ELEMENTAL CONCENTRATION AND NATURAL RADIO ACTIVITY STUDIES FOR SOME BIOLOGICAL AND GEOL OGICAL SAMPLES TAKEN FROM SELECTED ZONES OF ETHIOPIA BY THE METHOD OF INSTRUMENTAL NEUT RON ACTIVATION ANALYSIS (INAA)

By

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A DISSERTATION SUBMITTED TO ADDIS ABABA UNIVERSITY COLL EGE OF NATURAL AND COMPUTATIONAL SCIENCES DEPARTMENT OF PHYSICS IN PARTIAL FULFILLMENT FOR THE REQUIREMENTS OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN NUCLEAR PHYSICS

November 2015

ADDIS ABABA UNIVERSITY

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Title:

Elemental Concentration and Natural Radioactivity Studies for Some Biological and Geological Samples Taken from Selected Zone of Ethiopia by the Method of Instrumental Neutron Activation Analysis(INAA)

Department: **Physics**

Degree: **Ph.D** Year: **2015**

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Acknowledgement

Accomplishment of a study of such scale can not be anticipated with out the contribution of many individuals and institutions next to the Almighty God. It would be thus fair to mention people and institutions that have lend a hand for the successful completion the dissertation. primarily, I am sincerely indebted to my advisor, Prof. A.K. Chaubey, for his insightful professional assistance and academic support, all through the duration of the study.

I like to thank you my dearest wife, Ewunetwa Engida (Aynal), for all your patience, courage, sacrifice and support in all aspects of life at home and social environment when I was completely occupied in this program. I love you not because your current support, but from the beginning when we see each other and am honestly humbled by your never ending support. I dedicate this work to you and our daughter, Merado Teklemariam.

I am also reverently thankful to Center for Energy Research and Training (CERT), Ahmadu Bello University, Nigeria, Zaria, for their help and willingness to use the research reactor and facilities to perform the experiment in this pursuit.

I am also thankful to Jimma University and the department of physics at Jimma University for sponsoring my study leave.
I thank Addis Ababa University office of Research and Graduate studies for the support and funding of the dissertation.

Finally, I am grate full of the staff of Department of physics at Addis Ababa University, staff of CERT at Ahmadu Bello University and all my colleagues for their support, encouragement and comments.

Teklemariam Tessema

List of Original Publications

1. T.Tessema Teklemariam, A.K.Chaubey, W.Tsegaye Birhanu, Bala Bello Muhammad Dewu, Idris Isa Funtua. *Multi Elemental Analysis of Medicinal Plant Flower Hygenya Abyssinia Locally called Chima Used in Rural Part of Ethiopia (Gurage Zone, Shamene) as a Medicine to Cure from Tapeworm.* The International J.of Science Technology, Vol 2, issue 12, page 157, (Nov,2014).

2. T. Tessema Teklemariam, A.K. Chaubey, W. Tsegaye Birhanu, Y.A. Ahmed and M.O.A.Oladipo *Multi Elemental Analysis of mineral soil "Ewoa" used for cooking, cloth washing, etc. in Gurage Zone, Shamene, Ethiopia.* International J. of Engineering and Scientific Research (IJSER)Volume 3,126, Issue 5, (May, 2015).

3. W.Tsegaye Birhanu, A.K.Chaubey, T.Tessema Teklemariam , Bala Bello Muhammad Dewu, Idris Isa Funtua and N. Abubakr. *Elemental analysis of soil around Aykle in Chilga district North Gondar, Ethiopia using technique of Instrumental Neutron activation analysis (INNA)* Int. J.of Ad. Scientific and Technical Research, Vol 6, issue 4,page 445, (Dec, 2014).

4. W. Tsegaye Birhanu, A.K Chaubey, T. Tessema Teklemariam, B. B. Muhammed Dewu, M.O.A Oladipo, Y.A. Ahmed, and N. Abubakr *Analysis of essential elements in Ethiopian finger millets (Eleusine coracanda) by instrumental neutron activation analysis (INAA).* Int. J. of Basic and Applied Sciences,Vol 4, issue 1,page 82-88, (January, 2015).

5. W. Tsegaye Birhanu, A.K Chaubey, T. Tessema Teklemariam, B. B. Muhammed and Idris Isa Funtua. *Application of Instrumental neutron activation Analysis (INAA) in the analysis of Essential Elements in Six Endemic Medicinal Plants..* International Journal of Sciences: Basic and Applied Research (IJSBAR) Volume 19,No. 1 Page 223-227, (January, 2015).

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

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Abstract

This dissertation is devoted to the use of NAA to be applied for the determination of the qualitative and quantitative elemental analysis of selected samples. It involves the use of the knowledge of nuclear reaction particularly (n, γ) reaction and implement its practical applications to determine element types and their concentrations in the sample. In lab, a total of Five different biological and geological samples were studied, four samples were studied for their qualitative and quantitative elemental analysis and one soil sample was studied for its natural radioactivity. Long lived and short lived radionuclides spectra were measured using HPGe gamma detector. Using known values of gamma-ray energies emanating from calibrating point gamma sources, an energy calibration curve and full energy peak efficiency curve were determined and plotted. The best fit line matched the data with a least squares fit, R^2, of approximately equal to 1.

A gamma spectrum is created by taking measurements of emitted gamma-rays from different radio nuclei which emit many gammas of differing energies. Special softwares, acquisition software MAESTRO and analysis software WINSPAN, installed in computers identify an unknown radioisotope by measuring features on the gamma spectrum and comparing them to known spectra, and calculate the concentrations of the elements which gives out the gamma radiation. The peaks of different energies in the spectrum were tested analytically using the half lives of radionuclides whether the assignment of an element to each peak by the analysis software is correct. The analysis methodologies were validated by analyzing the IAEA-multi elemental standard having the same matrices as the sample.

The irradiation facility used was the Nigeria Research Reactor-1 (NIRR-1) at the Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria. A high resolution gamma-ray spectrometer comprising of HPGe detector coupled with associated electronics and basic spectroscopy softwares were employed in the analysis. From the analysis of samples of biological and geological origin, different concentrations of elements were obtained and an effort is made to explain the function of the elements for human or animals. In this dissertation a mineral soil was measured for its radioactivity and the concentration of radioactive materials were analysed and the level of radiation hazard due to the soil is calculated.

Chapter One

1 Introduction

Analytical science to develop the methodology for the investigation of properties and structure of matter at level of single nucleus, atom and molecule, and scientific analysis to determine either chemical composition or elemental contents in a sample are indispensable in basic research and development, as well as in industrial applications (1).

Following the discovery of neutron by J. Chadwick in 1932 (Nobel prize, 1935) and the results of F. Joliot and I. Curie in 1934, neutron activation analysis was first developed by G. Hevesy and H. Levi in 1936. They used a neutron source ($^{226}Ra + Be$) and a radiation detector (ionization chamber) and promptly recognized that the element Dy (dysprosium) in the sample became highly radioactive after exposure to the neutron source. They showed that the nuclear reaction may be used to determine the elements present in unknown samples by measuring the induced radioactivity (2).

Thereafter, the development of the nuclear reactors in the 1940s, the application of radiochemical techniques using low resolution scintillation detectors like NaI (Tl) in the 1950s, the development of semiconductor detectors (Ge, Si, etc.) and multichannel analyzer in the 1960s, and the advent of computers and relevant software in the 1970s, the nuclear technique has advanced to become an important analytical tool for determination of many elements at trace level (2). In spite of the developments in other chemical techniques, the simplicity and selectivity, the speed of operation, the sensitivity and accuracy of NAA have become and maintained its role as a powerful analytical technique. Neutron activation analysis is a primary non destructive method of measurements (1).

Nowadays, there are many elemental analysis methods that use chemical, physical and nuclear characteristics. However, a particular method may be favored for a specific task, depending on the purpose. Neutron activation analysis (NAA) is very useful as sensitive analytical technique for performing both qualitative and quantitative multi elemental analysis of major, minor and traces components in variety of terrestrial samples and extra-terrestrial materials (3). In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree. It is usually used as an important reference for other analysis methods (3).

Neutron Activation Analysis (NAA) is a technique to determine amounts of elements in a sample including the type of the elements present in it. It is based on the following principle (3; 4): An atomic nucleus exposed to a neutron flux of energy E_n has an isotope-specific probability per unit time of absorbing a neutron (neutron capture cross section). The reaction product is most of the time unstable, i.e. radioactive, and the process is therefore called activation. In that case, it then decays with a probability of λ per second to a stable or another unstable nucleus by emission of isotope's specific gamma radiation. Interaction of this gamma radiation with the material of the gamma detector during counting of the activity will lead directly to an interpretation of the features within the gamma spectrum (1; 2).

The instrumental detection of any particle or radiation depends upon the production of charged secondary particles which can be collected together to produce an electrical signal. Charged particles, for example, alpha- and beta particles, produce a signal within a detector by ionization and excitation of the detector material directly. Gamma rays are uncharged and consequently cannot do this. Gamma-ray detection depends upon other types of interaction which transfer the gamma-ray energy to electrons within the detector material. The electrons which received the gamma energy (excited electrons) have charge and lose their energy by ionization and excitation of the atoms of the detector medium, giving rise to many electronhole pairs.
The number produced is proportional to the energy of the electrons produced by the primary interaction. The detector must be constructed of suitable material in such a way that the electron hole pairs can be collected and presented as an electrical signal (3; 4).

Samples of a research interest, any material a solid or liquid (ice freeze), should be irradiated in a neutron flux, in a reactor neutron or in isotopic neutron source so that the gamma activity from the sample is being counted for identification of the kind of elements contained with in it, and the concentration of the elements in the sample can be calculated using the information gathered from the gamma spectrum.

In this dissertation an attempt was made to minimize the gap of lacking a scientific data for an environment in Ethiopia regarding the toxicity and the nutritional value of common foods, elemental concentrations and their uses in traditional plant medicines and the measurement of natural radioactivity of a mineral soil. The technique used for the generation of the data was based on creating unstable nuclei or activation of the element

contained in the sample by irradiating it with the flux of reactor neutrons.

1.1 Outline

This dissertation includes ten chapters all of which focuses on its different experimental and theoretical aspects. In chapter two the background of the study, the scientific laws, equations and principles that could be used during the experiment of the dissertation are explained in detail.

In Chapter three, the general methodology employed in the determination of qualitative and quantitative analysis of selected samples using a nuclear reactor neutron beam and HPGE detector system is explained and the way how the samples were collected including the location is discussed. Further more all the major materials and chemicals that were used during the experiment are presented.

The manner in which gamma ray is detected using high resolution High purity Germanium detector and NaI(Tl) detector are discussed in chapter four. The factors which affect the counting of the full energy of the gamma photon which enters in to the detector is being considered in the chapter including the detail of characterizing the HPGE detector and NaI(Tl) detector used during the experiment. The characterization focuses on the detector's energy calibration and full energy peak efficiency.
Chapter five presents all the techniques and results of the qualitative and quantitative elemental analysis of a medicinal plant flower used as a local medicine for the purpose of curing from parasites like tape worm by the people of the research area.

Chapter Six is devoted to exploring the elements in a mineral soil, locally called "Ewoa" , qualitatively and quantitatively. The chapter presents all the details of the methodology during the experimental work. In the next chapter, chapter Seven, the mineral soil "Ewoa" is tested for its natural radioactivity or the concentration of Uranium, Thorium and Potassium is calculated. The calculation includes the hazard level of the NORM radiation from the mineral soil so that the study of the mineral soil becomes complete.

In chapter Eight, the detail analysis and methodology of common and popular food type in Ethiopia called "Atmet" for its quantitative and qualitative elemental analysis using Instrumental Neutron Activation analysis is explored intensively.

In Chapter Nine, two medicinal plant species that are in use in Ethiopia are studied for their elemental concentrations using thermal neutron activation analysis. In the chapter,

the elemental concentration of each of the plants compared with the other is explained, and the methodology of the experimental work is described in depth.

Conclusion and Recommendation from the results of the research were explained in chapter Ten.

Chapter Two

2 Review of Literature

2.1 Instrumental Neutron Activation Analysis and Calibrations

Neutron activation analysis (NAA) is a very precise technique mainly used to determine trace concentrations of elements in samples (2) or to acquire information on the spatial distribution of a neutron field via neutron activation detectors (5). In INAA a sample is first irradiated with neutrons of speed $2200 m/s$ coming from e.g. a research reactor or other sources. Depending on the neutron flux, energy spectrum and reaction cross sections, the target nucleus undergoes a nuclear reaction, (n,γ), and the resulting nucleus will immediately de-excite under emission of characteristic prompt gamma rays into a more stable configuration. This configuration is mostly a radioactive nucleus with a certain half-life $t_{1/2}$ which will further decay under emission of characteristic delayed gamma rays into a stable product nucleus. An illustration in the case of a neutron capture reaction is depicted in figure1.

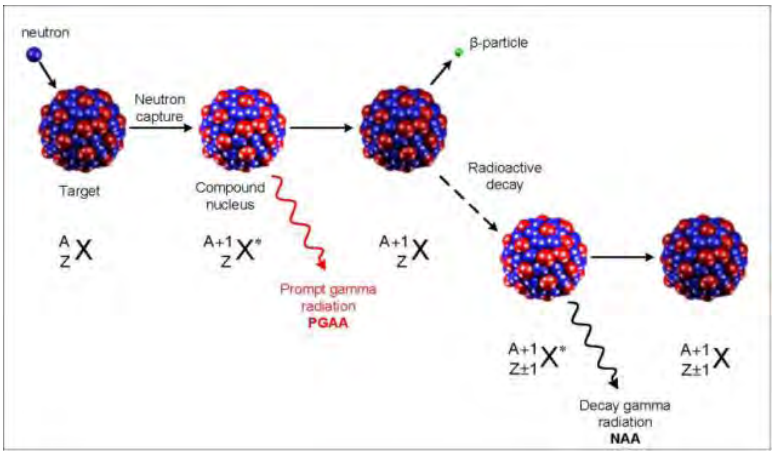

Figure 1: Thermal neutron reaction with target nucleus.

Monitoring the emitted gamma rays with a gamma detector gives information on the concentration of different elements in the sample. By using several thin foils of known composition at different locations as sample, one can obtain information on the spatial distribution of the neutron field. Such foils are called neutron flux monitors (neutron activation detectors) or activation foils.

2.1.1 Absolute calibration in INAA

If a sample is subjected to a neutron flux $\phi(E)$, radio-nuclei are formed. The reaction rate R per nucleus capturing a neutron is given by:

$$R = \int_0^\infty \sigma(v)\phi'(v)dv \tag{1}$$

where:
$\sigma(v)$ is the (n, γ) cross section as a function of neutron velocity.
$\phi'(v)$ is the neutron flux per unit of velocity interval as a function of neutron velocity.
In nuclear research reactors (which are intense sources of neutrons) three neutron flux distribution can be distinguished (2), the regions of which are shown in Figure 2.
The three regions of neutron flux are:

1. Fission or fast neutrons released in the fission of ^{235}U. Their energy distribution ranges from $100keV$ to $25MeV$ with a maximum fraction at $2MeV$. These neutrons are slowed down by interaction with a moderator, e.g. D_2O, to enhance the probability of them causing a fission chain reaction in the ^{235}U.

2. The epithermal neutron component consists of neutrons (energies from $0.5eV$ to about $100keV$). A cadmium foil 1 mm thick absorbs all thermal neutrons but will allow epithermal and fast neutrons above $0.5eV$ in energy to pass through. Both thermal and epithermal neutrons induce (n, γ) reactions on target nuclei.

3. The thermal neutron component consists of low-energy neutrons (energies below $0.5eV$) in thermal equilibrium with atoms in the reactor's moderator. At room temperature, the energy spectrum of thermal neutrons is best described by a Maxwell Boltzmann distribution with a mean energy of $0.025eV$ and a most probable velocity of $2200m/s$. In general a 1MW reactor has a peak thermal neutron flux of approximately $10^{13}n/cm^2$.

The (n, γ) cross section function, $\sigma(v)$, versus v can be interpreted as a $\sigma(v) \sim 1/v$ dependence, or $\sigma(E) \sim \frac{1}{E^{1/2}}$ dependence. In this region $\log \sigma(E)$ versus $logE$ is linear with slope $\frac{-1}{2}$, on which above some electron volts of energy several resonances are superposed.

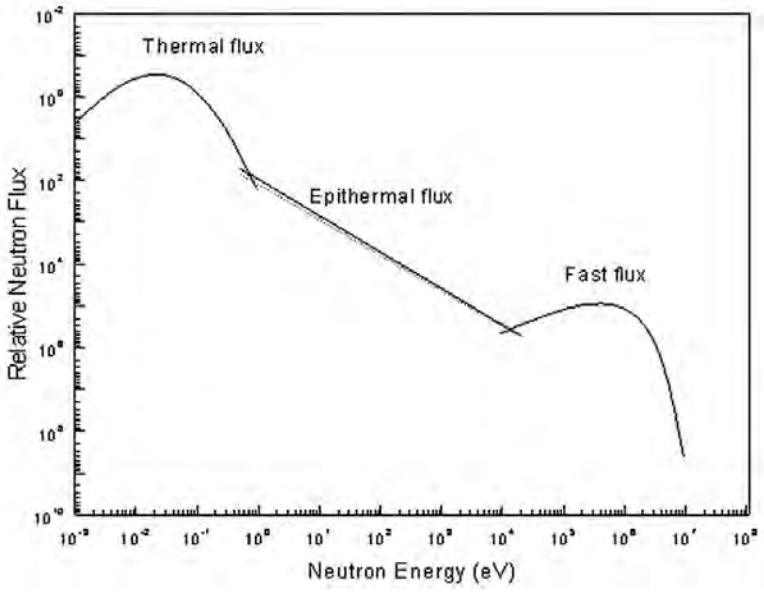

Figure 2: A typical reactor neutron energy spectrum showing the various components used to describe the neutron energy regions,(taken from (6))

$$R = \int_0^{v_{cd}} \sigma(v)\phi'(v)dv + \int_{v_{cd}}^{\infty} \sigma(v)\phi'(v)dv \tag{2}$$

$$R = \int_0^{v_{cd}} \sigma(v)\phi'(v)dv + \int_{E_{cd}}^{\infty} \frac{\sigma(E)\phi(E)dE}{E} \tag{3}$$

where:

$\sigma(E)$ is the $(n.\gamma)$ cross section as a function of neutron energy.

$\frac{\phi(E)}{E}$ is the neutron flux per unit of energy interval as a function of energy.

v_{cd} is the speed of neutrons at cadmium cut off energy ($E_{cd} = 0.55$ev).

For the most probable situation and $\phi(v) = n(v)v$, equation (3) becomes:

$$R = \sigma_0 v_0 \int_0^{v_{cd}} n(v)dv + \int_{E_{cd}}^{\infty} \frac{\sigma(E)\phi(E)dE}{E} \tag{4}$$

The flux $\phi(v)$ is thermal neutron flux (ϕ_{th}) and $\phi(E)$ is epithermal neutron flux(ϕ_{epi}), $n = \int_0^{v_{cd}} \mathrm{n(v)dv}$.

$$R = \sigma_0 v_0 n + \phi_{epi} I_0(E) = \sigma_0 \phi_{th} + \phi_{epi} I_0(E) \tag{5}$$

Where $I_0 = \int_{E_{cd}}^{\infty} \frac{\sigma(E)dE}{E}$ is called resonance integral in the region where the theoretical $\sigma \sim \frac{1}{E}$ is accepted. If the relation $\sigma(E) \sim \frac{1}{E}$ not accepted, the resonance integral becomes:

$$I_0(\alpha) = \int_{E_{cd}}^{\infty} \frac{\sigma(E)dE}{E}(1ev)^{\alpha} \tag{6}$$

Where α is the epithermal fluence rate contribution factor.

$$R = \sigma_{eff}\phi_{th} \tag{7}$$

From Eq.5 and Eq.7, it follows that:

$$\sigma_{eff} = \sigma_0[1 + \frac{Q_0(\alpha)}{f}] \tag{8}$$

where:

$$Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_0} \text{ and } f = \frac{\phi_{th}}{\phi_{epi}}$$

The time dependence of the number of radio-nuclei in the sample is determined by the balance between the rate of new isotopes being formed and the radioactive decay of the ones already formed:

$$\frac{dN}{dt} = RN_0 - N\lambda \tag{9}$$

In which N_0 is the number of target nuclei which is constant, λ denoting the decay constant, this first order differential equation can easily be solved by taking the following boundary conditions:

$$N(0) = 0, [\frac{dN}{dt}]_{t=\infty} = 0 \tag{10}$$

At $t = 0$, the radio-nuclei are yet to be created and at $t = \infty$ a state of equilibrium exists. The disintegration rate of the produced radionuclide at the end of the irradiation time t_i follows from the solution of Eq. 9 is:

$$D(t_i) = N(t_i)\lambda = N_0R(1 - e^{-\lambda t_i})$$

So at the end of irradiation, at t_i , the sample is left with N radio nuclei, such that:

$$N = \frac{RN_0}{\lambda}(1 - e^{-\lambda t_i}) \tag{11}$$

At the end of any time 't' the number of the radioactive nuclei is then given by;

$$N(t) = \frac{RN_0}{\lambda}(1 - e^{-\lambda t}) \tag{12}$$

In order to determine the count n_γ, the irradiated sample is measured by a detector for some time (t_c) starting at (t_d) , the time since the end of irradiation (t_i) . The number of radio-nuclei decaying in that time interval is "the radio nuclei present at $t = t_c$ is subtracted from the number at $t = t_d$".

$$n_\gamma = Ne^{-\lambda t_d} - \tfrac{N}{\lambda}e^{-\lambda(t_d+t_c)}$$

"N" is the number of radio nuclei just at the end of irradiation.

$$n_\gamma = Ne^{-\lambda t_d}[1 - e^{-\lambda(t_c)}] \tag{13}$$

Using (11) and (13),

$$n_\gamma = \frac{RN_0}{\lambda}(e^{-\lambda t_d})(1 - e^{-\lambda t_i})(1 - e^{-\lambda t_c}) \tag{14}$$

It is clear that the number of photons emanating from the radioactive decay that are detected by a radiation detector (counted experimentally) is different compared to the value that one can obtain using Eq. 14. This is because of several factors, the main are:

i . Full energy Peak efficiency of the detector ($\epsilon_p(E)$).
It is the probability that the full photon energy is deposited in the detector. The higher the efficiency is the higher the detection of the photon.

ii . Gamma emission probability ($I_\gamma(E)$).
It reflects the fact that there is only a certain probability, between all possible transitions from one excited state to another, that a photon of energy E_γ is emitted in the γ-decay. These probabilities are tabulated and can be found for instance in (8).

iii . There is a correction for cascade coincidences as well. The decaying radio- nuclei can turn into a stable nucleus by emitting photons as it passes through several transition states. These photons have different energies and escape angles. It is however

possible that several photons reach the detector simultaneously. This is called a cascade coincidence. We speak of true coincidences when the cascading photons are emitted in the same decay of a radio-nuclei with a very small time delay. The other case is referred to as a false coincidence, they are in general negligible unless the activity of the radioactive sample is very high. From the level scheme figure 3, we expect three gamma-peaks in our spectrum: at $412keV$, $676keV$ and $1088keV$. However, a transition energy of 1088 keV can be released in a single transition (2+ $\rightarrow$ 0+) or in two consecutive transitions (2+ $\rightarrow$ 2+ $\rightarrow$ 0+) that will be recorded together as a true cascade coincidence. As such the area of the $412keV$ and $676keV$ full energy peak will decrease and the $1088keV$ peak area will increase. When dealing with only two excited states, the calculation of the cascade correction factors is very straightforward. In more complicated level schemes, other peaks at the sum of transition energies for which there is no single transition energy alternative, might arise as well. For more than two excited levels the calculation quickly turns into k_0 standardization method(7).

