other instrumental techniques due to interferences resulting from the matrix elements. It involves the decomposition of the irradiated sample by the suitable method of separation such as chemical based ion exchange or precipitation in order to separate specific elements of interest. Radiochemical method is also very important when the amount of an element is very small so that the neutron induced gamma-rays activities associated with this element cannot be detected due to the effect of background activities or activities originated from other elements (Abd, 2009). Karijaha (1971) well explained that if two radionuclides with nearly equal half lives emit gamma-rays of nearly same energy during (n,γ) reaction, undoubtedly gamma interference takes place and the elemental contents of the two radionuclides couldn't be exactly identified or determined quantitatively by INAA technique. Therefore; the RNAA technique is the best option to use. Even though, RNAA technique is the most accurate measurement and extreme sensitivity in neutron activation analysis, it is rarely used because it is costly and time consuming in addition to its destructiveness.

On the other hand, in nuclear activation, the most important and widely used technique

in industrial and research laboratories for the analysis of large varieties of materials composition is the instrumental neutron activation analysis (Cristache et al., 2008; Enei et al., 2011). INAA technique is purely instrumental, very sensitive and nondestructive on the sample under investigation (Cristache et al., 2008). In short, INAA doesn't cause any physical and chemical change (or damage) on the sample of interest under invetigation. Thus, if needed be, the sample can be used repeatedly.

Instrumental neutron activation analysis in turn can be classified as : Thermal neutron activation analysis (TNAA), Epithermal neutron activation analysis (ENAA) and Fast neutron activation analysis (ENAA) based on the energy distributions of the neutrons in a nuclear reactor.

2.3.3 INAA classification based on Neutron energy distribution

The energy distribution of neutrons in a reactor is a broad spectrum that consists of thermal, epithermal and fast neutrons (Alfassi, 1995).

Thermal Neutron Activation Analysis

Thermal neutrons are produced in a research reactor within the energy range between 0 and 0.5 ev (Alfassi, 1995) as shown in figure 2.8. It is due to successive collisions of high energy fission neutrons with light and heavy waters (known as moderators) inside the reactor that the energy of the neutrons goes down and become in thermal equilibrium with the atoms of moderators. At room temperature the energies of these neutrons show a Maxwell-Boltzmann distribution with a maximum at 0.025 eV (De Bruin, 1983). In addition, the cross-section of thermal neutrons is proportional to the inverse of the neutrons' velocity and the most probable velocity is 2200 ms^{-1} at 0.025 eV. In most reactor irradiation positions, 90-95% of the neutrons produced are thermal neutrons.

Instrumental NAA that is based only on thermal neutron fluxes is known as Thermal

Neutron Activation Analysis (TNAA). Thermal neutron activation analysis takes the advantages of high intensity of neutron beams and large thermal cross-section for most isotopes (Frontasyeva et al., 2001).

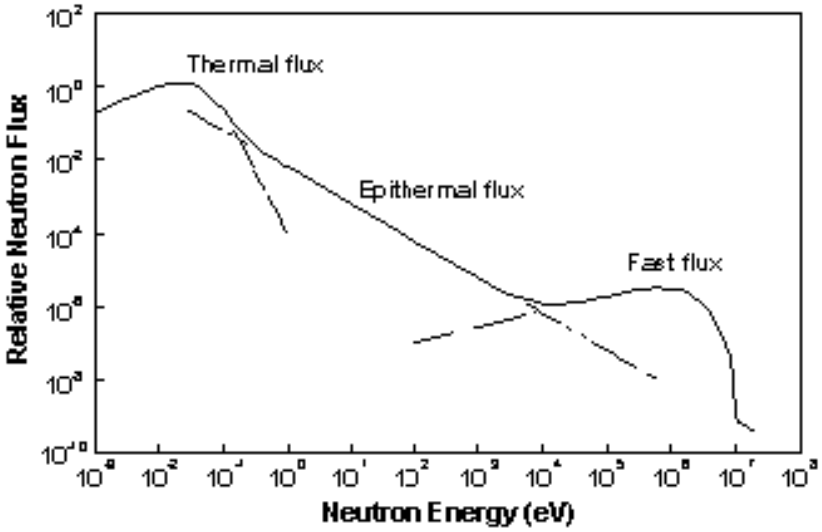

Figure 2.8: Schematic diagram of neutron flux spectrum as function of energy in a research reactor neutron (Frontasyeva, 2011)

Epithermal Neutron Activation Analysis

Neutrons in the energy spectrum from 0.5 eV to 100 eV are known as Epithermal neutrons. In this region the neutron flux distribution is not proportional to the inverse of the velocity but it is proportional to inverse of the energy. The other unique property of epithermal neutrons is their cross-section as function of energy show strong resonance peaks phenomena as shown in figure 2.9. The flux and the resonance energy of this region is more important to identify and determine chemical elements in sample of interest whose cross-sections are very small. To get epithermal neutron flux separated from thermal neutron flux in a reactor, a cadmium foil of 1 mm thick is inserted into one of the irradiation channels inside the reactor. The purpose of the cadmium foil is to absorb

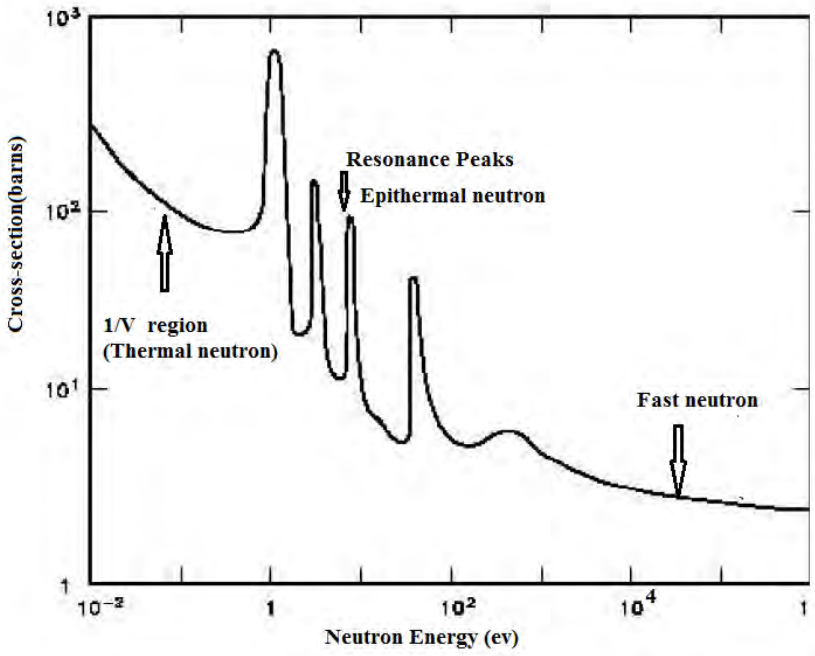

Figure 2.9: Neutron cross-section as a function of energy in a research reactor

all thermal neutrons but it will allow epithermal and fast neutrons to pass through it. In general, about 2 % of the reactor's total neutron flux is the epithermal neutron flux. Thus, neutron activation analysis that is based on only epithermal neutron flux is known as Epithermal Neutron Activation Analysis (ENAA).

Fast Neutrons Activation Analysis

Fast neutron activation analysis (FNAA) is the third type of activation analysis. The energy range of fast neutron component is above 0.5 Mev as shown in figure 2.8. Fast neutron consists of the primary fission neutrons which still have much of their original energy following fission. Actually, fast neutrons don't induce (n, γ) reactions but instead they induce nuclear reactions where the ejection of one or more nuclear particles (n, p),(n, n') and $(n, 2n)$. This type of technique induces particles reaction is known as fast neutron activation analysis (FNAA). Fast neutrons with energies of several MeV's

can be produced with a neutron generator in an isotopic neutron source.

2.3.4 The Kinetics of Neutron Activation

As discussed in the preceding section, neutron activation is a nuclear analytical process in which neutron radiation in the form of flux induces radioactivity in a targeted material. There are two basic processes that undergo during sample irradiation within the channels of a nuclear reactor: (1) the formation of radionuclides by neutron capture and (2) the decay of radionuclides by particle emission accompanied by gamma rays. The rate of growth of the nuclear product is thus the difference between the rate of formation of the product nuclei (RN_0) and the rate of decay of the radionuclides (λN^*), and is expressed as

$$\frac{dN^*}{dt} = RN_0 - \lambda N^* \tag{2.3.1}$$

Where, R is the reaction rate, N_0 is the number of atomic nuclei in the sample before irradiation, N^* is the number of product radionuclides during decaying and λ is the decay constant in sec^{-1}.

Integrating equation 2.3.1 between $t = 0$ at $N = N_0$ and $t = t_i$ at N= N^*, the following mathematical equation is obtained at the end of sample irradiation.

$$N^* = \frac{RN_0}{\lambda}(1 - e^{-\lambda t_i}) \tag{2.3.2}$$

Where, N^* is the number of radionuclides at the end of sample irradiation.

The activity A of the radionuclides at the end of irradiation is given by

$$A = \lambda N^* = RN_0\lambda(1 - e^{\lambda t_i}) \tag{2.3.3}$$

As can been seen in figure 2.10, the activity (A) of the target sample bombarded by neutron fluxes grows exponential until it reaches the saturation level where the rate formation of the radionuclide is the same as its rate of decay.

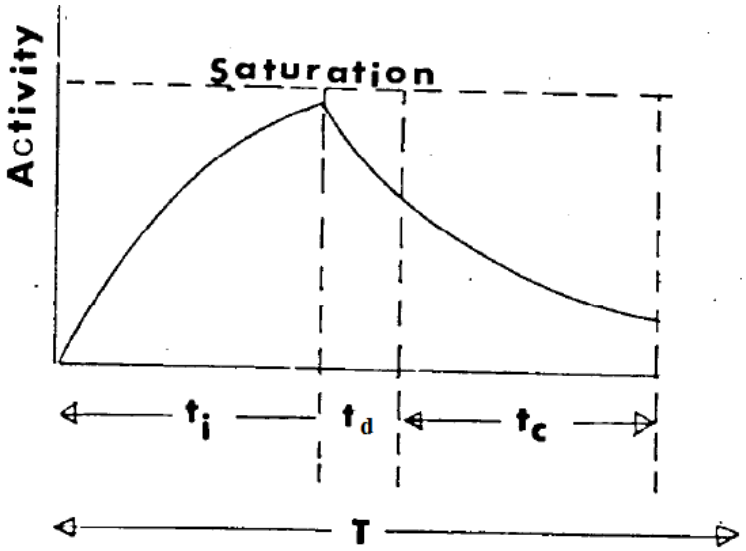

Figure 2.10: Sample Activity as function irradiation(t_i), decay time(t_d) and counting time(t_c)

The rate of decay for the radionuclide after the end of irradiation is given by

$$\frac{dN}{dt} = -\lambda N \tag{2.3.4}$$

Where, N is the number of atoms of the radionuclide at any decay time t_d.

Integrating and simplifying equation 2.3.4, the numbers of the radionuclide (N_D) at the end of the decay time (t_d) as shown in figure 2.10, is given by

$$N_d = N^* e^{-\lambda t_d} = \frac{RN_0}{\lambda}(1 - e^{\lambda t_i})(e^{-\lambda t_d}) \tag{2.3.5}$$

If the activity of the radionuclide is counted for counting period of time (t_c), the number of atoms of the radionuclide at end of the counting time t_c is determined by

$$\begin{aligned} \frac{dN}{dt} &= -\lambda N, \;\; N_c = N_d e^{-\lambda t_c} \\ N_c &= \frac{RN_0}{\lambda}(1 - e^{-\lambda t_i})e^{-\lambda t_d} e^{-\lambda t_c} \end{aligned} \tag{2.3.6}$$

where, N is the number of decaying atoms at any counting time (t_c); N_d and N_c represent the number of atoms of the radionuclide at the start of counting and at the end of counting respectively.

Finally, the number of atoms decayed ($\triangle N_c$) during the counting period as shown in

figure 2.10 is determined by taking the difference between the number of atoms at the beginning of the counting and end of counting period (Alfassi, 1998).

$$\triangle N_c = RN_0(1 - e^{-\lambda t_i})e^{-\lambda t_d}\frac{(1 - e^{-\lambda t_c})}{\lambda} \tag{2.3.7}$$

The net peak count produced due to the response of the detector at the end of counting depends on three major factors known as the number of atoms of a radionuclide ($\triangle N_c$), the branching ratio (I_γ) of the radionuclide and the absolute detector efficiency (ε) and is mathematically expressed as

$$C = \triangle N_c I_\gamma \varepsilon = RN_0 I_\gamma \varepsilon(1 - e^{-\lambda t_i})e^{-\lambda t_d}\frac{(1 - e^{-\lambda t_c})}{\lambda} \tag{2.3.8}$$

According to Alfassi (1998) the total nuclear reaction rate per nucleus (R) of neutron induced radioactivity in nuclear reactor is determined based on the following equation:

$$R = \int_0^\infty \sigma(E)\phi(E)dE = \int_0^\infty \sigma(v)\phi(v)dv = \int_0^\infty n(v)v\sigma(v)dv \tag{2.3.9}$$

where, $\phi(E_\gamma)$ and $\phi(v)$ are energy and velocity dependent radiation of neutron fluxes from a reactor, $\sigma(E_\gamma)$ and $\sigma(v)$ are energy and velocity dependent cross-sections respectively, n(v) is the neutron density as a function of velocity and $\sigma(v)$ is the nuclear cross-section as function of velocity and $\sigma(E_\gamma)$ is nuclear cross-section of the interacting nuclides at E_γ. The total reaction rate in a reactor as indicated in equation 2.3.9 can be separated into three terms based on the neutron energy distribution classification:

$$R = R_{th} + R_{epi} + R_{fast} \tag{2.3.10}$$

Where, R_{th}, R_{epi} and R_{fast} are the thermal, epithermal and fast neutron reaction rates respectively.

However, since the fast neutrons do not contribute the (n, γ) reaction, only the reaction rates of thermal and epithermal neutrons are considered and hence equation 2.3.10 is reduced to equation 2.3.11

$$R = R_{th} + R_{epi} \tag{2.3.11}$$

The total reaction rates in terms of thermal and epithermal can be represented as

$$R = \int_0^{E_{cd}} n(v)v\phi(v)dv + \int_{E_{Cd}}^{\infty} n(v)v\sigma(v)dv \tag{2.3.12}$$

The first part of equation 2.3.12 is thermal neutron reaction rate and can be expressed as

$$\int_0^{E_{cd}} n(v)v\phi(v)dv = v_0\sigma_0 \int_0^{E_{cd}} n(v)dv = v_0 n\sigma_0 = \phi_{th}\sigma_0 \tag{2.3.13}$$

Where, $n = \int_0^{E_{cd}} n(v)dv)$ is the the thermal neutron density, $\phi_{th}(v) = v_0 n$ is the radiation of thermal neutron fluence rate in $nm^{-2}s^{-1}$ in the energy range up to cadmium cut-off energy, $E_{Cd} = 0.55ev$, σ_0 is the thermal neutron cross-section at energy 0.025 ev, and v_0 the thermal neutron velocity $2200\text{m}s^{-1}$ at a temperature of 20^0c.

Similarly, the second part of equation 2.3.12 is the epithermal reaction rate and can be simplified as follows

$$\begin{aligned} \int_{E_{Cd}}^{\infty} n(v)v\sigma(v)dv = \phi_{epi}\int_{E_{Cd}}^{\infty} \frac{\sigma(E_n)dE_n}{E_n} = \phi_{epi}I_0 \\ I_0 = \int_{E_{Cd}}^{\infty} \frac{\sigma(E_n)dE_n}{E_n} \end{aligned} \tag{2.3.14}$$

Where, I_0 is the epithermal resonance cross-section which depends inversely proportional to $1/E_0$.

In epithermal neutron activation, there are two factors related to the ratio of neutron fluxes and the ratio of cross-sections with respect to the thermal and epithermal neutrons regions. These are known as the f, and Q_0 factors. $f = \frac{\phi_{th}}{\phi_{epi}}$ is the ratio of thermal flux to epithermal flux whereas $Q_0 = \frac{I_0}{\sigma_0}$ is the ratio of resonate integral to thermal cross-section. However, according to Hogdahl convection, practically epithermal resonance cross-section does not exactly inversely proportional to $1/E_n$ but shows a small deviation with a deviation parameter known as α (Nijinga et al., 2011). Therefore, the resonance integral (I_0) equation as indicated in 2.3.14 is modified and rewritten as

$$I_0(\alpha) = (1ev)^{\alpha}\int_{E_{Cd}}^{\infty} \frac{\sigma(E_n)dE_n}{E_n^{(1+\alpha)}} \tag{2.3.15}$$

Similarly, the Q-factor is modified as

$$Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_0} \tag{2.3.16}$$

The total reaction cross-section (R) in the reactor can be expressed mathematically as showing in equation 2.3.17 after substituting 2.3.13 and 2.3.14 in equation 2.3.11.

$$R = \sigma_{th}\phi_{th} + \phi_{epi}I_0(\alpha) \tag{2.3.17}$$

The total reaction cross section (R) in equation 2.3.17 is expressed in terms of ϕ_{th} and σ_{eff} as follow

$$\begin{aligned} R &= \phi_{th}\sigma_{th}(1 + \frac{Q_0(\alpha)}{f}) \\ R &= \phi_{th}\sigma_{eff} \end{aligned} \tag{2.3.18}$$

Where,

$$\sigma_{eff} = \sigma_{th}(1 + \frac{Q_0(\alpha)}{f}), \sigma_0 \approx \sigma_{th} \tag{2.3.19}$$

Cadmium Ratio

As discussed in section 2.3.3, the thermal and epithermal neutron fluxes of a reactor can be separated easily by placing a cadmium foil of 1 mm thickness inside one of the irradiation channels. Since cadmium has a high cross-section, it has the capability to absorb almost all thermal neutrons but it allows to pass only high energy neutrons whose energy is above the cadmium cut-off energy, $E_{Cd} = 0.55$ev. Thus, using cadmium foil, the flux ratio (f) and deviation parameters (α_0 in the epithermal region of the reactor can be determined by measuring the activities of selected monitors such as ^{197}Au, ^{58}Zr and ^{58}Zn flux without cadmium cover and with cadmium cover inside one of the irradiation channels of the reactor.

Thus, the cadmium reaction rate ratio would be determined by dividing the reaction rate of the monitors without cadmium to the reaction rate with cadmium cover based on the

following equation.

$$R_{0,mon} = \frac{R_{(without\,Cd)}}{R_{(with\,Cd)}} = \frac{\sigma_{th}\phi_{th,mon} + phi_{epi}I_0}{\phi_{epi}I_{0,mon}} \tag{2.3.20}$$

Simplifying equation 2.3.20 in terms of f and Q_0, the following equation is obtained

$$R_{mon} = 1 + \frac{\sigma_{th}\phi_{th,mon}}{\varphi_{epi}I_{0,mon}} \approx 1 + \frac{1}{fQ_{0,mon}} \tag{2.3.21}$$

Thus, rearranging equation (2.3.21) the flux ratio f can be obtained as follows

$$f = \frac{1}{Q_{0,mon}(\alpha)(R_{0,mon} - 1)} \tag{2.3.22}$$

However, according to De-Corte et al. (2005), in epithermal activation analysis, corrections are made from Q_0 to $Q_0(\alpha)$ and from I_0 to $I_0(\alpha)$ based on the deviation parameter α and thus the modified expressions are stated as follows

$$Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_{th}} = \frac{Q_0 - 0.429}{E_r^\alpha} + \frac{0.429E_a^\alpha}{(2\alpha+1)E_{Cd}^\alpha} \tag{2.3.23}$$

$$I_0(\alpha) = (\frac{I_0 - 0.429\sigma_{th}}{E_r^\alpha} + \frac{0.429\sigma_{th}}{(2\alpha+1)E_{Cd}^\alpha})E_a^\alpha \tag{2.3.24}$$

Where, $E_a^\alpha = 1^\alpha$ is the 1 eV arbitrary energy, and $E_{cd}^\alpha = 0.55^\alpha$ is the effective cadmium cutoff energy and E_r^α is the effective resonance energy.

The thermal and epithermal neutron activation analyses can be determined once the total nuclear reaction rate (R) of the reactor is known. Therefore, substituting equation (2.3.17) into equation (2.3.8) and then making rearrangement, the following mathematical expression is obtained to determine the mass (m_i) of the (i^{th}) element in a given sample interest containing many elements:

$$m_i = \frac{MC\lambda}{\theta\varepsilon N_{av}I_\gamma(\sigma_{th}\phi_{th} + \phi_{epi}I_0(\alpha))(1 - e^{-\lambda t_i})e^{-\lambda t_d}(1 - e^{-\lambda t_c})} \tag{2.3.25}$$

or

$$m_i = \frac{MC}{(\sigma_{th}\phi_{th} + \phi_{epi}I_0(\alpha)\theta\varepsilon N_{av}I_\gamma SDC_c} \tag{2.3.26}$$

Where,

C = net Photo-peak count N_{av} = Avogadro number (mole^{-1})

M = Atomic molecular mass of the isotope (g), θ = Isotopic abundance (%)

ϕ_{th} = Thermal neutron flux(n$cm^{-2}s^{-1}$) σ_{th} = Effective nuclear cross-section(in b)

ε = full energy peak detection efficiency, I_γ = Intensity of specific gamma lines (in %)

$S = 1 - e^{-\lambda t_i}$ (Irradiation Saturation factor), $D = e^{-\lambda t_d}$(Decaying factor)

$C_c = \frac{1-e^{-\lambda t_c}}{\lambda}$ (Corrected Counting factor) $\lambda = \frac{ln2}{T_{1/2}}$ is the decay constant (s^{-1})

and $T_{1/2}$ = Half-life in second.

The mathematical expression obtained in equation 2.3.26 is known as the **master equation of Absolute Neutron Activation Analysis**.

In the case of purely thermal neutron activation analysis, the epithermal values (ϕ_{epi} and $I_0(\alpha)$) in equation 2.3.26 would be ignored and then the expression is reduced into equation 2.3.27

$$m_i = \frac{MC}{\phi_{th}\sigma_{th}\theta\varepsilon N_{av} I_\gamma SDC_c} \tag{2.3.27}$$

Similarly, the concentration (ρ_i) of the i^{th} element in a sample can be determined by dividing the mass (m_i) of the element to the mass of the whole sample (m_{sam}) and is obtained as follows

$$\rho_i = \frac{m_i}{m_{sam}} = \frac{MA}{N_{av} m_{sam}\phi_{th}\varepsilon\sigma_{th}\theta I_\gamma SDC_c} \tag{2.3.28}$$

Where, $A = \frac{C}{t_m}$ is the activity or count rate (in cps), C is the net peak count and $C_c = \frac{1-e^{-\lambda t_c}}{\lambda t_m}$ is the corrected counting time

2.3.5 Standardization

In Neutron Activation Analysis, there are three basic methods of analysis based on the standard used. Those are Absolute method, Relative method and K_0 method of analysis. Each method of analysis has its own merits and demerits.

2.3.5.1 Absolute method of Analysis

Absolute method is one of the three NAA methods that are used for mass and concentration determination of elements in a given sample of interest. It is a direct analysis by inserting nuclear parameters obtained from nuclear data tables, irradiation parameters and measuring parameters without using any standard reference material (SRM). The sensitivity and accuracy of absolute method depend on:

- nuclear parameters of the elements such as isotope abundance (θ) , cross-section (σ), gamma intensity (I_γ), atomic mass (M), decay constant (λ) and half- life ($T_{1/2}$),
- the irradiation parameters such as neutron flux (ϕ), irradiation time (t_{irr}), decaying time (t_d), and counting time (t_c) and
- measurement conditions like mass of the sample (M_{sam}), net peak activity (A) and detector efficiency (ε),

Taking all physical and nuclear parameters into consideration, the concentration of each radionuclide in a sample can be determined using the following mathematical expression.

$$\rho_i = \frac{MA}{N_{av} M_{sam} \phi_{th} \varepsilon \sigma_{th} \theta I_\gamma SDC_c} \tag{2.3.29}$$

Where, A is the net peak count rate and M_{sam} is the weight of the sample.
Nevertheless, absolute method of analysis has certain limitations due to the uncertainties that appear from the nuclear parameters unless otherwise the values of nuclear parameters are determined correctly.

2.3.5.2 Relative method of Analysis

Relative method is essentially very simple method of analysis as compared to absolute method of analysis. In relative method, each sample is simultaneously co-irradiated with a standard containing known amounts of elements to be determined. When both samples

and standards are counted under identical conditions and geometries, uncertainties that could appear due to nuclear parameters (such as σ, ϕ, I_γ, θ and ε) will be eliminated through cancellations. Thus, the concentration (ρ_i) of the i^{th} element in sample can be determined based on the following simplified expression

$$\rho_i = \rho_{std}\frac{A_i\ (e^{\lambda t_d})_i}{A_{std}\ (e^{\lambda t_d})_{std}}\ \frac{M_{std}}{M_{samp}} \tag{2.3.30}$$

where

ρ_i= the concentration of the i^{th} element in the sample (in ppm or bpm)

ρ_{std} = concentration of the same element in the standard (in ppm or bpm)

$A_i = \frac{C_i}{t_m}$ is activity or count rate of the i^{th} element in sample (in cps)

$A_{std} = \frac{C_{std}}{t_m}$ is the activity or count rate of the same element in standard (in cps)

M_{std} = the total mass of standard (in g)

M_{samp} = the total mass of the sample in (in g)

t_d = decay time (in second)

$T_{1/2}$ = the nuclide half life time (in second and $\lambda = \frac{ln2}{T_{1/2}}$ in s^{-1}

However, when the samples of different masses are not irradiated and measured under identical conditions, the concentration of the i^{th} element in the sample can be determined using the equation (2.3.31)(Frontasyeva, 2011)

$$\rho_i = \rho_{std}\frac{A_i}{A_{std}} \times \frac{1-e^{-\lambda t_{ir,std}}}{1-e^{-\lambda t_{ir,i}}} \times \frac{e^{-\lambda t_{d,std}}}{e^{-\lambda t_{d,i}}} \times \frac{1-e^{-\lambda t_{c,std}}}{1-e^{-\lambda t_{c,i}}}\frac{m_{std}}{m_{sam}}\frac{\phi_{std}}{\phi_{sam}} \tag{2.3.31}$$

Where, m_{sam} and m_{std} are the total masses of the sample and standard in grams respectively

2.3.5.3 K_0 Method of Analysis

The K_0 method of analysis is the third alternative method of NAA in which elemental analysis is carried out by the simultaneous irradiation of a sample with a single comparator usually, ^{198}Au (Murrie et al., 2013). In K_0 Neutron activation, accurate knowledge of

nuclear data of such resonance integrals, neutron cross sections for (n,γ) reaction, isotope abundance (θ), Intensity of specific gamma lines (I_γ), detector efficiency and atomic mass (M) of both sample and the comparator are required for the correct quantification of each element in the sample under investigation. The concentration of each element in the sample is determined based on the following equation:

$$\rho_i = \frac{A_a}{A_{std}} \times \frac{1}{k_{0,std}} \times \frac{f + Q_{0,std}(\alpha)}{f + Q_{0,a}(\alpha)} \times \frac{\varepsilon_{std}}{\varepsilon_a} \tag{2.3.32}$$

Where, $A_a = \frac{N_p}{t_m W_s SDC}$ and $A_{std} = (\frac{N_p}{t_m SDC})_{std}$ represent the specific activities of the sample and standard respectively, N_P is net count peak at full energy, W_s and W_s are masses of the sample and standard (usually gold) respectively, $f = \frac{\phi_{th}}{\phi_{epi}}$, $Q_0(\alpha) = \frac{I_0}{\sigma_0}$, ε_a and ε_{std} are the full energy peak efficiencies of the unknown element and standard respectively, $S = (1 - e^{-\lambda t_{irr}})$, $D = e^{-\lambda t_d}$, $C = \frac{(1-e^{-\lambda t_c})}{\lambda t_c}$, t_{irr} is irradiation time, t_d is decay time, and t_c is the counting or measuring time.