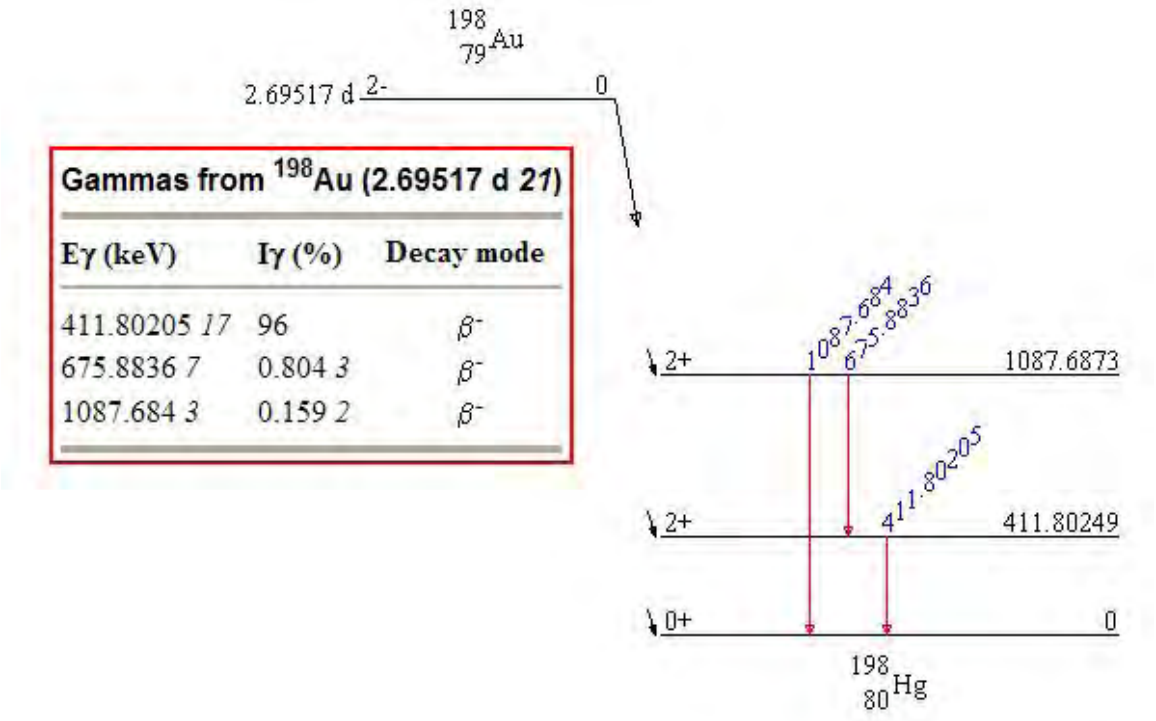

Figure 3: The gamma emission probabilities and decay level scheme for ^{198}Au.(taken from (8))

iv . Isotopic abundance (θ), It refers to the percentage presence of the isotope of interest in the element compared to other isotopes of the element.

So the total number of detected photons(n_γ) becomes:

$$n_\gamma = \frac{\epsilon_p(E).I_\gamma(E).R.N_0.\theta}{\lambda}(e^{-\lambda t_d})(1-e^{-\lambda t_i})(1-e^{-\lambda t_c}) \tag{15}$$

Using (7) and $N_0 = \frac{m}{M}N_A$, we can find an expression for the total count as:

$$n_\gamma = \frac{\epsilon_p(E).I_\gamma(E).\sigma_{eff}.\phi_{th}.m.N_A.\theta}{\lambda.M}(e^{-\lambda t_d})(1-e^{-\lambda t_i})(1-e^{-\lambda t_c}) \tag{16}$$

where: M is atomic weight, m is the mass of the element in the sample, and N_A is Avogadro's number.

During the experiment the total peak count is measured, one can calculate for the amount of the element in the sample (calculate for m in Eq. 16) using the following equation called NAA equation.

$$m = \frac{\lambda.M.n_\gamma.(e^{\lambda t_d})}{\epsilon_p(E).I_\gamma(E).\sigma_{eff}.\ \phi_{th}.N_A.\ \theta\ (1-e^{-\lambda t_i})(1-e^{-\lambda t_c})} \tag{17}$$

In absolute calculation, the values of the physical parameters $\theta,\ N_A,\ M,\ \sigma_{eff},\ I_\gamma,\ \lambda$, are taken from literature, and the parameters $n_\gamma,\ \epsilon_p(E),\ t_i,\ t_d,\ t_c$ and ϕ_{th} are determined experimentally. The draw back of this calibration is mainly due to the parameters $\sigma_{eff},\ I_\gamma,\ \lambda$ are not precisely known for many (n,γ) reactions and radionuclide, and in some cases θ is also not accurately known. Since the various parameters were often achieved via independent methods, their individual uncertainties will add up in the combined uncertainty of measurement of the elemental amounts, leading to a relatively large combined standard uncertainty. But for the other parameters $n_\gamma,\ m,\ \phi,\ \epsilon_p(E),\ t_i,\ t_d,\ t_c$ are determined, calculated or measured for the given circumstances and uncertainties can be established.

2.1.2 Relative calibration in INAA

There are two methods used in the relative calibration.

I. **Direct comparator method.** The unknown sample is irradiated together with a calibrator containing a known amount of the element(s) of interest. The calibrator is measured under the same conditions as the sample (sample-to-detector distance, equivalent sample size and equivalent matrix). From comparison of the net peak areas in the two measured spectra the mass of the element of interest can be calculated (7):

$$m_{x(unk)} = m_{x(std)}\frac{(\frac{n_\gamma}{t_c.e^{-\lambda t_d}(1-e^{-\lambda t_c})})_{unk}}{(\frac{n_\gamma}{t_c.e^{-\lambda t_d}(1-e^{-\lambda t_c})})_{std}} \tag{18}$$

where: $m_{x(unk)}$ is the mass of the element of interest x in the sample, and $m_{x(std)}$ is the mass of the element in the standard or comparator both in gram.

In this procedure many of the experimental parameters - such as neutron fluence rate, cross section and photo peak efficiency cancel out at the calculation of the mass and the remaining parameters are all known. This calibration procedure is used if the highest degree of accuracy is required. The relative calibration on basis of element calibrators is not immediately suitable for laboratories aiming at the full multi-element powers of INAA. It takes considerable effort to prepare multi-element calibrators for all the elements measurable via NAA with adequate degree of accuracy in a volume closely matching the size and the shape of the samples.

II. **The k0-comparator method/ $K0$ Standardization.**

The k0-based neutron activation analysis (k0-NAA) technique, developed in 1970s, is being increasingly used for multi element analysis in a variety of matrices using reactor neutrons (7).In the k0-based neutron activation analysis the evaluation of the analytical result is based on the so-called k0- factors that are associated with each gamma line in the gamma-spectrum of the activated sample. These factors replace nuclear constants, such as cross sections and gamma-emission probabilities, and are determined in specialized NAA laboratories. This technique has been reported to be flexible with respect to changes in irradiation and measuring conditions, to be simpler than the relative comparator technique in terms of experiments but involves more complex formulae and calculations, and to eliminate the need for using multi element standards. The k0-NAA technique, in general, uses input parameters such as (7):

1. the epithermal neutron flux shape factor (α),
2. sub cadmium-to-epithermal neutron flux ratio (f),
3. modified spectral index $r(\alpha)$ $\sqrt{T_n/T_0}$,
4. Westcotts $g(T_n)$-factor,
5. the full energy peak detection efficiency (ϵ_p),
6. nuclear data on Q_0 (ratio of resonance integral (I_0) to thermal neutron cross section (σ_0) and
7. k_0.

The parameters from the first to the fourth in the list shown above are dependent on each irradiation facility and the fifth parameter is dependent on each counting facility. The neutron field in a nuclear reactor contains an epithermal component

that contributes to the sample neutron activation (5). Furthermore, for nuclide with the Westcotts $g(T_n)$-factor different from unity, the Hgdahl convention should not be applied and the neutron temperature should be introduced for application of a more sophisticated formalism (5), the Westcott formalism. These two formalisms should be taken into account in order to preserve the accuracy of k0-method.

The applicability of HGDAHL convention is restricted to (n, γ) reactions for which Westcotts $g(T_n)$-factor is equal to unity (independent of neutron temperature) and neutron temperature ratio is unity since thermal neutrons are considered i.e. the neutron temperature T_n is equal to temperature T_0. Compared with relative method k0-NAA is experimentally simpler (it eliminates the need for multi-element standards, but requires more complicated calculations).

The k0-NAA method is at present capable of tackling a large variety of analytical problems when it comes to the multi-element determination in many practical samples. During the three last decades Frans de Corte and his co-workers focused their investigations to develop a method based on co-irradiation of a sample and a neutron flux monitor, such as gold and the use of a composite nuclear constant called k0-factor (7). In addition, this method allows to analyze the sample without use of the reference standard like INAA method. (The definition of the k0-factor and the detail of its deriving is as given in (7; 9)):
Since the k0 -standardization method was introduced in NAA(7), it has been broadly applied in the reactor in the world. The concentration of a element in the k0 -method is calculated using a principle that, a standard having approximately the same matrix as the sample with known mass (W_{stndrd}) of the element is irradiated for equal irradiation time simultaneously with a sample of known mass (W_{samp}) and counted with the same detector at fixed geometry, so that the concentration of the element in the sample ρ is give by the equation:

$$\rho = \frac{(\frac{N_p}{DCWt_c})_{samp}}{(\frac{N_p}{DCWt_c})_{stndrd}} \tag{19}$$

where D=exp(-λ t_d), C=1-exp(-λ t_c) and N_p=net number of of counts in the full-energy peak corrected for pulse losses, t_c=counting time, t_d=cooling time, λ=decay constant of the element. This is under the assumption of the neutron flux is the same for the sample and the standard(10).
In ENAA, the method called K_0 standardization was used. The equation for the

concentration of the element having 1/E, (n,γ) cross-sections in the epithermal energy region, Hgdahl convention is followed and the concentration (ρ(ppm)) of an element in the sample is calculated as:

$$\rho(ppm) = \frac{(\frac{\frac{N_p}{t_c}}{SDCW})_{samp}}{(\frac{\frac{N_p}{t_c}}{SDCW})_{std}} \frac{1}{k_0} \frac{f + Q_0(\alpha)_{std}\epsilon_{p,(std)}}{f + Q_0(\alpha)_{samp}\epsilon_{p,(samp)}} \tag{20}$$

$$k_0 = \frac{M_{std}\theta_{samp}\sigma_{0,samp}\gamma_{samp}}{M_{samp}\theta_{std}\sigma_{0,std}\gamma_{std}} \tag{21}$$

$$Q_0(\alpha) = \frac{Q_0 - 0.429}{(E_{ri})^{\alpha}} + \frac{0.429}{(2\alpha + 1)(E_{cd})^{\alpha}} \tag{22}$$

$$Q_0 = \frac{I_0(\alpha)}{\sigma_0} \tag{23}$$

$$f = \frac{\phi_{th}}{\phi_{epi}} = (R_{cd} - 1)Q_0(\alpha) \tag{24}$$

Where,

$samp$ = element to be analyzed in the sample., std=standard

N_p = peak area corrected for pulse loses.

W_{samp} = Molar mass of the analyte, M_{samp}= sample mass.

$\epsilon_{p,samp}$ = Full energy detector efficiency, at the energy peak of the analyte.

$\epsilon_{p,std}$ = full energy detector efficiency at the comparator peak.

ϕ_{th} = Thermal neutron flux.

ϕ_{epi} = Epithermal neutron flux.

θ = Isotopic abundance.

σ_0 = Thermal neutron (n, γ) cross section.

γ = Absolute gamma intensity (gamma emission probability of the isotope)

α = The measure of the deviation of the epithermal neutron fluence shape from the $\frac{1}{E}$ shape.

I_0 = resonance integral.

E_{cd} = cadmium cut-off energy, E_{cd}=0.55ev

E_{ri} = effective resonance energy.

Mentioning only the parameters which are specific to the k0-standardization, the user is confronted in practice with the following situation (2; 7):

(a) All relevant nuclear data (k_0, Q_0, E_γ) should be obtained from experimentally verified data center.

(b) Factors which should be determined experimentally are, peak efficiency curve i.e, log (eff) versus log (E_γ) for point sources at specific detector distance, f and α.

2.2 Epithermal Neutron Activation Analysis (ENAA)

The most important source for determination of trace elements by activation analysis is the nuclear reactor, due to its relatively high flux of bombarding particles and the relatively high cross section for the radiative capture reaction (n, γ) of thermal neutrons. The neutron energy spectrum in a nuclear reactor is usually divided, for convenience into three portions and their relative abundances are dependent on the reactor structure. The most abundant fraction is thermal neutrons, i.e. those neutrons which are in thermal equilibrium with the moderator atoms. Their most expected energy is equal to kT (where k is the Boltzmann's constant, T is the neutron temperature), which at room temperature is equal to about 0.025 eV. The neutrons with energy above that of the thermals are divided into fast neutrons, those which are directly from fission and have not been moderated at all and their energy is mainly above 1 MeV, and epithermal neutrons, i.e. partly moderated and having energy between 1 eV and 1 MeV (11). Usually in activation analysis, use is made of the whole spectrum of neutrons although the samples are activated mainly by the (n, γ) reaction of the thermal neutrons due to their higher flux and larger cross sections. However, the use of thermal neutrons has several drawbacks in some cases.

In many matrices the main elements are strongly activated by the thermal neutrons (e.g. Na and CI in biological samples and Na, A1 and Mn in rock samples) and their Compton scattered gamma rays interfere with the measurement of the gamma rays of the trace elements. In other cases, some of the elements cannot be determined either due to the too long half-life of the produced radio nuclide or since it does not emit gamma rays. In some cases, these difficulties can be overcome by the use of epithermal neutron activation. In this method the samples are activated not with the whole spectrum of reactor neutrons but rather after passing through a filter to remove the thermal neutrons. Although the activation is with both epithermal and fast neutrons, it is usually called epithermal neu-

tron activation analysis (ENAA). The main bulk elements ($Na, CI, A1, Fe, Mn$) have a fairly high cross section for the radiative capture reaction (n, γ) with thermal neutrons. However, fortunately these cross sections follow the common $1/v$ law, which means that the cross-section is inversely proportional to the square root of the energy of the neutrons and hence these elements are activated considerably less by the epithermal neutrons. In contrast, some of the trace elements of interest have high resonance integrals indicative of a relatively high cross section of (n, γ) reaction with epithermal neutrons (12).

Consequently, the use of filters (absorbers) for the thermal neutrons will lead to relative enhancement of the activity due to the trace elements(7; 11). Cadmium, Cd, or boron, B, is normally chosen as the thermal neutron filter although the choice will depend on whether the filter is to be handled. Cd activates well to produce short- and long-lived nuclides, so if the sample is to be unloaded there may be a risk of a high radiation dose. For short-lived nuclides, where there is no time to unpack the sample, the activity of the filter will be too high to count the sample. B, which is not activated except for trace impurities, is preferred in these situations. The problem is avoided altogether by the installation of a permanent facility so the choice of filter material can be made solely to optimize enhancement of the nuclide of interest. In the work (13), have shown how the thickness of Cd and B affects the neutron cut-off energy of the filter. For Cd the cut-off is at 0.55 eV for 1 mm thickness (6).

In a reactor, the flux density of the epithermal neutrons per unit energy interval is considered to be inversely proportional to the neutron energy. In fact, this assumption is valid only if the following conditions are satisfied:-

a . The medium in which fast neutrons are being slowed down is homogeneous and infinite.

b. The slowing down power is energy-independent.

c. The fast neutron sources are homogeneously distributed.

d. There is no absorption during the moderation processes.

e. The moderating atoms have the same mass as the neutron and behave as free particles.

In practice, however, these conditions are not met in a nuclear reactor. Thus, deviations from the E^{-1} law can occur in irradiation channels and errors could be induced in the resonance integral. In order to take into account all the effects mentioned above, several representations and formalisms (7; 9) have been established. Among these, the $E^{-(1+\alpha)}$ distribution has been the most frequently used in recent years as given in Eq. 20. The term α is a positive or negative coefficient which is assumed to be energy-independent, its

values depending on the reactor configuration.

Knowledge of the coefficient α in the irradiation channel is required to correct the resonance integral values for the accuracy of the single comparator method in neutron activation analysis. The K0 analysis is best applicable for the ENAA in most of the laboratories having no analysis software installed computers.

2.3 Neutron Sources

Neutron activation analysis requires the flux of neutrons which can be obtained from neutron sources (2). A neutron source is any machine that emits neutrons, irrespective of the mechanism used to produce the neutrons (14). Neutron source devices are used in physics, engineering, medicine, nuclear weapons, petroleum exploration, biology, chemistry and nuclear power.

The following are some of the main sources of Neutron:
Spontaneous Fission. Certain isotopes undergo spontaneous fission with emission of neutrons (14; 15). The spontaneous fission of uranium, plutonium, or other heavy elements is an important source of neutrons. An understanding of this complex process can be aided by visualizing the nucleus as a liquid drop. The strong, short-range nuclear forces act like a surface tension to hold the drop together against the electrostatic repulsion of the protons. In the heaviest elements the repulsive forces are so strong that the liquid drop is barely held together. There is a small but finite probability that the drop will deform into two droplets connected by a narrow neck (saddle point). The two droplets may spontaneously separate into two fragments. Within 10^{-13} s of scission, each of the two fragments emits a number of prompt neutrons and gamma rays.

Neutrons can be produced by nuclear fission in a reactor (14; 15).
Because neutrons are emitted in fission, a self-sustaining chain reaction is possible by lowering the energy of the newly produced neutrons to thermal region. The thermal neutrons being captured by the fuel nucleus induces fission and produces two to three neutrons (2.5 neutrons per fission as an average.) An illustrative picture of fission of the uranium capturing thermal neutron is shown in the figure 4.
Highly Enriched Uranium Fuel (93%), ($^{235}U_3O_8 + Al$), can be used in a research reactors like the Nigerian Miniature Pool type Research Reactor. In modern reactors the enrichment of the fuel is around 20 percent. The neutrons born in fission have an average kinetic energy of about 2 Mega-electron volts, 2 MeV. They are slowed to thermal energies (20 -

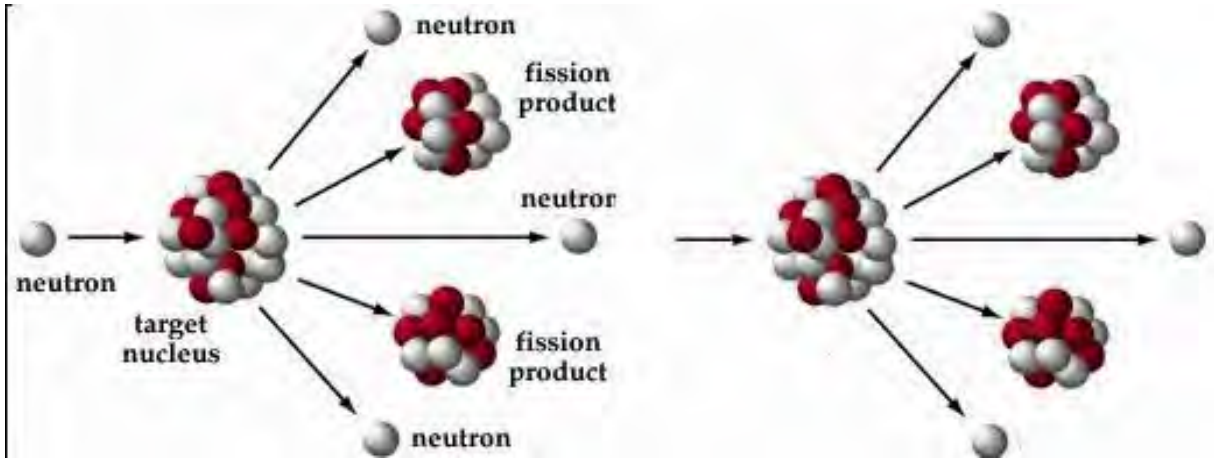

Figure 4: Diagram of fission of a fissile nucleus capturing thermal neutrons. (Taken from (14)).

400 milli- eV) by scattering from the molecules of the heavy water (D_2O) moderator in the reactor (14). In thermal equilibrium, the neutron energy spectrum is determined solely by the temperature of the moderator (a Maxwell-Boltzmann distribution), analogous to the motion of atoms in an ideal gas. To reach lower energies, therefore, we introduce D_2O Coolant. In general, reactors produce continuous neutron beams (14).

(α, n) reaction (15).
Neutrons are produced when alpha particles impinge upon any of several low atomic weight isotopes which include beryllium, carbon, oxygen etc. and produces a reaction with them (α, n) reaction. Example of such a reaction can be, $\alpha + {}^{18}O \rightarrow {}^{21}Ne + \text{n}$. (α, n) reactions can be used to construct a neutron source by intermixing a radioisotope that emits alpha particles such as radium or polonium with a low atomic weight isotope, usually in the form of a mixture of powders of the two materials. The useful lifetime for these types of sources is highly variable, depending upon the half life of the radioisotope that emits the alpha particles. The size and cost of these neutron sources are also comparable to spontaneous fission sources. Usual combinations of materials are plutonium - beryllium (PuBe), americium-beryllium (AmBe), or americium- lithium (AmLi).

(γ, n) reaction (15).
The (γ,n) reaction can produce neutrons in any element if the gamma-ray energy is high enough. The typical minimum threshold energy ($\backsim$8 MeV) is much higher than the energies of gamma rays emitted from radioactive nuclides. However, the (γ, n) threshold energies for beryllium (1.66 MeV) and deuterium (2.22 MeV) are anomalously low. Radioisotopes Which Decay With High Energy Photons, (γ, n) reaction, Co-located With

Beryllium or Deuterium Gamma radiation with an energy exceeding the neutron binding energy of a nucleus can eject a neutron. Two examples and their decay products:
$^{9}Be + \gamma$ (>1.7 Mev) $\rightarrow$ 1 neutron + ^{4}He
^{2}H(deuterium) + γ (>2.26 MeV) $\rightarrow$ 1 neutron + ^{1}H

Some accelerator-based neutron generators exist that work by inducing fusion between beams of deuterium and/ or tritium ions and metal hydride targets which also contain these isotopes.

Plasma Focus Neutron Source (15).
The plasma focus neutron source produces controlled nuclear fusion by creating a dense plasma within which ionized deuterium and/or tritium gas is heated to temperatures sufficient for creating fusion.

Accelerators. Light Ion Accelerators Traditional particle accelerators with hydrogen (H), deuterium (D), or tritium (T) ion sources may be used to produce neutrons using targets of deuterium, tritium, lithium, beryllium, and other low-Z materials. Typically these accelerators operate with energies less than 1 MeV range. (14)

Neutron scattering. (n,n') reaction can occur in heavy nuclei with neutron energies of roughly 0.1 to 1.0 MeV or higher (15). This reaction is possible if the target nucleus has energy level slow enough to be excited by the neutron. The (n,2n) reaction can increase the number of neutrons present, but the threshold energy in most elements is in the range of 10 MeV. For deuterium, beryllium, and tungsten the thresholds are lower, but the number of extra neutrons produced is likely to be small. The possibility of (n,2n) reactions should be considered only when the neutrons are known to have high energy and when deuterium, beryllium, or tungsten are present.

2.4 Naturally Occurring Radioactive Materials (NORM)

NORM are radioactive materials that exists in nature. From the beginning the earth was created, NORM can be found almost everywhere, in soil, air, public water supplies, oil and even in our bodies (16).

There are approximately 70 naturally occurring radionuclides on earth. Most of them are heavy elements radioactively present in the natural decay chains, but there are several important radioactive light elements, such as ^{3}H, ^{14}C, ^{40}K, etc. These radioactive species

are ubiquitous, i.e they exist every where at the same time, occurring in plants, animals, the air we breathe, the water we drink, the soil, etc. For example, in a typical US diet,one ingests $\backsim$ 1 PCi/day of ^{238}U, ^{226}Ra, and ^{210}Po (17). The air we breath contain 0.15 PCi/L of ^{222}Rn, the earth's crust contains 10ppm and 4ppm of the radio nuclei Th and U respectively. One should not forget that the interior heat budget of the planet earth dominated by the contribution from the radioactive decay of uranium, Thorium and potassium.

The naturally occurring radionuclides can be classified as (18):

a. Primordial. Nuclides that have survived since the time the elements were formed.

The primordial radionuclides have half-lives greater than 10^9years or are the decay products of these nuclei. This class includes ^{40}K ($t_{1/2} = 1.277x10^9y$), ^{87}Rb ($t_{1/2} = 4.75x10^{10}y$), ^{238}U ($t_{1/2} = 4.467x10^9y$), ^{235}U ($t_{1/2} = 7.04x10^8y$) and ^{232}Th ($t_{1/2} = 1.41x10^{10}y$) as its most important members. (Additional members of this group are ^{115}In, ^{123}Te, ^{138}La, ^{144}Nd, ^{147}Sm, ^{148}Sm, ^{176}Lu, ^{174}Hf, ^{187}Re, and ^{190}Pt.) (18; 19)

^{40}K is a β-emitting nuclide that is the predominant radioactive component of normal foods and human tissue. Due to the 1460 keV γ-ray that accompanies the β-decay, it is also an important source of background radiation detected by γ-ray spectrometers. The natural concentration in the body contributes about 17 mrem/year to the whole body dose. The specific activity of ^{40}K is approximately 855 PCi/g potassium. Despite the high specific activity of ^{87}Rb $\backsim$ 2400 PCi/g, the low abundance of rubidium in nature makes its contribution to the overall radioactivity of the environment small (18; 16).

There are three naturally occurring decay series. They are the uranium ($A = 4n+2$) series, in which ^{238}U decays through 14 intermediate nuclei to form the stable nucleus ^{206}Pb, the actinium or ^{235}U (A = 4n + 3) series in which ^{235}U decays through 11 intermediate nuclei to form stable ^{207}Pb and the thorium (A = 4n) series in which ^{232}Th decays through a series of 10 intermediates of stable ^{208}Pb as shown in figure 5.

The notation 4n+2, 4n, 4n+3 refers to the fact that the mass number of each member of a given chain is such that it can be represented by 4n, 4n+2, 4n+3 where n is an integer. (There is an additional decay series, the 4n+1 series that is extinct because its longest lived member, ^{237}Np, has a half-life of only $2.1x10^6$ y, a time that is very short compared to the time of element formation.)

The uranium series contains two radionuclides of special interest, $^{226}Ra(t_{1/2} = 1600y)$ and its daughter $^{222}Rn(t_{1/2} = 3.8days)$. ^{226}Ra (and its daughters) are responsible for a major fraction of the radiation dose received from internal radioactivity. Radium is present in rocks and soils and as consequence in water, food and human tissue.

^{226}Ra decays by α- emission to ^{222}Rn. The later nuclide is the principal culprit in the radiation exposures from indoor radon. Although radon is an inert gas and is not trapped in the body, the short lived decay products are retained in the lungs when inhaled and if the ^{222}Rn decays while it is in the lungs. Indoor radon contributes about 2mSv/yr of the average radiation exposure. Under normal circumstances, radon and its daughters attach to dust particles and are in equilibrium amounts, these dust particles can also deposit in the lungs. These may result lung cancer, for instance in the U.S. 5,000 - 10,000 cases of lung cancer are due to radon exposure (18; 16).

b. Cosmogenic. Shorter lived nuclides formed continuously by the interaction of cosmic rays with matter.

Cosmogenic nuclei are produced by interaction of primary and secondary cosmic radiation with nuclei in the stratosphere. The most important of these nuclei are ^{3}H,^{14}C, and ^{7}Be. These nuclei move in to the troposphere through normal exchange process and are brought by the earth's surface by rain water. Equilibrium is established between the production rate in the primary cosmic ray interaction and the partition of the radio nuclides amongst the various terrestrial compartments leading to approximately constant specific activity of each nuclide in particular compartment. When an organism dies after being in equilibrium with the biosphere the specific activity of the nuclide in that sample will decrease since it is no longer in equilibrium. This behavior allows for dating.

c. Anthropogenic. Wide variety of nuclides introduced in to the environment by the activities of man, such as nuclear weapons tests, the operation of nuclear power plants etc.

This group of nuclides includes the previously discussed cases of ^{3}H and ^{14}C, along with the fission products and the trans uranium elements. The primary sources of these nuclides are nuclear weapons tests and nuclear power plant accidents. Except

for ^{3}H and ^{14}C the anthropogenic contributions from nuclear weapons testing or use which is the most significant source of man made environmental exposure are negligible compared to other sources of natural radioactivity. (The principal component of these large releases of radioactivity was shorter-lived fission products like ^{131}I, which have decayed, leaving ^{137}Cs,^{90}Sr, and the Pu isotopes (18; 19; 20).

2.4.1 NORM Chains

Three naturally occurring radioactive decay chain families are found in significant amounts on earth. Others also exist which resulted from atomic weapons explosions to make ^{239}U, ^{241}Am, etc. The three primordial series of nuclides are called the Uranium, Thorium and Actinium series.

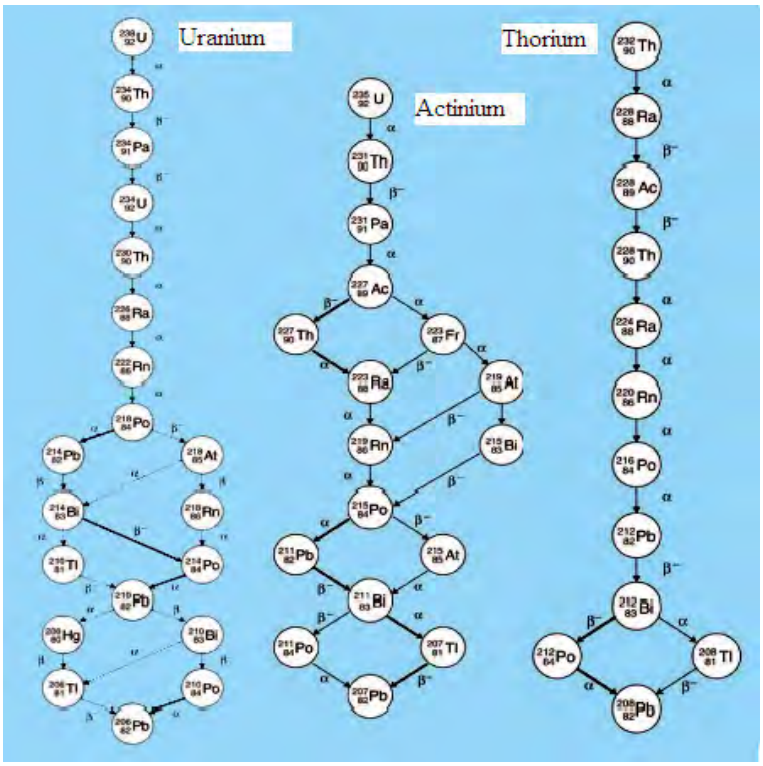

Figure 5: Diagram of natural decay chains (18).

Radioactive decay series can be defined as groups of isotopes representing various stages of radioactive decay in which heavier members of the group are transformed into successively lighter ones, the lightest being stable (18).
Most naturally occurring radioactive material obeys a chained series of transformation

rather than decaying in a single step. During the decay the nuclei in the chain emit various types of radiation (mostly either beta or alpha particles), until ending in a radioactively stable nuclide. Usually the concentrations of parent isotopes decrease as the decay progresses. In the mean time, the concentration of their daughter products increases (18).

In the earths crust ^{238}U constitutes 99.27 % of natural Uranium by mass, in comparison, ^{235}U makes up only about 0.72 %. As illustrated in figure 5, the Uranium decay chain, headed by ^{238}U ends via 18 intermediate stages at stable ^{206}Pb. The Actinium series starts with ^{235}U producing 15 daughter radio nuclides and stops at ^{207}Pb. Finally, the beginning of Thorium decay chain is ^{232}Th and ends at ^{208}Pb, including 10 daughter products (17). In a radioactive decay chain the parent nucleus decays with a certain decay constant, and while the parent decays, the daughter nucleus concentration starts to grow to some point and then decay away with another decay constant. The process continues until it reaches a final stable nuclide. Radioactive equilibrium takes place when each radioactive nuclide decays at the same rate of the parent nuclide this happens only when the half life of the parent is much larger than that the half life of the daughter product. After about 7 half lives of the daughter, the mother and daughter activities become equal. This kind of equilibrium is called secular equilibrium (18). Therefore, Measuring the activity of the daughter is the same as measuring the activity of the parent indirectly at the secular equilibrium. In order to reach at the time of secular equilibrium, the sample should at least be kept for about 7 half lives of the radioactive daughter before the start of the measurement.

Chapter Three

3 Method and Materials

3.1 Method

3.1.1 Basic Description of the Analytic Method

Activation analysis is an analytical technique that allows one to determine the amount of a given element X contained in some material Y. The basic steps in the activation technique are as follows:

i. Irradiate sample of the material Y with a source of neutron radiation so that X will change in to $(X + n)^*$, an unstable radioactive isotope of X. This isotope further decays by giving some particle radiation, mostly beta particle, then becomes radioactive daughter of $(X + n)^*$ which is Z^*.

ii. Using instrumental techniques, isolate Z^* from all other elements in Y and measure its activity. Instrumental isolation of the activity of interest involves the detection of radiation that can uniquely identify the nuclide in question.

iii. Calculate the amount of X present (using Eq. 17). Use of Eq. 17 is for absolute activation analysis which is done rarely because it needs detailed knowledge of the flux, energy of the bombarding particle in the sample, capture cross section, decay branching ratios, etc. A better technique, comparator technique, is to irradiate and count a known amount of pure X under the same conditions as the sample of material Y then use Eq. 18 to calculate the concentration.

3.1.2 Advantages and Disadvantages of the Method (Activation Analysis)

The use of Activation analysis has advantages over other techniques in the following aspects.

Use of activation analysis can lead to measurement of elemental abundances of the order of 10^{-6} to 10^{-12}g. Although the high sensitivity of activation analysis is perhaps its most striking advantage, there are a number of other favorable aspects as well. Activation analysis is basically multi elemental technique. Many elements in the sample will become radioactive during irradiation; and if each of these elements can be "isolated" instrumentally, their abundances may be determined simultaneously. Activation analysis

is non destructive and highly accurate method of analysis.

Activation analysis is not with out its drawback, however. Among them the need to use expensive equipment and irradiation facilities, the inability to determine the chemical state of the elements in question, the need to work with significant level of radioactivity which brings some health related problems to the personnel working in the INAA laboratory, with their attendant radiation safety and legal problems and the relatively longer time needed to complete analyses.

3.1.3 Method of Uncertainty Considerations

Neutron Activation Analysis Laboratories of Nuclear and Energy Research have been using instrumental neutron activation analysis (INAA) in studies like environment monitoring, reference material certification, food and diet analysis and archeology. According to internationally accepted instructions, the sources of uncertainty for the relative method of INAA applied to geological and biological materials were sample mass, elemental standard mass, element decay constant, sample activity, elemental standard activity and different time uncertainties (21). In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source.

Among the techniques of standardization the comparator method for which the individual uncertainty components associated with measurements made with neutron activation analysis (NAA) were considered in this section. This description assumes basic knowledge of the NAA method, and that experimental parameters including sample and standard masses, as well as activation, decay, and counting times have been optimized for each measurement. It also assumed that the neutron irradiation facilities and gamma-ray spectrometry systems have been characterized and optimized appropriately, and that the choice of irradiation facility and detection system is appropriate for the measurement performed. Careful and thoughtful experimental design is often the best means of reducing uncertainties. The comparator method involves irradiating and counting a known amount of each element under investigation using the same or very similar conditions as used for the unknown samples. Summarizing, relative calibration by the direct comparator method renders the lowest uncertainties of the measured values.

Each of the separate contributions to uncertainty is referred to as an uncertainty component. The expanded uncertainty provides an interval within which the value of the

measurand is believed to lie with a higher level of confidence (22).

The comparator method involves irradiating and counting a known amount of each element under investigation using the same or very similar conditions as used for the unknown samples. Summarizing, relative calibration by the direct comparator method renders the lowest uncertainties of the measured values.

Under proper conditions the counting systems and the associated programs have a great influence on the neutron activation analysis methods. However it is important to be aware of the limitations of each of the components which may give rise to erroneous results without any warning. The components cumulative effect can be obtained using Eq.25, the propagator equation (22). The equation gives the total uncertainty contributed from each of the components of Eq.17 which were believed to bring limitations on the result of the analysis.

$$\sigma_{C(x)} = C(x)\sqrt{(\frac{\sigma(m_{x(std)})}{m_{x(std)}})^2 + (\frac{\sigma(m_{x(samp)})}{m_{x(samp)}})^2 + (\frac{\sigma(n_\gamma)}{n_\gamma})^2 + (\frac{\sigma(t_i)}{t_i})^2 + (\frac{\sigma(\lambda)}{\lambda})^2 + (\frac{\sigma(t_d)}{t_d})^2 + (\frac{\sigma(t_c)}{t_c})^2} \tag{25}$$

The major components which were given a special focus were:

a. Linear attenuation coefficient (μ_l).

Linear attenuation coefficient (μ_l) is almost purely dependent on the matrix composition and mass, which is reasonably well known. The amount of material to be irradiated and to be counted is often set by availability, sample encapsulation aspects and safety limits both related to neutron self-shielding and gamma-ray self-absorption effects. For these reasons practically the sample mass is often limited to approximately 250 mg for biological samples and 150 mg for geological samples so that the effect of gamma attenuation and neutron self shielding were minimized to negligible values.

b. The neutron flux.

These are clearly set by the available irradiation facilities, in the control consul of the reactor. But for the comparator method of INAA, the neutron flux cancels out so that there is no its effect in the uncertainty of the results.

c. The duration of the irradiation time.

This is set by practical aspects, such as the limitations in total irradiation dose of

the plastic containers because of radiation damage, the half life of element of interest (long or short irradiation time). The maximum irradiation time for polyethylene capsules is usually limited to several hours, for instance 5 hours at a flux of $5x10^{11}cm^{-2}s^{-1}$. The uncertainty associated with the irradiation time is minimized to zero because the irradiation time is controlled by automated system of the control consul, it displays the exact time of irradiation reducing the time taken by the sample to inter in to the reactor and retrieve it from the reactor.

d. The duration of the counting time.

A very long counting time may set limits to the number of samples processed simultaneously in case the radioactivity decays considerably during this counting time. Care was taken on the strength of the sample activity to be counted, before it is put in to the detector facility in order to minimize the detector dead time and it was kept below 10%. The detector dead time was registered and reduced from the total counting time by a facility in the acquiring software MAESTRO. So that the uncertainty associated with the counting time was taken in to account and minimized to zero.

Special care was taken to register the time at the instant of the start of counting the activity of the sample to avoid the uncertainty associated with the decay time.

e. Sample mass and standard mass.

The amount of material to be irradiated and to be counted was limited by the aspect of minimizing self shielding and attenuation. But to measure exact dried mass of the samples and standards a technique of oven drying was employed. Example, a mass of around 250 mg from a homogenized sample of biological material was measured and placed in to a ceramic cup washed with distilled water and rinsed with acetone, then put in to an oven at $60C^0$ for 6 hrs then its mass was measured and registered, again it is put in to the oven for 6 hrs at $60C^0$ then measured and registered, the same procedure was repeated until the sensitive micro gram mass balance displays constant mass of the sample. By such a technique the uncertainty that can be aroused from the mass of the sample was minimized to negligible effect.

f. The detectable total induced radioactivity.

The total induced radioactivity that can be measured is set by the state-of-the-art of counting and signal processing equipment, with additional radiation dose (back ground radiation), shielding considerations, the detector size, counting geometry, the gamma energy intensity, the decay constant. The detector's characteristics were set in advance by determining its efficiency at different geometries and its calibration

results. Uncertainties from such aspects were measured by the analysis software WINSPAN using repeated measurements of the spectrum and analyzing the concentration from each measurements. The uncertainty values obtained during the repeated measurements were give as "±" with the value of the concentrations.

3.1.4 Study Area

A region in North-East of "Welkite" zone of Ethiopia called "Eja wereda", its map is shown in the Fig.6, is taken as the area for focus of this dissertation. This is because the environment of "Eja" is potentially rich rural part, which grows all crops including very known plant called "Eset" which the people in the surrounding eats its products called, "Wusa" with "Kitfua", "Atmet" and "Wohta".

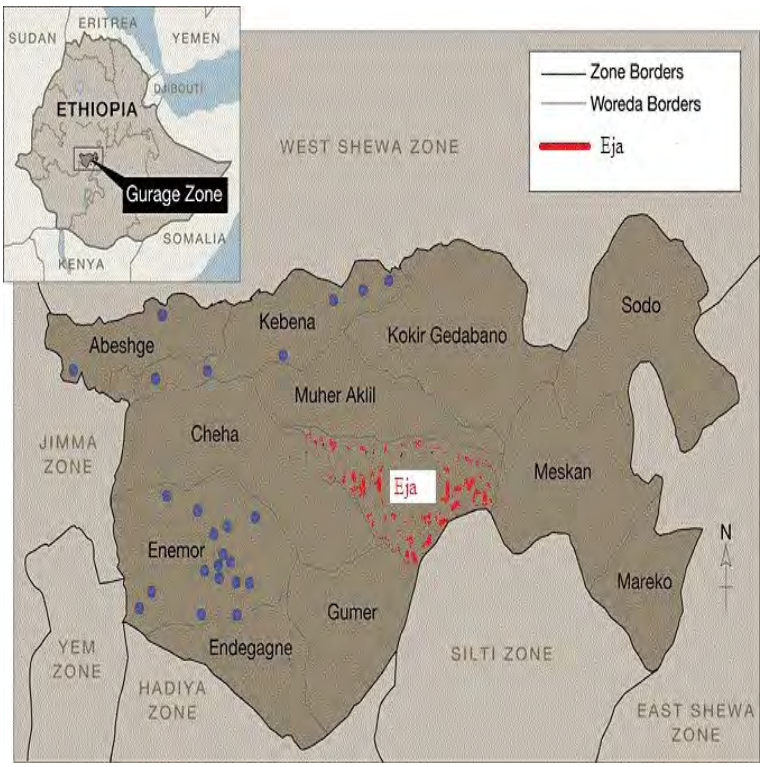

Figure 6: The map of the research area.

In the region there are plant medicines of Ethiopia origin plants locally called "Abesha Ded", "Chima", "Zigba",etc. The plants are found inside three forests of the region "Kotergedra", "Genemar" and "Yame". There is mineral soil called "Ewoa" in the region in which the people use for different purposes, for animal food spice, kooking spice of cabbage and washing clothes. This area is known to the researcher due to having long experience as he is the member of "Eja" community.

3.1.5 Scope and Sample Collection

The scope is to explore the region for potentially available samples and produce some scientific data using the practical application of the well known nuclear reaction (n, γ). The following five areas (four based on INAA and one based on NORM measurement) were the concerns of the dissertation.

i. Multi elemental analysis of the flower of the flowering plant, called "Chima" which the people in the region uses as a medicine for intestinal parasites mainly for tapeworm.

ii. Multi elemental analysis of a mineral soil called "Ewoa", which the surrounding people uses it as a spice and medicine for animals, some times for cooking and washing cloths.

ii. The NORM measurement of the mineral soil called "Ewoa".

iii. Multi elemental analysis of the major food of the society in the surrounding, "Atmet".

v. Comparison of elemental concentrations in two medicinal plants "Astara" and "Guariye" used by the society as a healing for wound and bone related problems.

Samples were collected in the manner which represents the surrounding area of the Shamene region. The detail of the collection of sample of the materials which were the focus of the dissertation are given in each chapters where the procedure of the experiment and the result of the analysis of the samples were described in depth.

3.1.6 Sample Irradiation and Spectrum Acquisition

The samples were thoroughly mixed to ensure homogenization and were properly dried, then irradiated in a reactor and facilities at the Nigerian Research Reactor-1 (NIRR-1). A similar procedure were adopted for IAEA Standard Reference Materials (SRM) and Certified reference materials(CRM). The purpose of the SRM and CRM is for quality control of the experimental procedure.

Each of the sample and the standards were counted in High Purity Germanium solid state detector (HPGe) which was connected with multi channel analyzer. A computer supported with acquisition softwares was used to store channel number, peak Energy, peak area and Peak count informations including the spectrum of each of the samples. The informations were used to calculate for the qualitative and quantitative search of elements which constitute the sample.

3.1.7 NORM Measurements

This has to do with the presence of Naturally Radioactive Materials in the sample. Samples were dried, Mixed homogeneously, packed and sealed in to a cylindrical plastic containers which fit the geometry above the a Sodium iodide scintillation counter (NaI(Tl)) kept inside a lead shield. The filled plastic container will be kept for at least 28 days, until the transient equilibrium is attained (19). The samples were counted for NORM determination using NaI(Tl) detector for eight hours. Standard reference material sealed with the same manner were counted with the same detector at the same geometry as the sample for quality assurance.

3.2 Materials

During this work the following facility, instruments and chemicals were used.

3.2.1 Facility and Instruments

i. Thermal and epi-thermal neutron source, Nuclear reactor facility

In this work NIRR-1 facility which is displayed in the figure Fig. 7 was used for the purpose of irradiating samples. The NIRR-1 is swimming pool-type reactor with a power of 30 kWh at the Center for Energy Research and Training, Ahmadu Bello University, Zaria which uses high-enriched uranium (93%) as fuel and heavy water (D_2H) as moderator and coolant.

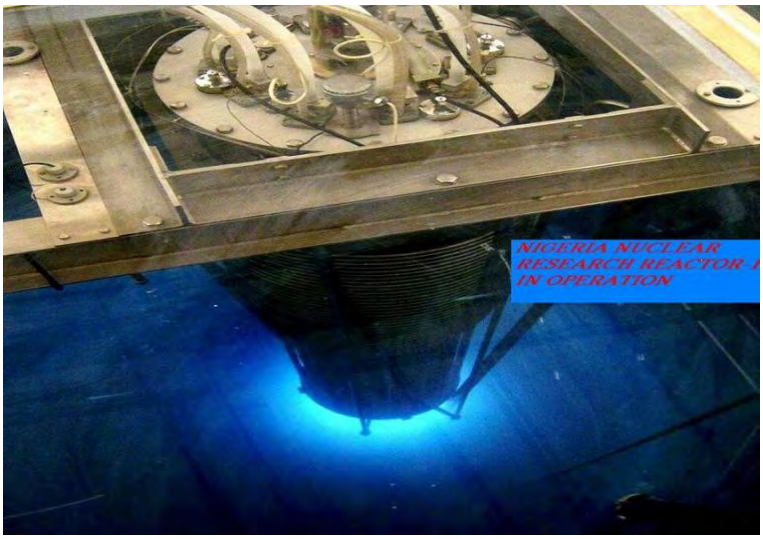

Figure 7: Pool type Nigerian Nuclear research reactor NIRR-1

ii. Gamma ray detector

High resolution gamma-ray spectrometer and NaI(Tl) gamma ray detector were used in this study. High-purity Germanium (HPGe) detector was, (Model:AL30 ORTEC, Serial: DCC 97A202) having 30 percent relative efficiency with energy resolution of $1.95keV$ for ^{60}Co photo peak at 1332 keV. The detector was as shown in the figure8. The NaI(Tl) gamma detector was model 905-4, and 3 inch by 3 inch crystal. The detector was as shown in the figure 9.

Figure 8: High-purity Germanium HP(Ge) detector inside lead shielding

Figure 9: NaI(Tl) gamma detector inside lead shielding

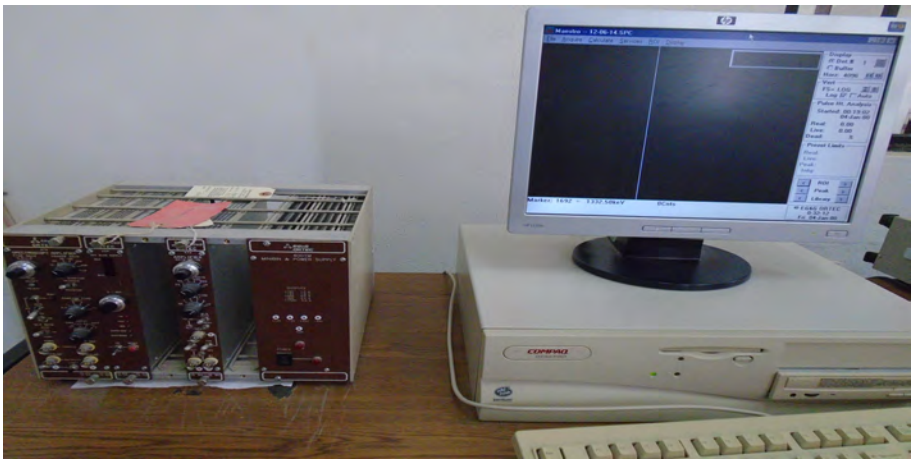

Figure 10: Analysis softwares MAESTRO and WINSPAN installed in computers connected with MCA

Figure 11: Micro gram mass balance measuring NORM sample

Figure 12: Heat regulating oven

Figure 13: polyethylene vials

Figure 14: Plastic containers used to seal NORM samples

Figure 15: Radiation servey meter

Figure 16: Desketor

iii. Multichannel analyzer (MCA), and associated electronics

High Voltage supply model 659 ORTEC, 5kV- spectroscopy amplifier model 672 ORTEC, was connected to an ORTEC 570 spectroscopy amplifier, Multichannel Analyzer, acquisition interface card ADC with computer and basic spectroscopy software (Winspan 2003 and MAESTRO) were used. The system was connected as shown in the figure 10.

iv.Standard point sources of gamma, ^{137}Cs**,**^{60}Co**,** ^{241}Am**,** ^{27}Na

Energy and efficiency calibration of the detector was done using standard gamma sources.

v. Micro gram Mass Balance

The mass of environmental samples taken from the research area and the sample of standard reference materials were measured using very sensitive digital micro gram mass balance shown in the figure 11.

vi. Heat regulating oven

Different wet samples were dried in an oven at different temperatures and for different length of time. The picture of one of such ovens is shown in the figure 12

vii. Polyethylene Vials

polythene vials were used holding the sample of mass between 150 g and 200 g for geological samples and between 200 mg and 250 mg for biological samples tightly closed and sent in to the reactor for irradiation through pneumatically air tight tube, the vials were of different size to hold samples horizontally in to the reactor core. One type of the vials used were as shown in the figure 13.

viii. plastic containers of different size to seal NORM samples

Samples for the measurement of Naturally occurring radioactive materials (NORM) were packed in to a plastic containers that can hold about 300 g to 500 g. Samples were sealed tightly till secular equilibrium. The containers were having the same geometry as the sample putting space of the NaI(Tl) gamma detector's lead shielding. Some of such sealed containers were as shown in the figure 14.

ix. Hand Gloves, Plastic sheet, Spachula, Forceps

In order to keep samples from any contamination while preparing for irradiation, two new hand gloves were used for each and every sample prepared and the gloves were put in a garbage before the start of preparing the next sample. A spatula and forceps were used to pick a sample in to its holder or reduce it from the holder when it is needed. One spachula and one forceps were used while preparing one homogeneous

sample and changed when another sample preparation was being started. De-ionized water and acetone were used to clean washed the forceps and spachulas, after dried in an oven they were re-used.

x. Hot air blower

Hot air blower is a machine which blows a hot air at a temperature enough to weld plastic holders when it is plugged at 220 v line and operated. It was used to seal a sample in a plastic sheet before it is put in to irradiation vial.

xi. Radiation Survey Meter

When a sample was irradiated and retrieved from the reactor, the activity of the sample which freshly appeared from the reactor is tested using digital radiation survey meter at some far distance using a long handle for radiation safety. If the activity of the sample is high, it was kept in place until it cools to the safest activity approximately 30 micro seviert/hr and the activity is such that the detector dead time is kept below 10%.