The composite nuclear constant k_0 in equation (2.3.32) is determined experimentally using the following equation

$$k_0 = \frac{M_{std}}{M_a} . \frac{\theta_{std}}{\theta_a} . \frac{I_{\gamma_a}}{I_{\gamma_{std}}} . \frac{\sigma_{0a}}{\sigma_{0std}} \tag{2.3.33}$$

Since elements which could not be detected by absolute and relative methods can be detected by K_0 neutron activation analysis, the K_0 method is more preferable method of analysis. In addition, in K_0 neutron activation analysis, uncertainty that appears due to nuclear parameters is very much less as compared to the absolute and relative methods of analysis.

2.4 Radiological Effects of Natural Radionuclides

Radiation is a part of the physical environment. The main cause for the background radiation at the Earth surface are radionuclides whose origins of primordial (^{40}K, ^{238}U and ^{232}Th), cosmogenic (^{3}H, ^{7}Be, ^{12}C, ^{22}Na) and anthropogenic (^{137}Cs, ^{90}Sr, ^{85}Kr, ^{239}Pu)

types of radionuclides. As studies suggest about 87% of the radiation dose received by mankind in the human environment is due to natural primordial and cosmogenic radiation sources, and the remaining is due to anthropogenic radiation (UNSCEAR, 1993). In particular, long-lived radioactive elements such as ^{40}K, ^{238}U and ^{232}Th have existed as being the source of background radiation starting from the creation of the earth. In other words, terrestrial radionuclides also known as primordial radionuclides are long-lived radionuclides with half live equivalent to the age of the earth and are widely spread and present in almost all geological materials in the Earth's crust in varying amounts in soils, water, air, food, building materials and even in the tissues of living things.

There are three major long-lived radioactive series in nature known as Uranium-235, Uranium -238 and Thorium-232 series as displayed in page 72 in a book written by U.S Environmental Protection Agency (2006). Uranium series starts with ^{238}U which has a half-life of 4.5×10^{10} decay to a stable ^{206}Pb nucleus after 14 successive decay series during which 8 alpha particles and 6 beta particles are emitted accompanied by gamma radiation during the beta emission of some radionuclides in chain. In a similar manner, thorium series start with $^{232}Th(100\%)$ as parent nucleus end with ^{208}Pb as stable nuclei after making 10 successive decay series during which 6 alpha particles and 4 beta particles are emitted accompanied by gamma radiation during the beta emission in chain.

To measure the activity concentration of the natural radioactive elements ^{238}U and ^{232}Th in the decay series, a secular equilibrium should be established between the parent and the successive radionuclides, and the equation of secular equilibrium can be expressed in a simplified way as

$$\begin{aligned} \lambda_P N_P = \lambda_D N_D = ... = \lambda_n N_n \\ A_P = A_D = ... = A_n \end{aligned} \tag{2.4.1}$$

Where, λ_P is the decay constant of the parent nucleus $^{238}U(^{226}Ra)$, λ_D is the decay constant of daughter nucleus in the series, N_P is the number of parent atomic nuclei before starting decaying, N_D is the number of daughter after secular equilibrium is established,

A_P the activity of the parent nucleus equal to the activity of the daughter nucleus A_D at secular equilibrium and n represents the daughter nuclide in the decaying series. For further details please to refer Krane (1988).

Since the activity concentration of ^{238}U is not directly measured, it is measured after secular equilibrium has been established with the activities of ^{214}Bi (at 609.31, 1120.3 & 1764.49 keV) and ^{214}Pb (at 295.22 & 351.93 keV). Similarly, the activity concentration of Th-232 is determined after secular equilibrium has been established with the activities of ^{208}Tl at (583.19 & 2614.53 keV); ^{212}Pb (at 238.63 & 300.09 keV) and ^{212}Bi (at 273.3 keV) whereas the activity concentration of ^{40}K is measured directly using its single decay at energy 1460.83 keV (Saleh et al., 2013; Harb et al., 2014).

2.4.1 Activity concentration

The activity concentrations of natural radionuclides (^{238}U, ^{232}Th and ^{40}K) in rocks, soils, building materials, water, air, etc., are determined based on the following expression (Harb et al., 2014)

$$A_{E_\gamma} = \frac{C_p}{\varepsilon(E_\gamma) \times I_\gamma(E_\gamma) \times M} \tag{2.4.2}$$

Where, $C_p = \frac{NP}{t_c}$ is the photo-peak count rates (in cps) corrected for background photo-peaks at energy E_γ; NP is the number of counts for the photo-peak area, t_c is the counting time in second, $\varepsilon(E_\gamma)$ is the detector efficiency at E_γ; I_γ is the number of gammas per disintegrations of the radionuclide at E_γ and M is the mass of the sample in kg.

2.4.2 Radiological effects

Since, the distribution of ^{238}U, ^{232}Th and ^{40}K in the environment is not uniform so that with respect to the radiation, the radiological effect of the radioactivity can be measured via radium equivalent activity (in Bq/Kg), gamma absorption dose rate (D in $nGyy^{-1}$, and external and radiation hazard indices.

Radium Equivalent Activity

Since the distribution of natural radionuclides cannot be uniform throughout in soils, rocks, building materials, air, liquid, etc., **radium equivalent activity** (Ra_{eq}) was introduced to define the uniformity in respect to exposure of radiation arising from ^{238}U , ^{232}Th and ^{40}K. It is a radiation index that widely used in the assessment of radiological hazards. Radium equivalent activity is a weighted sum of the activities of ^{226}Ra ($in\ ^{238}U\ series$), ^{232}Th and ^{40}K based on the estimation that 370 $BqKg^{-1}$ of ^{226}Ra, 260$BqKg^{-1}$ of ^{232}Th and 4810 $BqKg^{-1}$ of ^{40}K produce the same gamma ray dose rate (UNSCER, 2000).
The radium equivalent activity index is determined based on the following expression (UNSCEAR, 2000; Beretka & Mathew, 1985)

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \tag{2.4.3}$$

Where, A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively, expressed in $Bqkg^{-1}$

Absorbed Dose rate in the Air

The assessment of radiological hazard due to exposure of external terrestrial gamma-ray radiation from ^{226}Ra (^{238}U), ^{232}Th and ^{4}K in rocks, soils and building materials can also be measured using Absorbed Dose Rate in Air (ADRA) at about 1m above the ground. It is computed based on the following equation (UNSCEAR, 2000)

$$D(nGyh^{-1}) = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K \tag{2.4.4}$$

Where, D is absorb dose rate in $nGyh^{-1}$, A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{4}K respectively, expressed in $Bqkg^{-1}$, the dose coefficients 0.462, 0.604 and 0.0417 in units of $nGyh^{-1}$ per $Bqkg^{-1}$ are adopted from UNSCEAR (2000).

Internal and External radiation indices

The natural radioactivity of building materials can be estimated using internal and external radiation indices based on the following expressions (UNSCEAR, 2000; Harb et al., 2014)

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{2.4.5}$$

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{2.4.6}$$

For safe use of material in the construction dwellings, the external index (H_{ex}) and internal index (H_{in}) should be each less than unity.

2.5 Gamma-ray spectroscopy

In nuclear physics, the measurement of the gamma-rays radiation by gamma-ray spectroscopy system is one of the most important mechanism to get basic information about the nuclear structure and properties of an atomic nucleus such as nuclear energy levels, position of the levels, gamma-emission probabilities, deformations, vibrations, angular distribution and correlations related to spins, magnetic moments, quadrupole moments; and nuclear electric and magnetic transition properties, etc.

In addition, gamma ray spectroscopy has been found a very important analytical device for identifying and determining the chemical composition of samples of interest drawn from the natural environment. The history of gammaray spectroscopy for detecting and measuring gamma-rays emitted from natural and induced radioactive isotopes started in the early of 1950s immediately after Thallium doped Sodium Iodide (NaI[Tl]) scintillation detector came into use. NaI[Tl] scintillation detector gamma ray spectrometry has been used for many years. Nowadays, however; the high purity germanium detector gamma ray spectroscopy takes the lead in nuclear analytical technique due to its best energy resolution and sensitivity.

Modern gamma ray spectroscopy system consists of HPGe or NaI(Tl) detector, preamplifier and amplifier circuits, Multichannel analyzer (MCA) connected to a personal computer (PC) as shown in block in figure 2.11. Each component of the gamma spectroscopy system plays an important role and feed to each one after the other until a gamma ray acquisition spectrum is produced on the screen of the PC computer.

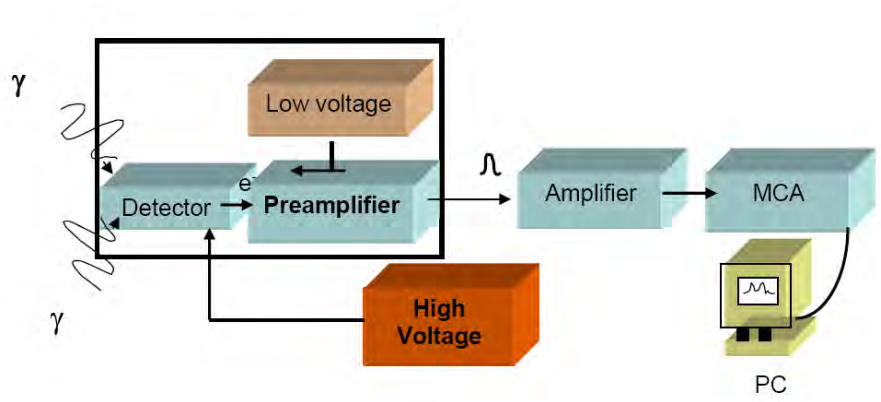

Figure 2.11: Gamma-ray spectroscopy System

2.5.1 Crystal Detectors

The major role of a crystal detector in gamma spectroscopy as shown in figure 2.11 is to detect gamma-rays emitted from radioactive isotopes and transform them into small electrical impulses in such a way suitable for amplification. In so doing, there are three basic physical processes known as photoelectric effect, Compton Effect, and pair-production ongoing on within the detector material for gamma ray detection and then transformation into electrical impulses. In photoelectric effect, the incident gamma ray energy is totally converted to hole-electron pairs at the detector surface. These hole-electrons pairs are then collected by the electric field established across the detector and the signal pulses are produced.

These signal pulses produced by the detector are proportional to the deposition of the energy of the incident gamma-rays that produced the interaction resulting in a photo-peak

in the spectrum with pulse height proportional to the full of gamma radiation.
In the case of Compton-effect, only part of the initial energy is transferred to the atomic electron for ejection and the remaining energy appears as a secondary photon. Therefore, Compton events will produce a well-distributed and a continuous background low-energy area in the spectrum.
In pair production process, when the incident gamma ray energy comes closer to the nucleus of the detector's atom, it experiences a probability of transformation all of its energy into electron- positron pair of equal mass under the influences of the coulomb field of the nucleus. As the positron and negatron deposit their energy through elastic scattering within the entire of the detector, two pulses with equal height are produced simultaneously; the output pulse from the detector would be the sum of the two pulses. For detailed understanding of the interaction of gamma ray with matter, please refer Knoll (1989); Gilmore (2008).
There are actually different types of detectors. Among them two groups of solid state radiation detectors known as scintillation and semiconductor detectors are most dominant and commonly used in gamma ray detection. In fact, each of these two detectors have their own advantages and limitations. For example, NaI[Tl] scintillation detector has better efficiency but it has a poor energy resolution which in turn produces poor spectral quality of the gamma spectrometry. On the other hand, the HPGe semiconductor detector has a wonderful energy resolution but it has a poor efficiency. Endorsing its low efficiency, nowadays, HPGe semiconductor detector is recognized as gold standard for detection and identification of characteristic gamma rays emitted from unstable radioactive isotopes.

2.5.2 NaI(Tl) scintillation gamma-ray spectrometry

Surprisingly, NaI(Tl) detector gamma spectroscopy still remains the most popular for measuring gamma radiation in the low background laboratory even though it has poor energy resolution. In particular, NaI(Tl) detector gamma spectroscopy is more applicable

for the study of natural radioactive elements in the low background laboratory room.

2.5.3 High Purity Germanium gamma-ray spectrometry

The high purity germanium (HPGe) semiconductor crystal is considered as the best and active volume that is used to detect the gamma rays with a high resolution. The main function of this detector is to generate charges, which are in proportion to the energy deposited in the detector by the incoming photon and then these charges are converted into pulses by an integral charge sensitive preamplifier.

In gamma ray acquisition spectroscopy system, the HPGe or NaI(Tl) crystal detector is mounted in a vacuum chamber to be protected from moisture and considerable contaminant similar to the schematic diagram as shown in Figure 2.12. This detector works under the supply of liquid nitrogen from cryostat inserted in a liquid nitrogen Dewar in order to keep the detector at a very low temperature. Otherwise, since germanium has a relatively narrow energy band gap as temperature increases thermal generation charge carriers increase which then induce a noise that destroys the energy resolution of the detector. Therefore; to reduce such noise liquid nitrogen at a temperature of (77^0K) is needed for cooling and maintaining the (HPGE) detector working at normal condition. Moreover, the preamplifier is located near the detector as part of the cryostat package to reduce electronic noise.

2.5.4 Preamplifier and Amplifier

In gamma ray spectrometry, preamplifier has three basic functions: (1) conversion of charge produced within the active volume of the detector to a voltage pulse, (2) pulse amplification, and (3) pulse shaping and then transmits the signal pulse toward the main amplifier for further amplification. In addition, preamplifier is also important for impendence matching between the high impedance of the detector to the low impedance of the

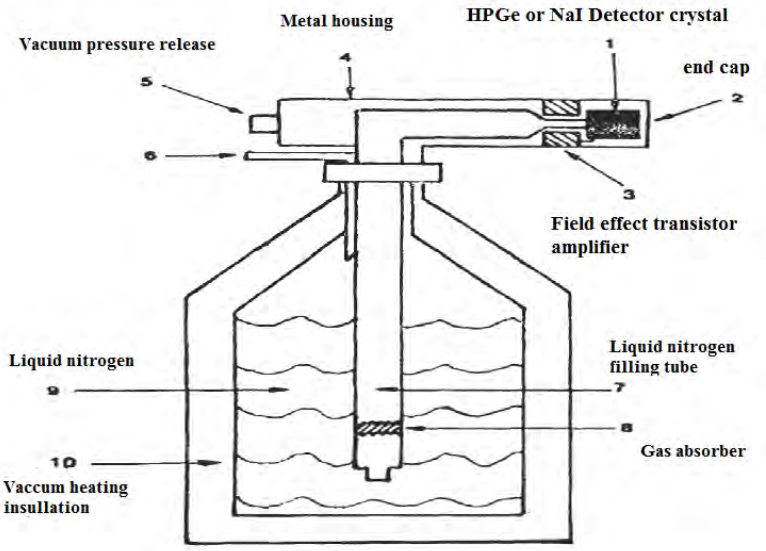

Figure 2.12: A typical germanium detector, crostal and liquid nitrogen reservoir

coaxial cables connected to the amplifier. Most detectors are considered as a capacitor into which a charge is deposited as a result of the interaction of gamma-ray energy or photons. During the charging process a small current flows and a voltage pulse is dropped

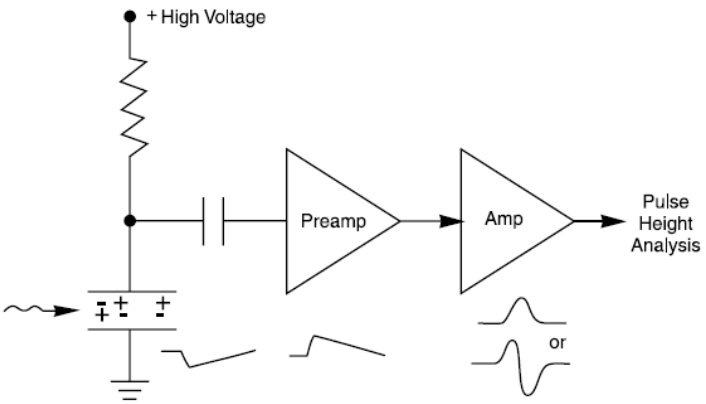

Figure 2.13: Basic circuit showing detector, Preamplifier and Amplifier

across the bias resistor as shown in figure 2.13. The rise time of the preamplifier output pulse is related to the collection time of the charge and ranges from a few nanoseconds to few microseconds while its decay time is the RC (resistor-capacitance) time constant characteristic of the preamplifier itself. Most preamplifiers are charge sensitive. Simply,

the output voltage pulse is proportional to the input charge.

The voltage pulse produced at the output of the preamplifier is not suitable for the measurement of peak height. So it needs to be amplified and well shaped to the desired level using the main amplifier circuit as shown in figure 2.13 next to preamplifier circuit. Finally, at the output of the amplifier, a smoothed signal height that is proportional to the energy of the detected gamma-rays or photons by the detector and becomes the input to the multichannel analyzer.

2.5.5 Multichannel Analyzer (MCA)

The major role of a Multichannel Analyzer(MCA) in gamma spectroscopy is to sort out the electrical pulse by height and decide in which channel it falls according to energy levels of the gamma-rays deposited in the detector. MCA is constructed from the combination of an analog to digital converter (ADC) circuit, a histogramming memory circuit and a visual display units as shown in figure 2.14. Each circuit in MCA has its own function. For instance, the role of analog to digital (ADC) in MCA circuit is to convert the amplified signal pulse output of the amplifier circuit as shown in figure 2.14 into digital pulse heights as illustrated in figure 2.15. The hitsogrammer circuit in figure 2.14 in turn

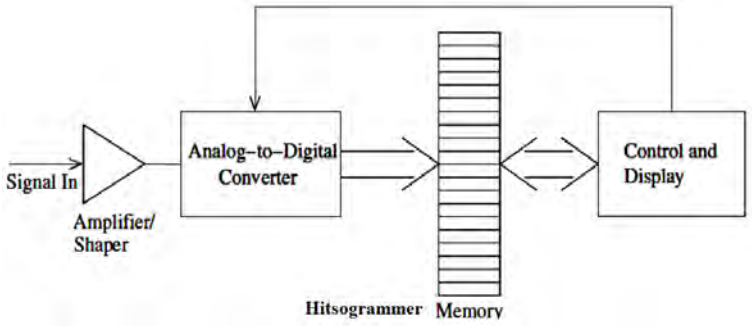

Figure 2.14: MCA functional Block Diagram

adds a count in a channel corresponding to the digital value of the pulse height. This

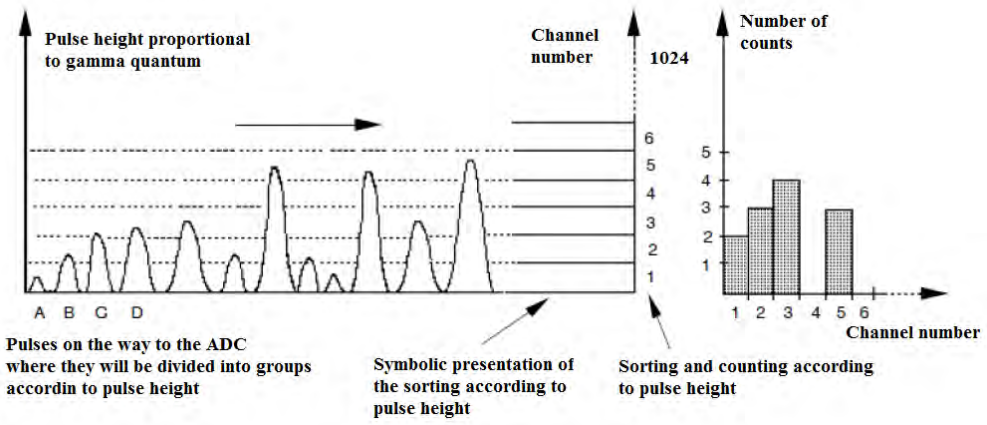

Figure 2.15: A flow chart showing how signal pulses are converted to digital histogram by ADC circuit

histogram represents the spectrum of input pulse heights. Simply, MCA is run as a pulse-height analyzer (PHA).

The overall working principle of the gamma spectrometry is that each event that falls on the detector produces a voltage proportional to the energy of γ-rays which caused the event. The event is amplified by amplifier circuit and then added to the MCA channel corresponding to its energy range. The control and display unit of MCA reads the memory content versus memory location, which is equivalent to the number of pulses against energy and appear as energy spectrum which is a plot of intensity (counts per second) versus energy like that of the energy spectrum in figure 2.16. For instance, the concentration of each neutron induced radioisotope in a given sample is determined by computing the areas under one of the peaks displayed in the gamma-ray spectrum. The spectrum obtained after neutron activation consists of many photo-peaks corresponding to each element in the sample as shown in figure 2.16.

However, theoretically, if we consider one of the photo-peaks of the gamma-rays spectrum in figure 2.16, it seems to be an ideal sharp photo-peak. In practice, however; the gamma rays of a single energy appear as a peak, which can be approximated by a Gaussian function as shown in figure 2.17. The peak position (x_0) of the Gaussian corresponds to

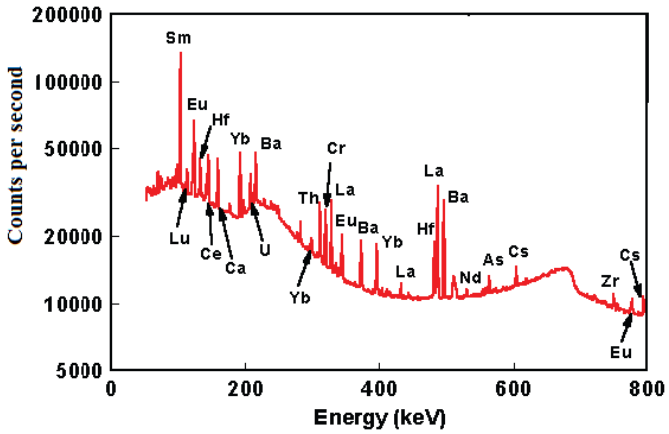

Figure 2.16: Spectrum diagram showing a plot of intensity (counts per second) versus energy

the energy of the gamma ray but the width of the Gaussian conveys information about how precisely the HPGe and NaI detectors measure the energy of the gamma ray.

In high resolution HPGe detector, the peak is nearly symmetric and the peak positions

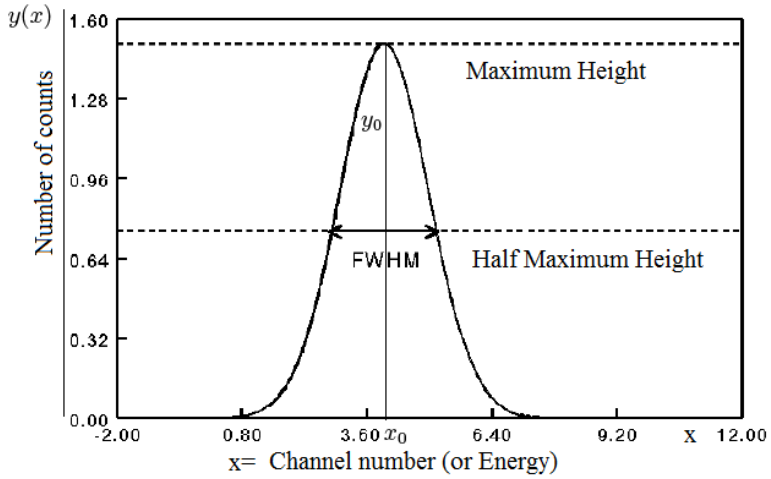

Figure 2.17: Photo-peak in Gaussian distribution function

are chosen at the peak centers defined by the axis of symmetry as shown in figure 2.17. The photo-peak area of the signal is expressed using full Gaussian function (Knoll, 1989)

$$\begin{aligned} Y(x) &= Y_0 e^{\frac{(X-X_0)^2}{2\sigma^2}} \\ &= \frac{A}{2.5066\delta} e^{\frac{(X-X_0)^2}{2\sigma^2}} \end{aligned} \tag{2.5.1}$$

Where,

Y(Xx) = number of counts at channel h

x_0= symmetric function of the peak centroid,

$\frac{A}{2.5066\delta}$ =the maximum vale of the Gaussian function ,

A=peak area (net area of the fitted peak)

σ = peak width= 0.42466FWHM

σ^2= variance

2.5.6 Energy Resolution

Energy resolution is an essential requirement of many experiments of analytical techniques. For instance, HPGe detector has an excellent energy resolution which can help to separate and resolve various close gamma-rays peaks in a complex energy energy spectrum despite its poor efficiency. The energy resolution (R) of a detector is determined by

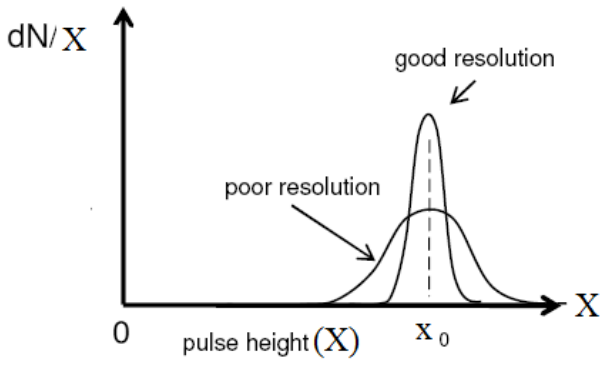

Figure 2.18: Energy resolution of a detector

$$R = \frac{FWHM}{X_0} = \frac{\Delta X}{X_0} \tag{2.5.2}$$

Where, the Full Width at Half Maximum , FWHM= Δ X shown in figure 2.17 is measured in keV and X_0 is the photo-peak energy centroid in keV.

As the value of R becomes smaller, the better will be the energy resolution of the detector to separate very closer energies. Usually, resolution is generally specified in terms of the

full width at half maximum (FWHM) using 122 KeV photo-peak of Co-57 and the 1332 KeV photo-peak of Co-60 of known activities. According to Ahmed (2013), for most NAA applications, a detector with R = 1.0 KeV resolution or below at 122 KeV and R = 1.8 KeV or below at 133 Kev is sufficient and excellent.

On the other hand, energy resolution can be affected by the number of electron-hole pairs created in the detector, incomplete charge collection, and electronic noise contributions and detector geometry (Knoll, 1989). The effect of such factors thus depends on the properties of the detector and the gamma-ray energy so that care should be taken to minimize such factors.

2.5.7 Energy Calibration

The calibration of any analytical system is needed critically to achieve accurate results. Similarly, in nuclear analytical technique, energy calibration is very useful to determine the width and location of region of interest and also to find the energies of unrecognized gamma rays. The energy calibration function can usually be a first or second degree of polynomial, describing the energy dependence of the channel number in a spectrum.

$$E_\gamma = A + B.X + C.X^2 \tag{2.5.3}$$

where, E_γ is the energy deposited in a detector, X is the spectral channel number for the center of peak corresponding to E_γ and A, B and C are constant to be determined for calibration. For a two-point calibration, equation (2.5.3) can be reduced into a linear function as shown in equation (2.5.4).

$$E_\gamma = B.X + A \tag{2.5.4}$$

where, $m = B = \frac{E_{\gamma 2} - E_{\gamma 1}}{X_2 - X_1}$ is the slope of the linear equation, A is the intercept.