All the staff members of the research center have to test the position where he/she is working every time with such meters tied with the safety wear. When the radiation of the position is hazardous which gives more than the health physics standard of the working personnel, he/she has to move away from the place. The picture of one of such radiation survey meters used during the experiment is shown in figure 15.

xii. Desketor

After samples were prepared for irradiation, they have to be kept away from exposure to atmospheric moisture till the time of irradiation, otherwise it brings an error in the result of the analysis. For this reason an air tight container called Desketor with in which silicates were placed to dry the air enclosed in it while putting the samples. The picture of Desketor used during this experiment is shown in the figure 16.

xiii. High capacity computer, Hard Disc, and Flash Discs

High capacity computers were used in order to connect them with the detectors and save repeated spectrum of samples detected. Analysis and acquisition softwares were installed in to the computers to make analysis using the informations from the saved spectrum. Back up of informations have to be saved by the user using flash discs and hard disc.

3.2.2 Chemicals

For the purpose of quality control of the method used during analysis, multi element standards were irradiated and counted with the same manner and procedure as the sample. Some of multi element standards (Lichen, tomato leaves, apple leaves, spinach, coal fly ash, soil 7) used were as shown in the figure 17.

Figure 17: Multi standard comparators

Chapter Four

4 Gamma Ray Detectors

Gamma ray detectors are devices which contains materials sensitive to interaction with gamma ray of any energy and produce charge to be collected and taken as an output pulse. In order for a gamma ray to be detected, it must interact with the matter with in the detector. Fortunately, the electromagnetic nature of gamma-ray allows them to interact strongly with the orbital electrons in the atoms of all matter. The key process by which a gamma ray is detected is photoelectric effect, where it gives up part or all of its energy to an electron. The emitted electrons collide with other atoms and liberate many more electrons. The liberated charge is collected, either directly (as with a proportional counter or a solid-state semiconductor detector) or indirectly (as with a scintillation detector), in order to register the presence of the gamma ray and measure its energy. The final result is an electrical pulse whose voltage is proportional to the energy deposited in the detecting medium (26). There are many types of radiation detectors, in this section we focus only on the High Purity Germanium (HPGe) Detector and NaI(Tl) Gamma Detector, which were used during the experiment stage of the dissertation.

4.1 Detector Parameters

Qualitative and quantitative analysis of radionuclides in materials requires the use of reliable gamma-ray detection system such as HPGe detector. The quality of the measurements depends on the calibration and the performance testing of the detector among others like sampling methods, contamination, accuracy in weighing of samples, interference from background radiation, etc. Analysis of gamma emitting radionuclides in a given material is usually performed by the well established method of gamma-ray spectrometry (24). The energies of gamma-rays emitted from radionuclides in a sample of the material are usually displayed in a spectrum as a function of the pulse height. The spectrum of a mixture of a number of different radionuclides measured in a material contain peaks. For the purpose of studying these peaks correctly, the detector has to be characterized or calibrated.

There are two main parameters (Resolution and Efficiency), which have decisive role on the measuring performance of a gamma ray detector.

4.1.1 Detector Resolution

The resolution of a detector is a measure of its ability to clearly separate two peaks that are close together in energy. The parameter used to specify the detector resolution is the full width of the (full-energy) photo peak at Half its maximum height (FWHM). If a standard Gaussian shape is assumed for the photo peak, the FWHM is given by

$$FWHM = 2\sigma\sqrt{ln2} \tag{26}$$

where, σ is the width parameter for the Gaussian (27). High resolution (small FWHM) not only makes individual definition of close-lying peaks easier but also makes the subtraction of the Compton continuum less uncertain because it is a smaller fraction of the total activity in the peak region. The more complex a gamma-ray spectrum is, the more desirable it is to have the best energy resolution.

High Purity Germanium (HPGe) is good radiation detection technology that provides sufficient information to accurately and reliably identify radionuclides from their gamma ray emissions. HPGe detectors have greater improvement in resolution as compared to that of Sodium Iodide (NaI) detectors. A detector with high resolution usually gives more accurate assays than one with low resolution. The resolution of a germanium detector is typically 0.5 to 2.0 keV in the energy range of interest for NAA applications, whereas the resolution of a NaI detector is 20 to 60 keV (27; 28). It is easier to determine accurately the area of full-energy peaks in a complex spectrum when the peaks do not overlap, and the probability of overlap is less with narrower peaks. The background continuum under the full-energy peaks is easier to subtract from a high-resolution spectrum because it is a smaller fraction of the total activity in the peak region.

4.1.2 Detector Efficiency

There are four types of the detector's detecting efficiencies, the overall efficiency of the detector which we call absolute photon detection efficiency, is obtained by combining all the four types of efficiencies of the given detector as given in the Eq. 27. The basic definition of absolute photon detection efficiency (ϵ_{tot}) is the ratio of "total number of detected photons in the full-energy peak" to the "total number of photons emitted by the source" (26; 27).
This total efficiency can be expressed as the product of four factors:

$$\epsilon_{tot} = \epsilon_{geom}\epsilon_{absp}\epsilon_{sample}\epsilon_{int} \tag{27}$$

The geometric efficiency (ϵ_{geom}) is the fraction of emitted photons that are intercepted by the detector. **The absorption efficiency** (ϵ_{absp}) takes in to an account of the effects of intervening materials (such as the detector housing, special absorbers, etc.) that absorb some of the incoming radiation before it interacts with the detector volume. This term is especially important for low-energy photons for which absorption effects are most pronounced. **The sample efficiency** (ϵ_{sample}) is the reciprocal of the sample self-absorption correction. This quantity is the fraction of emitted gamma rays that emerge from the sample material to the gamma actually produced.**The intrinsic efficiency** (ϵ_{int}) is the probability that a gamma ray that enters the detector will interact and give a pulse in the full-energy peak.

NaI (Tl) detectors are known to have a comparatively poorer resolution than germanium detectors, but are preferable in some specific types of analyses (e.g. identify and measure activities of NORM) due to their relatively high efficiency, besides, they operates under room temperature conditions (i.e. without use of liquid nitrogen as in HPGe detectors) (27; 28).

4.2 HPGE detector

HPGe detectors are made by highly refining the element germanium and growing it into a crystal. The crystal goes through a series of processing steps culminating in the attachment of positive and negative contacts which turn it into an electronic diode. The special property of this diode is that it conducts current in proportion to the energy of a photon (gamma ray) depositing energy in it so that the relationship between energy and current is so precise in HPGe detectors (26).

Germanium semiconductor detectors are now the detectors of choice for high energy-resolution γ-ray studies. These detectors directly collect the charges produced by the ionization of the semiconductor material. One electron-hole pair is produced on the average for every 3 eV absorbed from the radiation. These pairs drift under an external electric field to the electrodes where they generate the pulse. The high number of information carriers leads to a small percentage fluctuation and this is the reason for the high energy-resolution of HPGe detectors (28). The block diagram of the detection using HPGe detector for the NAA system is shown in the fig. 18.

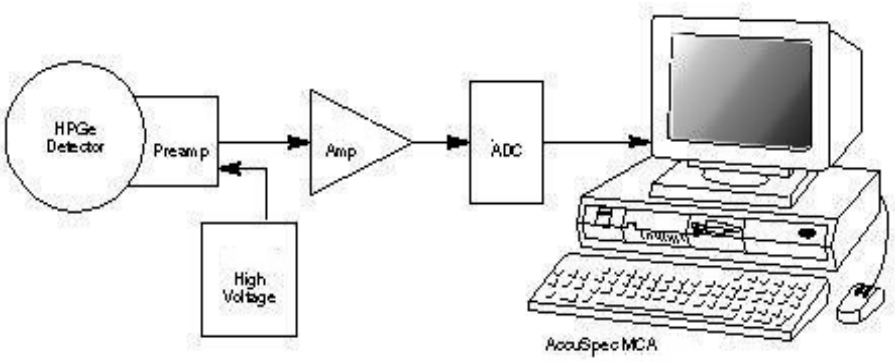

Figure 18: Block diagram of a multichannel-analyzer-based gamma-ray spectroscopy system for complex NAA applications.

4.3 Calibration of HPGe Detector used During the Experiment

In general, there are two calibration steps to determine the performance of a gamma spectrometry system (24).
Firstly, energy calibration, where the pulse height scale is calibrated in terms of gamma ray energy to enable the exact identification of photo peaks present in the spectrum produced by the detector system. Energy calibration of the detector system is performed by measuring mixed standard sources of known radionuclides with well defined energies in the energy range of interest.
Secondly, the efficiency calibration, which involves measuring reference standard sources to obtain efficiency versus energy throughout the region in the energy range of interest. In order to calculate activities of the nuclides, the user has to supply the computer program with detector efficiency as a function of the gamma-ray energy (efficiency curve) (29).

4.3.1 Energy calibration of the HPGe Detector

The counting of irradiated samples during the experiment were done using the High Purity Germanium (HPGe) detector introduced in section 3.2.1 and figure 8, its energy calibration was performed and plotted as shown in the graph 19.

The energy calibration of the detector was performed using ^{137}Cs (gamma energy 889.3 keV) and ^{60}Co (at energies 1173.2 keV and 1332.5 keV) sealed standard radioactive sources. This was done by putting both sources on the detector simultaneously, overlapping one over the other, and the gammas were acquired (or measured) for some time. The expected

Channel	Energy(Kev)
1127	889.3
1477	1173.2
1664	1332.5
0	0

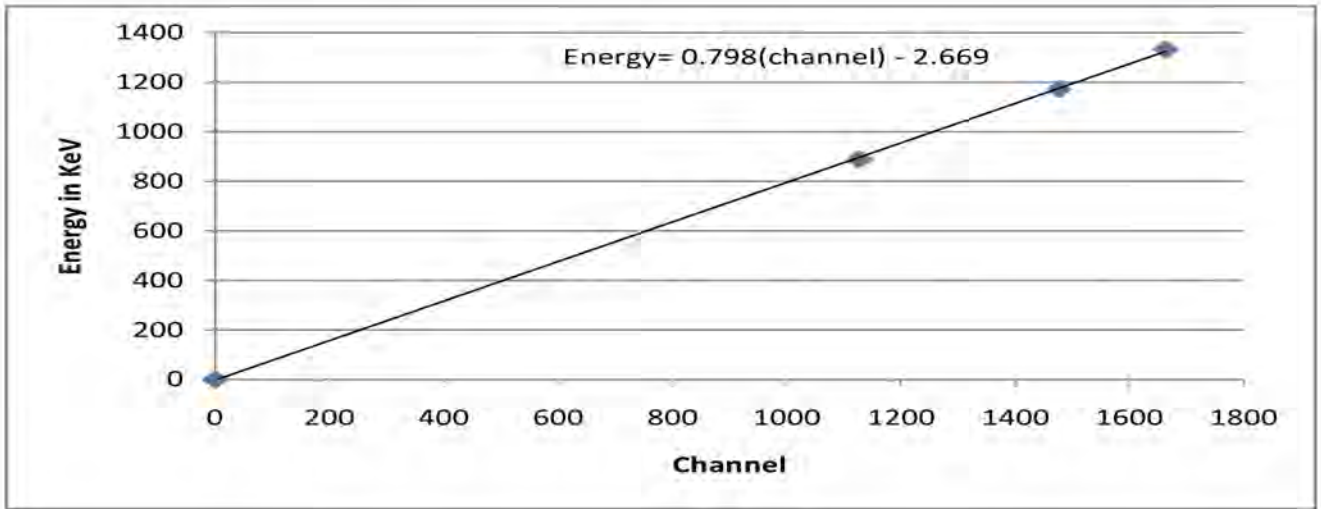

Figure 19: Experimental energy calibration curve of the HPGE detector for three different peaks of cobalt and cesium.

three gamma rays were seen appearing in the spectrum and adjusting the knobs (course gain, fine gain, shaping time, etc..) on the amplifier till all the three peaks appears and clearly resolved, i.e. the position on the energy/channel axis of the spectrum. The energies 889.3 keV, 1173.2 kev and 1332.5 keV versus the channel obtained were as shown in the table inside figure 19.

A straight line was drawn connecting the points on the Energy versus Channel plane and a linear fit of the curve (the equation of the straight line) was obtained. The peaks of ^{152}Eu at 121.78 kev and at 1408 keV was used in confirming the accuracy of the calibration procedure. It was seen that the two energy peaks with respective channel number lies on the calibration line.

Once it is done and the energy versus channel number was obtained for the three peaks of the standard sources, the energy calibration was checked or tested per every batch of sample putting the two standard sources and adjusting the energies and channel numbers in the acquisition software MAESTRO window to the same values as the first time regularly under the same condition of amplifier course gain 7 and the shaping time 3 micro second to prevent any shift in the spectra. This shift may occur due to the effect of electronic noises.

The relation between channel and energy is linear and mathematically represented by the equation [Y= 0.798X-2.669] as shown in figure 19, where "Y" is gamma peak in kev and "X" is the channel number where the peak appears. The equation was fed to the acquisition software MAESTRO to find the energy for any other peak.

4.3.2 Efficiency calibration of the HPGe detector

In $\gamma - ray$ spectrometry with HPGE detectors, it is a common practice to approximate the detector efficiency for full-energy peaks by an analytical function, fitted to the experimental efficiency data points, and many nuclear measurements require accurate knowledge of the shape of the efficiency curve in particular energy range(24). As the number of energy peaks obtained from standard radioactive sources are limited, functions are required to fit the detector efficiency at a wide range of energies. Therefore comparing the results of the fits of specific functions and choosing the best fit is a key point in γ-ray spectrometry.

Several kinds of functions, some of them are displayed in the table 1, could be used to fit the efficiency of HPGE detectors (24). The function, ln-ln scale, has been used to calculate the efficiency fit for the HPGE detector used in this dissertation and the efficiency values that can be calculated with the fit function were tested for the range of gamma energies of interest. How to fit the detecting efficiency better with commonly used functions is very important to most γ-ray spectrometry analysis laboratories, other wise the error associated with the efficiency of the detector affects the analysis most (30).

In the, 59.54 Kev - 1408 KeV, energy range the radioactive sources ^{137}Cs, ^{152}Eu, ^{241}Am, ^{226}Ra, ^{22}Na, ^{60}Co were used in the calibration. The performance of the functions depends on the degree of a polynomial of order i. The order of the fit function is of great importance (30).

The aim of this section was to obtain the optimum condition for the fitting function, the ln - ln scale. And to study the performance change of the function with its fitting orders with the help of the energy peaks of the standard sources, finally to chose the best order of the fit function. The calibrating sources them selves and the radioactive source ^{22}Na were used to validate the result. The experimentally obtained efficiency of ^{22}Na was not used while plotting the experimental efficiency of the detector and determining the order of the fit function in the ln - ln scale. After the function was obtained, the efficiency of the energy peak of sodium was calculated and the result obtained was compared with the experimentally obtained value. Furthermore the efficiencies of all of the calibrators

No	Name	Function
1	log - log scale	$\log\epsilon = \sum_{i=0}^{n} a_i (logE_\gamma)^i$
2	log scale	$\log\epsilon = \sum_{i=0}^{n} a_i (E_\gamma)^{-i}$
3	ln -ln scale	$\ln\epsilon = \sum_{i=0}^{n} a_i (lnE_\gamma)^i$
4	ln scale	$\ln\epsilon = \sum_{i=0}^{n} a_i . (E_\gamma)^{-i}$

Table 1: Four kinds of functions to be used in the peak efficiency fit for HPGE detector.

No	Source	half life(seconds)	Activity(Bq) initial (A_0)	Energy peaks(Kev)	$P_\gamma/perdecay$
1	^{22}Na	8.22E+07		1274.5	0.9994
2	^{60}Co	1.66E+08	38400	1173.2	0.9988
3	^{60}Co	1.66E+08	38400	1332.5	0.9998
4	^{137}Cs	9.53E+08	36900	661.7	0.8462
5	^{152}Eu	4.26E+08	38000	121.78	0.2822
6	^{152}Eu	4.26E+08	38000	244.69	0.0751
7	^{152}Eu	4.26E+08	38000	344.29	0.2641
8	^{152}Eu	4.26E+08	38000	778.92	0.13
9	^{152}Eu	4.26E+08	38000	964.1	0.1448
10	^{152}Eu	4.26E+08	38000	1112.07	0.1355
11	^{152}Eu	4.26E+08	38000	1408	0.2071
12	^{241}Am	1.36E+10	36500	59.5	0.3575

Table 2: The radioactive point sources used in the calibration of the detector.

energy peaks were calculated using the function and the results were compared with the experimentally obtained efficiency values.

A set of radioactive sources including ^{137}Cs, ^{152}Eu, ^{241}Am, ^{22}Na, ^{60}Co were used to obtain the gamma ray response in the energy range between $59.54KeV$ - $1408KeV$ all were in the form of point sources. With these radiation sources nearly uniform distribution of the calibration peaks can be obtained, for the energy range mentioned above. The applied calibration point sources, energy peaks, half lives, initial activities (the activity when the sources were prepared), the branching ratios, have been grouped together in table 2. The nuclear data for the sources were as in (31).
Efficiency is the ratio between the responses of the instrument (counting rate) and the value of the physical quantity which is in this case the photon emission rate. It depends on the distance between source to the detector, the energy peak and the presence of intervening materials between the active volume and the source (32).

The activity of the radioactive sources at the time of the experiment (present activity)

was calculated using the initial activity and the time the sources stayed from the manufacturing time (cooling time) using the activity equation, the emission rate which is the product of the gamma intensity p_γ and present activity, the net peak area, the counting rate (the ratio of the net peak area to the counting time(3600sec)) and the experimentally determined efficiency of the detector for three different source to detector distances, (2cm, 5cm and 15cm which were used during the counting stage of the irradiated samples), are given in the table 3.

As shown in figure 20, the absolute photo peak efficiency varies with the range of energy. At low energies, the absolute efficiency increases with energy to some point (about 120keV) because in the detector material the dominant interaction is the photoelectric effect. Whereas, in the energy range from 120keV up to 1000keV the Compton scattering with the electrons of the detector crystal takes place and some of the gamma rays are scattered and escape from the detector without detection, therefore, not all the photon energies contribute to the full energy peak. At very high gamma ray energy, pair production is dominant, the single and double escapes predominantly minimize the gamma photons detected in this region, that is why the efficiency in the high energy region is small compared to other regions. In addition, the attenuation from the detector window, detector geometry and source detector distance also is an issue and affect the efficiency.

Using the experimentally obtained efficiency values at the gamma energy peaks of the radio nuclei, ^{137}Cs, ^{152}Eu, ^{241}Am, ^{22}Na, ^{60}Co, a polynomial fit of the plot of "$ln(eff)$ versus $ln(E)$" was found, (where E is the energy of gamma in the unit of KeV). While searching for the polynomial fit, polynomial of degree 2,3, 4, and 5 were tried and the efficiency of the energy peaks of the point sources used during calibration were calculated using the polynomial fits of different order to reproduce the experimental efficiency. One of the orders of the polynomial fit function was to be chosen using the criteria if the calculated efficiency values compared with the experimental efficiency values has small deviation.

The fit function which gives best values of efficiency was chosen as an efficiency function for the detector system used in the experiment.

The function was tested using the energy peak of sodium, ^{22}Na at KeV energy of 1274.5. The efficiency of the energy peak was priorly determined experimentally has been calculated using the fit function and the result was compared. All the results of full energy peak efficiency calculated from the fit function are named "theoretical" in this chapter for the seek of simplicity.

Geo.	Source	E_γ (Kev)	present activity(Bq)	Net peak area(count)	count rate (count/sec)	Emission rate (disintegration/sec)	Efficiency (%)
2cm	^{22}Na	1274.5	2602.46	89082	24.745	2600.898	0.9514
2cm	^{60}Co	1173.2	10354.83	411786	114.385	10342.4	1.1060
2cm	^{60}Co	1332.5	10354.83	375496	104.3044	10352.76	1.0075
2cm	^{137}Cs	661.7	29356	1634761	454.1003	24841.1	1.8280
2cm	^{152}Eu	121.78	22781.05	1082664	300.74	6428.813	4.6780
2cm	^{152}Eu	244.69	22781.05	212678	59.077	1710.857	3.4531
2cm	^{152}Eu	344.29	22781.05	611197	169.777	6016.476	2.8219
2cm	^{152}Eu	778.92	22781.05	149998	41.666	2961.537	1.4069
2cm	^{152}Eu	964.1	22781.05	149448	41.5133	3298.696	1.2585
2cm	^{152}Eu	1112.07	22781.05	126257	35.0714	3086.832	1.1362
2cm	^{152}Eu	1408	22781.05	164118	45.5883	4717.956	0.9663
2cm	^{241}Am	59.5	35921.27	386699	107.4164	12841.85	0.8365
5cm	^{22}Na	1274.5	2600.61	89082	24.745	2600.898	0.4708
5cm	^{60}Co	1173.2	10354.83	411786	114.385	10342.4	0.5190
5cm	^{60}Co	1332.5	10354.83	375496	104.3044	10352.76	0.4719
5cm	^{137}Cs	661.7	29356	1634761	454.1003	24841.1	0.8107
5cm	^{152}Eu	121.78	22781.05	1082664	300.74	6428.813	2.0313
5cm	^{152}Eu	244.69	22781.05	212678	59.077	1710.857	1.6077
5cm	^{152}Eu	344.29	22781.05	611197	169.777	6016.476	1.2784
5cm	^{152}Eu	778.92	22781.05	149998	41.666	2961.537	0.6715
5cm	^{152}Eu	964.1	22781.05	149448	41.5133	3298.696	0.5931
5cm	^{152}Eu	1112.07	22781.05	126257	35.0714	3086.832	0.5386
5cm	^{152}Eu	1408	22781.05	164118	45.5883	4717.956	0.4533
5cm	^{241}Am	59.5		386699	107.4164	12841.85	0.3357
15cm	^{22}Na	1274.5	2605.69	9113	2.5314	2604.127	0.0972
15cm	^{60}Co	1173.2	10357.73	39760	11.0444	10345.3	0.1067
15cm	^{60}Co	1332.5	10357.73	36489	10.1358	10355.65	0.0979
15cm	^{137}Cs	661.7	29354.25	137887	38.3019	24839.57	0.1542
15cm	^{152}Eu	121.78	22777.91	80614	22.3928	6427.93	0.3484
15cm	^{152}Eu	244.69	22777.91	18499	5.1386	1710.62	0.3004
15cm	^{152}Eu	344.29	22777.91	54060	15.0167	6015.65	0.2496
15cm	^{152}Eu	778.92	22777.91	14483	4.0231	2961.13	0.1359
15cm	^{152}Eu	964.1	22777.91	14320	3.9778	3298.24	0.1206
15cm	^{152}Eu	1112.07	22777.91	12326	3.4239	3086.41	0.1109
15cm	^{152}Eu	1408	22777.91	16004	4.4455	4717.31	0.0942
15cm	^{241}Am	59.5	35921.12	25800	7.1667	12841.8	0.0558

Table 3: Full energy peak efficiency of the detector for three geometries.

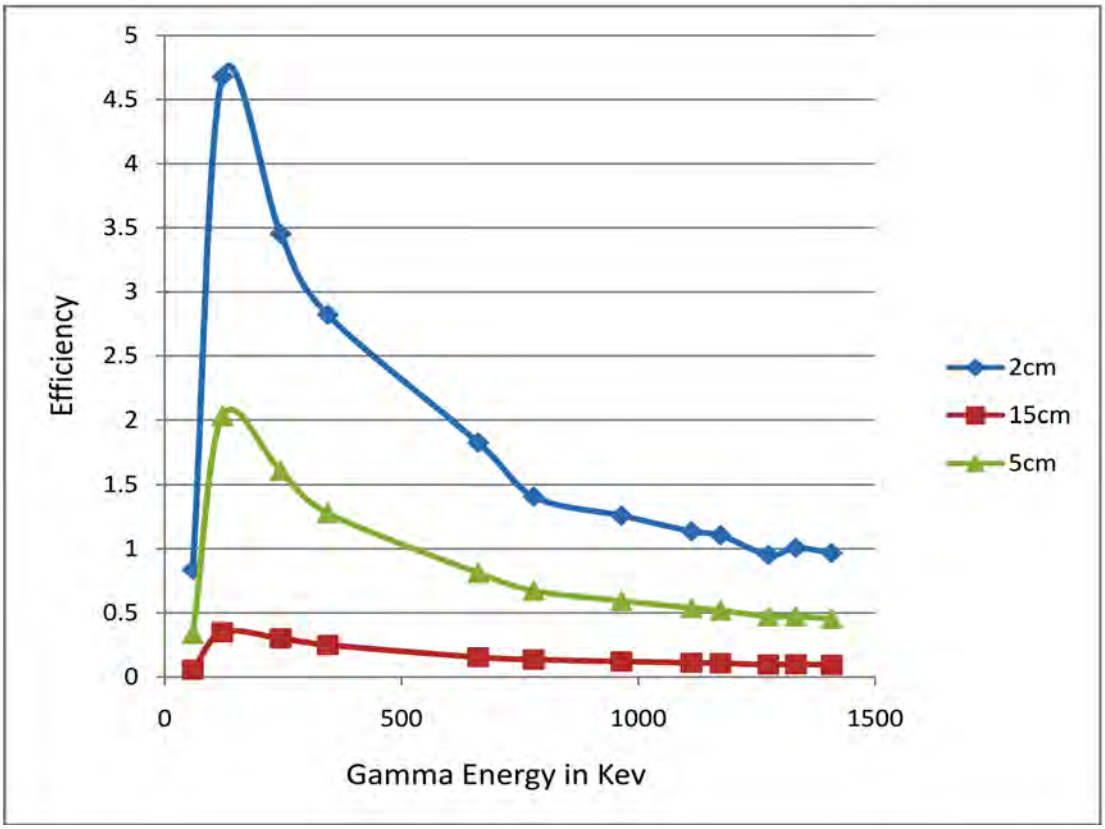

Figure 20: Experimental efficiency of the HPGE detector for three different distances used in the counting geometry of this research.