In NAA, calibration with standard radioactive sources such as ^{137}Cs, ^{57}Co, ^{60}Co, etc of known energies is done to correlate the channel number with the corresponding gamma energy as depicted in figure 2.19.

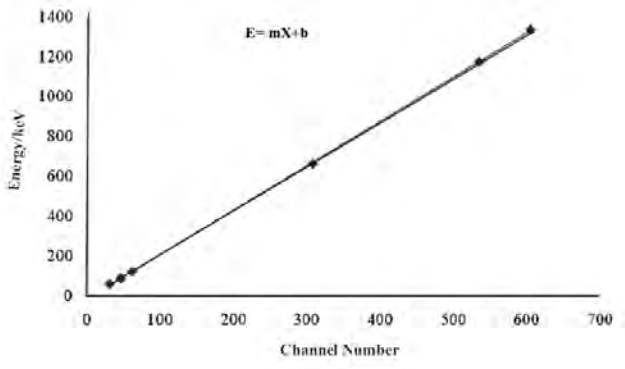

Figure 2.19: Energy Calibration of the gama ray spectroscopic system

2.5.8 Detector efficiency

The efficiency of a detector is defined as a measure of its ability to detect gamma-ray or x-ray radiation. It measures of how many pulses occur for a given number of gamma rays emitted from radioisotopes. There are different types of efficiency which have been in use for gamma ray detection, namely: absolute efficiency, intrinsic efficiency, relative efficiency and full energy photo-peak efficiency. Among these the full energy photo-peak efficiency is the most significant parameter of the detector and is independent of the detector geometry. The efficiency of a detector can be determined using equation(2.5.5) by measuring the gamma-rays emitted from a standard radioactive sources such as ^{22}Na, ^{60}Co, ^{137}Cs, ^{152}Eu and ^{241}Am of known activities.

$$\varepsilon = \frac{A}{A_0 P_\gamma e^{-\lambda t}} \tag{2.5.5}$$

Where, A is the net peak activity in count per second, A_0 is the original activity of the sources at the time of standardization(or fabrication), P_γ is the absolute γ-ray emission probability, t is the time elapsed since the standardization until the time of measurement and λ is the decay constant.

2.5.9 Source of Errors

Radioactive decay and other nuclear reactions are random events and therefore must be described quantitatively in statistical terms. This means measurement based on observing the radiation emitted in nuclear decay is subjected to some degree of statistical fluctuation (Knoll, 1989). In most nuclear analytical techniques, the statistical model used to describe the radioactive decay is the binomial distribution. For example, let us consider that a sample containing N radionuclides decay with a probability of P(n) where n is the population decay in certain interval of time. From statistics, the probability distribution is represented by a binomial distribution as

$$P(n) = \frac{N!}{(N-n)!n!}p^n(1-p)^{N-n} \tag{2.5.6}$$

where, n the number of trials in the population decay, p is the success probability per trial, the number of events occurred.

The mean value and the variance of the binomial distribution can be expressed in equation as follow

$$\begin{aligned} \overline{n} = \mu &= \sum_{n=0}^{n=N} nP(n) = Np \\ \sigma^2 &= \sum_{n=0}^{n=N} (n-\overline{n})^2 = \overline{n}(1-p) \end{aligned} \tag{2.5.7}$$

The mean value (μ) and the variance of the distribution (σ^2) are $\mu = np$ and $\sigma^2 = np(1-p)$ respectively. However, the binomial distribution can be reduced to poisson distribution under the conditions that the probability p is very small and the number of trials N $\rightarrow \infty$ such that μ= np remains finite (Leo, 1992). Thus, the probability of observing n events (decay atoms) in poisson distribution is given by

$$P(n) = \frac{(\overline{n})e^{-n}}{n!} \tag{2.5.8}$$

In radioactive decay, $\overline{n}$ is represented in terms of λt

$$P(n) = \frac{\lambda t e^{-\lambda t}}{n!} \tag{2.5.9}$$

In Poisson distribution, the variance can be expressed in terms of the mean as shown in equation 2.5.9 but the distribution couldn't likely to be symmetric for $\mu \leq 20$.

$$\begin{aligned} \sigma^2 &= \mu \\ \sigma &= \sqrt{\mu} \end{aligned} \tag{2.5.10}$$

However, as μ gets larger above 20, the distribution function becomes more symmetric and approaches the Gaussian distribution as shown in figure 2.17 and equation 2.5.1. This implies that the full-energy peaks are usually well described by a Gaussian function and thus $\sigma^2 = \mu$ is more pronounced nearly the centroid of the Gaussian function.

In experimental analysis, uncertainties that appear due to the statistics can affect the experimental data. Suppose, in instrumental neutron activation analysis uncertainties can appear due to nuclear parameters and measured parameters and the final results (R_f) of the analyzed data can be expressed in the form of

$$\begin{aligned} R_f &= R \pm \Delta R \\ \Delta R &= \sigma = \sqrt{\mu} \end{aligned} \tag{2.5.11}$$

Where, R is the mean value of the experimental result and $\Delta R = \sigma = \sqrt{\mu}$ is standard deviation or error due to nuclear parameters and measured parameters as shown in equation 2.5.12

$$\Delta R = R\sqrt{(\frac{\Delta A}{A})^2 + (\frac{\Delta \phi}{\phi})^2 + (\frac{\Delta \theta}{\theta})^2 + (\frac{\Delta \sigma}{\sigma})^2 + (\frac{\Delta I_\gamma}{I_\gamma})^2 + (\frac{\Delta \varepsilon(E_\gamma)}{\varepsilon(E_\gamma)})^2 + ..} \tag{2.5.12}$$

Where, A is the activity peak count rate of an element, ϕ is the reactor neutron flux, θ is the elemental mass abundance, σ is the cross section of an element, I_γ is the gamma ray intensity, $\varepsilon(E_\gamma)$ is detector efficiency, etc.

Minimum detectable Activity (MDA)

The minimum detectable activity (MDA) is defined as the smallest concentration of a radionuclide, which can be determined reliably with a giving detection system. For low

level radioactivity measurements, it is essential to reduce the background counts and to increase the detection efficiency. The critical level can be determined based on equation (2.5.17):

$$L_c = K_\alpha \sigma_0 \tag{2.5.13}$$

The the minimum detection limit (L_d) is given by the following equation;

$$L_d = L_c + K_\beta \sigma_D \tag{2.5.14}$$

Where, K_α and K_β ar the abscissas of the normal distribution corresponding to the probability levels $1 - K_\alpha$ and $1 - K_\beta$ respectively.

In gamma ray spectroscopy, the detection limit can be determine in terms of activity. Thus the minimum detectable activity can be determined based on the following expression

$$MDA = \frac{L_d}{\varepsilon m t_{liv}} \tag{2.5.15}$$

Where, m is the mass of the sample, t_{liv} is the live counting time and ε is the efficiency of the detector.

Chapter 3

Materials and Method

3.1 Introduction

The methodology part of this thesis discusses where and how the research was conducted. The discussion includes how best the sample collection, sample preparation, sample irradiation, the experimental calibration and efficiency determination were performed. In addition, it also discusses the method of data and error analysis.

3.2 Materials

The research materials or facilities used for this study were the Nigerian Research Reactor (NIRR-1) swimming pool-type reactor operating at 30.5 kW as shown in figures 3.1 and 3.2, which was installed and commissioned in 2004 at "Center for Energy Research and Training (CERT)", in Ahmadu Bello University, Zaria, Nigeria. According to the report of Yamusa et al. (2013), the NIRR-1 nuclear reactor uses high-enriched uranium as fuel and light water as moderator and coolant.

In addition to the nuclear reactor, other accessory facilities and related instruments such as Oretc HPGe detector and Ortec Multichannel analyzer gamma spectrometer, NaI(Tl) gamma spectrometer, a four-digit Meter model weighing balance, polyethylene capsules or vials, Maestro and Winspan 2004 software packages were in use for the element

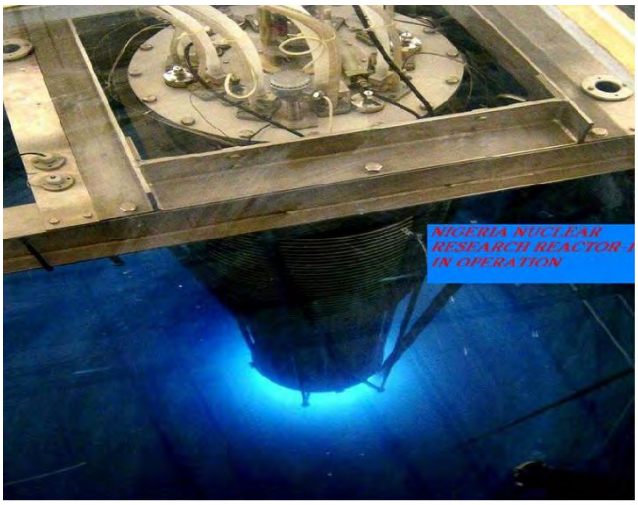

Figure 3.1: Sectional view of the Nigerian Research Reactor-1(NIRR-1) swimming pool-type

Figure 3.2: The Pneumatic Rabbit System for sample sending and retrieving out the reactor

characterization and for measuring the radiation levels of the samples under investigated.

3.3 Research Method

The research method that was chosen for present research was the reactor based experimental method. After the samples were collected on random basis and purposeful means from the sampling sites, they were taken to the research laboratory and then processed in such a way suitable for experimental irradiation in a nuclear reactor. The samples were

irradiated by Thermal neutron sources of the Nigerian Research Reactor (NIRR-1). Then the activities of the neutron induced radioisotopes in the samples were measured using HPGe detector gamma ray spectroscopy and the analysis was done using gamma ray spectrum analysis software known as WINSPAN 2004. Based on the gamma ray spectrum analysis software, the elements of interest in the samples were identified by their energies and half-lives displayed on the gamma-ray spectrum qualitatively and the concentration amounts of those elements were determined quantitatively using intensity (photo-peak area per second) and other related measurable nuclear parameters irradiation, decay, and counting times, etc.

Similarly, the activity concentrations and radiation doses of the long-lived radioactive elements in the rocks considered in this study were also measured experimentally based on the NaI(Tl) scintillation detector gamma ray spectroscopy and the analysis was done using gamma ray spectrum analysis software package known as Maestro.

3.4 HPGe detector Gamma ray spectrometry

The activities of irradiated samples in this work were measured using a PC-based gamma-ray spectrometry set-up that consists of a coupled Ortec coaxial HPGe detector and computer based multi-channel analyzer (MCA) connected via associated electronic circuits as shown in figure 3.3. The gamma-ray spectrum that was displayed at the screen of a

Figure 3.3: Ortec HPGe gamma detector and MCA connected to a Desktop computer

desktop computer consisted of many full photo-peak energies which were unique to each of the elements in the sample. While the entire process goes on, the intrinsic germanium (HPGe) detector as shown in figure 3.3 should be maintained at room temperature or below 77^0K by the continuous supply of liquid nitrogen during the counting periods to avoid statistical errors caused by the thermal current leakage in the detector.

The analysis of the samples and standard reference materials were performed by the gamma-ray spectrum analysis software package known as WINSPAN 2004, a software developed at CIAE, Beijing, China. Finally, the gamma rays which are unique (or the finger print) to each of the elements in the samples were identified through their half-lives and energies qualitatively. In addition, the concentrations of those elements were determined quantitatively.

3.4.1 Energy Calibration

In nuclear analytical technique, energy calibration is a must before any measurement starts. It specifies the relationship between the channel numbers (where the photo-peak positions observed on the gamma rays spectrum) corresponding to the gamma ray energies. Energy calibration curve is obtained by plotting the energy of selected nuclei versus corresponding channel number as shown in figure 3.4. In this study, the selected energies of certain nuclides as shown in table 3.1 with their corresponding channel numbers were taken to make energy calibration of the HPGe gamma ray spectroscopy.

The energy calibration can be determined using the data in table 3.1 based on the first or second degree of polynomial

$$E_\gamma = A + B.Ch + C.Ch^2 \tag{3.4.1}$$

Where, E_γ is the energy deposited in a detector, Ch is the spectral channel number for the center of peak corresponding to E_γ and A, B and C are constant to be determined for calibration.

Table 3.1: Radionuclides, Energy and channel number used for energy calibration detector based

Nuclide	Energy(in keV	Channel number
^{137}Cs	94.7	1376
^{60}Co	1173.2	1470
	1332.5	1670
^{152}Eu	121.78	244
	244.5	486
	344.29	689
	778.9	1556
	3964	1924
	1408	2812

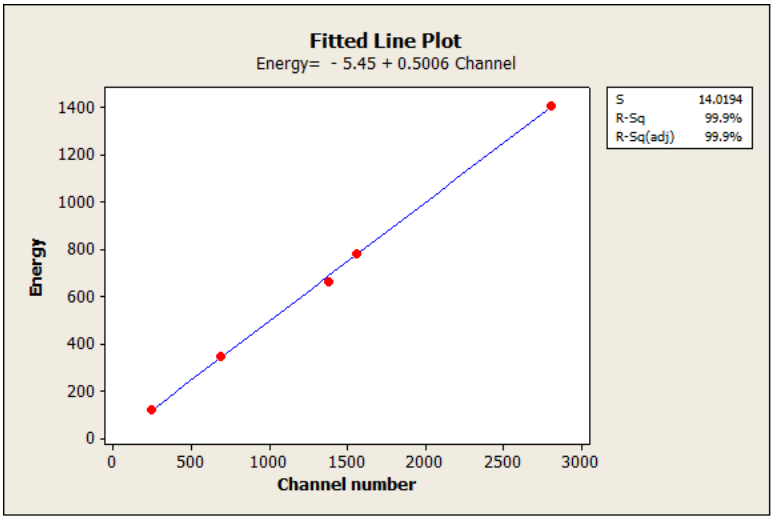

Figure 3.4: Energy versus channel number calibration using standard sources

Accordingly, the energy calibration in this study was done using the energies and channel numbers: (121.78keV, 244), (344.27keV, 688), (661.6keV, 1376) and (1408keV, 2812). Thus, the energy versus calibration plots with the calibration equation is shown in figure 3.4 with calibration function displayed on the curve is

$$E(kev) = -5.45 + 0.5006Ch + 0.00000Ch^2 \tag{3.4.2}$$

Where, A=-5.45, B=0.5006 and C =0 ,E (kev) is the energy and Ch is the channel number

3.4.2 HPGe Detector Efficiency

Detector efficiency is one of the basic analytical technique in nuclear physics. It is the ability to detect all the gamma rays emitted from the radioactive nuclides. Even though

Table 3.2: Efficiency determination for 2 cm, 5 cm and 15 cm Geometries

Nuclide	Energy in Kev	half life *insec*	Decay constant $\lambda(s^{-1})$	γ-emission probability I_γ	Efficiencies (%)at Geometries 2cm	5cm	15cm
^{241}Am	59.54	1.36E+11	5.08E-12	0.357	0.292476	0.336199	0.0558851
^{152}Eu	121.78	4.20E+08	1.65E-09	0.2837	4.687405	2.04646	0.3464358
^{152}Eu	244.69	4.20E+08	1.65E-09	0.0751	3.47841	1.607749	0.300317
^{152}Eu	344.29	4.20E+08	1.65E-09	0.2658	2.8243882	1.270272	0.2479663
^{137}Cs	661.66	9.51E+08	7.29E-10	0.8521	1.816236	0.80545	0.1531857
^{152}Eu	778.92	4.20E+08	1.65E-09	0.1296	1.421604	0.67356	0.1357011
^{152}Eu	964.11	4.20E+08	1.65E-09	0.1462	1.25557	0.587439	0.1209767
^{152}Eu	1112.08	4.20E+08	1.65E-09	0.135	1.1487350	0.540593	0.1113166
^{60}Co	1173.2	1.66E+8	4.17E-09	0.9998	1.1048748	0.51849	0.1067368
^{22}Na	174.53	8.21E+07	8.44E-09	0.9994	0.9544799	0.470791	0.097207
^{60}Co	1332.5	1.66E+08	4.17E-09	0.9998	1.007504	0.471899	0.0978773
^{152}Eu	1408	4.20E+08	1.65E-09	0.2085	0.966826	0.45031	0.0935824

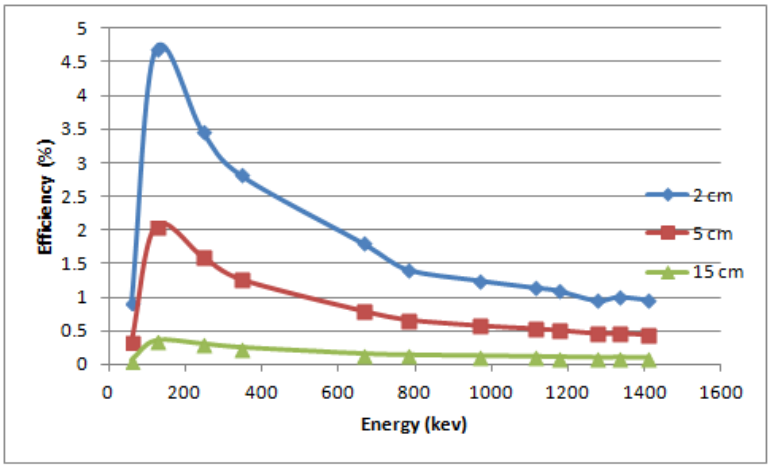

Figure 3.5: Efficiencies as function of gamma-ray energy at geometries 2, 5 and 15cm from HPGe detector

there are various types of efficiencies, this study has interested only on the full energy peak efficiency (FEPE) which is independent of the detector geometry. The full-energy peak of efficiency (ϵ) is the most significant parameter used in a gamma-ray spectrometry system. It is defined as the fraction of the photons of a particular energy emitted by

radioactive nuclides that contributes to the corresponding full-energy peak observed in the pulse height spectrum.

The full energy peak efficiency of the Ortec coaxial HPGe detector in this study was determined based on the following equation:

$$\varepsilon_\gamma(E_\gamma) = \frac{A}{N_0 I_\gamma(E_\gamma) e^{-\lambda t}} \tag{3.4.3}$$

Where, $\varepsilon_\gamma(E_\gamma)$ is the full peak efficiency at energy E_γ, A is the net peak area count per second, N_0 the initial activity of the standard calibrated source at the time of standardization (in Bq), $I_\gamma(E_\gamma)$ is the absolute γ-ray emission probability at E_γ and t is the elapsed time since standardization and λ is the decay constant.

The full energy peak efficiency of HPGe detector in the analysis of essential elements in this study was determined using standard radioactive elements such as ^{22}Na, ^{60}Co, ^{152}Eu, ^{137}Cs and ^{241}Am as shown in tables 3.2 for 2 cm., 5 cm and 15 cm geometries. The plot of efficiency versus energy for 2 cm, 5 cm and 15 cm is plotted as shown in figure 3.5.

To extrapolate the peak efficiency of an element in a sample with known gamma ray energy, the logarithmic value of the gamma ray energy versus the logarithmic value of the efficiency is plotted using the energy and efficiency values in table 3.2. After plotting, a logarithmic polynomial function consisting of log (E_γ) and log (ε) is displayed. Thus, by inserting the logarithmic energy value of the gamma rays obtained from the element in the sample to logarithmic polynomial function displayed, the photo-peak efficiency of that element can be determined.

3.4.3 NaI(Tl) Efficiency determination

Similar to the photo-peak efficiency of elements as determined in HPGe detector gamma ray spectroscopy, the photo-peak efficiency of naturally occurring radioactive materials can be determined based on the NaI(Tl) scintillation detector gamma ray spectroscopy.

The standard radioactive elements used for the efficiency determination of NaI (Tl)

Table 3.3: Efficiency calibration of NaI(Tl) detector

Nuclide	Energy in (kev)	Half life $in(s)$	Decay constant $\lambda(s^{-1})$	γ-emission probability I_γ	Efficiency
^{152}Eu	244.69	4.26e+08	1.65e-09	0.0751	0.08587806
^{152}Eu	344.29	4.20e+08	1.65e-09	0.2658	0.12124236
^{137}Cs	661.66	9.51e+08	7.29e-10	0.8521	0.1096264
^{152}Eu	778.92	4.20e+08	1.65e-09	0.1296	0.0660196
^{60}Co	1173.2	1.66e+8	4.17e-09	0.9998	0.03622464
^{60}Co	1332.5	1.66e+08	4.17e-09	0.9998	0.03259074
^{152}Eu	1408	4.20e+08	1.65e-09	0.2085	0.02712978

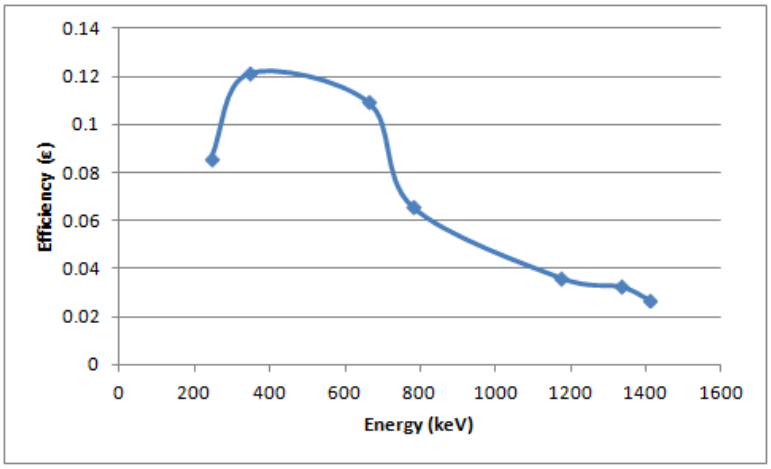

Figure 3.6: Efficiency versus energy calibration of NaI(Tl) gamma rays spectroscopy

detector were ^{60}Co, ^{137}Cs and ^{152}Eu, and the efficiency of the detector was computed using mathematical expression in equation 3.4.3. Moreover, the extrapolated photo-peak efficiency of the natural radioactive element of interest was determined as shown in table 3.3 with the same procedure that was done for the extrapolated photo-peak efficiency determination of the HPGe detector gamma ray spectrometer. The extrapolated photo-peak efficiencies of the natural radioactive nuclides of ^{214}Bi ($in\ ^{226}$Ra series), ^{208}Tl ($in\ ^{232}Th\ series$) and ^{40}K have been determined as displayed in chapter 4 under section 4.2 in table 4.7.

3.4.4 Energy Resolution

The energy resolution of the HPGe detector system was set at Full Width Half at Maximum (FWHM) = 1.33 keV at 1332 keV resolution using ^{60}Co.

3.4.5 Error in Analysis

In experimental analysis, errors are totally unavoidable but can be minimized to the acceptable limits. In INAA, for instance, uncertainties usually appear from counting statistics such as neutron flux (ϕ), irradiation time (t_{irr}), decaying time (t_d), counting time (t_c) and dead time (t_{dead}) as well as from the measured parameters such as the mass of the sample (m_{sam}), net peak activity (A) and detector efficiency (ε).

In the present study such overall uncertainty for each element of interest in the irradiated sample was determined as the square root of the sum of measured activity as shown in equation 2.5.12 on page 53 using the gamma-ray spectrum analysis softwares packages known as WINSPAN 2004.

The relative method was extensively used for NAA calculation in this work for the very reason that uncertainty that appear due to nuclear parameter became insignificant. According to user's Mannual (2010) prepared by **Bright Stone International** for gamma spectrum analysis softwares packages WINSPAN 2004, in relative method of analysis if the irradiation and measurement conditions of the control sample and SRM (standard reference materials) are the same, some nuclear parameters such as θ, σ, I_γ, M and λ would be offset to each other and do not cause an impact on the analysis of the results because these experimentally confirmed parameters with very small errors are usually adopted as constants by the software packages.

Moreover, the dead time measured by the multichannel analyzer gamma rays spectrometer was on average 5% that is below 10%. According to the protocol of the CERT in

Nigeria, the dead time counting should be less than 10%. Otherwise, the control experiment sample should be repeated or avoided. Therefore, the energy resolution is not affected due to the effect of the dead time.

Gamma ray self absorption by the sample mass was corrected using the mixture gamma ray mass absorption:

$$\mu = \Sigma w_i \mu_i (\frac{cm^2}{g}) \tag{3.4.4}$$

Where, μ is the total photon mass absorption coefficient for our mixture, w_i is the weight fraction of i^{th} element in the mixture and μ_i is the photon mass absorption coefficient. The mean value of the gamma ray mass self absorption coefficient was used for the calculation of the actual intensity of the photon. The intensity from the full energy photo peak is corrected using the photon intensity mass absorption based on the following equation

$$I(x) = I_o e^{-\mu x} \tag{3.4.5}$$

Where, I_0 is the intensity at the upper surface of the sample and $I(x)$ is the intensity of the photons at thickness x = 5 mm the from upper surface of the sample

$$\frac{I(X)}{I_0} = K = e^{-\mu x} \tag{3.4.6}$$

By substituting the total photo mass absorption as determined in equation 3.4.5 for the analyzed elements in the sample and the thickness of the sample into equation 3.4.7, the value of k was obtained ≈ 1 for the majority of the samples. This implies that the gamma ray self absorption by the sample can be considered as insignificant.

Statistical error that is caused by the masse of the sample or the SRM sample was also corrected using four-digit Melter model weighing balance. Apart from the correction made by the four-digit Melter model weighing balance, the mass of the sample with four digits in gram as measured by the weighing balance was again rounded off into two digits in g by the WINSPAN 2004 softwares packages and thus the estimated errors due to sample mass measurement was negligible.

3.5 Study Area

In this study representative samples were collected from the specific areas of the Amhara regional state. The Amhara regional state is one of the biggest regions in Ethiopia and is found in North and Northwest Ethiopia as illustrated in figure 3.7. The region has different

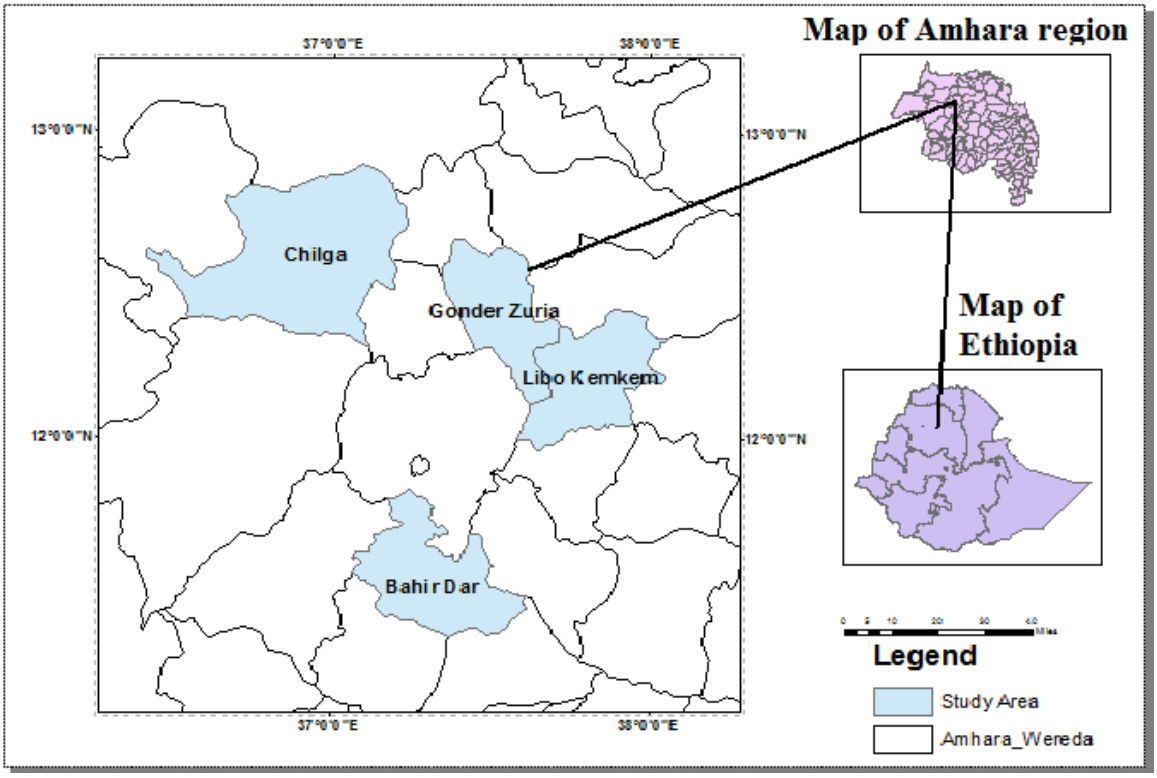

Figure 3.7: Map of the Study Area

geographical and climatic conditions starting from semi-low land areas to highland areas. From the specific areas of the Amhara region known as Chilga woreda, Gondar zuria (surrounding), Libo kemekem and Bahirdar city as shown in figure 3.7, representative samples of soils, rocks, medicinal plants and finger millets were collected and taken to the research laboratory for the purpose of multi-elemental analysis based on neutron activation analysis and for investigating the level of radioactivity in rocks using the NaI (Tl) gamma ray spectrometer.