Energy(Kev)	eff(Exp.)	ln E	ln eff(Experimental)	ln eff(Theoretical)
59.5	0.8365	4.08597	-0.1786	-0.1875
121.78	4.678	4.8022	1.5428	1.453
244.69	3.453	5.4999	1.2393	1.227
344.29	2.822	5.8415	1.0874	1.105
661.7	1.828	6.4948	0.6032	0.5903
778.92	1.4069	6.6579	0.34	0.3298
964.1	1.2585	6.8712	0.2299	0.2398
1112.07	1.1362	7.0139	0.1276	0.1189
1173.2	1.10598	7.06749	0.10073	0.0998
1274.53	0.9514	7.1503	-0.04982	-0.04283
1332.5	1.0075	7.1948	0.007476	0.00698
1408	0.9663	7.2499	-0.0343	-0.0319

* Theoretical means the efficiency values calculated from the fit function.

Table 4: Experimental and theoretical values of efficiency at known energy peaks for 2cm geometry.

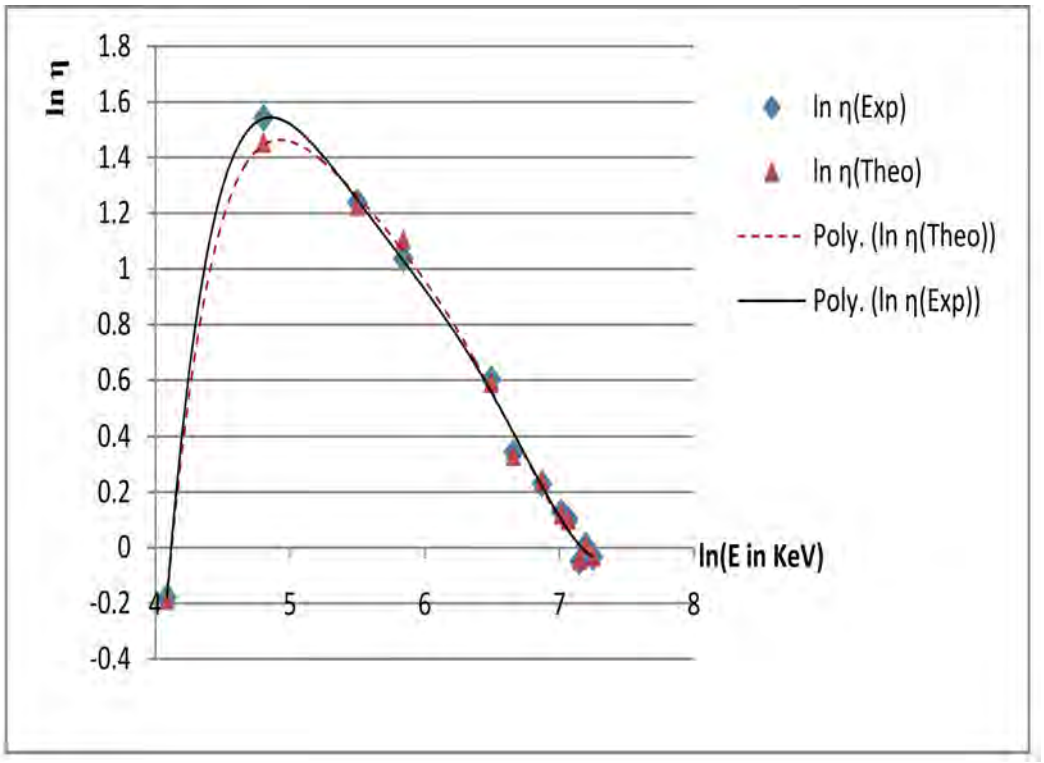

Figure 21: Experimental and theoretical natural logarithm values of efficiency versus energy curve at 2cm geometry

Energy(Kev)	ln E	ln eff(Experimental)	ln eff(Theoretical)
59.5	4.08597	-1.09145	-1.08627
121.78	4.8022	0.7087	0.65132
244.69	5.4999	0.4748	0.45826
344.29	5.8415	0.2456	0.2909
661.7	6.4948	-0.2099	-0.3522
778.92	6.6579	-0.39826	-0.43753
964.1	6.8712	-0.52256	-0.54669
1112.07	7.0139	-0.61879	-0.62744
1173.2	7.06749	-0.65583	-0.6612
1274.53	7.1503	-0.75332	-0.71889
1332.5	7.1948	-0.75099	-0.75317
1408	7.2499	-0.79108	0.79947

Table 5: Experimental and theoretical values of efficiency at known energy peaks for 5cm geometry.

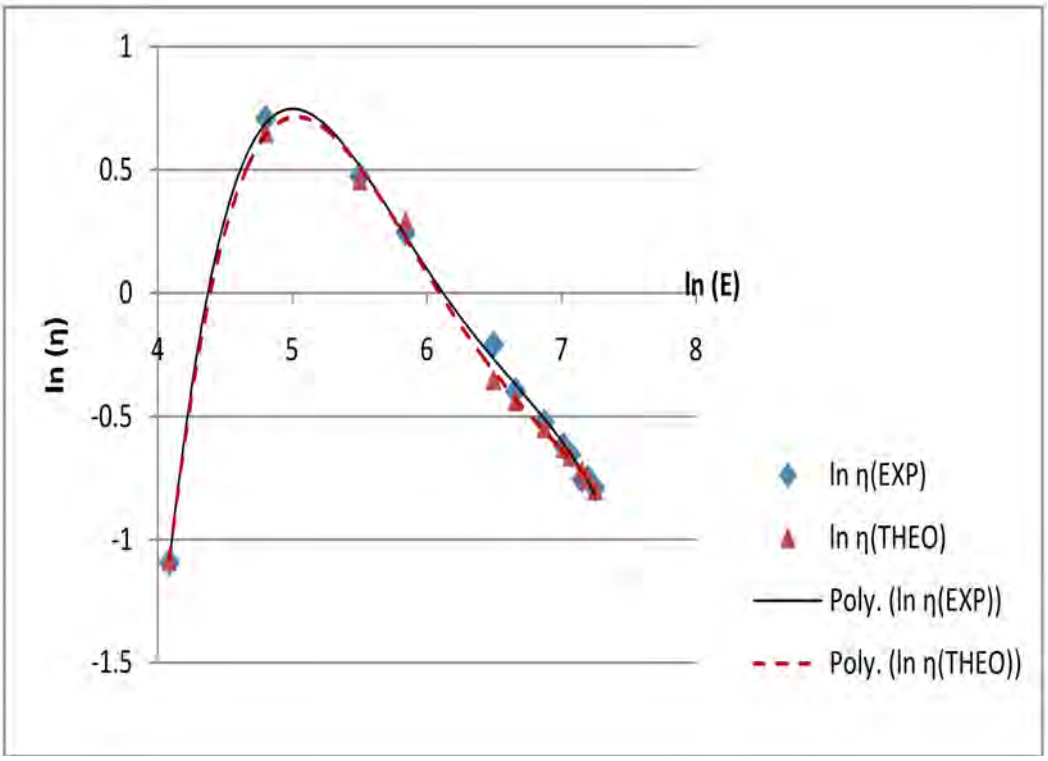

Figure 22: Experimental and theoretical natural logarithm values of efficiency versus energy curve at 5cm geometry.

Energy(Kev)	eff(Exp.)	ln E	ln eff(Experimental)	ln eff(Theoretical)
59.5	0.0558	4.08597	-2.8858	-2.8976
121.78	0.34837	4.8022	-1.0545	-1.0336
244.69	0.3004	5.4999	-1.20266	-1.2215
344.29	0.24963	5.8415	-1.38778	-1.407
661.7	0.154197	6.4948	-1.8695	-1.8403
778.92	0.13586	6.6579	-1.996	-2.0969
964.1	0.1206	6.8712	-2.11525	-2.1225
1112.07	0.1109	7.0139	-2.1988	-2.213
1173.2	0.10675	7.06749	-2.2372	-2.2577
1274.53	0.0972	7.1503	-2.331	-2.346
1332.5	0.097877	7.1948	-2.324	-2.3157
1408	0.09424	7.2499	-2.36192	-2.3623

Table 6: experimental and theoretical values of efficiency at known energy peaks for 15cm geometry.

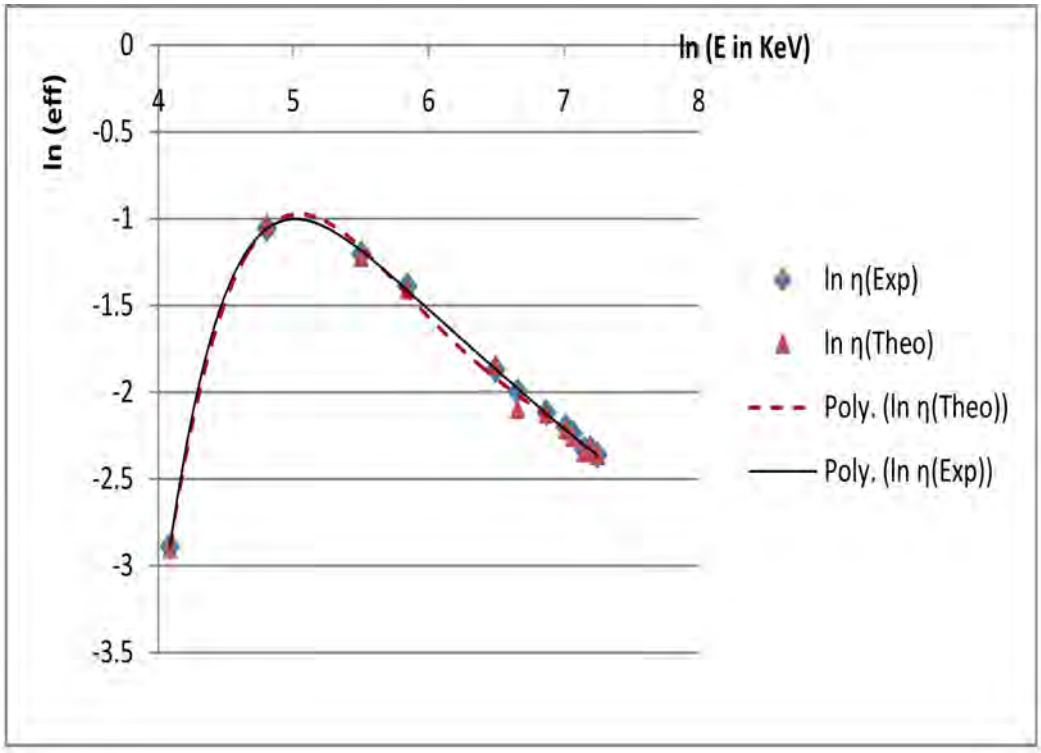

Figure 23: Experimental and theoretical natural logarithm values of efficiency versus energy curve at 15cm geometry

The results obtained for three different geometries, 2cm geometry, 5cm geometry and 15cm geometry, were as shown in the tables 4, 5 and 6. The plot of the data were shown in the figures 21, 22 and 23 respectively.

The exponentially fit function used for the 2cm, 5cm and 15cm geometries were fourth order $ln - ln$ scale function, because fourth order fit function gives best result.
After choosing the function and the order of polynomial fit the equation of the functions was fed to the analysis software program WINSPAN for each of the three geometries before analysis was performed.

4.4 NaI(Tl) Gamma Detector

NaI(Tl) consists of a single crystal of thallium activated sodium iodide optically coupled to the photo cathode of a photomultiplier tube. When a gamma ray enters the detector, it interacts with orbital electrons of its crystal.This creates excited states in the crystal that decay by emitting visible light photons. This emission is called a scintillation, that is why this type of sensor is known as a scintillation detector. The thallium doping of the

crystal is critical for shifting the wavelength of the light photons into the sensitive range of the photo cathode. Fortunately, the number of visible-light photons is proportional to the energy deposited in the crystal by the gamma ray. After the onset of the flash of light, the intensity of the scintillation decays approximately exponentially in time, with a decay time constant of 250 ns (28).

NaI(Tl) detectors are commonly used to identify and measure activities of Naturally occurring radioactive materials (NORM), because the spectrum of NORM contains small number of peaks compared to complex spectrum of samples, so that high resolution detector is not required (26; 28).
The NaI(Tl) detector produces a pulse of charge that lasts for about 1μs at the anode output of the photomultiplier tube. The preamplifier collects that charge on the input capacitance and turns it into a voltage pulse at the preamplifier output (26; 28).
The block diagram of an experimental set up to measure the activity of NORM sample is shown in the figure 24.

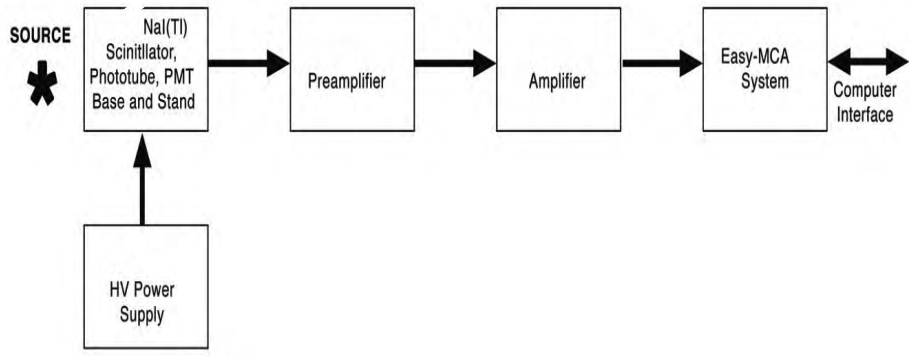

Figure 24: Simple block diagram of the electronics for gamma-ray spectrometry with NaI(Tl) detector.

4.5 Characterizing NaI(Tl) Gamma Spectroscopy used During the Experiment

4.5.1 Energy Calibration of the NaI(Tl) detector

The energy calibration of the NaI(Tl) gamma detector (described in section 3.2.1) was done using an IAEA mixed standard (IAEA-RGKUTh). The spectrum obtained was as indicated in figure 25. The peak positions were adjusted by slightly shifting the coarse and fine gain of the preamplifier and finally kept fixed in positions.

Element	Isotope Used	Gamma energy (Kev)	Energy window (Kev)
K	^{40}K	1460.0	1350.56 - 1615.92
Ra	^{214}Bi	1764.0	1670.32 - 1967.25
Th	^{208}Tl	2614.5	2494.43 - 2791.7

Table 7: The energy region of the gamma line used during spectrum acquisition.

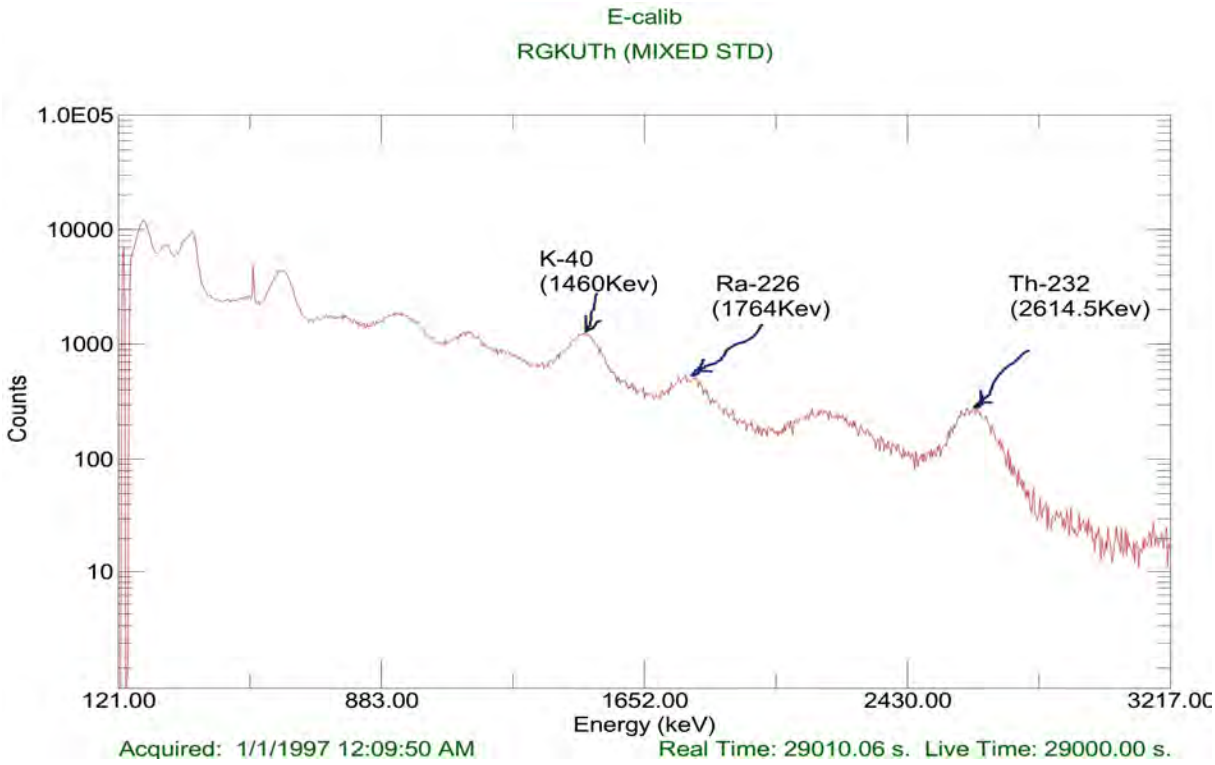

Figure 25: Spectrum of Energy calibration of the detector obtained from the energy calibration mixed standard IAEA-RGKUTh.

The energy peak and Energy window positions were as shown in table 7.

The counting of the NORM samples, the laboratory background and standard reference materials were made with out shifting the calibration. Three energy peaks versus the channel numbers displayed in the table 8 were plotted and shown in the figure 26, which is called the energy calibration curve. But the fit obtained was not needed to be used since the energy peaks themselves were to be detected from the NORM sample under study. Hence the task was just waiting for an energy peak at the same position as the channels given in the table 8 after putting the sample in position. The energy associated with each of the peaks equal to the energies associated with the three channels shown in the table 8.

Energy (KeV)	Channel Number
1460	458
1764	552.8
2614.5	821.5

Table 8: Energy and its respective Channel obtained during the energy calibration of NaI(Tl) gamma detector.

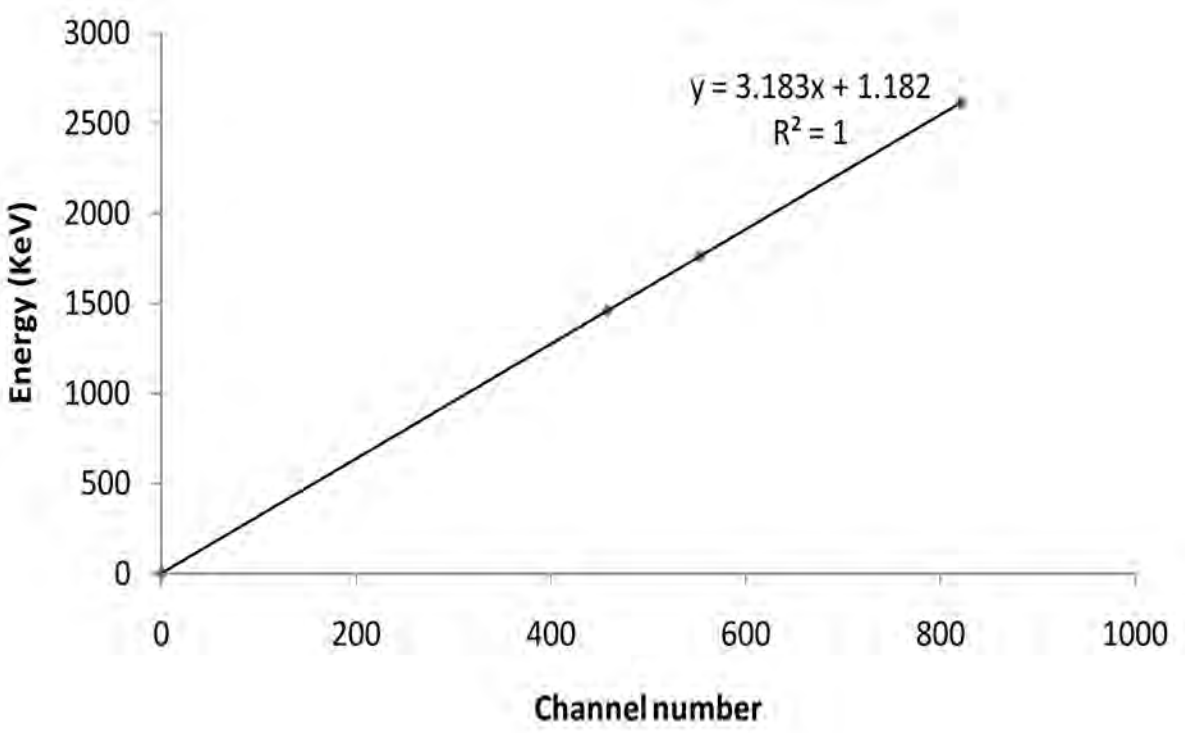

Figure 26: Energy calibration curve of NaI(Tl) gamma detector using the energy calibration standard mixed IAEA-RGKUTh.

4.5.2 Full Energy Peak Efficiency of the NaI(Tl) Detector

The performance of the detector was determined by relating the amount of radiation emitted by the source to the amount of radiation measured by the detector, the relationship is as shown in Eq. 28.

$$\epsilon_i = \frac{I_s - I_b}{\rho\ C\ m_s} \tag{28}$$

Where, ϵ_i is the efficiency of the detector corresponding to the a gamma peak in IAEA standards (IAEA-RGK-1), (IAEA-RGU-1) and (IAEA-RGTh-1) which were used for the efficiency calculation and quality assurance of the radionuclides potassium, Uranium and Thorium respectively, I_s is the activity count of the radionuclide of interest in the standards (IAEA-RGK-1 at 1460 keV, IAEA-RGU-1 at the peak 1764 keV and IAEA-RGTh-1 at the enrgy peak of 2614.5 keV) in counts/second, I_b is the background activity at the energy peak of the radionuclide of interest in counts/second, ρ is the photon emission probability of the gamma of the radionuclide of interest in (IAEA-RGK-1, IAEA-RGU-1 and IAEA-RGTh-1), C is the certificate concentration of the radionuclide of interest in the standards (IAEA-RGK-1, IAEA-RGU-1 and IAEA-RGTh-1) in Bq/Kg as given in (34) and m_s is the mass of the sample (IAEA-RGK-1, IAEA-RGU-1 and IAEA-RGTh-1) in Kg.

The gamma emission probabilities ρ of the energies were used as: $\rho = 0.11$ at 1460 keV, 0.161 at 1764 keV and 0.36 at 2614.5 keV (8).

In order to get the experimental values I_b and I_s, counting of the background and the IAEA standards has been made. The background activity of the laboratory, putting empty container inside the sample cavity of the detector shielding, was counted for 29000 seconds and all the informations on the resulting spectrum was saved to be used in the calculation of the background activity of each of the three radioactive nuclei.

The result of the background activity of the radioactive nuclei were subtracted from the measured activities of the samples. This gives the net activity of the mineral soil.
The spectra that was generated from laboratory background during spectrometric analysis was as shown in the figure 27 and the result of the count I_b, (Net Peak area/live time), at three energy peaks were shown in the table 9.

Three IAEA reference materials were counted for 29000 seconds each with the same procedure as the sample and the lab background for the purpose of controlling the quality of the measurement as well as for determining the full energy peak efficiency of the NaI(Tl) detector at three different gamma peaks.

The reference material IAEA-RGK-1 is counted for the purpose of checking the analysis of potassium and determining the NaI(Tl) efficiency at a peak 1460 KeV. In the procedure the standard (IAEA-RGK-1) was prepared with the same procedure and mass as the sample.

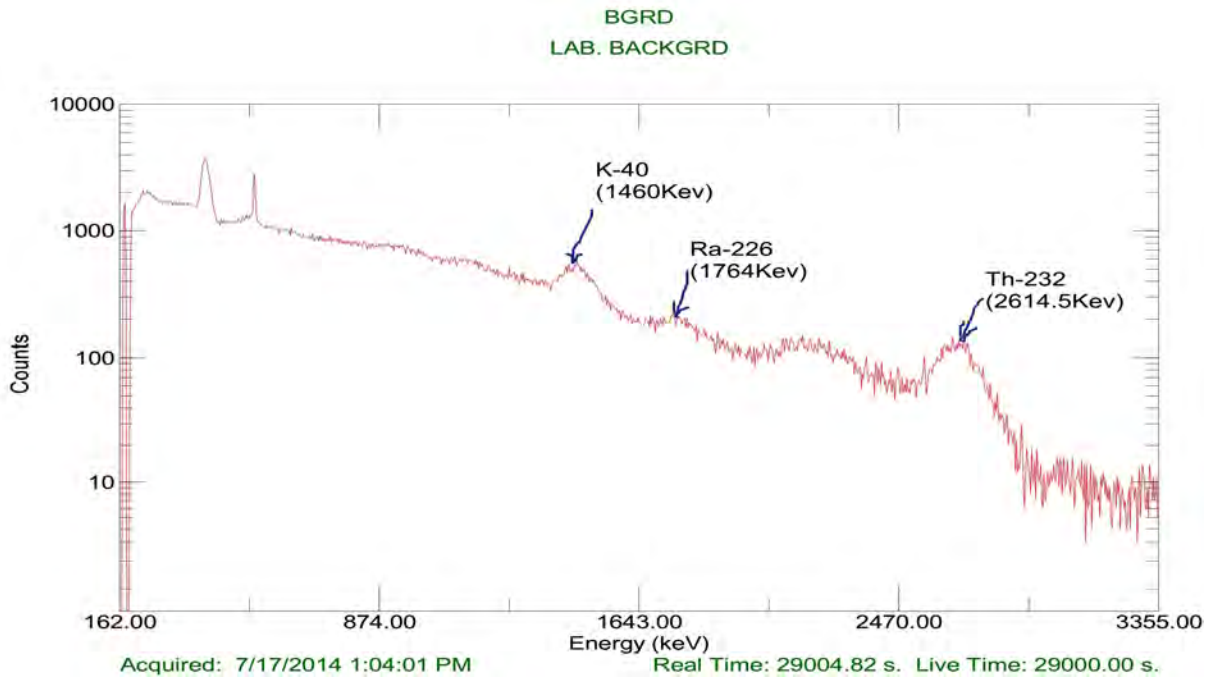

Figure 27: Spectrum of the lab background.

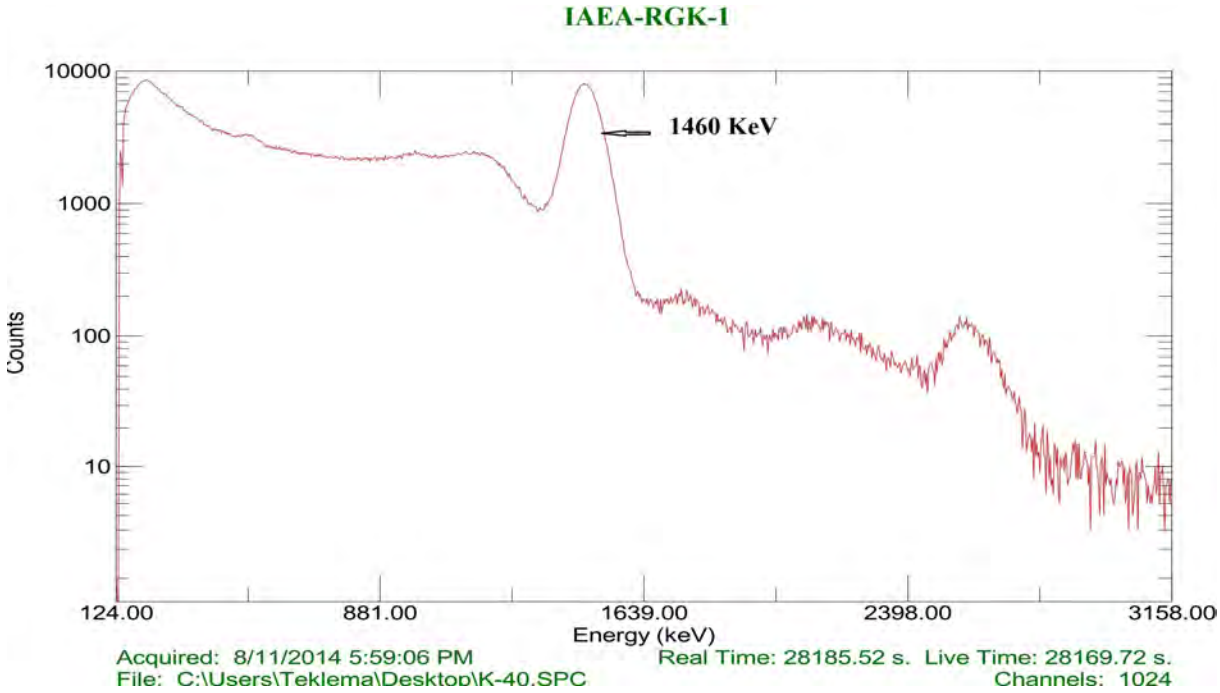

Figure 28: The spectrum obtained by the IAEA standard (IAEA/RGK-1) showing the potassium energy peak.

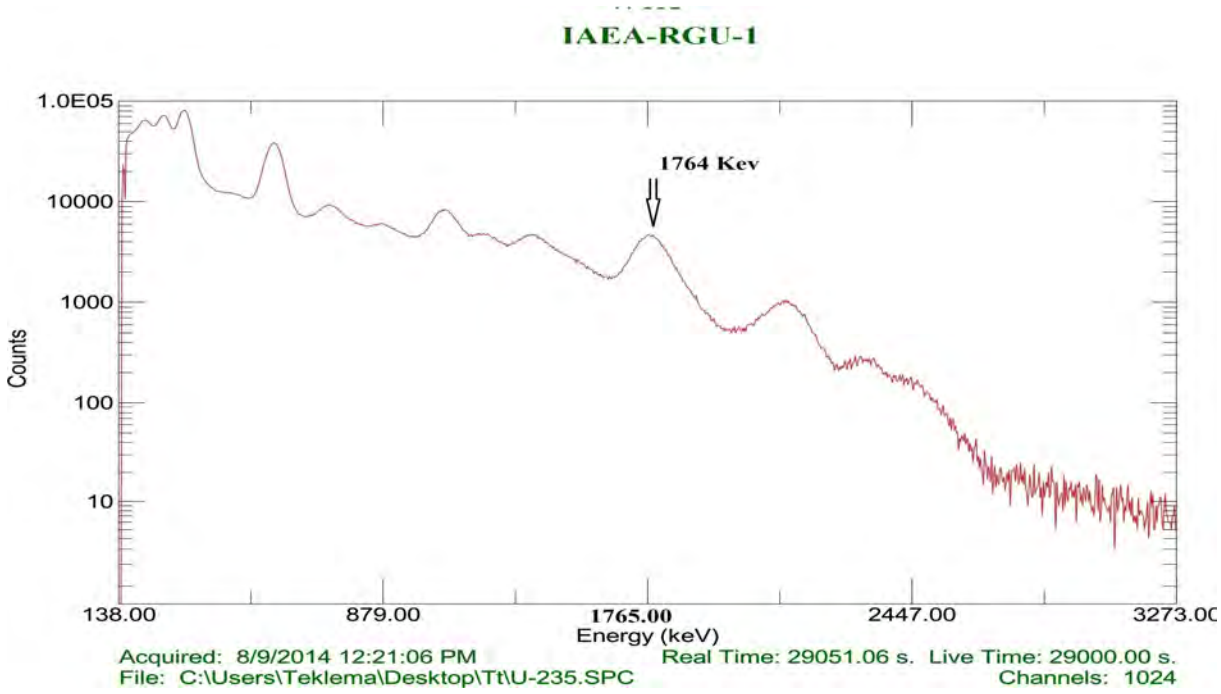

Figure 29: Spectrum of the Uranium standard IAEA-RGU-1, showing the energy peak of Radium-226.

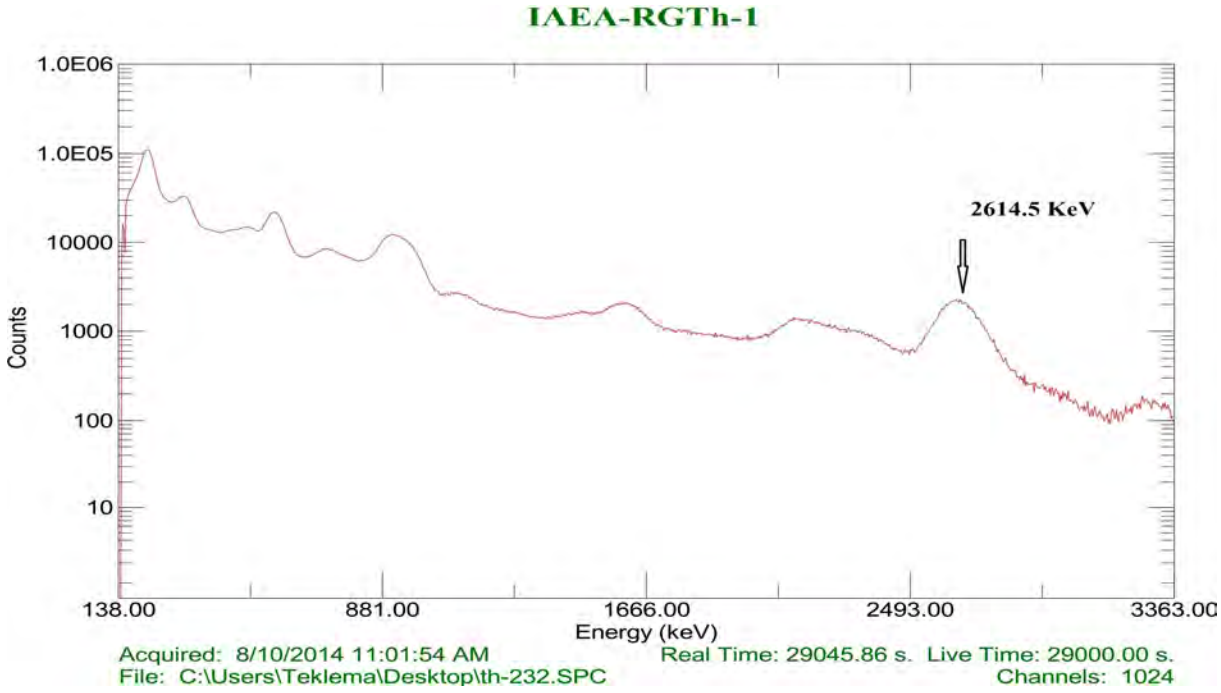

Figure 30: The spectrum obtained by the IAEA standard (IAEA-RGTh-1), showing the gamma peak of Thorium-232.

Counting of the activity concentration of (IAEA-RGK-1) was made in the same procedure and geometry as the sample and background, from which the potassium count rate was obtained to calculate the efficiency of the detector at the energy peak of potassium.

With the same procedure explained for (IAEA-RGK-1) for the analysis of potassium and obtaining the 1460 KeV peak efficiency of the NaI(Tl) detector, the standard reference material (IAEA-RGU-1) was counted for determining the efficiency of the NaI(Tl) detector at 1764 KeV gamma peak and a reference material (IAEA-RGTh-1) was counted for measuring the 2614.5 KeV peak efficiency of the NaI(Tl) gamma spectrometer. The spectrum obtained during the counting of the reference materials were as shown in figure 28, 29 and 30.

The obtained efficiencies, using Eq.28, corresponding to the three radionuclides were given in the Table 9.

Radio nuclide	IAEA standard	Energy peak(Kev)	I_s(c/s)	I_b(c/s)	ρ	Certificate Concent. (Bq/Kg)	m_s (Kg)	ϵ
^{40}K	RGK-1	1460	8.970	0.1995	0.11	14000	0.5	0.0113
^{238}U	RGU-1	1764	4.265	0.0278	0.161	4940	0.5	0.0106
^{232}Th	RGTh-1	2614.5	2.876	0.093	0.36	3250	0.5	0.0047

Table 9: Full energy peak efficiency of the NaI(Tl) detector at the energy peaks of ^{40}K, ^{226}Ra and ^{232}Th, (C(Bq/Kg values were taken from (34), and ρ values were from (8)).

Chapter Five

5 Multi elemental analysis of the Flower of a Medicinal Plant Called "Chima"

5.1 Introduction

In the under developed countries, the people of far-flung rural areas still depend upon herbal medicines and minerals. The foundation of usage of herbal and mineral medicine is the experience of thousands of years. Herbal medicines, also known as medicinal plants are known for their effectiveness and are widely practiced in almost every part of the world. They also are available in remote parts of Ethiopia at relatively lower cost.

World Health Organization (WHO) supports the use and application of herbal medicines by its agency called International Regulatory Cooperation for Herbal Medicines. It was established in 2006 under the WHO and is a global network of regulatory authorities responsible for regulation of herbal medicines(33). These medicines are used for curing various diseases like kidney disorder, cancer , diabetes, cardiovascular problems, urinary tract diseases, parasites. Herbal medicine could be obtained by either one of or concoction of flowers, fruits, barks, roots, seeds, and leaves from one or more plants. The major component of these medicines contains organic compounds some of which have biological activity.

These medicinal plants have been little explored on their elemental contents. Four non-metallic elements (H, O, C and N) account for 99 percent of all elements in all biological systems. Seven elements Na, K, Ca, Mg, P, S and Cl provide another 0.9 percent of the total content and trace elements share the remaining 0.1 percent(33). There are reports suggesting that trace elements deficiencies can lead towards the impaired growth during infancy and childhood. In biological system, some trace elements have been classified as essential, the others as toxic and the rest of undecided role. Trace elements play crucial role in various biochemical functions because some metals form integral part of enzymes. In addition to the essential elements present in herbs, they might contain toxic elements from the environment. Researchers have measured As, Cd, Cu, Hg and Pb in various food articles. It is therefore, very important to analyze all kind of food particles including herbal medicines for their mineral contents. Herbal medicines belonging to different countries have been explored for their elemental composition, because of the presence of

research facilities like nuclear reactor. But we found no literatures in the related area of research focused to the environment described in section 3.1.4.

The objective of this chapter is to report elemental contents and concentration of the flower of flowering plant Hygenya Abyssinia "Chima" which is Ethiopia origin by instrumental neutron activation analysis (INAA). It focuses mainly on the experimental methodologies used and discusses the results obtained.

Briefly the plant Hygenya Abyssinia, shown in the figure 31 "locally called Chima" grows in Ethiopia only. The plant is flowering plant and people in the area described in the section 3.1.4, uses the powdered form of the dried flowers as an anti tapeworm medicine, it works effectively. The powder is taken after it is mixed thoroughly with a glass of water. There is no constant measurement regarding the amount of the powder for adults and children. The plant gives flower in the months November to December, people in the surrounding collect these flowers and keep dry for use in the other months of the year.

Figure 31: Picture of Hygenya Abyssinia, "Chima"

Neutron activation analysis (NAA) is a very precise technique mainly used to determine trace concentrations of elements in samples or to acquire information on the spatial distribution of a neutron field via neutron activation detectors (4). In INAA a sample is first irradiated with thermal neutrons from research reactor or an isotopic neutron source etc.. Depending on the neutron flux, energy spectrum and reaction cross sections, the target nucleus undergoes a nuclear reaction and the resulting compound nucleus, is always at excited state, will immediately de-excite under emission of characteristic prompt gamma rays into a more stable configuration. This configuration is in general a radioactive nucleus with a certain half-life $t_{1/2}$ which will further decay by beta or other to an excited state. These excited nucleus decays under the emission of characteristic delayed gamma rays into a stable product nucleus.

A sample is irradiated together with a comparator containing a known amount of the element of interest, it can be a multi element standard. The standard is measured under the same conditions as the sample (sample-to-detector distance, equivalent sample size and equivalent matrix). From comparison of the net peak areas in the two measured spectra the mass of the element of interest can be calculated using the Eq.18, (7).
In this procedure many of the experimental parameters - such as neutron fluence rate, cross section and photo peak efficiency cancel out and the remaining parameters are all known. In full multi-element INAA techniques the standard should be multi elemental standard. IAEA (International Atomic Energy Agency) makes considerable effort to prepare multi-element standards for all elements measurable via INAA with adequate degree of accuracy in a volume closely matching the size and the shape of the samples.

5.2 Method

5.2.1 Sample collection

"Chima" is the local name of flowering plant and a name given for the medicine which is prepared from the flower of the plant. The scientific name of the plant is "hygenya Abyssinia". The plant grows in the "Kotergedra" forest particularly in "Yechma Gobet", "Yame" and "Genemar" of Shamene region in the Gurage zone of Ethiopia, Eja. Samples of flower were collected from different "Chima" trees and the flowers were grouped according to the forest they are collected from. Different samples from the same forest were dried exposing to dry air at room temperature then powdered using a mortar and homogenized together to get one sample for irradiation. By the same procedure three different samples of the flower were prepared. The three samples were packed in polythene pocket and taken

to the minister of agriculture of Ethiopia to obtain permission in order to transport them abroad to where a reactor and facilities were available. After obtaining the permission by a letter reference number 334807, the samples were transported to Nigeria, Ahmadu Bello University(ABU), Center for Research and Training(CERT) to irradiate them, count the resulting activities and analyze.

5.2.2 Sample preparation

The powder form of the samples brought from Ethiopia were dried in an oven, shown in the figure 12, at a temperature of $45C^0$ till constant mass then prepared for irradiation in the NAA sample preparation laboratory, Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria Nigeria. The samples as well as Standard Reference Material(SRM) were weighed between $200mg$ - $250mg$ using a Mettler Toledo balance, model AE 24, shown in the figure 11.

The reference material used was apple leaves (NIST-1515) supplied by International Atomic Energy Agency(IAEA), Vienna, Austria, for verification and quality control purpose. A total of eight samples were prepared, four for short irradiation and four for long irradiation. Three of short irradiation samples were obtained by taking one from each of the three "Chima" samples transported from Ethiopia and the other sample is prepared from the SRM. The same procedure is applied to prepare long irradiated four samples. All the samples were coded, a code "KGR" was used for the name of the sample collected from "kotergedra", a code name "GNMR" was used for the sample collected from "Genemar" and "YAME" was the code name of the sample collected from "Yame" and "NIST 1515" was used for the apple leaves, packed in a plastic and put in pre - cleaned air tight polyethylene vials. The samples in the vial were kept in, "Desketor shown in the figure 16", an air tight container containing silicates in order to keep them away from moisture due to humidity of the atmospheric air till the date of irradiation.

5.2.3 Irradiation and Counting

The irradiation facility used at Ahmadu Bello University, CERT is the Nigeria Research Reactor-1 (NIRR-1) which is a Chinese Miniature Neutron Source Reactor (MNSR) with a nominal thermal power of 31.1 kW pool-type, with a maximum thermal neutron flux of 10^{12} neutrons cm^{-2} s^{-1}, the picture of it is shown in the figure 7.

During this work the reactor was made to run at half of its maximum power. So that the flux in the inner sites of irradiation was $2.5 * 10^{11}\ cm^{-2}\ s^{-1}$ and in the outer sites was $1.25 * 10^{11}\ cm^{-2}\ s^{-1}$ as noted from the control consul.
There is an automated system which works with air pressure, to transfer samples pneumatically in to irradiation site of the reactor and retrieve them from the reactor through a rabbit transfer tube to the counting laboratory. There were six irradiation sites of the reactor which were situated around its core, one outer channel(B_4) , one cadmium fixed channel for Epithermal irradiation (A_2),four inner channels (A_1, B_1, B_2, B_3).

The analysis of the plant flower in this work can be divided into two different techniques on the basis of the half-lives of the radionuclides of interest, as described in the next section 5.3,.
The first technique is to use a short irradiation (5 min) in order to asses those nuclides with short half lives. In this process samples were irradiated for five minutes in the outer irradiation site, B_4, with a flux of $1.25 * 10^{11}\ cm^{-2}\ s^{-1}$.
The second technique used was long irradiation, which is useful for the analysis of long half life nuclides. In this case the samples were irradiated in the one of inner channels (A_1) for six hours, the flux in this site of irradiation was $2.5 * 10^{11}\ cm^{-2}\ s^{-1}$. The elements to be determined in this technique were important and are affected by short life nuclide interferences, that is why long irradiation was used.

A multi-elemental standard called apple leaves (NIST 1515) was used for the purpose of validation of the results of the analysis. For calibration purposes, an energy calibration is performed with each batch of samples using two standards, Cobalt ^{60}Co and cesium ^{137}Cs to reset the detector energy calibration back to the state described in section 4.3.1.

After irradiation the samples were left to cool until the activity of the samples become approximately $30 microseviert/hr$, and taken to the counting facility furnished with high purity germanium detector, figure 8, connected with computers supported by analysis softwares, figure 10, MAESTRO and WINSPAN, to measure gamma-ray spectra of the samples and standards.
In all counting, dead time was less than 10% and pile-up corrections were applied by the software allowing the count for real time count. These system of computer and detector gives an out put spectrum with energy peaks. 5 cm geometry was used for the first regime of short irradiation counting and 2 cm geometry was used for the second regime of short irradiation counting, for the first counting of long irradiated samples and second counting of long irradiation.

5.3 Peak Testing

In the spectrum acquired from multi channel analyzer, there are many peaks associated with gamma of specific energy. To exactly identify the kind of radio nuclide from which the gamma energy comes, the rate of counts of a peak were repeatedly registered four to five times with some interval period of time. From the data *time* vs $ln(A/A0)$ graph was plotted, where A is activity at time t, and $A0$ is activity at $t = 0$ /initial activity/ and the linear fit of the data was found. From the linear fit of the plot the half life was determined, i.e the slope of the linear fit is equal to the negative of the decay constant λ, $(\lambda = ln2/T_{1/2})$, where $T_{1/2}$ is the half life of the radio nucleus releasing the gamma ray at that peak.

But the WINSPAN software assigns a nucleus to each peak according to the technique of nuclide identification fed to it, in this work the software was fed with the half life of an element including its peak energies with abundance. Since counting was made two to three times at different length of cooling time for every sample, the software retrieves information about an activity of a particular peak at least at three different times which helps it to find the linear plot and calculate half life and compare it with the given value, the half life fed to it from literatures. Furthermore the program calculates the concentration of an element from each counting, three times (default), and takes the average concentration of the element in the sample and the standard deviation.

Peak testing was performed manually for each of the peaks in the spectrum, When a peak was tested with the half life of the radio nucleus and if there is any discrepancy between the nucleus assigned by the software and the test, the analysis for that particular nucleus will be rejected otherwise the result of the analysis by the software was accepted. Unfortunately no nucleus was rejected, because all the assignments by the software were correct.

During counting and irradiation, the elements of interest (EOI) were divided in to four groups,

i. **First short:** These group of elements of interest comprises of those radionuclides having half life in the order of seconds and minutes /half life less than 1hr/ like, Magnesium, Aluminum, Calcium, Titanium, vanadium, Copper, Selenium.
   The irradiation period of a sample to see for such short half life nuclides in this work

was only for five minutes. Because they depopulate or decay out during irradiation if a longer period of irradiation is used. Counting was repeated after 5 minutes to 10 minutes for the search of such nuclides.

ii. **Second short:** These are EOI nuclides having half life in the order of an hour and less than 15hrs such as silicon, potassium, manganese, copper, selenium, dysprosium. For the search of such nuclides counting was made in the sample irradiated for first short EOI. If some of these elements are not identified they can be obtained in the next group first long EOI analysis.

iii. **First long:** Such elements have half lives in the range above 15 hrs and less than 10 days. Some of such group EOI are, bromine, lanthanum, samarium, etc.
For the search of such elements the sample was irradiated for six hrs, and counting was repeated after a week and two weeks period.

iV. **Second long:** These group of EOI, has halve life beyond 10 days, such as iron, cobalt,barium, thorium, hafnium, mercury, etc. Irradiation and counting for such group of elements is similar to first long EOI.

All group of the EOI was tested one by one to check the peak in the spectrum corresponds to the element assigned by the software. As an example three peaks testing procedures were given below.