3.5.1 Analysis of Essential and/Toxic elements in soils around Aykle town in Chilga Woreda, North Gondar zone

Sample Collection and Preparation

A total of six soil samples (0-5 cm depth) was obtained from six different sampling sites known as Serako, Nara Micheal, Nara awrdarda, Dilanba, Alemtsehay and Yihuseraba from around the town of Aykle in Chilga Woreda. Aykle town in Chilga Woreda is located at 60 km west of Gondar city in northwest Ethiopia lying at latitude of $12^0 32' 54.44''$ N and longitude of $37^0 05' 11.22''$ E. The name of sampling sites and their corresponding codes including GPS coordinates are shown in table 3.4.

The samples were dried in open air for a few days and then put in a standard oven as

Table 3.4: Sample code, sampling site and GPS coordinate of the study areas

Sample code	Sampling site	GPS coordinate
SSO1	Serako	Lat.12^0 $33'49.49''$N, Long.$37^0 3' 39.10''$E
SSO2	Nara Michael	Lat.12^0 $32'29.42''$N, Long.$37^0 6' 1.54''$E
SSO3	Nara Awrdarda	Lat.12^0 $32'22.84''$N, Long.$37^0 4' 38.95''$E
SSO4	Dilanba	Lat.12^0 $33'51.21''$N, Long.$37^0 4' 41.56''$E
SSO5	Alemtsehay	Lat.12^0 $33'56.36''$N, Long.$37^0 5' 51.34''$E
SSO6	Yihuserako	Lat.12^0 $32'14.30''$N, Long.$37^0 3' 41.05''$E

shown in figure 3.8 for 12 hours ; crushed into powder form using the agate mortar as shown in figure 3.9 and then passed through 100 micron mesh sieve to get a homogenized powdered form. After the samples were pulverized, small representative sub-mass in the range of 150- 250 mg from each sample was weighted using a four-digit Melter model weighing balance as depicted in figure 3.9 and heat sealed in a cleaned sheet similar to the image shown on the right side of figure 3.10.

Similarly, for the purpose of quality assurance and data validation of INAA, two standard reference materials (SRMs), namely: Soil-7 (IAEA) and Coal fly ash (NIST 1633b) whose

Figure 3.8: Standard oven with temperature regulator for drying samples

Figure 3.9: Four-digit Meter model weighing balance (on left side) and Agate Mortar (on right side)

Figure 3.10: polyethylene heat sealed sheet containing sample

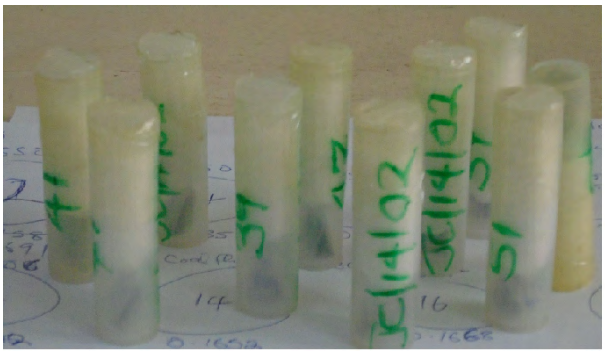

Figure 3.11: The $7.4cm^3$ Snap-top polyethylene capsule vials containing sample and standard reference material sample ready for irradiation

mass was equivalent to the mass of soil sample were weighed and heat sealed separately in a pre-cleaned polyethylene sheets. Finally, the samples and standard reference materials were packed together in a polyethylene vial for irradiation as shown in figure 3.11.

3.5.2 Analysis of Essential Elements in six Endemic Ethiopian Medicinal Plants obtained from Gondar City and Taragedam areas

Sample Collection and Preparation

Six different medicinal (or herbal) plant samples were obtained from Gondar city and from Taragedam areas near Addis Zemen town in Lemo kemkem Woreda in south Gondar,

Ethiopia. According to Geographical Position System (GPS), the Taragedam area is located at latitude of $12^0 08' 38.48''$ N and longitude of $37^0 44' 42.77''$E as shown in figure 3.12. Similarly, Gondar city where the sample of Millettia ferruginea was taken is located at latitude of $12^0 36'$ $29.04''$ N and longitude of $37^0 28' 9.96''$E. The samples were washed

Figure 3.12: Medicinal plants collected from Taragedam areas near Addis Zemen town, in South Gondar zone, Northwest Ethiopia

off, dried in an open air and girded by agate mortar into powder formation. The powder form of each sample was then passed through a 100-mesh sieve to get a fine powder in a homogeneous state. To avoid any moisture content the powder form of the samples were dried again at $45^0 c$ in an oven as shown in figure 3.8 for 24 hrs and then were put in a desiccators for another 24 hrs.

Finally a small representative sub-mass in the range of 0.250-0.300 g was weighed from each sample using a four-digit Meter model weighing balance as shown in figure 3.9 and heat sealed in a polyethylene sheet for irradiation as shown in figure 3.10. Similarly, for the purpose of quality assurance, a standard reference material of biological origin, known as appeal leaves (NIST 1515) whose mass equivalent to the mass of the medicinal

plant was also prepared for irradiation. Both samples and Standard Reference Materials (SRMs) were then packed together in polyethylene vial for irradiation.

3.5.3 Finger millet Sample Collection from local market of Bahirdar City

Sample Collection and Preparation

Three finger millet species white, black and mixed were obtained from the local market of Bahirdar city in Northwest, Ethiopia as shown in figure 3.13. Bahirdar city, the capital

Figure 3.13: Area of finger millet (or cereal crop) market in Bahirdar city

city of the Amhara regional state, is located at geographic coordinates of $11^0 35' 37"$ North latitude and $37^0 23' 26"$East longitudes. The samples were washed off by deionized water. After the samples were taken to the research laboratory, they were dried, pulverized and sieved to get the fine powder in a homogenized state. The fine powder was dried again at $45^0 C$ in an oven for 24 hrs until a constant weight was obtained. Finally, a small mass in the range of 0.250-0.300g from each sample was weighed by four-digit Meter model weighing balance and heat sealed in a cleaned polyethylene sheet. In addition, for the purpose of quality assurance a standard reference material (SRM) of biological origin

known as apple leaves (NIST 1515) which was equivalent to the mass of the samples was prepared and packed together with samples in such a way suitable for short and long irradiation schemes.

3.5.4 Determination of activity concentrations and radiation doses of natural radioactive nuclides in rocks around Gondar City

Sample Collection and Preparation

A total of five rock samples were collected from five different locations around Gondar city in Northwest Ethiopia. The rocks of the selected locations are usually utilized for purposes of house and road constructions in the form of gravel similar to the two sampling sites as shown in figure 3.14 and 3.15. About 400g of rock sample from each sampling site was collected, packed in polythene and labeled each by giving a sample code for easy identification as shown in table 3.5. The sample of rocks were dried for a week time and

Figure 3.14: Crashed rocks in the form of gravel collected from Gondar airport sampling site

Figure 3.15: Rocks and Crashed Rocks from Suru Damaza sampling site

crushed to fine powder with the use of agate mortar as shown in figure 3.9. The powered form of each rock sample was heated again in a standard oven at 100 ^{0}C for 24 hours to avoid moisture contents within the powder form of the rock samples.

Packaging of the samples into radon-impermeable cylindrical plastic containers which were selected based on the space allocation of the detector vessel 7.62 cm by 7.62 cm in

Table 3.5: Sample code, sampling site and GPS coordinate of the study areas

Sample code	Sampling site	GPS coordinate
SR1	Arno Seneba	Lat.12^0 $21'45.62''$N, Long.$37^0 33' 55.19''$E
SR2	Dngay Gores	Lat.12^0 $34'18.84''$N, Long.$37^0 25' 31.40''$E
SR3	Srur Damaza	Lat.12^0 $33'0.18''$N, Long.$37^0 23' 8.06''$E
SR4	Dabecha Rufauel	Lat.12^0 $32'29.80''$N, Long.$37^0 21' 54.94''$E
SR5	Gondar Airport	Lat.12^0 $31'25.39''$N, Long.$37^0 25' 43.58''$E

Figure 3.16: Rock Samples Packed in plastic containers for 4 weeks

dimension (geometry) was done (Umar & Jonah, 2012). To prevent radon-222 escaping, the polyethylene container lid was tightly sealed and wrapped using thick cello-type and filling the lid assembly gap with candle wax to block the gaps between lid and container as shown in figure 3.16. The radionuclides ^{238}U, ^{232}Th and their daughter products such as radon and the next progenies in the rock were allowed to reach a secular radioactive equilibrium by storing the samples for 30 days prior to gamma spectroscopy measurements.

3.5.5 Sample Irradiation and Counting

In INAA, the samples and standard reference materials packaged together in a capsule were irradiated simultaneously in the Nigerian Research Reactor (NIRR-1) irradiation sites using pneumatic-rabbit system. For this experimental work, the nuclear reactor was adjusted to produce a thermal neutron flux of $2.5 \times 10^{11} n.m^{-2}.s^{-1}$ in the outer irradiation channels and a thermal neutron flux of $5 \times 10^{11} n.m^{-2}.s^{-1}$ in the inner irradiation channels. There are two sets of transfer system connected to the reactor core of the NIRR-1 as shown in figure 3.2. The pneumatic transfer system type A has been connected directly to two sections of the irradiation channels: to inner irradiation channel A_1 and outer irradiation channel A_2. The other multi-functional transfer system known as the pneumatic system type B has been connected to three inner irradiation channels (known as B_1, B_2 and B_3) and to a single outer irradiation known channel B_4. Both pneumatic transfer system types A and B are used to send the sample into the reactor channels and then to retrieve the sample back outside the reactor's irradiation channels.

There are also two stages of sample irradiation schemes designed to capture neutron induced isotopes of short half-lives and long half-lives at the Nigeria research reactor (Oladipo et al., 2012). An arrangement of elements with short life are determined using the short live irradiation scheme, the sample is then sent to channel B_4 for either 1 minute or 5 minutes depending on the sample matrix, while channel B_2 is used for long lived irradiation.

In short irradiation, the geological samples and biological samples were irradiated for 1 minute and for 5 minutes respectively in the outer irradiation channel (B_2) of the reactor. After a decay time of 2-12 minutes, each sample was placed on top of a 2 cm height sample holder (H_2) above the detector and then the first round of counting was taken for 10 minutes with radiation counting at this position denoted as S1. The second round of counting of the same sample was taken again for 10 minutes after the cooling of time of

Table 3.6: Radionuclides produced by (n, γ)reaction during short and long irradiations and their corresponding half- lives $(\tau_{1/2})$, gamma energies (in kev), irradiation time (t_{irr}), decay time (t_d) and counting time(t_c)

Element	Target nuclide	Product nuclide	$\tau_{1/2}$	$E_\gamma(in\ kev)$	$Measured\ time\ parameters$
	First short	Irradiation (1S)			
Mg	^{26}Mg	^{27}Mg	9.46 min	1014.4	t_{irr}=1 or 5minutes
Al	^{27}Al	^{28}Al	2.24 min	1779.0	t_d= 3-15: mintues
Cl	^{37}Cl	^{38}Cl	37.2 min	2167.7	t_c =10 mintues
Ca	^{48}Ca	^{49}Ca	8.72 min	3084.5	Sample holder geometry H_2
Ti	^{50}Ti	^{51}Ti	5.76min	320.1	
V	^{51}V	^{52}V	3.75 min	1434.1	
	Second short	Irradiation Scheme (2S)			
Dy	^{48}Dy	^{49}Dy	2.33hrs	94.7	t_{irr}=1 or 5minutes
Na	^{23}Na	^{24}Na	15.0 hrs	2754.0	t_d=3-4hours
K	^{41}K	^{42}K	12.4 hrs	1524.5	t_c=10minutes
Mn	^{55}Mn	^{56}Mn	2.58 hrs	1810.7	Sample holder geometry H_2
	First long	Irradiation Scheme (1L)			
As	^{75}As	^{76}As	26.4hr	559.1	
La	^{139}La	^{140}La	40.3 hrs	1596	
Ho	^{165}Ho	^{166}Ho	56.8 hrs	80.6	t_{irr}=6hours
Sm	^{79}Sm	^{80}Sm	46.3 hrs	103.2	t_d=3-4days
Br	^{81}Br	^{82}Br	35.3 hrs	776.5	t_c=30minutes
U	^{238}U	^{239}Np	56.6hrs	277.6	Sample holder geometry H_1
	Second long	Irradiation Scheme (2L)			
Co	^{59}Co	^{60}Co	5.263yrs	1332.5	
Cr	^{50}Cr	^{51}Cr	46.3 hrs	320.1	
Sc	^{45}Sc	^{46}Sc	83.8 days	889.3	
Fe	^{58}Fe	^{59}Fe	44.5 days	1291.6	
Sb	^{121}Sb	^{122}Sb	64.8 h	564.2	
Zn	^{64}Zn	^{65}Zn	244 days	1115.6	t_{irr}=6 hours
Eu	^{151}Eu	^{152}Eu	13.3 yrs	1408	t_d=9-11 days
Rb	^{85}Rb	^{86}Rb	18.7 days	1076.6	t_c=1 Hour
Ba	^{130}Ba	^{131}Ba	11.8 days	496.3	Sample holder geometry H_1
Nd	^{146}Nd	^{147}Nd	11 days	91.1	
Hf	^{180}Hf	^{181}Hf	42.4days	482.2	
Lu	^{175}Lu	^{176}Lu	6.71 days	208.4	
Ta	^{181}Ta	^{182}Ta	115 days	121.4	
Tb	^{159}Tb	^{160}Tb	72.3 days	879.34	
Tm	^{169}Tm	^{170}Tm	129days	84.3	
Yb	^{174}Tb	^{175}Tb	4.19 days	396.3	
Th	^{232}Th	^{233}Pa	27 days	312	

3 to 4 hours and the radiation of counting during the second round is denoted as S2. In short irradiation scheme radionuclides with half-lives in the order of minutes were detected and analyzed as shown in table 3.6.

In the case of long irradiation, about 6-7 samples including the standards were irradiated for period of 6 hrs in the inner channel (B_2) of the same facility. The first round of counting was carried out after a waiting period of 3 to 4 days for 30 minutes to capture radionuclides with half-lives in the order of hours or few days. This long term radiation is termed as L_1 and is carried out using the ($H_1 = 15cm$) holder above the detector. The second round of the counting for the same sample was done for 60 minutes after a cooling period of 9 to 11 days and is denoted as L_2. Radionuclides having half-lives in the order of days and years were determined.

For purpose of quality assurance and data validation of INAA, the same irradiation and counting procedure was also done for the standard reference materials: Soil-7 (IAEA), Coal fly ash (NIST 1633b) and apple leaves(NIST 1515).

3.5.6 Identifying Radioactive Elements by INAA

In neutron activation analysis, the types of elements in the sample under investigation could be identified by calculating the half life time of each element after determining the decay constant from the decaying activity curve of the element. A semi-logarithmic plot of the activity of the isotope versus decay time is plotted. Thus, the slope of the graph represents the decay constant (λ) from which the half-life time of the radioactive element can be determined using the following equation

$$\tau_{1/2} = \frac{ln2}{\lambda} \tag{3.5.1}$$

Where, $\tau_{1/2}$ is the half-life time and λ is decay constant.

Even though the decay curves of all elements were found difficult to include in this Thesis, a few of the decay curves of certain elements have been displayed in chapter 4 under

discussion parts.

Another option for identifying the types of elements in the sample can be done by analyzing the standards references materials (SRMs) obtained from IAEA and NIST (National Institute of standards and Technology), USA, along with the samples. If the elements in the analyzed standard materials are the same with the certified elements by IAEA and NIST, and with the analyzed elements in the samples under investigation, those elements should be included in the data.

3.6 Method of Data Analysis for NAA

As discussed in chapter 2 section 2.3.5, in instrumental neutron activation analysis (INAA), there are three basic methods of multi-elemental analysis known as: Absolute method, Relative method and K_0 method. However, in the present study the absolute and relative methods of neutron NAA were chosen.

3.6.1 Absolute method of analysis

Absolute method is a direct analysis of the irradiated samples without using standard reference materials if the nuclear parameters and measuring counting parameters are known. However, in most cases absolute method is subjected to error unless experimentally confirmed parameters are taken. In this study absolute method has been applied in the analysis of standard reference materials.

3.6.2 Relative method of analysis

Relative method of analysis is very easy to get accurate results. In this study, for instance, the relative method was chosen for the reason that uncertainties that could appear due to nuclear parameters such as cross sections, neutron flux, decay scheme and detector

efficiency would be minimized. Since the samples and standards were irradiated simultaneously and counted under the same conditions and geometries, the nuclear parameters get canceled (Yamusa et al., 2013) and thus only the parameters measured were the activity rates, irradiating time, cooling time and counting time of the irradiated samples as shown in equation 3.6.1. The concentrations of neutron induced radioisotopes in the samples of soils, medicinal plants or finger millets were determined using the equation on page under 36 section 2.3.5.2 and computed by WINSPAN 2004 software package.

3.6.3 Activity measurement and Method of analysis for natural radionuclides (^{238}U, ^{232}Th and ^{40}K)

The activity concentration levels of ^{238}U, ^{232}Th and ^{40}K in the rock samples in this study were measured using the gamma-ray spectrometric counting system that consisted of NaI (Tl) scintillation detector with dimensions of 7.62 cm by 7.62 cm, preamplifier, amplifier and a Canberra multichannel analyzer (MCA) connected via the associated electronics. The scintillation detector was housed in a 6 cm thick lead shielding and lined with cadmium and copper sheets (CERT, 1999; Umar & Jonah, 2012) to reduce background radiation entering it from the laboratory of measurement.

For accurate measurement, the gamma-ray spectrometric system was calibrated and tested its linearity using Geological Certified Reference Material (GCRM) samples known as potassium (RGK-1), Thorium (RGTh-1) and Uranium (RGU-1) obtained from International Atomic energy Agency (IAEA), Vienna (IAEA, 1987). Equal quantities of these standard sources of known energy were packed for about a month to attain a secular equilibrium. As per the protocol established in CERT (1999), Zaria, Nigeria,(CERT), the configuration and geometry of the system was maintained throughout the analysis.

Four weeks later each sample of rock including the GCRM sample was placed on the detector surface and counted for 29000 seconds. The net numbers of counts for each photo peak were obtained by subtracting the background counts from the total counts in the

same photo peak using an advanced ORTEC made MAESTRO multi-channel analyzer (MCA) emulation software. The MAESTRO program is a software package that was developed for data acquisition, storage display and data analysis of the acquired gamma spectra (Auwa et al., 2010). After the net area under each photo-peak counts of the spectrum was determined, the activity concentration for each of the radionuclide of interest in the rock sample could be calculated by the following expression(UNSCEAR, 2000).

$$A = \frac{C_p}{\varepsilon(E_\gamma I_\gamma(E_\gamma)M} \tag{3.6.1}$$

Where A is activity of the radionuclide of interest; C is the net peak count rate($C_p = \frac{PA_{Tcount} - PB_{Bcount}}{t_c}$ in count per second, PA_{Tcount} is the total peak area count, PA_{Bcount} is the background peak area count, t_c is the counting time in second, $\varepsilon(E_\gamma)$ is the efficiency of the detector at energy E,$\varepsilon(E_\gamma)$ is the extrapolated photo-peak efficiency at energy E_γ and M is the mass of the rock sample which is equivalent to the IAEA gamma Spectrometric reference material, 300g.

Thus, according the CERT (1999) protocol, the activity concentrations (A in $BqKg^{-1}$) of the natural radionuclides (^{40}K , ^{226}Ra and ^{232}Th) in the rock samples were determined by dividing the net count rate C_p (in count per second) of the photo-peak to the calibration factors K as shown in equation 3.6.3.

$$A(BqKg^{-1}) = \frac{C_p}{K} \tag{3.6.2}$$

Where, K is a constant calibration factor for each radionuclide determined by the detectors efficiency at constant geometry.

Thus, the K calibration factors for ^{40}K , ^{226}Ra and ^{232}Th determined in CERT were 0.000643, 0.000863 and 0.000877 respectively (Umar & Jonah, 2012). Similarly, activity concentration the radionuclides in unit of $BqKg^{-1}$ were converted to their corresponding mass concentration in unit of ppm. That was done by dividing the activity concentrations ($BqKg^{-1}$) of the three radionuclides (^{40}K , ^{226}Ra and ^{232}Th) to their conversion factors 313 for ^{40}K, 12.35 for ^{226}Ra and 4.06 $BqKg^{-1}$ for ^{232}Th (IAEA, 1989).

Chapter 4

Results and Discussion

4.1 Elemental Analysis of Chilga Soil using Instrumental Neutron Activation Analysis (INAA)

"The nation that destroys its soil, destroys itself" Frankline D Roosevelt

4.1.1 Introduction

Soil is an essential component of the terrestrial ecosystem upon which man and all living things directly or indirectly depend on as basic source of food (Enei et al., 2011). Soil by its nature is a heterogeneous mixture of different organic and inorganic substances, micro-organisms, minerals, rock particles, water and gases (Artiola et al., 2004; Shahabuddin et al., 2010) and varies from place to place. In particular, macro-nutrients such as K, Mg, P, S and N , and micro-nutrients like B, In, Mo, Co, Fe, Se, Cu, Mn and Zn are the most essential components of soil for the healthy growth of plants and high productivity of various crops in agriculture fields (Brian, 2008; Kogo et al., 2009; Kanias & Philianos, 2009).

Nowadays, however; soil pollution has become a common problem worldwide. Soil is polluted if the concentrations of heavy and trace elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, V, and Zn) resulting from natural and anthropogenic activities such as forest

fires, volcanic activity, flood-water transport, biogenic emissions and weathering process of parent rocks, the use of fertilizers, unwise human interventions for agricultural purposes, polluted water sewerages are in excess(Ernest, 2010; Oladipo et al., 2012; Morto-Berma & Segovia, 2002; Ernest, 2010). These excessive levels of elements which could be caused by natural and anthropogenic activities in soil can be introduced into the food chain via plants, cereal crops and ultimately into humans and animals that feed upon the plants and cereal crops. To put it simply, nutrients which are important for plants and crops can be toxic if their concentration amounts in soil are more than necessary.

Soil can have scarcities of essential mineral elements. Such mineral scarcities could arise from the unwise agricultural practices, water erosion, natural wind erosion, etc. On the other hand, the common problem of many soils in different parts of the world is soil acidity caused by rainfall and leaching, acidic parent material, organic matter decay or harvest of high yielding crops. Soil pH is among the obvious influencing factors of plant microbial activities and ultimately influence plant growth.

The soil of Chilga Woreda in North Gondar Zone considered in this study has shown less productivity over the years due to the assumed soil acidity, caused by the presence of excess cations of H^+ and leaching of nitrogen contents. Even though agricultural experts of North Gondar zone have advised farmers to use Urea and Daf fertilizers after testing the soil pH meter, the eexpected amount of production couldn't be still harvested from that soil. Thus, the present study was needed with the objective to find out the root cause of the soil pollution in the soil of Chilga Woreda by employing the technique of INAA.

4.1.2 Results

In soil physics analysis, prior to analytical analysis using INAA method or any other analytical method, the measurement of the pH meter is essential. The pH meter is a good indicator of the relative acidity or alkalinity of soil. It measures the amount of hydrogen ions in soil. A pH value measured below 7 indicates that the soil is acidic but when it

measures above 7 it specifies that the soil is alkaline.

In general, measurement of pH value below 5 indicates that a severe acidity exists in that soil. In the present study, however, the results of pH meter measurement as depicted in table 4.1 showed that the soils of Chilga woreda have been found acidic but not as such a severe acidic soil except the soil of Serako area.

Apart from the assessment soil pH meter, the main objective of this study was to

Figure 4.1: Six soil samples collected from six sampling sites of Chilga Woreda

Table 4.1: Results of the pH meter and Temperature of the soil samples (Abebe et al., 2007)

Sample code	PH Meter	Temperature
SSO1	4.39	22.2
SSO2	5.45	22.0
SSO3	6.87	22.0
SSO4	6.28	22.2
SSO5	6.26	21.9
SSO6	5.94	21.7

apply neutron activation analysis in the analysis of essential and toxic elements in soil samples of Chilga Woreda collected from six different sampling sites as shown in figure 4.1.

The concentration of each unknown element in the sample of soil was determined based on the following equation

Table 4.2: Elemental Concentrations of coal ash fly (NIST 1633b in ppm) used for quality control purpose, mean±SD

Element	This work	Certified value
Mg×(10^4)	0.4820 ±0.0760	0.482 ±0.008
Al×(10^4)	15.05±0.12	15.05 ±0.27
K×(10^4)	1.95±0.02	1.95±0.03
Ca×(10^4)	1.51±0.18	1.51 ±0.06
Fe×(10^4)	7.78±0.05	7.78±0.23
Na×(10^4)	0.201±0.001	0.201±0.27
Ti×(10^4)	0.791±0.054	0.791±0.140
As	136.2±0.04	136.2±2.6
V	295.7±92	295.7±3.6
Cr	198.2±4.4	198.2±4.7
Br	2.8±0.2	(2.9)
Ba	709 ±27	709±55
La	94.0±.3	(94)
Lu	1.20±0.03	(1.2)
Ho	3.50±0.24	(3.50)
Sr	1041±80	1041±14
Sm	20.00±0.04	(20)
Nd	85±3	(85)
Zn	210±11	(210)
Sb	6.00±	(6.0)
Th	25.7±0.03	25.7±1.3
Tm	2.1±0.3	(2.1)

Table 4.3: Elemental Concentrations of Soil-7 (IAEA Soil-7 in ppm) used for quality control purpose,mean±SD

Element	This work	Certified value	Confidence interval 95%
As	12.7±0.1	13.4	12.5-14.2
Co	8.5±0.3	8.9	8.9-10.1
Dy	3.7±0.4	3.9	2.5-5.3
Eu	1.3±01	1.0	0.9-1.3
Hf	4.6±0.2	5.1	4.8-5.5
Mn	634±3	631	609-650
Rb	56±4	51	47-56
Sc	8.4±0.1	8.3	6.9-9.0
Ta	0.7±0.2	0.8	0.6-9.0
Tb	0.7±0.1	0.6	0.5-0.9
U	1.18±0.22	2.6	2.2-3.3
Th	8.35±0.18	8.2	6.5-8.7
Yb	1.8±0.1	2.4	1.9-2.6

$$\rho_i = \rho_{std}\frac{A_i}{A_{std}}\frac{M_{std}}{M_{sam}}\frac{(e^{-\lambda t_d})_{std}}{(e^{-\lambda t_d})_i} \tag{4.1.1}$$

Where, ρ_i is the concentration of the i^{th} element in the sample, ρ_{std} is the concentration of the i^{th} element in the standard, M_{sam} is mass the sample, M_{std} is the mass of the standard reference material, A_i is the count rate of i^{th} element in the sample, A_{std} is count rate of the i^{th} element in the standard reference material, t_d is decay time, $T_{1/2}$ is the nuclide half life time and $\lambda = \frac{ln2}{T_{1/2}}$

Table 4.4: Elemental concentrations(in ppm) obtained in soils

Element	Soils (in ppm)						
	Serako	Nara Michael	Nara Awrdarda	Dilanba	Alemtsehay	Yihuserako	World top soil median
Mg	5592±951	3792±621	BDL	11100±921	7332±975	4529±811	5000
Al	93040±744	97170±875	116100±1696	88970±534	70070±631	83990±756	71000
Ca	13980±1761	9707±1514	5990±1120	24990±2099	68430±3832	14670±1848	15000
Ti	15470±727	20550±863	5160±857	13590±584	18760±7669	22290±758	5000
K	8444±1777	5007±130	4685±159	4923±172	10200±592	11990±504	40000
Fe	96720±484	117600±470	33690±337	90230±451	100600±12	90160±541	41000
Na	2340±5	1164±4	1890±6	3422±7	14430±14	5873±504	5000
V	329±9	425±8	223±6	2886±6	335±7	269±8	90
Mn	1544±5	2071±4	457±2	1745±4	1528±5	1549±5	1000
Dy	8.9±0.7	11±1	34±1	6.7±0.8	8±2	269±8	NA
As	3.2±0.2	5.2±0.1	3.4±0.2	1.1±0.1	0.7±0.2	3.2±0.2	6.0
Br	10.2±0.3	29.7±0.4	1.9±0.2	13.9±0.4	BDL±7	10.0±0.5	NA
La	27.2±0.2	38.6±0.2	117.9±0.2	14.8±0.1	26.7±0.2	47.03±0.23	NA
Sm	7.48±0.02	10.35±0.03	27.9±0.1	5.57±0.02	9.00±0.03	11.51±0.03	5.98
Ho	1.2±0.2	1.9±0.2	10.9±0.2	1.3±0.2	1.1±0.3	BDL	0.80
U	0.8±0.2	2.35±0.2	5.8±0.3	BDL	BDL	1.71±0.0	2.00
Sc	33.0±0.1	36.1±0.1	21.6±0.1	31.4±0.1	22.9±0.1	19.0±0.1	2.00
Cr	202±4	13±4	72±3	248±14	BDL	68±3	70
Co	57±1	57.3±0.6	18±0.2	64.7±0.6	46±1	33.3±0.5	8.0
Zn	115±9	124±9	44±1	167±9	144±9	141±9	90.0
Sr	BDL	BDL	BDL	BDL	394±83	BDL	NA
Rb	29±5	46±5	35±4	BDL	29±5	41±6	120
Sb	BDL	0.4±0.1	0.5±0.1	BDL	BDL	BDL	7
Ba	464±52	341±55	421±45	199±27	306±42	638±51	500
Nd	17±2	24±2	80±3	3.9±0.9	23±2	36.4±2.5	43.6
Eu	2.1±0.1	3.0±0.2	4.6±0.2	2.1±0.2	2.8±0.2	3.3±0.2	1.28
Tb	0.8±0.2	BDL	4.0±0.2	1.0±0.1	1.5±0.2	2.0±0.2	0.85
Tm	BDL	BDL	2.2±0.2	BDL	0.8±0.2	2.0±0.2	0.62
Yb	3.4±0.2	3.7±0.2	11.4±0.2	0.45±0.03	2.8±0.2	3.2±0.2	3.94
Lu	0.69±0.03	0.61±0.03	1.75±0.04	0.13±0.01	0.43±0.02	0.61±0.03	0.46
Hf	5.3±0.3	7.0±0.3	19.3±0.4	3.0±0.1	5.7±0.3	9.0±0.3	7
Ta	1.3±0.2	1.7±0.2	6.7±0.3	0.5±0.1	11.1±0.1	3.2±0.2	2
Th	4.7±0.2	6.3±0.2	15.5±0.2	1.1±0.1	2.1±0.2	6.2±0.2	6

[1]ppm= parts per million, BDL = Below Detection Limit

Table 4.5: Comparison of elemental concentration (in ppm) in terms of range, median and mean values between Chilga and worldwide soils (Bowen, 1975)

	Chilga soil			World top soil		
Element	Range	Median	Mean	Range	Median	Mean
Mg	3792-11100	5590	5350	400-90000	5000	23000
Al	70070-116100	91000	92000	10000-300000	71000	82000
K	33690-117600	93475	88167	2000-550000	40000	41000
Ca	5990-68430	14100	22961	700-500000	15000	15000
Fe	33690-117600	93475	88167	2000-550000	40000	41000
Na	1164-14430	2881	4853	1500-25000	5000	23000
Ti	5160-22290	17100	15970	1500-25000	5000	5600
V	223-2886	332	745	3-800	90	160
Mn	457-2071	1547	1737	20-10000	1000	950
As	0.7-5.2	3.2	2.8	0.1-40	6.0	1.5
Cr	13-248	72	121	705-1500	70	100
Br	1.9-29.7	10.20	13.14	2-270	0.37	NA
Ba	199-638	381.5	394.84	100-3000	500	500
La	14.8-117	32.9	45.3	1.9-29.7	NA	40.0
Ho	1.1-10.9	1.25	3.28	0.39-1.81	0.80	NA
Sc	0.8-5.8	2.03	2.64	0.4-6	2.00	NA
Sm	7.48-27.9	9.56	11.96	0.6-23	5.98	NA
Co	33.3-64.5	51.5	46.1	0.05-65	8.0	20.0
U	0.8-5.8	2.03	2.64	0.4-6	2.00	NA
Zn	44-167	135.2	122.5	1-900	90.0	75.0
Rb	29-46	35	36	1.5-1800	120	NA
Sb	0.4-0.5	0.225	0.225	1.00	7	NA
Nd	3.9-80	23.5	30.7	14.1-300	43.6	NA
Eu	2.1-4.6	2.9	2.9	0.1-2.6	1.28	NA
Tb	0.8-4.0	1.5	1.8	0.11-1.71	0.85	NA
Tm	0.8-2.2	2.0	1.7	0.34-1.2	0.62	NA
Yb	0.45-11.4	3.33	4.16	0.04-1.2	3.94	NA
Lu	0.13-1.75	0.61	0.70	0.1-0.95	0.46	NA
Hf	3-0-19.3	6.35	8.2	0.5-36	7	NA
Ta	0.5-11.1	2.45	4.08	NA	2	NA
Th	1.1-15.5	5.45	5.98	2-12	6	NA

In order to evaluate the exactness of the INAA method, two standard certified reference materials (SRMs) of geological origins known as IAEA-soil-7 and NIST 1633b Coal fly ash were irradiated and analyzed along with the soil samples.

The measured concentrations of different elements in IAEA-Soil-7 and in coal fly ashes (NIST 1633b) in this work were in good agreement with the measured concentrations of IAEA and NIST certified reference materials as shown in tables 4.2 and 4.3. In addition, the precision and trueness of the counting system was also calculated as percentage relative standard deviation (% RSD). It was seen that most of the percentage values were observed to be less than 16.5 % indicating high order of accuracy and precision of our data with the exception of U and Yb which deviated a bit high from the certified values.

4.1.3 Discussion

In the present study, the concentrations of 33 elements were quantified in six of the soil samples collected from Chilga Woreda using neutron activation analysis as tabulated in table 4.4. The concentration amounts of 33 elements obtained were compared with the concentration of worldwide top soil of the same elements as displayed in table 4.5. In short irradiation scheme, radionuclides with short half-lives such as Mg, Al, Ca, Ti, Na, K, Mn and V were captured and identified whereas in long irradiation scheme radionuclides with intermediate and long half-lives such as Dy, As, Br, La, Fe, Sm, Sc, Ho, U, Cr, Lu, Co, Zn, Sr, Rb, Sb, Ba, Nd, Eu, Hf, Ta, Tb, Tm, Yb, and Th were identified as tabulated in table 4.4. Among the measured elements Mg, Al, Ca, Ti, Na, K, Fe, Na and Mn were found in large proportions or amounts along all soil samples as depicted in figure 4.8; elements such as V, Sr, Ba and Zn were obtained in intermediate proportions as shown in figure 4.9 with Dy, As, Br, La, Sm, Ho, U, Sc, Cr, Co, Zn, Rb, Sb, Nd, Eu, Tb, Tm,Yb, Lu, Hf, Ta, and Tb measured at trace and ultra trace levels.

The concentration of magnesium in six soils ranged from 3792±621 ppm to 11100±921 ppm with highest in soil of Dilanba area. Although the range of Mg in soil of Chilga

Woreda was obtained within the world soil range limit (Bowen, 1975) the median and mean values of Mg in Chilga soils were found above the worldwide soil median and mean values. Magnesium is required by plants as secondary nutrient in the concentration range between 0.1 to 0.4% (Tisdale et al., 2004). The recommended daily intake of Mg is 350 mg/day for men and 300 mg/day for women.

Similarly, Calcium like Mg is an essential secondary plant nutrient. The concentration of calcium was determined in the range between 5990 ±120 ppm to 68430 ±3832 ppm. In particular, the soils of Dilanba and Alemtsehay accumulated high content of Ca above the world top soil median. The cause for high enrichment of Ca in these soils might be due to dead animals bones decay, bush burning exercise by farmers and weathering of calcareous rocks (Oladipo et al., 2012). Plants take Ca mainly from soil via their root uptake for the proper functioning of their cells and membranes. Lack of adequate Ca content in both plants and animal bodies can cause physiological disorders.

Potassium like Mg and Ca was found in the present study in large concentration. The

Figure 4.2: Soil of Narawdarda area

lowest and highest concentrations of K were found 4685±159 ppm and 11990 ± 504 ppm in Nara Awdarda and Dilanba soils respectively. This concentration range was found within the scope of the world top soil. According to Tisdale et al. (2004), K concentration required by plant is in the range from 1000 to 40000 ppm. Potassium is the most essential element for proper function of plants and human bodies. It is required for osmotic and ionic regulation in cells, for carbohydrate, protein, fat metabolizes, enzyme activation and muscle function of human body (Birch & Padgham, 1994). But according to this study the soils of Chilga Woreda have potassium deficiency. Such problem should be remedied by adding inorganic fertilizer that consists of K in appropriate amount.

Aluminum (Al) is most abundant element in the Earths crust. However, as studies

Figure 4.3: Soil of Naramichael area

suggest Al has no biochemical roles in both plants and human bodies. An increased level of Al in soil can be a potential toxic for roots of the plant or cereal crop. Moreover, it is likely to reduce the existence of other important cation nutrients like K, Mg and Ca

through competitive interaction (Emmanuel & Peter, 1995). In the present study, Al concentration was obtained in the range from 70050±631 to 116100 ±696 ppm. High content of Al was observed above the world median value in all soil samples with the exception of the soil of Alemtsehay. Particularly, the soil of Nara Awrdarda as shown in figure 4.2 scored the highest concentration of Al which is likely to produce highly acidic soil and can hinder the growth of cereal crops that grow on it.

Iron is the most essential mineral elements for both plants and animals. The concentration level of iron was observed the highest in soil of Nara Michael as shown in figure 4.3 in 117600 ±470 ppm and lowest in soil of in Nara Awrdarda 54930± 75 ppm. Elevated concentration of Fe above the world soil median was found in all soils except in the soil of Nara Awrdarda. This implies that the soils of Chilga are rich in Fe content. However, studies suggest that excess intake of Fe can be toxic to plants and humans rather than its benefits. The decay activity of Fe measured in this study is polluted as shown in figure 4.7.

The other macro-nutrient that was obtained in the soil of Chilga is titanium (Ti).

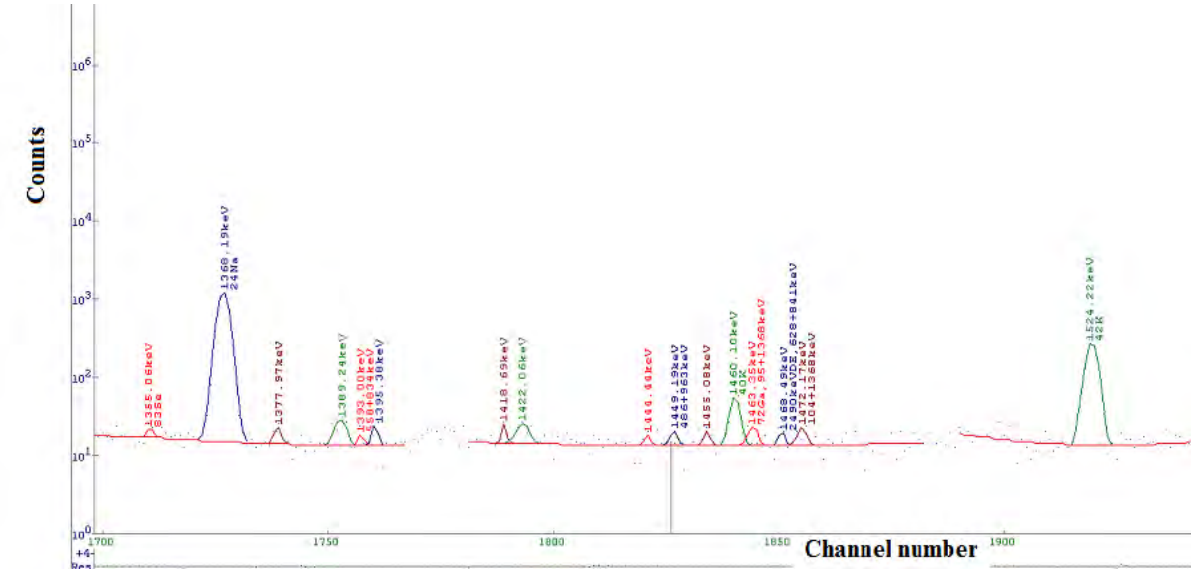

Figure 4.4: A typical Gamma ray spectrum for soil of Naramichael at $t_{irr} = 1$, $t_d = 3hrs$, $t_c = 30min$

Titanium mineral is resistance to weathering and is usually preserved in soils. According

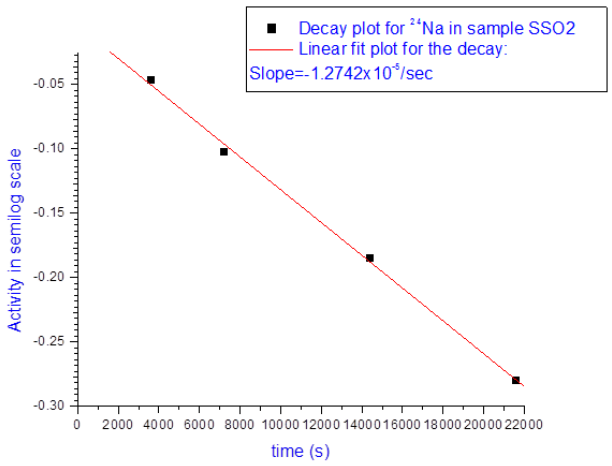

Figure 4.5: Decay curve of Na-24 in Soil of Naramichael

to the report of Elizabeta et al. (2012) some weeds like horsetail and nettle are known to accumulate more Ti, up to 80 mg/kg. Other studies also report that pure titanium has no biological role for both plant and animals but indirectly when it is in the form of titanium oxide it might have a part in the symbiotic fixation of nitrogen (N) in the nodules of legumes. The concentration of Ti obtained in this work ranged from 5160± 867 ppm to 22290 ± 758 ppm with highest concentration in soil of Yihuseraba.

Sodium is an essential element for the proper growth of plants and for the physiological metabolism of human body. It is useful for osmotic pressure and acid-base equilibrium with Cl in human body. The concentration of Na in the present work was found in the range from 1164±4 ppm to 14430±14 ppm with the highest concentration in soil of Yihuseraba. All soil samples accumulated Na below the world soil median except the soil of Yihuseraba. The decay curve for Na in sooil of Naramichael is plotted as shown in figure 4.5.

In all samples, except the soil of Nara Awrdarda, the concentration of manganese was recorded in the range from 457±2 ppm to 2071±4 ppm which is above the world soil median. This implies that the soils of Chliga were found rich in Mn contents. With regard to biological importance manganese is an essential micro-nutrient for plants and animals

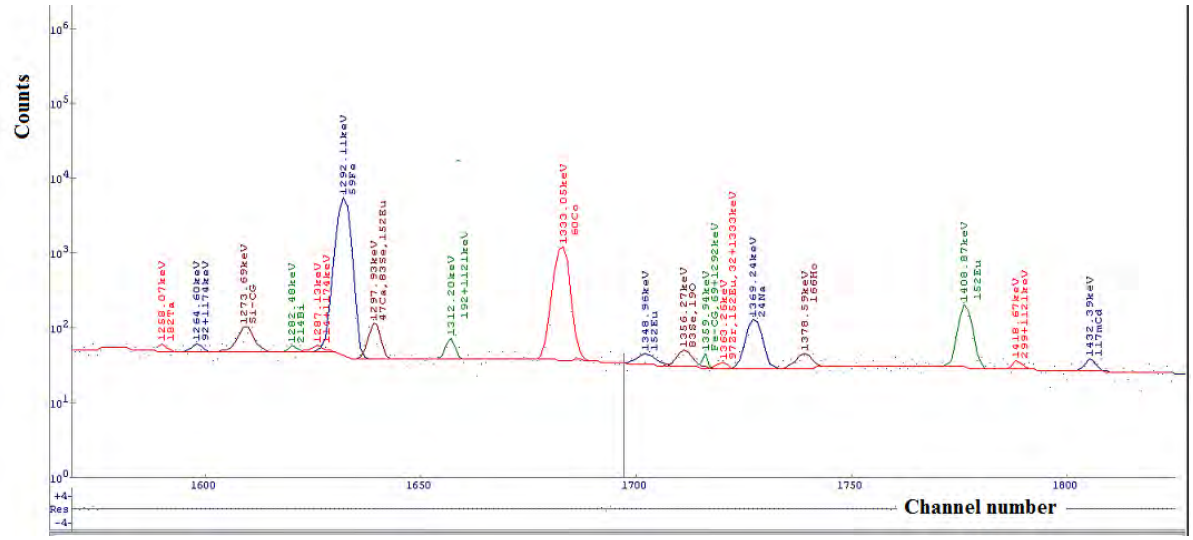

Figure 4.6: A typical Gamma ray spectrum for soil of Serako at $t_{irr} = 6hrs$, $t_d = 11days$, $t_c = 1hr$

health. Plants take Mn via root uptake in the range of 20 to 500 ppm. Manganese is required by plant as enzyme activator for nitrogen assimilation and for the manufacture of chlorophyll in green plants. A plant with low manganese turns into yellow.

Zinc, V, Ba and Sr were obtained in the category of minor concentrations as shown in figure 4.8. According to Brian (2008), zinc is an essential trace element found in varying concentrations in all soils, plants and animals. In this study, the concentration range of Zn along all samples of soils was obtained in the range from 44± 1 pm to 1679 pm with highest in soil of Dilanba. Except the soil of Nara Awrdarda, all soils accumulated Zn above the world soil mean and median implying that the soils of the research areas are rich in Zn even though there is a global nutritional deficiency in Zn.

The concentration level of strontium (Sr)in soil of Alemtsehaye area was quantified as 394±83ppm which is above the world median value but in all other soil samples it was detected below detection limit. Vanadium concentration in this study was obtained in the range of 223±6 ppm to 425±8 ppm above the world soil mean and median values with highest concentration in soil of Dilanba. Vanadium is required by micro-organism, cereal crops and small plants at very low concentration (Ross et al., 1973). Taking V as

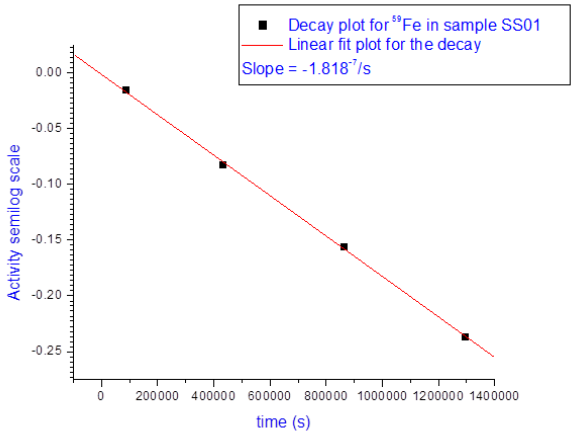

Figure 4.7: Decay curve of Fe-59 in Soil of Serako

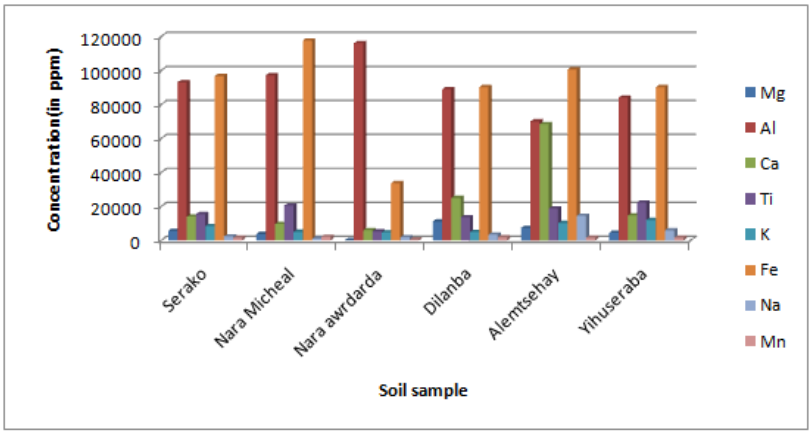

Figure 4.8: Macronutrients in six Soil samples

nutritional diet is important for bone formation, and cellular replication.

On the other aspect U, Co, As, Th and Cr were measured in traces. These elements can be toxic if their amounts in both plants and animals are in excess. For instance U, Co and Th are radioactive elements which cause radiological hazards in human body when taken via ingestion due to the fact that they are the emitters of alpha and beta particles, and gamma rays. Uranium concentration in soil of Nara Micheal was obtained 5.8 $\pm$ 0.3 ppm above the world median. Thorium like U is a natural radioactive element available at the surface of the Earth including soil. Thorium concentration in soils of Nara Micheal, Narawardarda and Yihuserba were obtained above the world soil median.

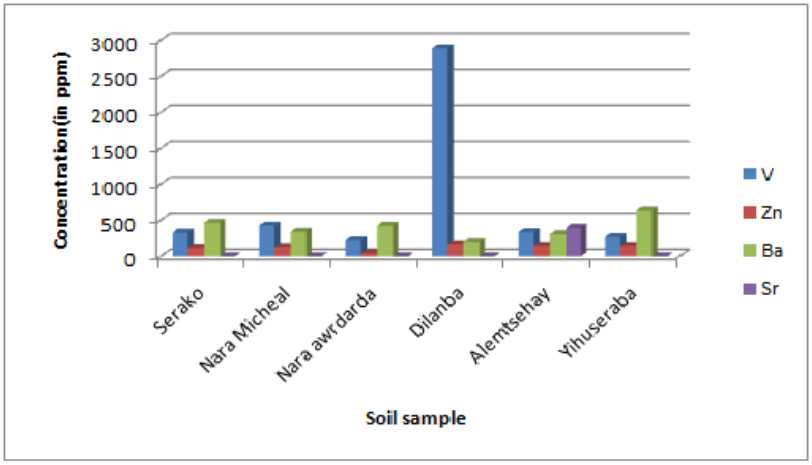

Figure 4.9: Micro-nutrients in six Soil samples

Similarly except Cr in soils of Nara Awrdarda and Alemtsehaye, Cr and Co concentrations were obtained in all samples above the world soil median but their concentration ranges were found within worldwide soil range. Chromium concentration in soil varies from place to place depending on the natural sources of the areas and the extent of contamination from anthropogenic sources. The highest Cr concentration was found 248±14ppm in soil of Dilanba and lowest 13± 4 ppm at Nara Micheal. Elevated concentration of Cr above the world soil median was observed in soils of Dilanba and Serako areas. With regard to its nutritional value, Cr is known to be an essential element for the normal carbohydrate, protein and fat metabolism in animals and humans bodies if appropriate amount is taken via the food chain. In addition, Cr has the function to reduce glucose tolerance and impaired insulin action, for weight reduction and prevention for the formation of Atherosclerotic plaques in blood vessels(Pechova & pavlata, 2013). Chromium can be toxic heavy metal in human body if it is taken more than necessary.

Rubidium (Rb) is another essential element for the production of hormones and various enzymes in human body (Nath, 2014). In this study, Rb concentration ranged from 29±5 ppm and 46±5ppm which is below the world soil median.

Europium, Dy, Br, La, Sc, Sb, Lu, Sm, Hf, Ho Nd, Ta, Tb, Tm and Yb are the other **nonessential elements** obtained in soils of Chilga Woreda in various proportions. As

studies suggest the biological and nutritional benefits of these elements have not been known so far.

To assess the similarity among the concentrations of six soil samples a cluster analysis

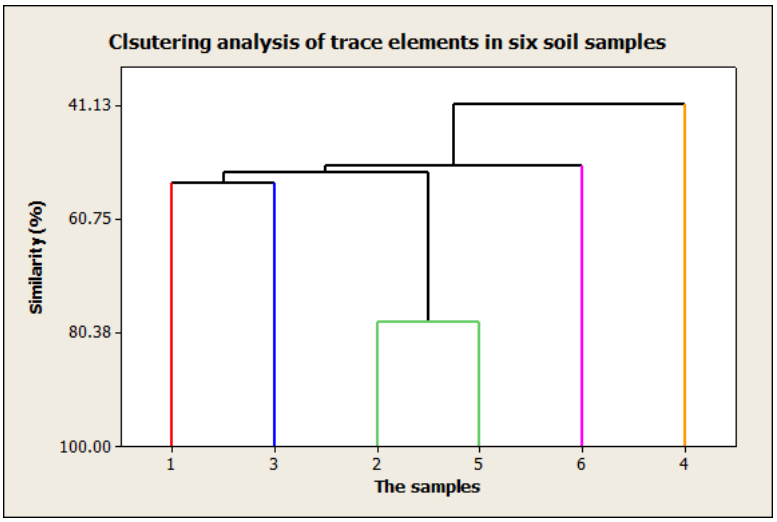

Figure 4.10: Cluster analysis of soils from Chilga Woreda

was also done using the cluster package contained in Minitab 16 window. The clustering was done in a two dimensional tree diagrams known as Dendrogram as shown in figure 4.10. Dendrogram is a multivariate diagram that helps to link together the similar concentrations of elements in the different samples. In figure 4.10, the highest clustering of soil samples was observed between soil of Serako and Yihuserba with the similarity level of 86.53 % followed by Serako and Dilanba with the similarity level 85.36%; Serako and Chelecbit in Narawdarda with the similarity level of 78.30%; Serako and Alemtsehaye with the similarity level of 51.69 % and the lowest clustering was seen between Serako and Narawdarda with the similarity level of 35.83%.