5.3.1 Magnesium Peak Testing

For the test of a peak assigned ^{27}Mg by the analysis software WINSPAN the activity of the peak centroid was registered at different times as shown in figure 32.
As can be seen from figure 32, the activity at the peak centroid was taken four times at different periods. From the linear plot of the "time vs ln(A/A0)" curve the fitting equation is given by $Y = -0.0012197X$, where Y is the value on $ln(A/A0)$ axis and X is the value on the time axis. From the relation,

$$\text{slope} = -\lambda$$
$$-\lambda = -0.0012197$$
$$\text{But, } \lambda = ln2/T_{1/2}.$$
$$\text{Substitution of } \lambda \text{ gives:}$$
$$T_{1/2} = 568.3 \text{ seconds}$$

Verification for Magnesium, A0 = 2873 c/sec

t(sec)	A(c/sec)	A/A0	ln(A/A0)
0	2873	1	0
600	1379.04	0.48	-0.73397
1800	318.9	0.111	-2.19823
3000	73.55	0.0256	-3.66516
3600	35.4	0.0123	-4.39816

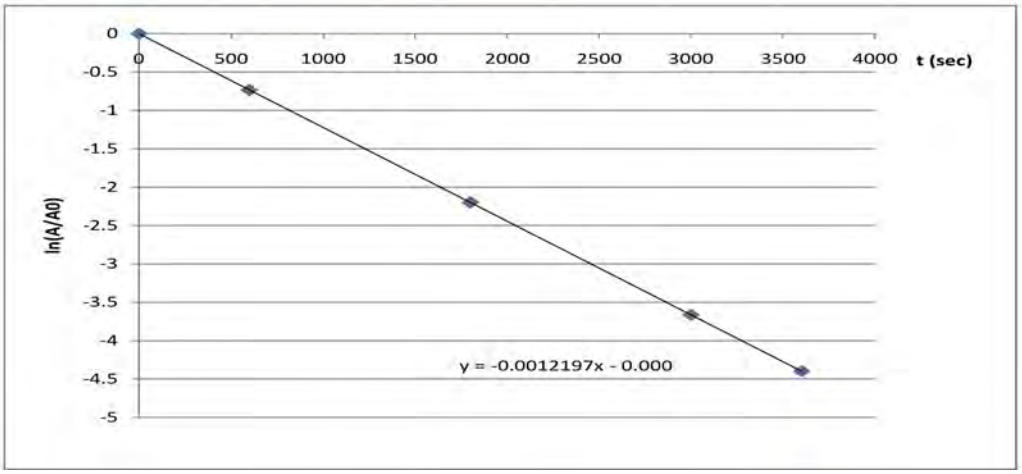

Figure 32: Time vs ln(A/A0) linear curve for Magnesium peak.

When we compare this time with the half life of magnesium 9.46 min = 567.6 seconds, it is exactly magnesium peak with an error less than 1%. Hence the analysis of the peak by the software for magnesium will be confirmed.

5.3.2 Aluminum Peak Testing

As can be seen from figure 33, the activity reading of the aluminum assigned peak by the analysis software WINSPAN has been taken four times at different periods.
By the same procedure as in section 5.3.1, the half life of the nucleus giving the gamma energy at the peak can be calculated from the slope of the linear curve shown in figure 33, and it is equal to 394.06 seconds. Comparing the calculated half life with the half life of radionuclides, it becomes nearer to the half life of Aluminum, (6.56 min = 393.6 seconds), with an error less than 1%. Hence the peak assignment by the software is confirmed, and the analysis of the aluminum concentration is accepted.

Aluminium peak verification (A0 = 899 c/sec)

t(sec)	A(c/sec)	A/A0	ln(A/A0)
0	899	1	0
300	530.05	0.5896	-0.528311
600	312.49	0.3476	-1.056703
900	184.29	0.205	-1.584745
1200	108.64	0.121	-2.111965

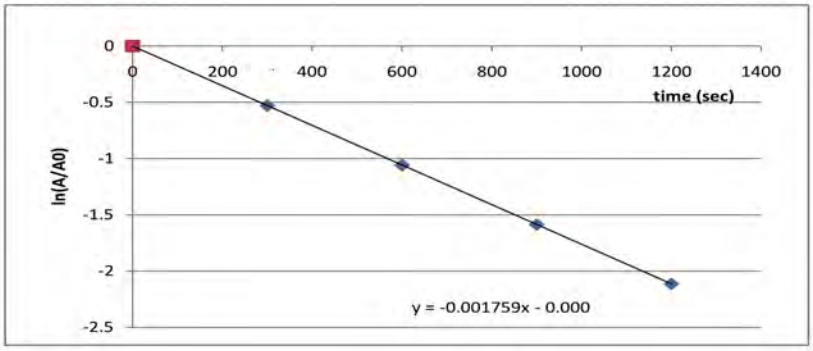

Figure 33: Time vs ln(A/A0) linear curve for Aluminum peak.

5.3.3 Manganese Peak Testing

With similar procedures as in sections 5.3.1 and 5.3.2 the half life of the peak energy assigned ^{56}Mn by the WINSPAN software in the spectrum was tested for its half life. The linear plot of the data of Manganese shown in the figure 34.
The slope of the linear fit is, slope $= -7.464X10^{-5}$, using the value of the slope and the relation,

$$T_{1/2} = ln(2)/|(slope)|,$$

One can calculate the half life of the radionuclide giving the peak energy as

$$T_{1/2} = 9286.54 \text{ seconds.}$$

The half life of Calcium from nuclear data table (35), is 2.58 hrs. = 9288 sec. When the calculated half life (9286.54 sec.) is compared with the half lives of radionuclides given

Mn peak testing, A0 = 332c/s

t(sec)	A (c/s)	A/A0	ln(A/A0)
0	332	1	0
14400	113.35	0.34141	-1.07467
18000	86.65	0.261	-1.34323
21600	66.23	0.1995	-1.61194
25200	50.6	0.1525	-1.88059

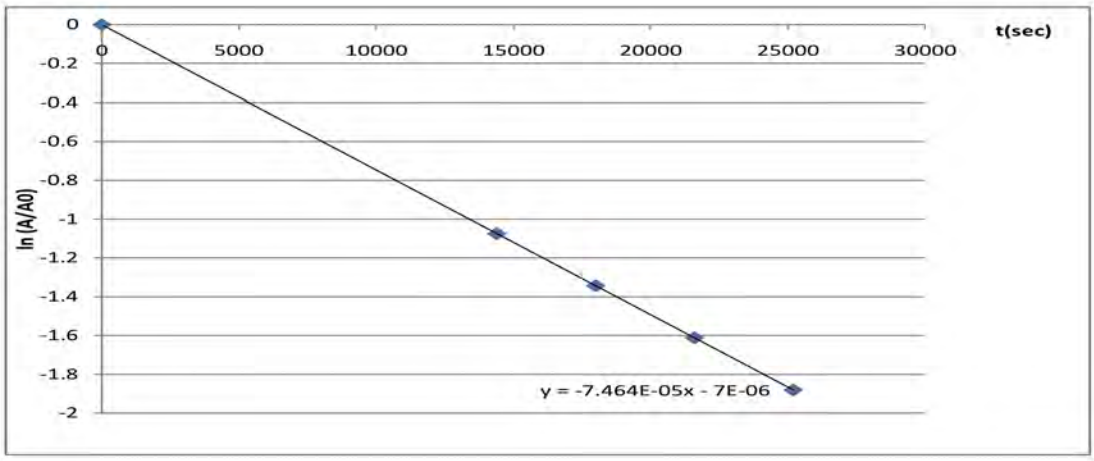

Figure 34: Time vs ln(A/A0) linear curve for Manganese peak.

in the data table, it is clearly seen that the calculated half life approaches the half life of Manganese, with a percentage error nearly 0.016%. Hence it is confirmed that the peak energy is exactly coming from Manganese. Therefore the analysis of the peak for manganese is validated.

5.4 Result and Discussion

From the experimental spectrum of irradiated samples, the spectrum shows various γ-ray energy peaks. The decay of each of γ-ray was followed and half life of radio nuclide were used by the software to confirm the element present in the sample. Information on data about the half life and principal gamma energy of the isotopes were as given in (35). Elemental concentrations in the three samples of "Chima" were calculated using Eq.18, using a computer supported by acquisition and analysis softwares MAESTRO and WINSPAN. The Standard reference material apple leaves (NIST 1515) was also analyzed for the purpose of quality control and comparison in this study. The quality control of INAA system is based on the results from the analyses of these standard samples, analyzed under the same conditions as the environmental samples. Careful consideration of these results yield information on accuracy and precision of the analysis.

Element	$E_\gamma(Kev)$	$T_{1/2}(Sec)$	present work (ppm)*	certified (ppm)	non certified (ppm)
K	1524.6	$4.464x10^4$	16100±161	16100±200	
Mg	1014.4	567.6	2710 ± 165	2710±80	
Al	1779	134.4	286 ± 5	286±9	
Cl	2167.7	2232	579 ± 20	579±23	
Ca	3084.5	523.2	15260 ± 443	15260±150	
V	1434.1	289.02	0.26 ± 0.08	0.26±0.03	
Mn	2113.1	$9.288x10^3$	54 ± 1	54±3	
Na	2754.0	$5.4x10^4$	24.4 ± 0.5	24.4±1.2	
Br	776.5	$1.271x10^5$	1.8 ± 0.3		1.8
La	1596.2	$1.451x10^5$	20 ± 0.08		20
Sm	103.2	$1.667x10^5$	3 ± 0.01		3
Sc	889.3	$7.197x10^6$	0.03 ± 0.007		0.03
Cr	320.1	$2.3933x10^6$	0.3±0.01		0.3
Fe	1291.6	$3.845x10^6$	83 ± 28	83±5	
Co	1332.5	$1.663x10^8$	0.09±0.01		0.09
Zn	1115.6	$2.9722x10^7$	12.5 ± 2.7	12.5±0.3	
Rb	1076.6	$1.6157x10^6$	10.2 ± 0.3	10.2±1.5	
Ba	496.3	$1.0195x10^6$	49 ± 11	49±2	
Nd	91.1	$9.504x10^5$	17 ± 1		17
Eu	91.1	$9.504x10^5$	0.2 ± 0.05		0.2
Tb	879.4	$6.2467x10^6$	0.4 ± 0.05		0.4
Yb	396.3	$3.6202x10^5$	0.3 ± 0.06		0.3
Th	312	$2.333x10^6$	0.03 ±0.1		0.03

*ppm=parts per million.

Table 10: Nist1515, certified and non certified values compared with the present work.

The results obtained from the analysis of standard reference material in the present study is displayed in table 10.

Table 10, presents the elemental concentrations in the reference material as analyzed by this work compared to the certified and non-certified values given in the certificate of the standard. From results obtained, it is observed that most of the elemental concentrations were agreed with an error below or equal to 10% of certified values. Since the concentrations of most of the elements are similar to their respective certified values except for those that are below detection limit, almost all of the elements listed in the certificate of the standard were considered. Those elements which are below the detection limit during the analysis of the standard were not analysed in the "Chima" samples too because of the uncertainty in the quality of the result.

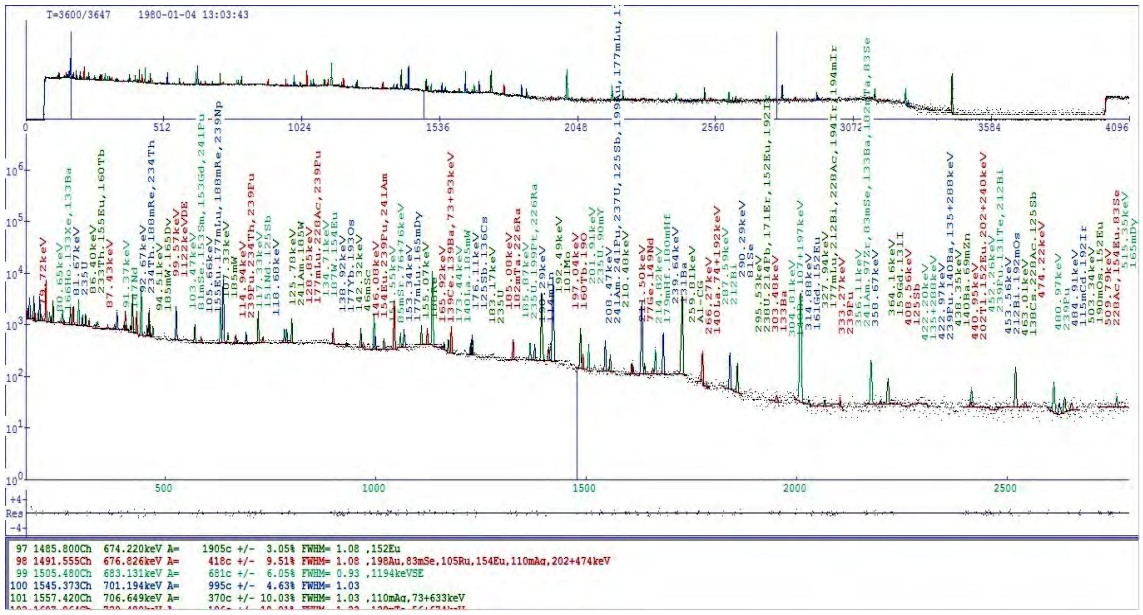

Figure 35: The second long spectrum of the sample chima containing all peaks of long half life nuclides in the selected region.

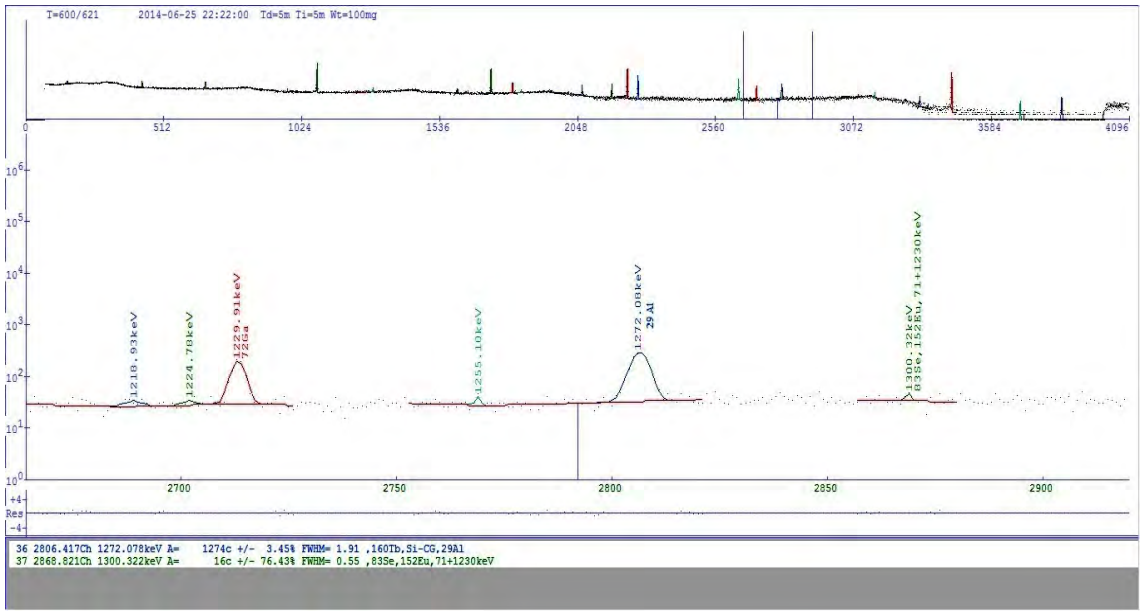

Figure 36: The region of a spectrum of the sample Chima containing Aluminum peak

The second long count spectrum of one of the sample of chima obtained during the experiment is given in the figure 35, the part of first short count spectrum obtained during the experiment in one of the chima samples containing Aluminum peak is as given in the figure 36 and containing sodium peak is as shown in Fig. 37.

The resulting elements in the "Chima" samples in this work were listed in table 11, the table includes the elemental concentrations and their uncertainties. It is observed that the uncertaintity values in most cases were $< 10\%$ suggesting high order of accuracy and precision of the data.

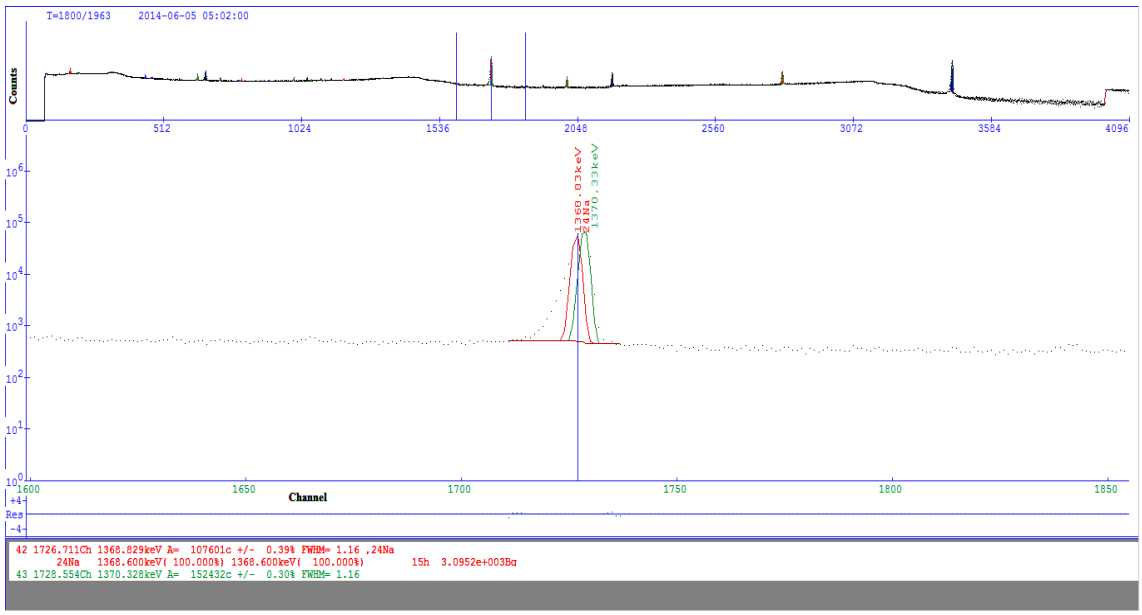

Figure 37: The region of a spectrum of the sample Chima containing Sodium peak

As can be seen from table 11, Magnesium (Mg), Aluminum (Al), Chlorine (Cl), Iron(Fe) and Calcium(Ca) found in a relatively higher concentration in all of the three samples. The elements, Manganese(Mn) and sodium(Na) are relatively in a moderate concentration. The other elements vanadium(V), Bromine(Br), Lanthanum(La), samarium(Sm), scandium(Sc),chromium(Cr), Cobalt(Co), Zinc(Zn), Rubidium(Rb), Barium(Ba), Neodymium(Nd), Europium(Eu), Terbium(Tb), Ytterbium(Yb),and Thorium(Th) are presented only in trace quantities.

The data showed that amounts of elements in the three different samples of "Chima" vary to certain extents; it is probably due to many factors which directly linked to the Elemental Composition of soil where the plants grown and the pollution of the flower on its tree due to atmospheric pollutants. The differences seen in the concentration of some

Element	$E_\gamma(Kev)$	$T_{1/2}(Sec)$	KGR(ppm)*	GNmR(ppm)	YAME(ppm)
K	1524.6	$4.464x10^4$	24630±369	24090±361	25010±375
Mg	1014.4	567.6	3523 ± 275	3700 ± 322	3415 ± 277
Al	1779	134.4	2948 ± 29	2979 ± 33	2750 ± 30
Cl	2167.7	2232	5458 ± 54	5568 ± 56	5572 ± 55
Ca	3084.5	523.2	8060 ± 379	7898 ± 379	7772 ± 55
V	1434.1	289.02	4.82 ± 0.38	6.31 ± 0.38	4.4 ± 0.5
Mn	2113.1	$9.288x10^3$	113.8 ± 0.5	107.1 ± 0.4	102.1 ± 0.4
Na	2754.0	$5.4x10^4$	516 ± 5	481 ± 3	449 ± 3
Br	776.5	$1.271x10^5$	32.21 ± 0.2	31.6 ± 0.2	32.5 ± 0.2
La	1596.2	$1.451x10^5$	6.07 ± 0.07	6.25 ± 0.01	6.20 ± 0.10
Sm	103.2	$1.667x10^5$	0.94 ± 0.01	0.96 ± 0.01	0.92 ± 0.01
Sc	889.3	$7.197x10^6$	0.56 ± 0.02	0.58 ± 0.02	0.55 ± 0.02
Cr	320.1	$2.3933x10^6$	0.47 ± 0.01	0.8 ± 0.21	0.69 ± 0.13
Fe	1291.6	$3.845x10^6$	1379 ± 54	1392 ± 50	1363 ± 50
Co	1332.5	$1.663x10^8$	0.23 ± 0.02	0.29 ± 0.04	0.20 ± 0.03
Zn	1115.6	$2.9722x10^7$	41 ± 3	28 ± 4	34 ± 4
Rb	1076.6	$1.6157x10^6$	34 ± 2	32 ± 2	38 ± 2
Ba	496.3	$1.0195x10^6$	64 ± 1.5	BDL	BDL
Nd	91.1	$9.504x10^5$	BDL	2.78 ± 0.85	BDL
EU	1408	$4.1972*10^8$	0.11 ± 0.03	0.12 ± 0.03	0.16 ± 0.04
Tb	879.4	$6.2467x10^6$	0.17 ± 0.04	BDL	0.18 ± 0.04
Yb	396.3	$3.6202x10^5$	0.57 ± 0.08	0.50 ± 0.08	0.55 ± 0.07
Th	312	$2.333x10^6$	0.08 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
Lu	208.4	$5.797x10^5$	$5.1x10^{-6}$	$7.1*10^{-6}$	$3.41x10^{-6}$

*ppm=parts per milion.

Table 11: Concentration of elements in the sample Chima.

of the elements is given in the fig 38.

There is an interest in herbal medicine for the treatment of main ailments by people to get cured from many disease types. The main advantage of herbal medicines is that they are naturally occurring products having relatively lower side effects. Trace elements play a major role in healing diseases, whereas excessive intake of some of these essential elements may adversely affect the human metabolic function (36; 37). At high concentrations these essential elements can lead to poisoning (38). The trace elements play a vital role in the medical value of plants as curative and preventive agents in combating disease, nutritive and catalytic disorders. The concentration of trace elements in plants is so meager that their importance was ignored for a long time.

The elemental concentrations were determined to verify the biological role of trace elements in anti parasitic medicinal plant flower are K, Mg, Al, Cl, Fe, Ca, Mn, Na, V, Br, La, Sm, Sc, Cr, Co, Zn, Rb, Ba, Nd, Eu, Tb, Yb, Th.
In different literatures, it is explained that the elements Fe, K, Mg, Na, Ca, Co, Mn, Zn and Cu have been classified as essential elements, Ni, Cr are possibly essential while Cd, Pb and Li are non essential elements for the human body. Among the various elements detected in different medicinal plants used in the treatment of different diseases, Calcium and potassium are found in major concentrations in these plants, this work also justifies a higher concentration of these elements relative to others (39).

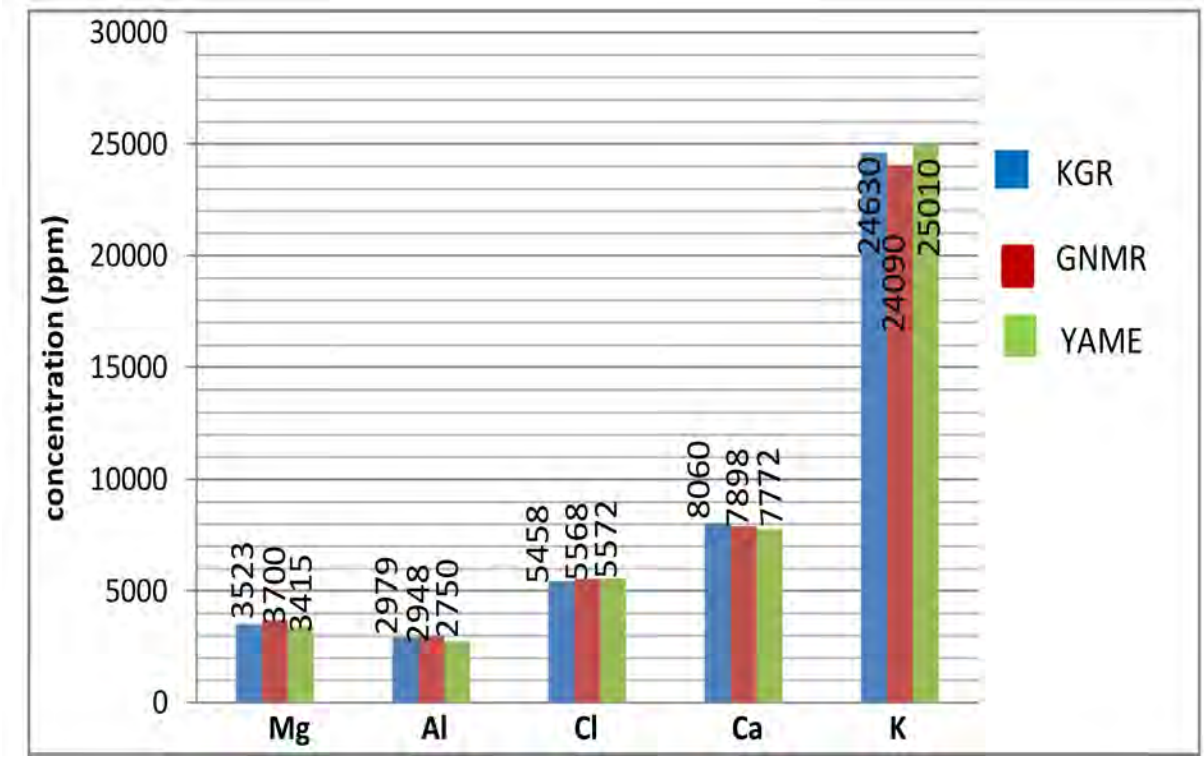

Figure 38: Column chart showing the differences in the concentration of major elements found in the "Chima" samples.