The results of cluster analysis showed that the soils of Serako and Yihuserba have almost similar elements with equivalent concentration contents and thus these soils have similar chemical properties. The same is true for Serako and Dilanba. On the other hand, the similarity between elements in soils of Serako and Narawdarda were found so weak implying the two soils contain different elements.

4.2 Determination of Natural Radioactivity Levels and radiation doses of radionuclides (^{238}U, ^{232}Th and ^{40}K) in rocks around Gondar city

4.2.1 Introduction

The sources of background radiation from radioactive materials present in the atmosphere, marine and terrestrial environments (Gafver & Faerevik, 2004) can be categorized into three categories depending on their origins: Primordial, Cosmogenic and Anthropogenic types(UNSCEAR, 1993). The background radiation in the natural environment is mainly contributed from primordial radioactive elements (^{238}U, ^{235}U and ^{232}Th) that have been produced since the creation of earth and due to cosmogenic radionuclides (such as ^{3}H, ^{7}Be, ^{14}C and ^{22}Na) created in the earth's atmosphere due to the interaction of high energy cosmic rays from the outer space with the atomic nuclei in the atmosphere (NCRP, 1975; Malain et al., 2012; Al-Beddri et al., 2014). In particular, long-lived naturally occurring radioactive materials (NORMs) such as ^{238}U, ^{235}U and ^{232}Th and their serial decays, and the single decay of ^{40}K represent for the major cause of radiation field in the natural environment (IAEA, 2003).

Radiation emissions due to anthropogenic (or manmade) radionuclides that base from nuclear power plants, medical centers, industrial nuclear plants, and nuclear research reactors are very small under normal circumstances. However, sometimes, unwise or inappropriate utilization of such radiation sources can be devastating and could be the cause of radiological hazards to all living things in the surroundings. One good example of such devastating radiation hazards had happened in march 2001, at Fukushima nuclear plant. Basically, the major ways by which humans are exposed to irradiation are radiation from sources outside the body (external exposure), radiation from radionuclides that are ingested through the consumption of food and water or due to the radiation from inhaled

radioactive gases (internal exposure)(UNSCEAR, 2000). In particular, natural radionuclides are widely distributed and present usually in various proportions in geological and biological formations such as soils, rocks, building materials, ground water, air, food items, plants and tissue of living things, and give rise to external and internal exposures.

Thus, for managing the effects of radiation exposure to human population due to both natural and man-made sources, the knowledge of radionuclides distribution and the radiation levels in the environment we live in is an indisputable fact (Avwiri et al., 2012). According to Fasae (2013) building materials such as concrete, plaster, cements, soils, rocks in the form of stones and industrial products can cause substantial radiation exposure if the materials contain elevated levels of natural radionuclides compared with that of undisturbed earth crust.

Thus, the present study was carried out with the objective to assess the activity concentrations and the radiation doses in rocks around Gondar city using the technique of NaI (Tl) detector gamma-ray spectrometer for the very reason that these rocks are widely used for house construction in the city. Radiological effects such as the radium equivalent activities, absorbed dose rate, external and internal radiation hazard indices were determined and compared whether the activity levels and radiological effects are within the scope of acceptable limits or not as stated in UNSCEAR (1988); ICRP (1990); UNSCEAR (2000). Moreover, the results obtained in this study can serve as a base line value for further assessment of the radiation pollution in different parts of the Amhara regional state.

4.2.2 Results

As discussed in the preceding section, the activity concentrations of the primordial long-lived radionuclides in the rocks around Gondar city were determined using NaI(Tl) gamma ray Spectrometry. Similarly, the activity concentrations of the IAEA gamma ray spectrometric reference materials known as RGK-1, RGU-1 and RGTH-1 were also analyzed

with same procedure as done for the rocks samples for the purpose of quality assurance.

From the results obtained it was observed that the measured activity concentrations

Table 4.6: Activity measurement in this work and IAEA certified value

GCRM Code	Mass concentration determined in This work	Activity concentration in This work	Mass concentration certified value by IAEA	Activity concentration certified value by IAEA	Relative STD (%)
RGU-1	4971.95±14.90	403.0±0.4	4940±30	400±2	0.6
RGTh-1	2937.286±28.19	723.5±7.0	3250±40	800±10	9.6
RGK-1	13450.55±30.48	(43±0.1)%	14000±400	(44.8±0.03)%	3.96

Table 4.7: Natural radionuclides, their gamma lines used and their transition probability gamma intensity (IAEA, 1990, 2007)

Parent nuclide	Daughter nuclide	Gamma-ray Energy in (kev)	Transition probability gamma intensity	extrapolated efficiency in this work
^{226}Ra(^{238}U)	^{214}Bi	1764.49	0.1652	0.0175
^{232}Th	^{208}Tl	2614.53	0.36	0.00812
^{40}K	-	1408.83	0.1067	0.020087

of the RGK -1, RGU-1 and RGTH-1 in this work were in good agreement with IAEA certified values as displayed in table 4.6 with the percentage relative standard deviation (RSD%) between the IAEA certified values and the measured values of this work less than 10 % for activity.

In general, the activity concentrations of the natural radionuclides in the sample of

Table 4.8: Net photo-peak Count rate(in cps)

Sample code	^{226}Ra	^{232}Th	^{40}K
SR1	0.01672494±0.0024164	0.0496382±0.0014887	0.10351657±0.00789604
SR2	0.0163107±0.0036159	0.049989±0.00106117	0.09817324±0.0090663
SR3	0.01558578±0.00482417	0.04785789±0.00124534	0.149137424±0.00789604
SR4	0.020221146±0.0020712	0.7379078±0.00110502	0.56134543±0.00841049
SR5	0.02334415±0.0039698	0.09324264±0.00144705	0.181326±0.00804393

Table 4.9: Specific Activity and Mass concentrations of ^{226}Ra (in ^{238}U series), ^{232}Th and ^{40}K in five rock samples

Sample ID	Specific Activity (in Bqkg^{-1})			Mass Concentration (in ppm)		
	^{226}Ra	^{232}Th	^{40}K	^{226}Ra	^{232}Th	^{40}K
SR1	19.38±2.80	56.66±1.31	160.99±12.28	1.57±0.23	13.95±0.08	5143.45±393.33
SR2	18.90±4.19	57.00±1.21	152.68±14.10	1.53±0.34	14.04±0.30	4877.95±450.48
SR3	18.06±5.59	54.57±1.42	231.94±12.28	1.53±0.45	13.44±0.35	7410.22±392.33
SR4	23.42±2.40	84.14±1.26	873.01±13.08	1.90±0.19	20.72±0.31	27891.69±417.89
SR5	27.05±4.60	106.32±1.65	226.95±10.83	2.19±0.37	26.19±0.41	7250.80±346.00
Mean in this work	21.36	59.60	282±12.51	1.74±0.33	17.67±0.29	100514±400
World median	35	30	400			
World range	17-60	11-64	400-850			

Table 4.10: Radium equivalent (Ra_{eq}), Absorbed dose rate (D in nGyh^{-1}), External and Internal hazard indices (H_{ex} & H_{in}), Activity concentration index and Annual Effective dose equivalent (in mSvy^{-1})

Sample code	Ra_{eq}	D	H_{ex}	H_{in}	$I_{\gamma x}$	Annual Effective dose equivalent
SR1	112.32	49.98±1.99	0.305±0.053	0.358±0.058	0.803	0.061
SR2	57.69	52.93±3.26	0.588±0.019	0.639±0.03	0.805	0.065
SR3	119.32	54.22±3.98	0.308±0.042	0.357±0.072	0.821	0.067
SR4	219.77	102.26±2.84	0.570±0.015	0.634±0.021	1.5791	0.126
SR5	114.47	91.053.57	0.532±0.20	0.604±0.033	1.801	0.112
Range in this work	57.69 -219.77	49.98±1.99-102.26±2.84	0.305-0.570	0.358-0.639	0.803-1.801	0.061-0.126
Mean in this work	124.45	70.09±3.13	0.522±0.13	0.518±0.04	1.161	0.086
Worldwide range	-	18-93	-	-	-	-
World recommend value	≤ 370	55	≤ 1	≤ 1	≤ 3	1

rocks were determined based on the following expression (UNSCEAR, 2000).

$$A = \frac{C_p}{\varepsilon(E_\gamma) I_\gamma(E_\gamma) M} \tag{4.2.1}$$

According to the protocol of the CERT for constant geometry conditions, the activity concentration of each radionuclide was determined easily by

$$A = \frac{C_p}{K} \tag{4.2.2}$$

Where, K is 0.000643, 0.000863 and 0.000877 for ^{40}K, ^{226}Ra and ^{232}Th respectively which represent the denominator as seen in equation 4.2.1.

On the other hand, the concentration mass of each radionuclide for ^{226}Ra, ^{232}Th and ^{40}K

in the rock sample were calculated by dividing the activity concentration in $BqKg^{-1}$ to the conversion factors 313, 12.35 and 4.06 $BqKg^{-1}$ respectively as given in IAEA Technical Report Series No. 295 (IAEA, 1989). It means that once the activity concentration of each radionuclide is calculated in unit of $BqKg^{-1}$ it is possible to convert into mass concentration in unit of ppm.

4.2.3 Discussion

The activity concentrations of ^{226}Ra(in ^{238}U series), ^{232}Th and ^{40}K in the rocks were determined and the results obtained are presented in table 4.9. Along all rock samples, the measured activity concentration of ^{226}Ra was found in the range between 18.06±5.59 $BqKg^{-1}$ and 27.05 ± 4.6 0 $BqKg^{-1}$ with a mean value of 21.36 $BqKg^{-1}$.

The range and mean activity concentrations of ^{226}Ra were obtained below the world activity concentration range and median (17-60 $BqKg^{-1}$ & 35 $BqKg^{-1}$) as reported by UNSCEAR (2000). With regard to mass concentration of ^{226}Ra in the rock samples, it was varied from 1.53 ± 0.34 to 2.19 ±0.37 ppm with highest mass concentration in Gondar Airport's rock.

With regard to the activity concentration of ^{232}Th along all samples of rocks, it varied from 54.57 ±1.42 $BqKg^{-1}$ to 106.32 ± 1.65 $BqKg^{-1}$ with a mean activity of 59.60 ± 2.34 $BqKg^{-1}$. Even though the activity of ^{232}Th in rocks of Arno Seneba, Dngay Gores and Srur Dmaza were obtained within worldwide range permissible limit but in rocks of Dabecha Rufauel and Gondar Airport, the activity concentrations of ^{232}Th were obtained which were above world range as tabulated in table 4.9. Similarly, the computed mass concentration ^{232}Th was obtained in the range from 13.44 ± 0.35 ppm to 26.19 ± 0.41ppm with the mean value 17.67 ± 0.29 ppm.

Basically natural potassium has three main isotopes known as ^{39}K, ^{40}K and ^{41}K. Among the three isotopes, ^{40}K is the only natural radioactive isotope with abundance of 0.012%. The activity concentration of ^{40}K in the study was found in the range from 152.68 ± 14.10

to 873.01 ± 13.08BqKg^{-1} with a mean value of 282±12.51 BqKg^{-1}. As can be seen in table 4.9 as well as in figure 4.11, the highest activity concentration of ^{40}K was recorded in the rock of Debecha Rufauel (873.01 ±13.08 BqKg^{-1}), which is beyond the worldwide range and mean values. This implies that the rock of Debecha Rufauel contains high contents of ^{40}K as compared to the rocks of other sampling sites.

Assessment of Radiological hazards

The radiological hazards due to exposure of radiation arising from naturally occurring radioactive ^{238}U, ^{232}Th and ^{40}K can be determined using the known radiological parameters and indices such as radium equivalent activity (R_{aeq}), absorption dose rate(D), external and internal radiation indices (H_{ex} and H_{in}.

Radium Equivalent Activity is a weighted sum of the activities of ^{226}Ra, ^{232}Th and ^{40}K based on the estimation that 370 BqKg^{-1} of ^{226}Ra, 260 BqKg^{-1}of ^{232}Th and 4810 BqKg^{-1} of ^{40}K produce the same gamma ray dose rate(UNSCEAR, 2000) and is determined using the following equation (Beretka & Mathew, 1985; Oyebanjo et al., 2012).

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \leq 370 \tag{4.2.3}$$

Where, A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively in BqKg^{-1}. The maximum value of Ra_{eq} in building materials should not be beyond 370 BqKg^{-1} for radiological safety (Abdulrahman et al., 2013).

The estimated radium equivalent Ra_{eq} activity of the rock samples in the present study varied from 57.69 to 219.77 BqKg^{-1} with the mean value of 124.45 which was obtained less than 370 BqKg^{-1} as recommended by UNSCEAR (2000).

The assessment of radiological hazard due to exposure of external terrestrial gamma-ray radiation from ^{226}Ra , ^{232}Thand ^{40}K in rocks, soils and building materials can also be measured using Absorbed Dose Rate in Air (ADRA) at about 1m above the ground. Based on the conversion factors 0.462, 0.604 and 0.0417 for ^{226}Ra , ^{232}Th and ^{40}K respectively

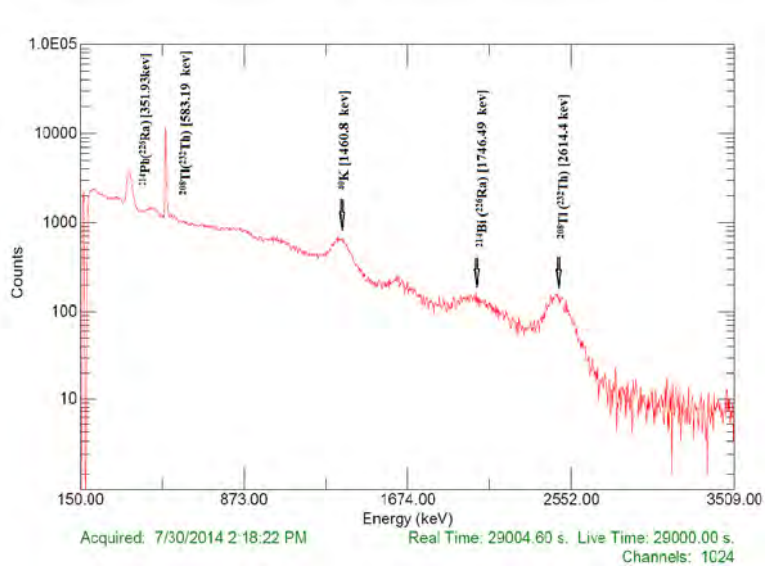

Figure 4.11: Typical gamma-ray spectrum obtained by the NaI(Tl) detector gamma spectrometry for rock sample Suru Damaza (SR3)

as set by UNSCEAR (2000), the activity concentration of each natural radionuclide was converted to absorbed dose rate in air using the following equation (Oyebanjo et al., 2012)

$$D(nGyh^{-1}) = 0.462A_{Ra} + 0.0604A_{Th} + 0.0417A_K \tag{4.2.4}$$

Where, D is the total absorbed dose rate in air in $nGyh^{-1}$, and A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in $BqKg^{-1}$ respectively.

In present study, the total gamma dose rate in the rock samples were obtained between 249.98 ± 1.99$nGyh^{-1}$ and 102.26 ±2.84 $nGyh^{-1}$with a mean value of 70.09 ± 3.13. A maximum dose rate 102.26 ± 2.84 $nGyh^{-1}$ above the world range 18-93 $nGyh^{-1}$ was observed in rock of Debecha Rufauel due to the fact that the mass as well as the activity concentrations of ^{40}K in this rock was found the highest as shown in figure 4.12.

Exposure of radiation arising from natural radionuclides of ^{226}Ra, ^{232}Th and ^{40}K is evaluated through external and internal hazard radiation indices (H_{ex} & H_{in}) and also by the activity concentration index ($I_{\gamma r}$). The three indices were estimated based on the following expressions (European Commission, 1999; Murugesan et al., 2011)

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{4.2.5}$$

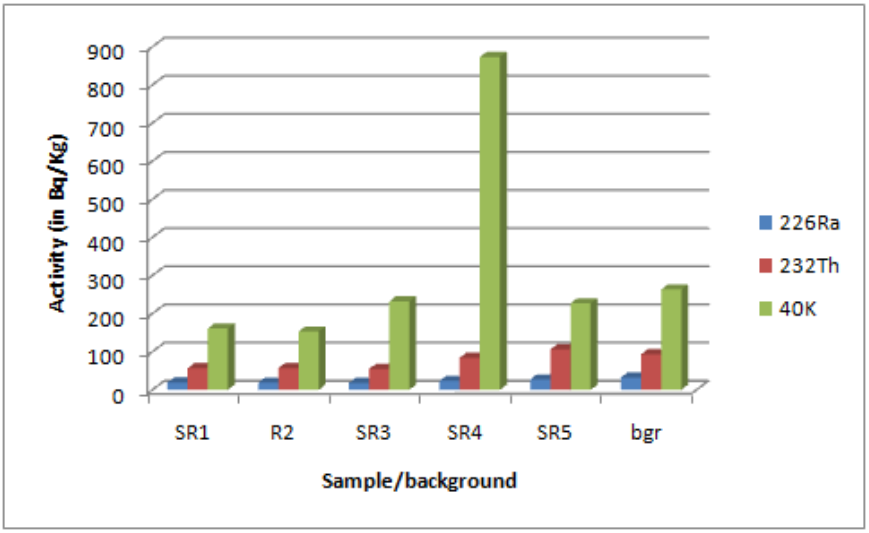

Figure 4.12: A graph of activity concentration distribution of ^{226}Ra(^{238}U), ^{232}Th and ^{40}K for six rock samples

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{4.2.6}$$

$$I_{\gamma r} = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \tag{4.2.7}$$

Where, A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in $BqKg^{-1}$ respectively.

External and internal hazard indices greater than unity can be significantly radiation hazard to human body. Accordingly, the external and internal hazard indices in all rocks under the present investigation were obtained < 1 which confirm that the environment safe is from radiological hazards. The estimated activity concentration index was also obtained between 0.803 and 1.801 which is below recommend values $I_{\gamma r}$ as indicated in table 4.10. The activity concentration index $I_{\gamma r}$ corresponds to $0.3mSvy^{-1}$ and $I_{\gamma r}$ corresponds to $1mSvy^{-1}$ indicating that the terrestrial gamma radiation emanating from the natural radionuclides in rocks used for building construction is as such insignificant to cause radiological related health risk.

Lastly, the total annual effective dose rate due to the natural activity of ^{226}Ra, ^{232}Th and ^{40}K in the rocks was calculated (UNSCEAR, 2000) as follows

$$E(mSvy^{-1}) = D(nGyh^{-1} \times 87640h \times 0.2 \times 0.7SvGy^{-1} \times 10^{-6} \tag{4.2.8}$$

Where, E is the total effective dose rate ($mSvy^{-1}$), D is the absorbed dose rate in $nGyh^{-1}$, 0.2 outdoor occupancy factors, 0.7 $SvGy^{-1}$ is a conversion factor recommended by UNSCEAR (2000)and 87640h is one year duration.

The annual effective equivalent dose rate was found in the range from 0.061 to 0.126 ($mSvy^{-1}$) along all rocks which is lower than the world average dose rate $1mSvy^{-1}$. According to ICRP, 1990, the maximum permissible annual effective equivalent dose for general public is 1 $mSvy^{-1}$.

4.3 Application of Instrumental Neutron Activation Analysis in the Analysis of Essential Elements in six Endemic Ethiopian Medicinal Plants

4.3.1 Introduction

Our earth is the source of tremendous and various types of plants. Many of these plants supply a large number of resources that provide the basic requirements of food, clothing and other necessities for the lives of both animals and humans. Among those important plants, traditional medicinal plants have been the source of medicinal treatment for many thousands of years to prevent and cure various human ailments before the birth of modern pharmacological based medicines and other health centers.

About 70-80 % of the world population use medicinal plants as a traditional system of medicine for primary health care, curing diseases and food supplements (Choudhury et al., 2007; Subramanian et al., 2012). Thus, taking into consideration the importance of medicinal plants, nowadays scientific research interests on medicinal plants have been growing up to study the essential and/or toxic elements in medicinal plants. Some researches, for instance; report that medicinal plants are enriched with trace elements, minerals, carbohydrates, proteins, fats and vitamins that are very important for the plants themselves and ultimately for animals and humans that take them as medicine for various ailments (Magili et al., 2014; Selvaraju et al., 2011). However, since most of the previous studies on medicinal plants focused on the organic constituents of the plants such as glycosides, alkaloids and essential oils (Mukherjee, 2003), their essential inorganic components could not be fully addressed. The medicinal part of a herbal plant could be its root, stem, bark, leaf, flower, fruit or seed.

Unless otherwise the medicinal plants are administered and taken wisely, consuming any assumed medicinal plant might have adverse effects on human and animal health so care should be taken (Obert, 2005). As worth mentioned by Dzomba et al. (2012) medicinal

plants can be contaminated by heavy metals during their growth via roots uptake and by the deposition of pollutants from the atmosphere on their leaves. Heavy metals like As, Cd and Pb can be toxic if their concentration amounts in plants are more than 1.0, 0.3 and 10 ppm respectively (WHO, 1998; Shad et al., 2008). Aside from heavy metal toxicities, the excess or deficiency of essential nutrients in medicinal plants can cause various complications and metabolic disorders in human body.

About 80 % of the Ethiopian population use traditional medicinal plants for immediate relief of illness, health care, spices of food and as a food supplement (Hawaze et al., 2012) but the elemental contents of these medicinal plants have not yet been studied satisfactorily. Belayneh et al. (2012), for instance, reported that some of the medicinal plants in Ethiopia have not been studied well but still await scientific studies. Similarly, Endashaw (2007), also reported that the modern research made on Ethiopian medicinal plants has been focused on inventories and checklists although some of them have been touched.

By taking the existence of such research gap into consideration the present study was needed to assess the chemical and essential medicinal elements of six Ethiopian endemic medicinal plants known as Artemisia Abyssinica, Lippia Adolensis, Celematics Longicanda, Echinops kebericho, Thymus schimperi and Millettia ferruginea using Instrumental Neutron Activation Analysis. Instrumental neutron activation analysis is considered as important technique in the analysis of geological and biological samples. The scientific names, the vernacular(or local) name and traditional uses of the six medicinal plants included in this study are listed in table 4.11.

Table 4.11: Medicinal plant samples used in this study

Sample Code	Scientific name	Local name	Part used	Traditional use
SMP1	Artemisia Abyssinica	Chikugn	Leave	Intestinal problems, infectious diseases, antileishmanial (acts against Leishmania parasites), colon cancer and cold
SMP2	Lippia Adolensis	Kesse	leave	Stomach ache, flavor of butter, and for washing wooden and ceramic utensils to give fresh and clean smell,treatment of skin infection diseases
SMP3	Celematics Longicanda	Nechyeazo hareg	Steam and bark	treatment of ear and antimicrobial activities on bacterial and fungal strains
SMP4	Echinops kebericho	Kebericho	Root	treatment of Diarrhea, head aches, typhus, malaria fever and cold; repellent of mosquitoes and snake; chewed for alleviating stomach ache, for expelling tapeworm and and for evil eye
SMP5	Thymus schimperi	Tosign	Leave	headache, cough, diabetics and control of gonorrhea. The dried leaves: flavor of tea, coffee, meat, vegetables. Some people also smoked it as cigarette
SMP6	Millettia ferruginea	birbra	Leave, Pod	For wound, for fish poison and inducing abortion

4.3.2 Results

The accuracy and precision of the relative method of INAA was evaluated by analyzing the standard reference material (SRM) known as apple Leaves (NIST 1515) obtained from the National Institute of Standards and Technology (NIST), USA. The sample of apple leaves was packed with the samples of medicinal plants and irradiated simultaneously inside the reactor channels. From the results obtained it was observed that the measured concentrations of elements in the irradiated apple leaves in this work were in a good agreement with the certified values as shown in table 4.12.

Table 4.12: Concentrations of elements in the irradiated standard reference material of apple leaves (NIST-1515 in ppm),mean±SD

Element	This work	Certified value
Mg(%)	0.2710 ±0.015	0.2710±0.008
K(%)	1.61±0.02	1.61±0.02
Ca(%)	1.5260±0.443	1.526 ±0.015
Al	286 ±5	286 ±9
Cl	579 ±20	579±23
V	0.26 ±0.08	0.26±0.03
Br	1.8±0.3	(1.8)
Mn	54±1	54±3
Na	24.4±0.5	24.4±1.2
Ba	49 ±11	49±2
La	20.00±0.08	(20)
Sm	3.00±0.01	(3.00)
Sc	0.030±0.007	(0.030)
Fe	83±26	83±5
Zn	12.5±2.7	12.5±0.3
Rb	10.2±0.3	10.2±1.5
Nd	17±1	17±1
Eu	0.20±0.05	(0.20)
Tb	0.40±0.05	(0.40)
Yb	0.30 ± 0.06	(0.30)

Table 4.13: Elemental concentrations obtained for six medicinal plants (in ppm)

Element	Artemisia abyssinica	Lippia Adolensis	Celematics Longicanda	Echinops Kebericho	Thymus Schimperi	Millettia ferruginea
Mg,$\times 10^4$	1.716 ±0.113	0.636±0.004	0.117 ±0.016	0.202±0.022	0.488± 0.035	0.469±0.025
K,$\times 10^4$	0.527±0.020	1.885±0.025	0.237±0.009	0.482±0.015	0.799±0.018	0.439±0.010
Ca,$\times 10^4$	1.418±0.081	1.599 ±0.054	0.268±0.019	0.346±0.026	1.617±0.063	1.691±0.054
Al	49500 ± 346	889.4±19.6	417±7	3069±36	6273±345	259±8
Cl	2053 ±62	8058±64	652±20	1362±30	2407 ±41	2584±39
V	256 ±4	3.79±0.41	2.24±0.14	14.33±0.53	15.04±0.99	0.91±0.17
Br	28.5±0.2	14.0±0.1	1.6 ±0.4	24.69 ±0.15	27.28±0.16	28.74±0.14
Mn	566±11	53.77±0.27	41.24±0.25	135.4±0.4	223.66±0.67	50.24±0.25
Na	1969±14	75±1	23.4±0.6	113±1	136 ±1	25.9±0.5
Ba	315 ±3	BDL	BDL	BDL	90±15	BDL
La	9.30±0.08	0.35±0.02	0.27±0.01	1.22±0.03	2.93±0.04	0.11±0.01
Sm	3.65±0.02	0.08±0.01	0.059 ±0.004	0.45±0.01	0.517 ±0.007	0.029±0.004
Sc	29.2±0.1	0.03±0.01	0.21±0.01	1.26±0.02	1.78±0.03	0.10±0.01
Fe	54930±275	522±34	382±35	2353±64	3580±75	323±28
Zn	BDL	38±3	11±2	BDL	37±3	38±3
Rb	22±4	14.5±2	BDL	7.69±1.41	BDL	BDL
Nd	9.23±2.10	BDL	BDL	BDL	BDL	BDL
Eu	0.86±0.05	BDL	BDL	0.52±0.02	14±3	BDL
Tb	1.20±0.17	BDL	BDL	BDL	BDL	BDL
Yb	3.15 ± 0.26	BDL	BDL	BDL	0.38±0.09	BDL

4.3.3 Discussion

According to this study, the concentration of 20 elements were determined quantitatively in six medicinal plants of different kinds. In our short irradiation and counting schemes (1S and 2S) nuclides with short half-lives such as Mg, Al, Ca, Cl, Na, K, Mn and V were determined whereas in long irradiation and counting schemes (1L, 2L) nuclides with long half-lives such as Br, La, Sm, Sc, Fe, Zn, Rb, Ba, Eu, Nd, Tb and Yb were obtained as tabulated in table 4.13. The elemental compositions of these medicinal plants varied which might be due to the preferential absorption of the plants for specific elements, mineral composition of the soils in which the plants were grown and due to climatic conditions (Debrah et al., 2011; Serfor et al., 2003; Lokhande et al., 2010). Even though, it is difficult to show all typical gamma ray spectra for six of the medicinal plants, as exemplariness, the gamma ray spectra of Echinops Kebericho and Artemisia abyssinica are displayed in

figure 4.13 and 4.15.

Among the 20 elements displayed in table 4.13 Mg, K, Ca, Cl, Al and Fe were obtained in large proportions as macronutrients as depicted in figure 4.16 along all medicinal plants whereas Ba, Mn and Na were obtained in intermediate proportions as micro-nutrients as shown in figure 4.17 with all other elements measured at trace levels. Macro-nutrients in human body are required to maintain the health of bones, teeth and blood, for supporting processes such as protein synthesis, cell growth, energy production, and for proper functioning of the heart and nervous systems.

Magnesium content was observed the highest 17160 ±1130 ppm in Artemisia abyssinica

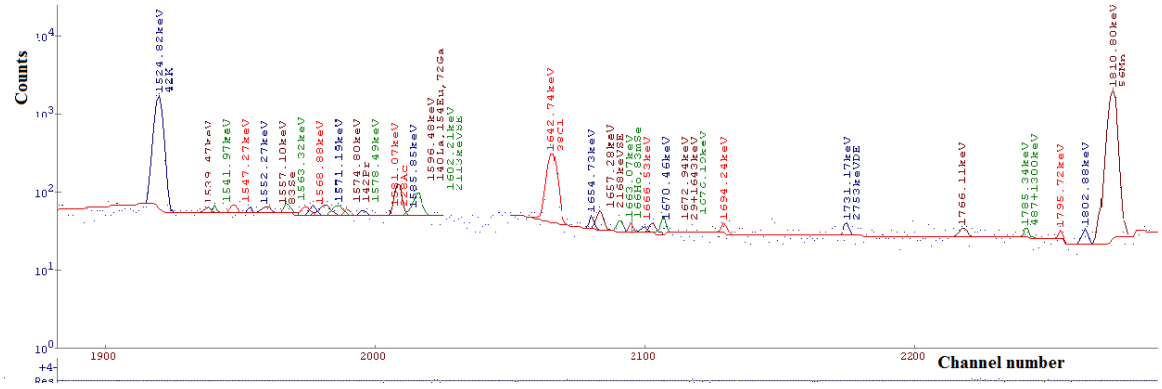

Figure 4.13: A typical gamma ray spectrum of Echinops Kebericho at t_{irr} = 5min, t_d = $4min$ and t_c = 10min

and lowest 1170±160 ppm in Celematics Longicanda. This concentration range was found in agreeable with the range of previous findings on other medicinal plants (Serfor et al., 2003; Ajasa et al., 2004; Abdul et al., 2012) except the concentration of Mg in Artemisia abyssinica in this study was observed the highest one. The minimum safe dietary concentration of Mg in plants for animal health is 2000 ppm (Little, 1982). With regard to pharmacological importance Mg is used for treatment of asthma, headache and stress. High concentration of Mg (in mg) plays important role in insulin action, protect against diabetes and serve as cofactor or components for enzyme systems (Magili et al., 2014). Low magnesium levels in human body are likely to cause hypertension, cardiovascular disease, and diabetes in human body. The necessary daily intake of Mg is 350 mg/day

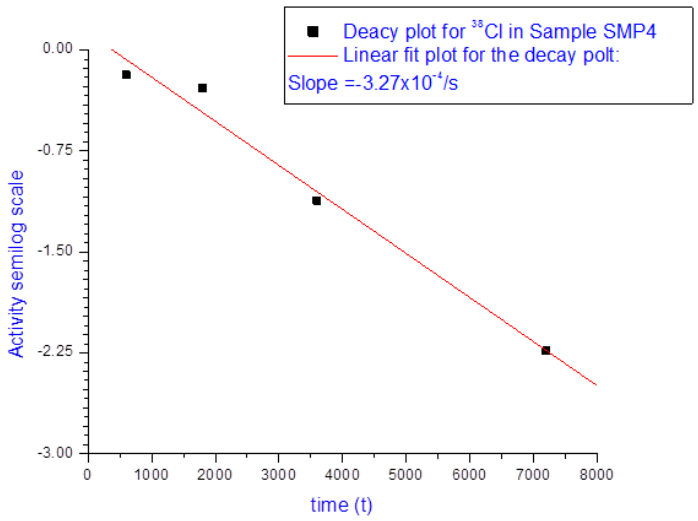

Figure 4.14: Decay curve of Cl-38

for men and 300 mg/day for women to maintain a healthy body.

High content of Ca is required for mineralization and enhancement of the qualities of bones and teeth (Charles, 1992). Calcium like Mg is important for blood clotting, relief of stress, proper functioning of the heart and nervous systems as well as for normal function of muscle system. Ca concentration in the present study was found in the range from 16910±540 ppm in Millettia ferruginea to 2680±190 ppm in Celematics Longicanda. This concentration range of Ca was found agreeable with the previous finding on medicinal plants (Serfor et al., 2003; Obiajunwa et al., 2002; Ndiokwere, 1989; Sharat et al., 2010).

K, Cl and Na are important electrolytes for the normal distribution of fluid balance in the intracellular and extracellular cells of human body. These elements are also very important for the proper balance of acid- base in human body. A high content of K was observed at macronutrient level in this study with concentration range varying between 2370±90 ppm in Celematics Longicanda and 18850±250 ppm in Lippia Adoensis. This concentration range was found to be agreeable with previous work on other medicinal plants (Serfor et al., 2003; Sharat et al., 2010). Potassium plays a vital role as electrolyte

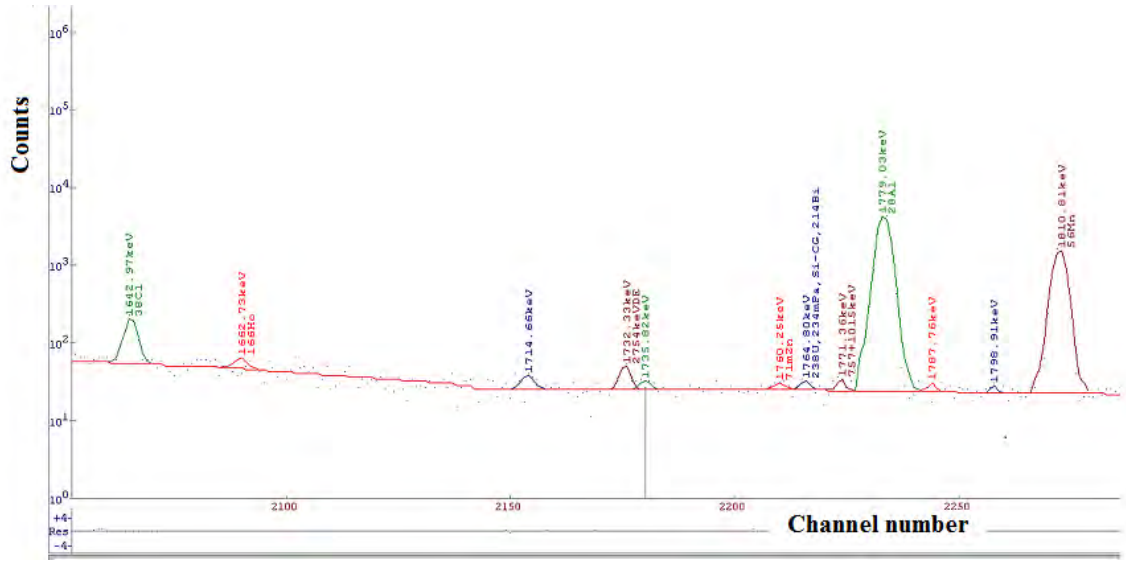

Figure 4.15: A typical gamma ray spectrum of Artemisia Abyssinica at t_{irr} = 5min, $t_d = 6min$ and t_c = 10min

in blood and for the smooth flow of communication signals from cell to cell but low level of K in human body causes diseases like heart stroke, diabetes and hypertension(Prag & Bhanu, 2013).

Chlorine (Cl) like K is an essential nutrient. It acts as an anion in the extracellular fluid in plasma, lymph, connective tissue and bone of human body (Yamusa et al., 2013). But high doses of chlorine intake result in malfunction of nervous system and organs on such as liver and lungs (Agaja & Omatsola, 2013). The concentration of chlorine was found between 8058±64 ppm in Lippia Adoensis and 1362±30 ppm in Echinops Kebericho. This range of concentration was found agreeable with the previous work on other medicinal plants (Serfor et al., 2003; Obiajunwa et al., 2002). The decay activity plot of Cl in Artemisia Abyssinica is plotted in figure 4.14.

Although aluminum (Al) is the third most abundant metal on Earth's crust, it has no known physiological importance in the human body (Garbossa et al., 1998). Most studies related to Al indicate that excess intake of Al causes diseases like neurological dementia (or kidney dialysis), Parkinson and Alzheimer. The daily average intake of Al by adult is in about 7 to 10 mg/day(Flarend, 2001).

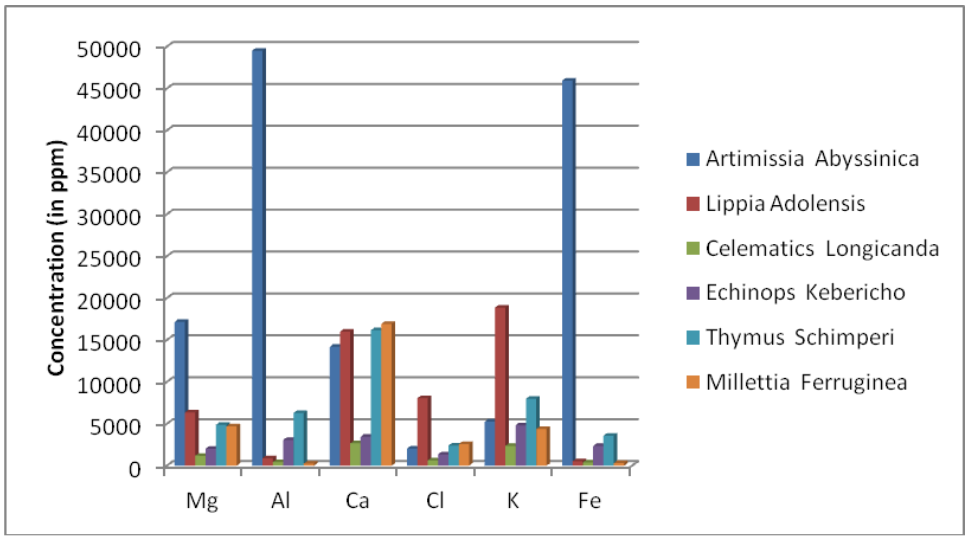

Figure 4.16: Macronutrient in six medicinal plants

Al concentration in this work was observed significantly high in Artemisia abyssinica 49500±346 ppm which is 191 times higher than that of 259±8ppm in Millettia ferruginea. The possible cause for the high concentration of Al in this study could be due to high absorption of Al by the plants from the soil. On a similar manner, the leaf of Artemisia abyssinica accumulated high content of iron 54930±275ppm. Iron concentration in this study was recorded between 323±28ppm in Millettia ferruginea and 54930±275 in Artemisia abyssinica. Biologically, Iron is required for proper growth of plants and is also responsible for the oxidation process of carbohydrates, protein and fat, and for the formation of hemoglobin in red blood cells and transporting oxygen in human body. According to (FAO)/WHO (1984), the permissible limit of iron for edible plants is 20 ppm (Muhammad et al., 2010). Low Fe content in human body causes gastrointestinal infection and nose bleeding (Hunt, 1994).

Sodium, manganese and barium in this study were found in the category of micronutrient as shown in figure 4.17. The concentration of Na in this work ranged from 23.4±0.6 to 1969 ±14 ppm and the leaf of Artemisia abyssinica accumulated high Na content as shown

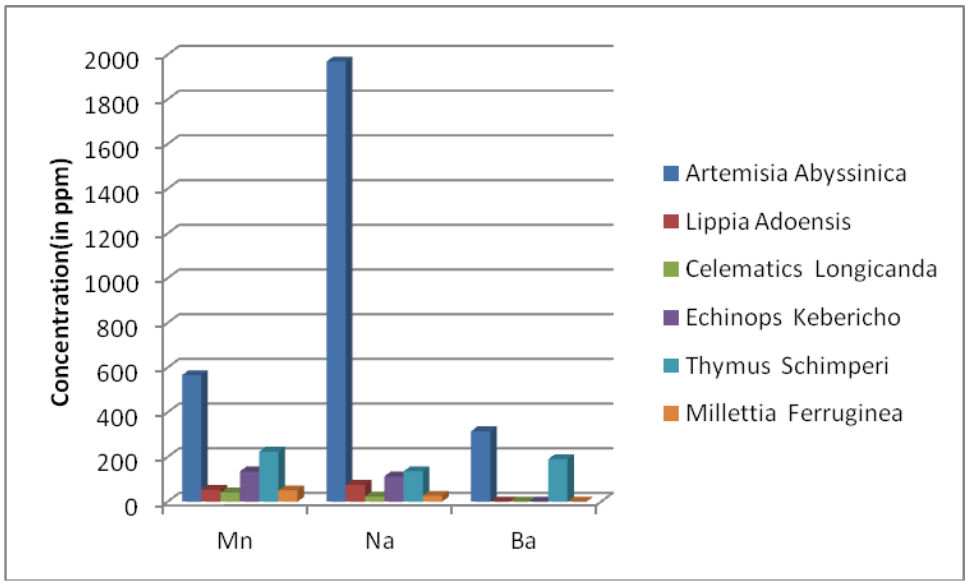

Figure 4.17: Micronutrient in six medicinal plants

in figure 4.17. This concentration range was found almost in agreeable with other works on other medicinal plants (Serfor et al., 2003). Thus, consuming Artemisia abyssinica as medicinal plant might cause seizer and comma. Similarly, manganese like Na is an essential micronutrient which is used for the normal bone structure, reproduction and normal functioning of the central nervous system, for eliminating tiredness, fatigue and nervous irritability (Guenther & Konieczynski, 2010)but higher amount of Mn accumulation in human body is not good for brain. Results of Mn obtained in this study showed that the leaf of Artemisia abyssinica is dominate in Mn accumulation (556±11ppm) and the lowest was noticed in Celematics Longicanda, (41.24±0.25)pm. Although Mn concentration in this study was found above the permissible limit, it was found in agreeable with the range of previous works on other medicinal plants (Magili et al., 2014; Ndiokwere, 1989).

Zinc and vanadium are very essential chemical elements. Zinc, for instance, is very important for wound healing, proper function of nervous system, metabolic function,bone formation, for growth and multiplication of cells and for the prevention and treatment of

diabetes Mellituses and malaria (Djama et al., 2011). The dietary limit of Zn for human body is 100 ppm (Jones, 1987). According to FAO/WHO (1984), the permissible limit of Zn for edible plants is 27.4 ppm (Abdul et al., 2012).

In this study, the highest concentration of Zn was found both Lippia Adoensis and Millettia ferruginea (83 ± 3 ppm) and lowest in Celematics Longicand (11±2 ppm).

Vanadium is a trace element that is useful treatment for prevention and treatment of diabetes Mellitus 2 (Agaja & Omatsola, 2013). It works the activities of insulin to produce reduced glucose levels in blood. Vanadium concentration was obtained high 256±4 ppm in Artemisia abyssinica and the lowest 0.91±0.17 ppm in Millettia ferruginea. The concentration of barium in Artemisia abyssinica and Thymus Schimperi samples was measured 315±3 ppm and 90±15 ppm respectively but in the other samples it was detected below detection limit. As studies suggest Ba ions at low concentration act as a muscle stimulant but at higher concentration, it affects the nervous system, causing cardiac irregularities, tremors, weakness, anxiety and paralysis.

On the other hand, some elements such as Br, La, Sm, Sc, Rb, Nd, Eu, Tb and Yb were measured in trace amount in some of the medicinal plant samples. But the functional roles of these elements have not been known so far. For instance, Br, La and Sm were measured at trace level in all samples but these elements have no known essential role in the human body (Sharat et al., 2010; Agaja & Omatsola, 2013). Similarly elements like Sc, Rb, Nd, Eu, Tb and Yb were found in Artemisia Abyssinia rather than in the other samples. The concentration ranges of these elements were obtained in the range of 0.52±0.02 ppm with Eu in Echinops Kebericho and 14±3 ppm in Thymus Schimperi.

The data sets as shown in table 4.13 are also subjected to cluster analysis to evaluate the similarities among the medicinal samples based on their elemental concentrations using the cluster package in Mintab 16 windows. As shown in figure 4.18, the highest clustering of the medicinal plants was observed between Celematics longicanada and Echinops Kebericho with the similarity level of 94.31% followed by Thymus Schimperi and Millettia

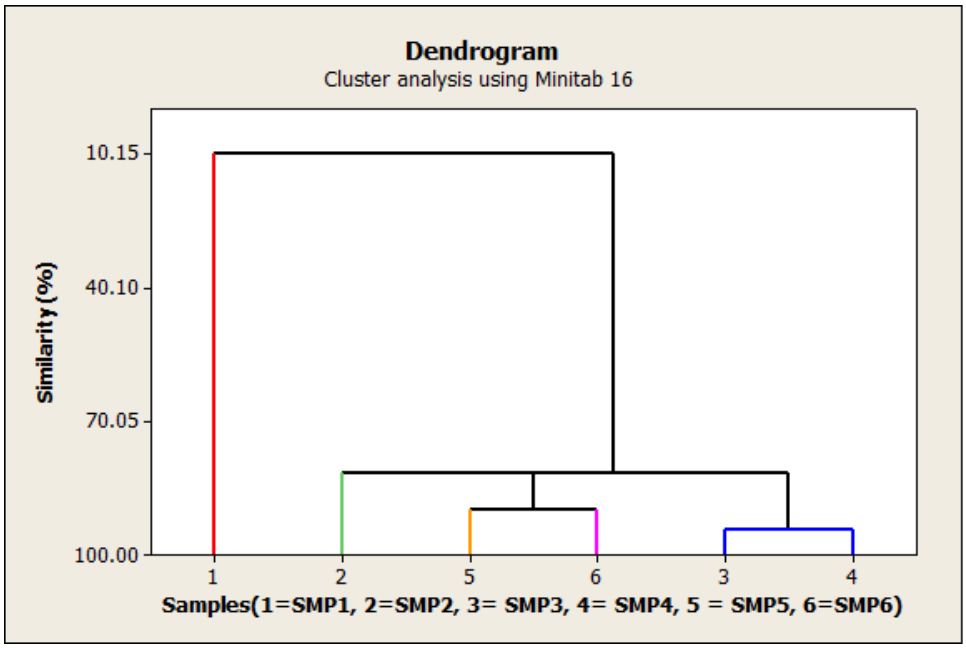

Figure 4.18: Cluster analysis of six medicinal plants

ferruginea with the similarity level 89.78% ; Lippia Adoensis and Thymus Schimperi with the similarity level of 81.861%, Lippia Adoensis and Celemetics Longicanda with the similarity level of 81.751% and the lowest clustering was seen between Artemisia Abyssinica and Lippa Adoensis with the similarity level of 10.15%. On one hand, the cluster analysis showed that Celematics longicanada and Echinops Kebericho have similar elements with equivalent concentration amounts and thus these plants could have similar curative properties. This is also true for Thymus Schimperi and Millettia ferruginea. On the other hand, the similarity between elements in Artemisia Abyssinica and Lippa Adoensis were found strongly weak indicating that these medicinal plants do not have similar curative properties.

4.4 Analysis of essential elements in Ethiopian finger millets (Eleusine coracanda) by Instrumental neutron activation analysis (INAA)

Cereal crops are the major source of food for the human population. One of those important sources of cereal food is finger millet (Eleusine coracanda). Finger millet is widely cultivated as an important staple food in many parts of eastern and central Africa and India (Rajalakshmi et al., 2014).

Finger millet is an excellent source of micro-nutrients, which could alleviate the wide spread micronutrient malnutrition in the developing countries Shashi et al. (2007) because of its better nutritional quality. It contains more percentage of different nutrients like calcium, iron, magnesium, phosphorus, potassium and zinc (Sonia & Zerihun, 2012; Shimelis et al., 2009; Pragya & Raghuvanshi, 2012; Krishania & Kalpana, 2013). The importance of Eleusine coracana is not only providing essential nutrients but it is also rich in nutritional values to the diet in terms of carbohydrate, protein, fat and inorganic minerals (Shimelis et al., 2009; Khouloud et al., 2013; Pragya & Raghuvanshi, 2012). Shashi et al. (2007) reported that the total carbohydrate content of finger millet is in the range of 72% to 79.5 % and its protein content in nearly 7% (Sonia & Zerihun, 2012).

Elements, in trace amounts, play an important role in metabolic processes and are essential for the general well-being of humans. This is because essential trace elements in their appropriate concentrations are very important for the physiological and metabolic processes and biomedical functions of the body.

Finger millet, apart from its nutritional values, has also significant medicinal properties for treatment and prevention of cancer initiation. In India, for instance, it is used traditionally as remedy for leprosy, liver disease, measles, pneumonia and small pox (Khouloud et al., 2013; Pragya & Sarita, 2012). In addition, Eleusine coracana gives to working class valor and strength to stay active without tiredness and regulate their body temperature

during intensive labor.

Finger millet also known as Dagussa (in Ethiopian Amharic language) is a native and indigenous food crop to Ethiopia and has been harvested in different parts of the country for centuries (Shimelis et al., 2009). Usually it is grown almost exclusively once a year like that of Ethiopian Tef (Eragrestis). Tef is a fine stemmed, tufted annual grass like finger millet and is categorized as cereal crop. In Ethiopia, Tef is widely cultivated for domestic consumption of millions of people. However, even though finger millet is nutritionally rich compared to Tef, it is not usually a preferred type of food. In Ethiopia, there is still a limited information about the nutritional values of finger millets.

Thus, the present study was carried out with the objective to find out scientific evidences what essential or toxic chemical elements are available in white, black and Sergegna finger millets. The method employed to study the elemental composition of three species of finger millets (as shown in figure 4.19) was the Instrumental Neutron Activation analysis (INAA). Finally, a comparison was done between the nutritional values of finger millet and Tef for evaluating which of the two cereal crops is significantly rich in chemical nutrients.

Figure 4.19: White, Sergegna and black types of finger millet

Figure 4.20: White finger millet, in powder and soup forms

4.4.1 Results

In the analysis of essential elements in white, black and Sergegna finger millets, the validity of INAA was evaluated by analyzing apple Leaves (NIST 1515) of biological origin.

As can be seen from the table 4.14, the measured concentration of apple leaves was in good agreement with the certified values by NIST.

In relative method, the concentration of each radionuclide in the three finger millets was

Table 4.14: Elemental concentrations of apple leaves (NIST-1515) used for quality control purpose in (ppm)[mean±SD]

Element	This work	Certified value
Mg(%)	0.2710 ±0.015	0.2710±0.008
K(%)	1.61±0.02	1.61±0.02
Ca(%)	1.5260±0.443	1.526 ±0.015
Al	286 ±5	286 ±9
Cl	579 ±20	579±23
V	0.26 ±0.08	0.26±0.03
Br	1.8±0.3	(1.8)
Mn	54±1	54±3
Na	24.4±0.5	24.4±1.2
Ba	49 ±11	49±2
La	20.00±0.08	(20)
Sm	3.00±0.01	(3.00)
Sc	0.030±0.007	(0.030)
Fe	83±26	83±5
Zn	12.5±2.7	12.5±0.3
Rb	10.2±0.3	10.2±1.5

determined using equation 4.1.1 through the manipulation of gamma-ray spectrum analysis software WINSPAN 2004, a software developed at CIAE, Beijing, China. Furthermore, the gamma rays which are unique (or finger print) to each of the elements activated in the samples were identified through their energies and half-lives qualitatively as shown in figure 4.21 and 4.22.

4.5 Discussion

In this investigation, the concentrations of 16 chemical elements in white, black and Sergegna finger millet were determined using INAA as tabulated in table 4.15. The

Table 4.15: Elemental concentrations (in ppm) obtained in three samples of finger millet

	Finger Millet (in ppm)		
Element	White	Black	Sergegna
Mg	1789±229	1886±411	1907 ±246
K	592±11	1076±20	2407±19
Ca	4403±299	4876±36	4786±297
Al	268 ±19	1469±59	541±15
Cl	387 ±21	219±19	467±20
V	BDL	4.3±0.7	0.9±0.2
Br	7.98±0.05	7.58±0.05	17.36 ±0.02
Mn	54.9±0.3	52.4±0.3	57.3±0.3
Na	2.73±0.06	10.73±1.6	10.65±1.2
La	0.095±0.008	0.34±0.10	0.30±0.01
Sm	0.07±0.01	0.087±0.003	0.061 ±0.002
Sc	0.07±0.01	0.46±0.01	0.115±0.009
Fe	194±36	775±42	156±18
Rb	6.2±1.7	BDL	13.6±1.9
Nd	9.23±2.10	BDL	BDL
Ba	57±15	BDL	BDL
Zn	15±3	24±3	16±2

elements obtained are Mg, Al, Ca, Cl, Na, Mn, K, Br, La, Sm, Sc, Fe, Zn, Rb, and Ba. Among these elements Ca, Mg, and K are the most important and were found in large concentrations (macronutrients) in three of the finger millet types as depicted in figure 4.24.

Finger millet is significantly rich in calcium compared to other cereals and millet species (Shobana et al., 2013). In this study, for instance, out of the three finger millet samples, the highest concentration of Ca was observed in white finger millet (4430±229 and the lowest in black finger millet (4876±36 ppm. The concentration of Ca in three of the finger millets were found higher than the concentration of Ca in white and purple Teff as seen in tables 4.16 and 4.17.

Magnesium like calcium was obtained in the category of macro-nutrient in three of the finger millets. The highest concentration of Mg was observed (1907±246 ppm) in mixed finger millet and lowest (1789±291 ppm) in white finger millet. This implies that mixed

Table 4.16: Chemical Composition of tef seed compared with of spring wheat, winter wheat, Winter barely and sorghum (in ppm) (Mengesh, 1966)

Chemical element	Purple Tef	White Tef	Spring Wheat	Winter Wheat	Winter barely	Sorghum
Mg$\times 10^4$	0.18	0.19	0.15	0.12	0.13	0.18
K$\times 10^4$	0.36	0.20	0.37	0.33	0.44	0.44
P$\times 10^4$	0.44	0.46	0.51	0.40	0.48	0.52
Ca$\times 10^4$	0.18	0.17	<0.1	<0.1	<0.1	<0.1
Mn(ppm)	21.2	30	53	36	12	29
Fe(ppm)	196	115	78.5	40	35	66.5
B(ppm)	14	13	12	11.5	11	16.5
Cu(ppm)	53	36	20	11	14	23.5
Zn(ppm)	67	67.5	60	39.5	45	44
Al(ppm)	83	0.12	<0.1	<0.1	<0.1	<0.1%
Sr(ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1%
Mo(ppm)	0.78	0.74	0.6	0.55	0.4	0.45
Co(ppm)	0.52	0.64	0.6	0.55	0.3	0.3
Na(ppm)	220	212.5	195	168.5	392	141.5
Ba(ppm)	19	23.5	7.5	6	7	<0.1

Table 4.17: Chemical Composition of white and purple Tef (in ppm) (Abebe et al., 2007)

Chemical Element	White Tef	Red Tef	Sergegna Tef
Ca	1240	1550	1470
Fe	377	>1500	>1500
Zn	28.6	40.2	38.6

finger is better in Mg content than black and white finger millet. As literatures suggest, taking Mg rich crops as a diet is very important to human body because Mg plays a major role in the proper functioning of nervous system, muscle control and blood pressure. However, human body which is subjected to low level of Mg content is easily exposed to illness such as hypertension, cardiovascular disease, diabetes, asthma, headache and stress Rajendran et al. (2007); Magili et al. (2014).

Potassium like Ca and Mg is the third macronutrient found in three of the finger millet as shown in figure 4.24. The highest concentration of K (2407±19 ppm) was found in

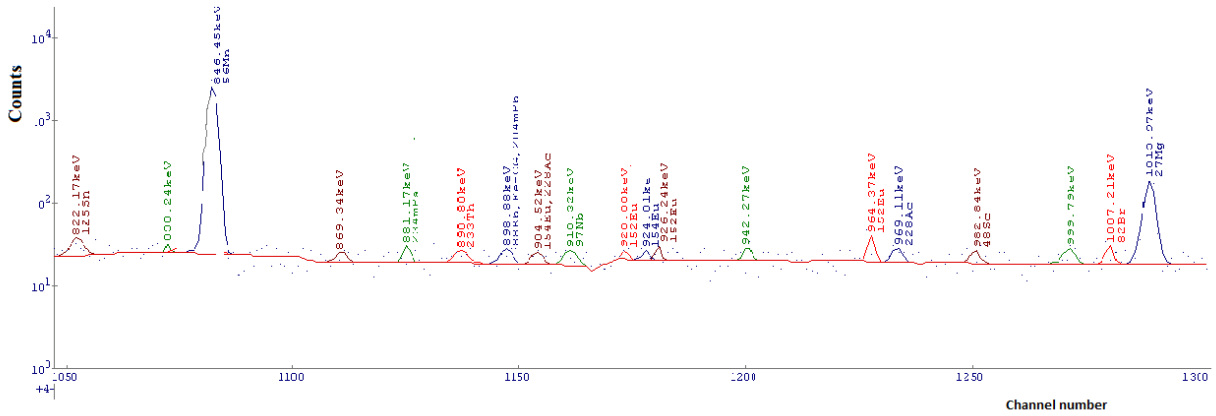

Figure 4.21: A typical gamma ray spectrum of black finger millet viewed partially at t_{irr} = 5min, t_d = 4 min and t_c= 10min

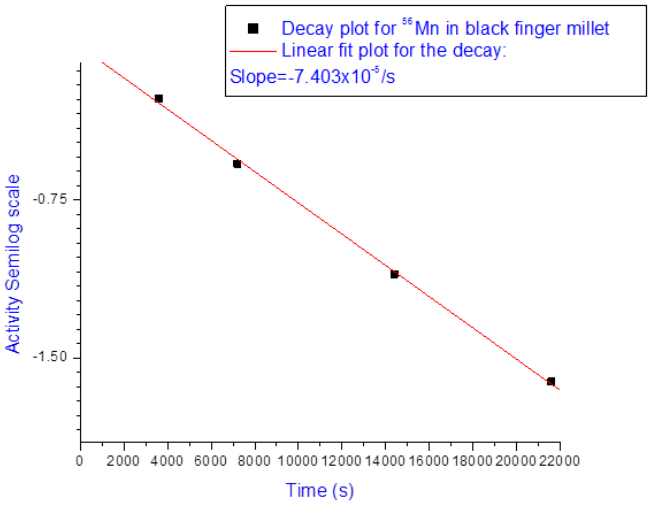

Figure 4.22: Decay curve of Mn-56 in Black finger millet

Sergegna finger millet and the lowest concentration of K (592±11 ppm) was found in white finger millet. The K concentration observed in white and purple Teff (Abebe et al., 2007) was higher than the concentration observed in the white and black finger millets. However, the concentration found in Sergegna finger millet was almost comparable. Potassium is an essential nutrient and functioning as electrolyte in the blood and helps the smooth flow of signals from cell to cell in human body. The recommended average intake of K is 2300mg/day for adult women and 3100 mg/for adult men. However, lack of K in human body causes diseases like heart stroke, diabetes and hypertension (Prag & Bhanu, 2013).

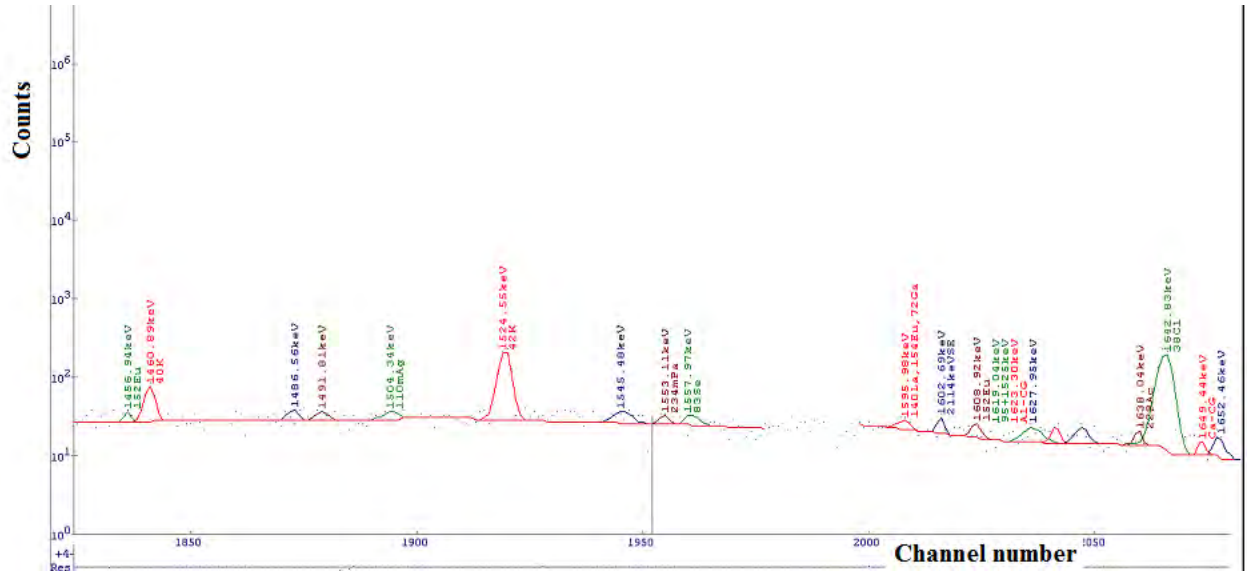

Figure 4.23: A typical gamma ray spectrum of white finger millet viewed partially at t_{irr} = 5min, t_d = 192 min and t_c= 10min

Therefore; according to the result of this study, as Sergegna finger millet contains a lot of K, it is possible to minimize diseases like stroke, diabetes and hypertension by taking processes Sergegna finger millet daily.

Aluminum, chlorine and iron were obtained at micronutrient levels in the three of the

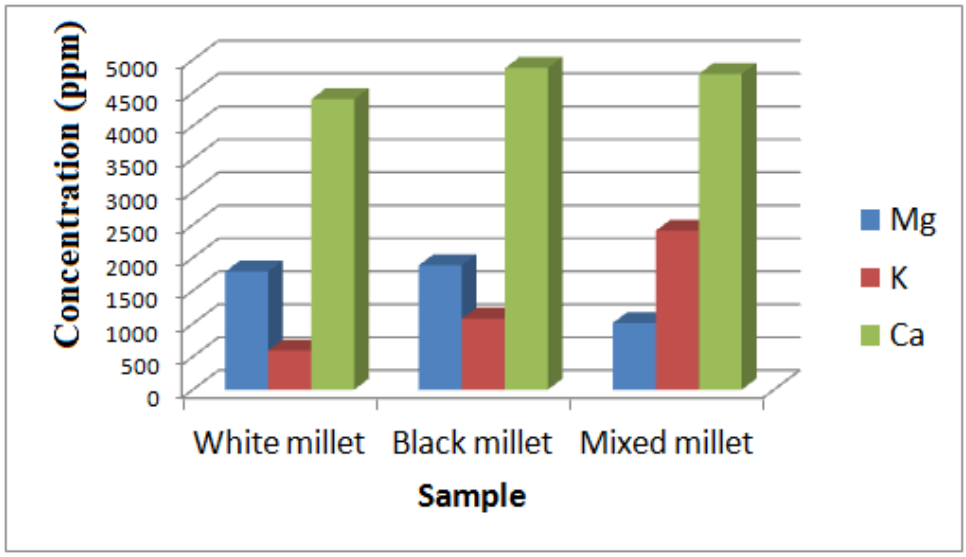

Figure 4.24: Macronutrients of finger millets

finger millets as depicted in figure 4.25. Although Al was categorized as micronutrient,

the concentration obtained in black finger millet (1469 ±59 ppm) was significantly high. The concentration found was 5.5 times higher than the Al concentration in white finger millet (268 ±19 ppm) and 2.7 times higher than the concentration found in Sergegna finger (541±15ppm). The possible cause for high concentration of Al in black finger millet could be due to the high absorption of Al by black finger millet from the soil where the finger millet had been grown. Moreover, the concentration of Al in three finger millet species was found significantly high as compared to the concentration of Al in two of the Tef species.

Chlorine (Cl) and iron (Fe) are the other most essential nutrients the human body

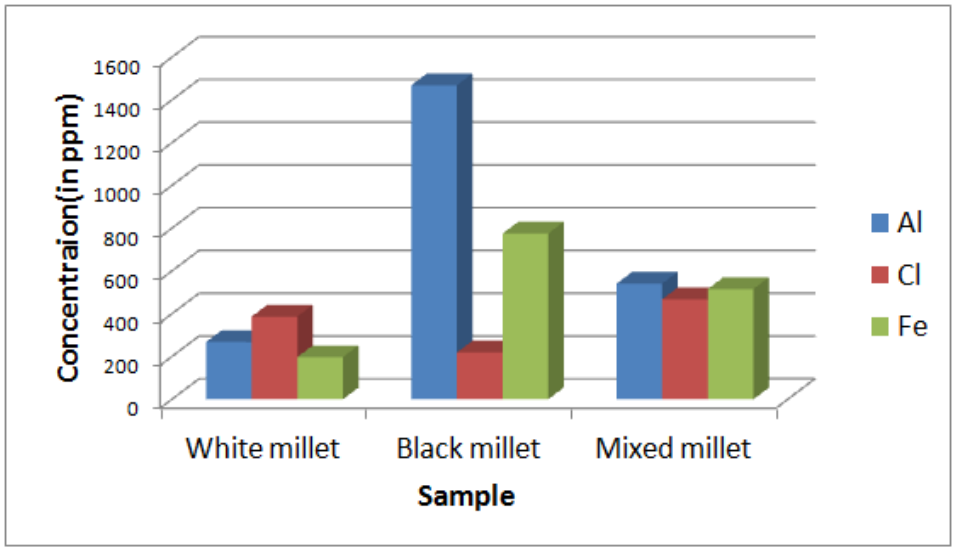

Figure 4.25: Micronutrients of finger millets

requires. The concentration of chlorine obtained in this work ranged from 219±19 ppm in black finger millet to 467±20 ppm in Sergegna finger millet as micronutrient. With regard to the biological importance, the role of chlorine in human body is to act as an anion in the extracellular fluid in plasma, lymph, connective tissue (Debrah et al., 2011). Similarly, Iron concentration recodred in three of the millet species ranged from 156±18 ppm in white millet to 775±42 ppm in black millet. The concentration amount of Fe in finger millet and Tef species was found relatively to be the same. According to the result

obtained in this study the concentration of Fe was above the permissible limit 20 ppm (Muhammad et al., 2010).

The concentrations of other essential nutrients such as Na, Mn, V, Rb and Zn were

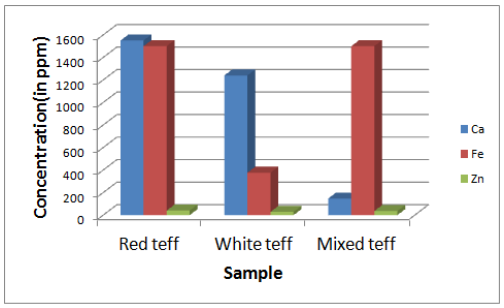

Figure 4.26: Two species of Teff: White and purple (Abebe et al., 2007)

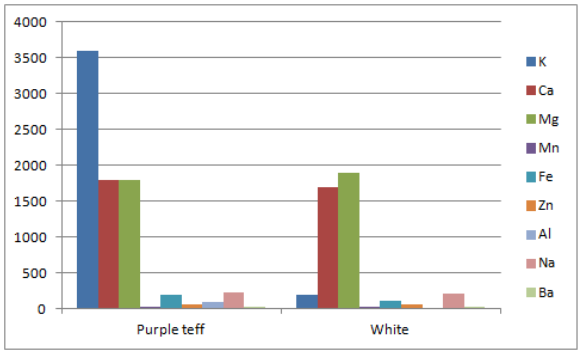

Figure 4.27: Three species of Teff: White, Red and Mixed (Mengesh, 1966)

measured at trace levels in all finger millet types. But vanadium (V) in white millet and rubidium (Rb) in black finger millet were recorded below detection limit.

The concentration of sodium found ranged from 2.73±0.06 ppm to 10.73 ±1.6 ppm at trace level. Biologically, sodium is important for maintaining acid-base equilibrium in the human body and also acts as electrolyte in transmitting nerve impulse and in relaxing muscles of the human body (Lokhande et al., 2010; Soefan et al., 2010). Excessive intake or the deficiency of Na in the human body could be subjected to water retention, high blood pressure, stomach ulcer and cancer, confusion, weakness, seizures, coma and even death (Lokhande et al., 2010).

Similarly, Zinc concentration was seen in trace amount. The concentration ranged from 15±3 ppm ppm to 24±3 ppm in three of the millets which was below the permissible limit, 27.4ppm. Zinc has both biological and pharmacological importance as discussed in medicinal plants under section 4.3. However, excess or low intake of Zn in human body could be the cause a number of metabolic disturbances such as abdominal pain, vomiting, diarrhea and insulin degradation.

The concentration of manganese (mn) was ranged from 52±3 ppm to 75.3 ± 0.3 ppm which was above the permissible limit. Mn is an essential element required for various bio-chemical and enzymatic processes. The permissible limit of Mn as estimated by FAO/WHO (1984) is 2ppm (Muhammad et al., 2010; uhammad et al., 1998). The other trace element obtained in this study was vanadium with the concentration of 4.3±0.7 ppm in black millet and 0.9±0.02 ppm in Sergegna millet but the concentration found in white finger millet was below detection limit. Vanadium is an essential nutrient found in many foods (Nath, 2014). It has a biological importance for bone formation, cellular and replications, and pharmacological importance for prevention and treatment of diabetes Mellituses 2.

Rubidium is an essential element for the production of hormones and various enzymes (Nath, 2014). The concentration of Rb found in this work ranged from 6.2 ±0.6 ppm to 13.6±0.9 ppm in white and Sergegna millets whereas in black millet it was recoded below detection limit.

Although in this stduy the concentrations of other nonessential elements such as Ba, Br, La, Sm and Sc were obtained in the range of 0.095 ± 0.008 ppm to 57 ±15pm in the finger millet samples, in many reports the biological and physiological importance have not yet been known.

Furthermore, this study confirmed that finger millet is better in nutritional quality and therapeutic values as compared to other cereal crops like tef (Eragorostis tef), wheat, barely and sorghum as shown in table 4.16. For instance, the concentrations of essential elements such as Ca, Mg, Mn and Fe observed in three of the finger millet are observed significantly higher than the concentrations of the same elements in Tef (Eragorostis tef), wheat, barely and sorghum as reported by (Mengesh, 1966; Abebe et al., 2007) as shown in figure 4.16 and 4.17. The other importance of finger millet is the fact that it contains essential elements such as Cl, V and Rb which are not foundn other cereal crops like Tef.

Chapter 5

Summary, Conclusion and Recommendation

5.1 Summary

As the results of this thesis were clearly stated in the previous chapters, instrumental neutron activation analysis has proved to be the most efficient and effective method to analyze the essential and/or toxic chemical elements in soils, herbal plants and finger millet. The strength of neutron activation is categorized by its versatility, reliability, sensitivity, accuracy and low detection limits over many elements. The quantified results of this experimental based study showed that the soil of Chilga Woreda, the traditional medicinal herbs collected from Taragedam areas and the three species of finger millets collected from the local market of Bahirdar city were proved to be rich in essential mineral constituents although some elements contained excessive amounts of toxins.

On the other hand, NaI(Tl) scintillation detector gamma ray spectroscopy was also found to be a good nuclear analytical technique for determining the activity concentrations and radiological hazards of long-lived radioactive elements such as Potassium (^{40}K), Uranium (^{238}U) and thorium (^{232}Th) in the laboratory of low energy background. As many studies suggest, nowadays, the natural radioactivity levels of building materials among others: rocks, cements, concretes and bricks are tested before using them for

construction industries to safeguard the public from exposure to radiation hazards. By taking such practice into consideration, this study was mainly focused on the assessment to the activity concentrations and radiation doses of natural radioactive elements in rocks around Gondar city in Northwest Ethiopia as these rocks are widely used for buildings and road constructions in the city in various forms such as taking the rocks as they are and in the forms of gravels of different sizes.

5.2 Conclusion

To investigate the elemental composition of soils in Chilga Woreda, Northwest Ethiopia, we have employed the INAA technique which has enabled us to determine the composition of 33 elements. Among 33 elements, the concentrations of Mg, Al, Ca, Ti, Na, K, Fe, Mn were found high. The concentration of the elements in the all samples ranges between 457 ppm to 117600 ppm with the highest concentration found in soil of Nara awdarda. Elements such as V, Ba, Zn and Sr were also obtained in the range from 44 ppm to 2886 ppm to the intermediate proportions whereas elements such as As, Ba, Br, Cr, La, Lu, Hf, Ho, Sc, Sm, Sb, Co, Rb, U, Nd, Eu, Ta, Tb, Th, Tm and Yb were measured at trace and ultra trace levels. But the soil of Dilanba accumulates exceptionally high content of V and is categorized at macronutrient level.

Compared with the world top soil median (Bowen1975), the median and mean concentration values of Mg, Al, Cr, Na, Co, Fe, V, Ti and Mn in Chilga soil were above the world top most soil mean and median values, whereas, the median and mean concentrations values of alkaline Earth metals such as Ca, K and Na were found to be below the corresponding world top soil mean and median values; as it can be clearly seen in table 4.4.

The results of the finding showed that the soil of Chilga Woreda is substantially enriched with essential mineral compositions. Soil types with such compositions are vital for the

normal growth of plants and boosting crop production and productivity. However; the existence of excess amounts of Al, Mn and Fe in the soils was acclaimed to having adverse effects on the growth of plants, due to their high toxicity levels. Moreover, the low concentration of alkaline earth metals such as Na, K and Ca as compared to the world soil median contributes a lot to the soil acidity.

Furthermore, in this study since the content of hydrogen in the soil of Chilga could not be detected by INAA method, a pH meter was taken as an option to determine the level of acidity caused by hydrogen ions in the soil. The results of the pH meter indicated that the soil of Chilga contains hydrogen ions in addition to acidic metals but it was obtained that the acidity was not very severe.

The other research problem that was assessed in the present study was the natural radioactivity levels of ^{40}K, ^{238}U and ^{232}Th, in rocks around Gondar city using technique of NaI (Tl) scintillation detector γ-ray spectrometry. The results of the study demonstrated that the activity concentration of ^{226}Ra (in ^{238}U series) of each rock was found to be lower than the worldwide mean and median as shown in chapter 4 table 4.9 and the activity concentration of ^{232}Th in each rock sample was above world median. Even though the activity concentration range and median of ^{40}K in rocks of Dabecha Rafael was recorded as above worldwide range and median, the activity concentrations in rocks of Arno Snaba, Dngy gores and Surur Damaza areas were confirmed below worldwide range and median values.

With regard to the radiological hazards such as the radium equivalent activity, absorbed dose rate, annual effective dose rate, and the external and internal radiation hazard indices in all rocks it was found out that they were below the world recommended values as can be seen in chapter 4 table 4.10. But exceptionally, the absorbed dose rate in rocks of Dabecha Rufauel and Gondar airport were recorded to be above the world recommended values. In sum,in accordance to the results of this study all rocks except the rock of

Dabecha Rufauel do contribute insignificant radiological health related risks to the general public.

Endemic Ethiopian Medicinal herbs which are traditionally used to treat various ailments were taken as the third researchable problem of this study. Medicinal plants are the natural products which are perceived by many as the gifts of nature or God. More than 70% of the world population who lack access to modern medicines use medicinal plants as treatments to cure their illnesses from various diseases and they are also use them as food supplements.

In the same way, more than 80% of the Ethiopian population who live in the rural areas including the population living even in urban areas use various types of medicinal plants for their immediate relief from illnesses as primary health care, and as food supplements. However, many of the medicinal plants that are used in Ethiopia and other developing countries are not based on scientific research. Rather, people usually take medicinal plants traditionally without having basic understanding about the pharmacological importance of those herbal plants. To recapitulate, researches conducted on the Ethiopian medicinal are ar rudimentary stage. Thus, undertaking an academic research upon such knowledge gap like this study was needed to find out what essential chemical elements are there in the six different types of endemic medicinal plants in Ethiopia as listed in 4 table 4.13.

In this work, hence, a total of 20 elements in six medicinal plants were determined quantitatively using the relative method of neutron activation analysis. According to the experimental results obtained K, Mg, Al, Ca, Cl and Fe were found in high proportions along all samples. Ba, Mn and Na were obtained in intermediate proportions in all samples. Elements such as Br, Eu, La, Sc, Sm, Nd, Rb, Tb, V and Yb were measured in trace levels. The concentrations of the elements varied in wide ranges from the lowest concentration of Eu in root of Echinops Kebericho (0.50±0.02 ppm) to the highest concentration of Na in leave of Artemisia abyssinica (54930±275 ppm). It was observed that the leaf of Artemisia abyssinica accumulated 19 elements significantly with the highest

concentrations. However, although the leaf of Artemisia abyssinica is well enriched with essential elements as can be seen in table 4.13, the excessive amounts of Al and Fe present in the medicinal plants may cause diseases such as neurological dementia, Parkison and Alzhemir rather than having medicinal benefit.

In general, the data obtained in this study showed that the six medicinal plants are well enriched with essential elements which are required for the metabolic process, proper growth and development of the human body, prevention and healing of various diseases and for the synthesis of new drugs which can be used for the control and cure of various diseases as stated in table 4.11. In particular, the elemental and concentration contents of Celematics longicanada and Echinops Kebericho plants were found to be almost similar and these plants could have similar curative properties. The same is also true for Thymus Schimperi and Millettia ferruginea. To summarize, the present study supports the claims made by traditional medicinal practitioners about the use of the six medicinal plants for curing various ailments.

The fourth research problem that was addressed in the present study was about the nutritional quality of finger millets. According to this study and other related finger millet studies, the composition of finger millet is of great importance for its nutritional and medicinal benefits.

In line with this study, when we compare the mineral contents of the three finger millets, the concentrations of Ca, Mg, K, Fe, Na, Cl, Zn, Rb and V in black and mixed finger millets were found to be higher than that of white finger millet as tabulated in chapter 4 table 4.15. Furthermore, this study has also confirmed that the mineral composition of finger millet is better than the mineral composition of Tef (Eragorostis tef) (Abebe et al., 2007). For example, essential elements such as Cl, V and Rb which are present in finger millet are not present in Tef(Eragrestis).

Therefore; finger millet which is in most cases used to make liquor (”Areki” and ”Tella”) in rural Ethiopia should be reconsidered to use it as stable food like tef, wheat and

barley because of its good nutritional quality and therapeutic importance. Apart from nutritional quality, finger millet has got immense potential for generating income, food security, and avoiding micronutrient deficiency. It is also considered as helpful famine crop as it is easily stored for long years.

From the medicinal point of view, the regular intake of finger millet could enhance the health status of the population at large. For instance, according to Prag & Bhanu (2013) elements like Mg, Zn, Mn, and V that have medicinal properties for the treatment and prevention of malaria, diabetes Mellituses, anemia, hypertension, stomach ulcer and cancer, and for wound healing and controlling blood pressure. Consequently, the present study has confirmed that three of the finger millets contain minerals Mg, Zn, Mn, and V with medicinal properties.

5.3 Recommendation

In accordance to the four major findings of the research, the following recommendations are suggested below:

- According the results of soil analysis showed in this study, the soil of Chilaga woreda, is tested rich in soil nutrients. The richness of the soil in nutrients, however; has been affected due to the existence of high concentration of contents of Al, Mn, Fe and H which cause soil acidity. Thus, the acidity of Chilga soil can be minimized (or remedied) possibly by adding inorganic fertilizers consisting sufficient amount of potassium, calcium carbonate and other liming materials in order to reduce acidity by neutralizing the acid reaction in soils. The carbonate component of lime consumes hydrogen ions present in the soil solution and raises soil pH. In addition, according to this study the soils of Chilga Woreda have potassium deficiency. Such problem should be remedied by adding inorganic fertilizer consisting K in appropriate amount

- The results of this study demonstrated that the rocks which are widely used for house construction in Gondar city do have insignificant radiological health risk to the public except the rock of Debecha Rufauel. Even though the rocks of this research areas have been confirmed to have insignificant radiological effects, in Ethiopia since research on natural radioactivity has been untouched, the radioactivity map of the country has not been done so far. Areas with high, moderate and low contents of terrestrial radioactive materials should be identified to prevent them from the vulnerability features and from the exposure to natural background radiation.

- According to the results of the present study, the six Endemic Ethiopian Medicinal Plants are rich enough with essential chemical elements such as K, Ca, Na, Mn, V, Mg and Zn that are useful for the treatment of various diseases. In particular, the samples of Echinops kebericho, celematics Longicanda, Thymus Schimper and Millettia ferruginea were found to be useful for preventing and curing various diseases such as asthma, headache and stress, stomach ache, cold, heart stroke, hypertension, wound healing, treatment of diabetes mellitus, etc. However, in Artemisia abyssinica high concentrations of necessary Al and NA were obtained. So, as per the result of this study, taking Artemisia abyssinica as medicine for the treatments of intestinal problems and infectious disease because one may be subjected to diseases like neurological dementia (or kidney dialysis), Parkinson, Alzheimer, coma and seizer. To sum up, the results of the study suggest that medicinal plants are potential candidates for drug development.

- Finger millet (or "Dagussa") is originally native cereal crop to the Ethiopia highland areas before it spread to other African and Asian countries. But in Ethiopia there has been limited information on nutritional quality of finger millet. As per the results of this study and other related studies on finger millet, finger millet has a better nutritional quality and medicinal values as compared to Tef (Eragrestis) and

other cereal crops. Therefore, according to this study it is recommended that finger millet as staple food in Ethiopia should be considered Therefor, this study suggest that finger millet should be reconsidered as a staple food in Ethiopia and should be taken as a daily meal.

- Finally, the scientific community of Ethiopia should seriously think to have nuclear research reactor for conducting scientific research.

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Declaration

This thesis is my original work, has not been presented for a degree in any other University and that all the sources of material used for the thesis have been dully acknowledged.

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