In this study, Bromine was obtained in the three samples and its concentration in the sample "KGR" is 32.21±0.2 ppm, the concentration in "GNMR" sample is 31.6±0.2ppm and it is 32.5±0.2 ppm in the "YAME" sample. The concentration of bromine in the "KGR" and "YAME" samples is higher than its concentration in the "GNMR" sample. Bromine is corrosive to human tissue in a liquid state and its vapors irritate eyes and throat. Bromine vapors are very toxic with inhalation. Humans can absorb organic bromines through the skin, with food and during breathing. Organic bromines are widely used as sprays to kill insects and other unwanted pests. This poisonous nature of the

element may act to kill the parasite tapeworm inside human intestine after people of this research area take 'Chima" as a medicine. High doses of bromine can cause problems in a human being too. The most known health effects that can be caused by bromine-containing organic contaminants are malfunctioning of the nervous system and disturbances in genetic materials, damage to organs such as liver, kidneys and lungs and they can cause stomach and gastrointestinal malfunctioning. Some forms of organic bromines, such as ethylene bromine, can even cause cancer, damage the nervous system and the thyroid gland (40).

Zinc was found in the all of the three samples. Its concentration variation shows that the sample "KGR" contains highest "41±3 ppm" compared to the other two, as can be seen from table 11. The medicinal advantage of Zinc is given in section 6:4.

Sodium was present at major levels with its highest concentration found in "KGR" at 516±5 ppm and the least concentration was 481±3 ppm in "GNMR" sample.

Potassium concentration was found to be the highest of all elements in all of the three samples. The largest concentration was found to be 25010 ±375 ppm in "YAME" sample. Its concentration was 24630±369 ppm in "KGR" and 24090±361 ppm in "GNMR" samples.

Toxic elements such as Cd, Hg and Sb were not detected in the sample. It does not mean that these elements are totally absent from the samples, but the concentrations of these elements present in the sample analyzed are found to be very low below the detection limit.
The use or importance of Potassium, calcium and sodium, are described in section 9.4,.

Barium(Ba) and Neodymium(Nd) are the elements which were not found in all the three samples. Barium was found in the "KGR" sample with a concentration of 64±1.5 ppm but its concentration in the other two "GNMR" and "YAME" samples was below detection limit(BDL). In other case Neodymium was detected in in GNMR sample with a concentration of 2.78±0.85 in parts per million but its concentration was below detection limit in the other two samples "KGR" and "YAME".
According to different literatures out of the known natural elements that play key role in the evolution of life, there are three groups of elements, the first group are macro elements which are found in all of green plants in high concentrations "Main organic elements", the second group called "secondary organic elements" and the third are "Trace elements". Main organic elements: H, O, C, N, S, P Secondary organic elements: Fe, Mg, Ca, Na, K

Organic trace elements: Li, B, J, Cl, Br, Al, Si, Ti, Mn, Co, Cu, Zn, Se, Mo, Bi, V, Rb.

In this work a focus was only on the investigation of the two groups, Secondary organic elements and organic trace elements. And the conclusion was that, the element bromine plays a vital role in the killing and discharge of the parasite tape worm from the human intestine. And, We hope that our results give sufficient information on the concentration of elements in the sample which can provide scientific data as an input for the environment.

Chapter Six

6 Multi Elemental Analysis of mineral soil called "Ewoa"

6.1 Introduction

In Ethiopia, large percentages of the populations are engaged in farming and cattle production. Mineral soils and plants play a vital role in these population to fatten the cattle. The minerals and mineral water were mostly being used as a medicine for the cattle (cows, sheep, goats, donkeys, horses, etc.). Particularly in the region called Gurage Zone, Shamene-Eja farmers use a mineral soil called "Ewoa" as a free choice mineral in order to keep the flesh that can be produced from the cattle be better quality and produce qualified Milk and Milk products, like butter and cheese.

When a grazing field contains "Ewoa", the animals always go to the soil which contains "Ewoa" unless they are forbidden, that means the animal themselves like to eat the soil called "Ewoa" than grazing. The people in the surrounding scatter the mineral soil over a surface of grazing field containing better grass, so that the animals graze it with out going to other places of the field, this opens up a lot of grazing possibilities by keeping the animals in a limited region of the grazing field from day to day. When ever there is a place in the field of grazing which contains "Ewoa", it's amazing that the livestock eats all the grass around it, plus they scratch the surface of the over grazed soil to get a better more of the mineral. Finally the animals dig a hole at the spot where the mineral soil concentrated more. Figure 39 shows one of such a spot in the field of grazing of cows in the research area.

Those animals which eat "Ewoa" able to graze more, look better, the milk and milk products from these animals taste good including the meat produced when the animals slaughtered. There are no available scientific data which gives information about the elemental composition of the mineral-soil "Ewoa". The aim of this chapter is to analyze this mineral soil using instrumental neutron activation analysis(INAA) to check for the elements present in the mineral soil(Ewoa) qualitatively and quantitatively.

Instrumental Neutron Activation Analysis (INAA) is a relatively straightforward technique for determining elemental abundances in a wide range of materials (2). The con-

Figure 39: A hole dug by grazing animals in the field at a spot where the soil contains the mineral soil "Ewoa".

centration of an element in the sample is calculated using equation 18 (41; 3).

In this work INAA is chosen for the elemental analysis of the mineral-soil samples for its multi-element analysis characteristic and for its precision over other methods (43). In this chapter, the INAA results are discussed which were achieved on determining the total element contents in the soil-samples. Results for Standard reference Material Coal Fly Ash (SRM 1633b) and $IAEA - SOIL - 7$ which were analyzed in the same manner as the soil-mineral samples for traceability purposes, were also reported (42).

6.2 Method

6.2.1 Sample collection

The mineral soil is not every where in the region of the research area. It is only found in special places of the surrounding, even not always but during particular season of a year. For this reason the researcher unable to collect sample of the mineral soil directly from the ground. A soil sample from places that animals over graze where the mineral soil is expected highly concentrated, is more of black soil than the gray powder of the mineral soil. For the purpose of getting a better concentrated sample of the mineral soil, samples were collected from three different markets, "Agena", "Shamene" and "Bole". These markets

are situated inside the region of the research area. The samples were dried exposing to dry air at room temperature and powdered to get three samples for irradiation. The three samples were packed in polythene pocket and taken to the minister of agriculture to obtain permission in order to transport them to Nigeria, Ahmadu Bello University(ABU), Center for Research and Training(CERT), where a reactor and facilities were used to irradiate the samples and count activities.

6.2.2 Sample preparation

The powder form of the samples brought from Ethiopia were dried, crushed with agate mortar to obtain a fine powder of the mineral-soil. The crushed soils were then transferred into an evaporating dish and oven dried at temperature of $100c^0$ for 5 hours to allow the moisture in the mineral-soil evaporate. Finally The samples were weighed between 150 mg - 200 mg using a Mettler Toledo balance, and packed in a plastic and put in pre-cleaned air tight polyethylene vials for irradiation in the NAA sample preparation laboratory, Center for Energy Research and Training, CERT, Ahmadu Bello University, Zaria..
With the same procedures standard reference materials coal fly ash (SRM 1633b) and SOIL 7, supplied by International Atomic Energy Agency(IAEA), Vienna, Austria, for verification and quality control purpose were prepared for analysis. The analysis of reference materials which has the same matrix with the unknown samples is one of the means by which the accuracy of the results can be assessed(44). Assessment of the results obtained from the analysis of the reference material(s) using the same technique as used for the unknown samples (being investigated) provide a means of accepting or rejecting the result on element to element basis. In other words, it will give an opportunity to know the result of the analysis of which element to be accepted and of which to be rejected.

6.3 Experiment

6.3.1 Nuclear reaction considered during the experiment

The identification of elements and their concentrations involves the detection of prompt gamma energy of a radioactive and unstable isotope of the element in the sample or detection of delayed gamma rays of the radioactive daughter while it is allowed to decay with its corresponding half life. One of a stable element in a sample swallows neutron performing a well known nuclear reaction (n, γ) when a sample containing unknown elements with unknown concentrations is irradiated in nuclear reactor of certain thermal neutron flux.

In this work samples were irradiated with thermal neutron flux, this is because the cross section of the capture reaction with thermal neutrons is very high, compared to epithermal and fast neutron capture reaction. So that the probability of a nucleus in the sample to capture thermal neutron in the flux is very high. Irradiation of a sample with epithermal neutron flux is suitable for analysis of elements which involve high interference with other (n,γ) reactions.

The elemental analysis of samples with thermal neutrons is, straight forward, non destructive, more amenable compared to other systems. Hence it is called a reference method for other techniques (3).

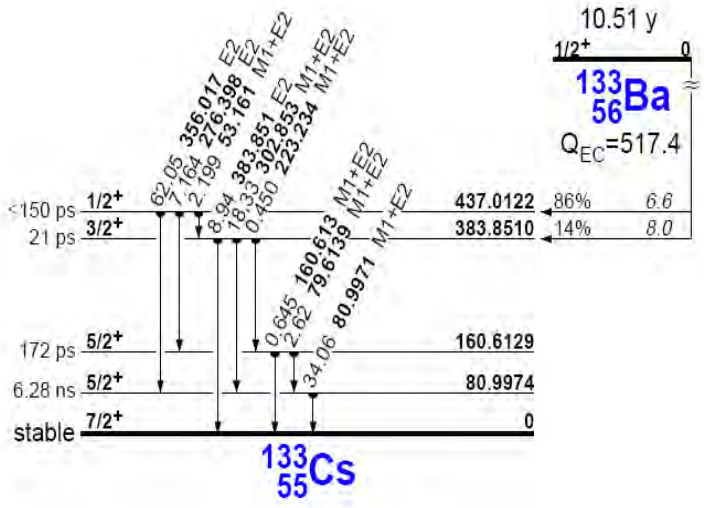

Figure 40: The decay of radioactive nucleus after thermal neutron reaction with stable isotope of the nucleus.

The gamma photon emitted from an element means the energy difference between the higher excited state of a radioactive nuclide of that particular element and the lower excited state or can be the ground state which is given out when it decays. The level scheme in the figure 40 give example of the decay scheme of an element barium considered in the elemental analysis of the samples in this experiment.

For the identification and concentration calculation of barium, the stable barium ^{132}Ba captures one neutron from the thermal neutron flux then the nucleus ^{132}Ba, becomes compound and radioactive barium ^{133}Ba, giving out prompt gammas when the compound nucleus decays to its ground state. The compound nucleus ^{133}Ba at the ground state be-

Element	Eγ(Kev)	$T_{1/2}(second)$	Element	Eγ(Kev)	$T_{1/2}(second)$
Al	1779	134.4	Hf	482.2	$3.6634 * 10^6$
Fe	1291.6	$43.845 * 10^6$	Th	312	$2.333 * 10^6$
Ca	3084.5	523.2	Sc	889.3	$1.197 * 10^6$
Ti	320.1	345.6	Br	776.5	$1.271 * 10^5$
Na	2754	$5.4 * 10^4$	La	1596.2	$1.45 * 10^5$
Mg	1014.4	567.6	Sm	103.2	$1.667 * 10^5$
K	1524.6	$4.464 * 10^4$	Yb	396.3	$3.62 * 10^5$
Mn	2113.1	$9.288 * 10^3$	Dy	94.7	$8.388 * 10^3$
Ba	496.3	$1.0195 * 10^6$	Ta	1221.4	$9.936 * 10^6$
Zn	1115.6	$2.9722 * 10^7$	Eu	1408	$4.1972 * 10^8$
V	1434.1	225	Tm	84.3	$1.8576 * 10^5$
Rb	1076.6	$1.6157 * 10^6$	Tb	879.4	$6.2467 * 10^6$
Cr	320.1	$2.393 * 10^6$	Lu	208.4	$5.797 * 10^5$
Nd	91.1	$9.504 * 10^5$	Sb	564.2	$2.3292 * 10^5$
Co	1332.5	$1.663 * 10^8$	U	277.6	$2.0376 * 10^5$
Cs	795.8	$6.5 * 10^7$			

Table 12: Gamma Energy and half life of elements used during analysis, (35).

gins beta-decay with a half life of 10.51 Yrs to an excited daughter ^{133}Cs in turn it decays to the ground state, there are six gammas which take the excited ^{133}Cs to its ground state. These gamma energy peaks appear in the spectrum which are called the delayed characteristics gamma energies of barium. Measuring one of these gammas, the gamma with 356.01 Kev is preferable due to its large branching ratio and low conversion coefficient, leads to the identification of the nucleus barium ^{132}Ba and obtain its concentration.

The gamma energy used in the analysis of an element is the energy which is best identified and clearly visible independently from energy peaks of other elements in the spectrum compared to other energies of the nucleus. The energy peaks and half life of elements (35) used during the analysis in the analysis were shown in the table 12. .

6.3.2 Irradiation

The irradiation facility used at Ahmadu Bello University, CERT is The Nigeria Research Reactor-1 (NIRR-1), as described in Section 5.2.3. The pneumatic system containing the tubes, the controller, and the sample acceptor is shown in the figure 41.
The irradiation of the mineral soil were in two different techniques on the basis of the half-life of the radionuclide. The first technique is to use a short irradiation (2 min), the second technique is to use a long irradiation (6 h).

Figure 41: The pneumatic rabbit system of the reactor used during irradiation.

For short irradiation, each of the samples were sealed in a rabbit capsules together with the standard reference material and put for irradiation one after the other in one of the outer irradiation sites,B_4, where the thermal neutron flux was $1.25 * 10^{11}\ n\ cm^{-2}\ s^{-1}$ using pneumatic rubber tube supported by air controlled pressure system for a duration of 120 seconds .

For long irradiation, samples were heat-sealed using a hot air blower, in a plastic sheet one by one and put in to polyethylene vial together with standard reference material for irradiation. The samples are irradiated for 6 hours in one of the inner irradiation channels, A_1, where the thermal neutron flux was $2.5 * 10^{11}\ n\ cm^{-2}\ s^{-1}$. This enables exposure to the maximum value of thermal neutron flux which was kept constant by monitoring the neutron flux reading from a fission chamber connected to the microcomputer-controlled room. After the samples have been irradiated they are retrieved via the same pneumatic transfer of the rabbit to the control chamber where they are collected and kept for counting.

6.3.3 Counting

Detection of gamma rays is performed using a high purity germanium detector, shown in the figure 8. This is linked via a multichannel analyzer to a PC with specialized software ('MAESTRO' and 'WINSPAN' programs).

An energy calibration was performed with each batch of samples, as in the section 4.1,

using two standards which put together in to the detector at the same geometry as the sample's counting geometry. The standards were, Cobalt (^{60}Co) and cesium (^{137}Cs).
For the short irradiation regimes, the first round of counting was performed starting from 10-15 minutes at 15 cm geometry after the end of irradiation (time of 2 minutes was irradiation time) depending on whether the activity from the irradiated sample measured by radiation survey meter is reasonably not harmful for the personnel in the counting room, less or equal to 30 μ Sv/h the limit set by health physics section of the center. The length of the counting time was 600 seconds. The second round of counting was performed for 10 minutes, starting 3 hrs - 4 hrs from the end of irradiation at either 5 cm or 15 cm geometry depending up on the dead time of the detector.

Regarding the long irradiation regime, the first round of counting was carried out for 30 minutes after decay time of 4 to 5 days at 2 cm geometry. The second round of long irradiation regime of counting was performed for 60 minutes after cooling time of 10 to 15 days at 2 cm geometry. The choice of the cooling time and sample-detector geometry is such that the detector's dead time is less than 10%.

6.4 Result and Discussion

With the aid of gamma ray spectrum software known as WINSPAN, the gamma rays of product radionuclides were identified by their energies and half life, as well as quantitative analysis of their concentrations were obtained using the energy peak informations, counting, cooling and irradiating time values including the energy peak efficiency of the detector. The software was developed according to Eq.18, and used to calculate the concentration of elements in the sample. The spectrum was directly acquired from the detector by acquisition software MAESTRO. The information was saved in a computer and made to be accessed by another computer with analysis software WINSPAN.

The results of the analysis of the Standard Reference Materials Coal-fly-ash ($SRM1633b$) and $IAEA-SOIL-7$ during this work compared to the certified values in the certificate of the standards (46; 47) were summarized in the tables 13, 14 and 15. It can be seen from the tables that the results of the concentration of the elements obtained during the present work were in good agreement with the certified values obtained from the certificate of the SRM 1633b (46) as shown in tables 13 & 14 and the certificate of $IAEA-SOIL-7$ (47) in table 15.
The non certified values obtained from certificate(46) were in a good agreement with the present work as given in table 14, but these uncertified values were not used for analysis

Element	present work (ppm)*	certified (ppm)*
Mg	4820± 76	4820±80
Al	150500±1053	150500±2700
Ca	15100 ± 767	15100±600
Ti	7910± 150	7910±140
V	295.7 ± 7.9	295.7±3.6
Mn	131.8 ± 1.2	131.8±1.7
Sr	1041 ± 18	1041±14
Na	2010 ± 4	2010±30
K	1950 ±234	1950±300
As	136.2±0.4	136.2±2.6
U	8.79 ± 0.34	8.79±0.36
Cr	198.2±4.4	198.2±4.7
Fe	77800± 2407	77800±2300
Ba	709± 55	70927
Th	25.7 ±0.3	25.7± 1.3

* ppm = parts per million.

Table 13: Coal fly ash (SRM 1633b), certified values compared with the present work.

purpose, except for the analysis of elements Br, Tm and Lu. We believe that the obtained concentrations of these three elements in the samples were not exact it can only be used as an information for the existence of the elements. For the rest of the elements which were not certified in the SRM 1633b but analysed in this work, we have used $IAEA-SOIL-7$ instead since most of them were found in the $IAEA-SOIL-7$ recommended with 95% interval of confidence (47).

The result of the analysis of $IAEA-SOIL-7$ during this work and its recommended values were as displayed in table 15, in the result all the analysed elements concentration lies in the 95% confidence interval.

The concentration of determined elements in the mineral-soil of Eja-shamene, Ethiopia are given in Table-16. The samples were identified as E.Bole, E.Shamene and E.Agena in the name of sampling locations, where "E.Agena" is a code given for Ewoa from Agena, "E,shamene" is for the mineral Ewoa from the market Shamene, and "E.Bole" is for the mineral soil collected from the market Bole. Thirty (30) elements were analysed for the mineral - soil as shown in the table-16. The Table shows that eight elements Al, Fe, Ca, Ti, Na, Mg, K and Mn were present as relatively major elements.
Instrumental neutron activation analysis (INAA) of the mineral-soil Ewoa gives, Aluminum , Iron and Calcium to be the most abundant elements which have concentrations

Element	present work (ppm)	non certified (ppm)
Dy	17 ± 0.5	17
Br	2.9 ± 0.2	2.9
La	94 ± 0.3	94
Sm	20± 0.04	20
Ho	3.5 ±0.24	3.5
Sc	41 ± 0.16	41
Co	50±0.6	50
Zn	210 ± 11	210
Rb	140 ± 8	140
Sb	6 ± 0.1	6
Cs	11 ± 0.7	11
Nd	85± 3	85
Eu	4.1 ± 0.2	4.1
Tb	2.6 ± 0.3	2.6
Tm	2.1± 0.3	2.1
Yb	7.6 ± 0.2	0.3
Lu	1.2± 0.003	1.2
Hf	6.8± 0.4	6.8
Ta	1.8 ± 0.2	1.8

Table 14: SRM 1633b, non certified values compared with the present work.

Element	present work (ppm)	recommended value(ppm)	95% confidence interval (ppm)
Dy	4.7± 0.6	3.9	3.2 - 5.3
La	27.9 ± 0.1	28	27 - 29
Sm	5.1± 0.3	5.1	4.8 - 5.5
Sc	8.36 ± 0.07	8.3	6.9 - 9
Co	8.5±0.1	8.9	8.4 - 10.1
Zn	106 ± 7	104	101 - 113
Rb	51 ± 6	51	47 - 56
Cs	5.8 ± 0.3	5.4	4.9 - 6.4
Nd	30± 2	30	22 - 34
Eu	1.3 ± 0.1	1.0	0.9 - 1.3
Tb	0.7 ± 0.1	0.6	0.5 - 0.9
Yb	1.9 ± 0.2	2.4	1.9 - 2.6
Hf	4.9± 0.2	5.1	4.8 - 5.5
Ta	0.7 ± 0.1	0.8	0.6 - 1.0

Table 15: $IAEA - SOIL - 7$, recommended values and 95% confidence intervals as given in (47) compared with the present work.

in the order of 10^5 ppm.

Aluminum: Aluminum was found to be more dominant element than the other elements in the present study. The region of spectrum of the sample in the first short counting of the sample is shown in the figure 42.

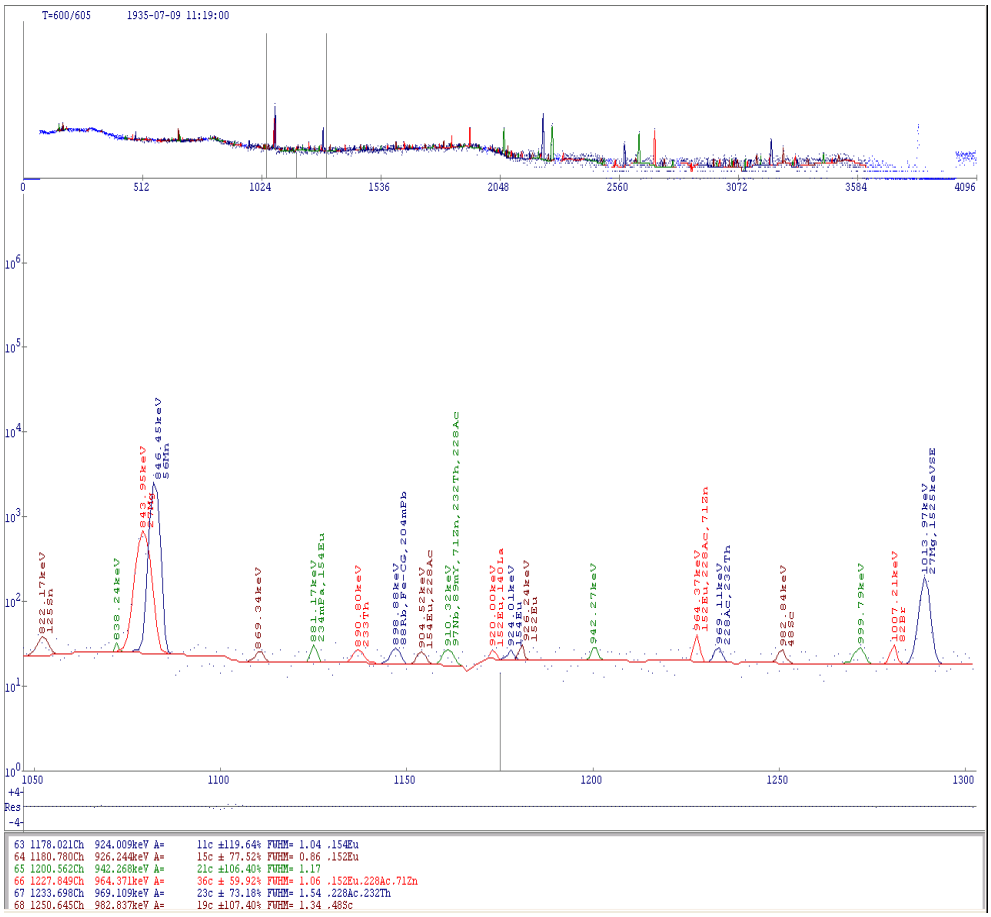

Figure 42: A region of spectrum of the sample "Ewoa".

The concentration of aluminum varies from 63830 ppm to 59100 ppm. The lowest and highest value of this element was recorded for E.Agena and E.Bole respectively. Variation of Aluminum in the samples may be the difference in the places where the mineral soil was collected, we thought of as being the slight differences in the concentration of the element in the crust.

Iron: As can be seen from Table 16, Iron(Fe) is the most abundant element next to Aluminum in all of the samples. In the present study, its concentration ranges from 45620 ± 365 ppm - 48760 ± 390 ppm. Relatively highest concentration is obtained from a sample

Element	E.Bole (ppm)	E.Agena (ppm)	E.Shamene (ppm)
Al	63830± 574	59100 ± 650	62230 ± 497
Fe	45620 ± 365	48760 ± 390	47550 ± 380
Ca	24550 ± 2479	28760 ± 2559	24250 ± 2449
Ti	7923 ± 594	2519 ± 571	7307 ± 540
Na	6610 ± 7	6469 ± 13	6370 ± 13
Mg	4067 ± 862	3520 ± 721	3837 ± 986
K	1511±181	1632±390	1645±209
Mn	1377 ± 5.5	1237 ± 3.7	1369 ± 5.4
Ba	343 ± 4	329 ± 4	314 ± 5
Zn	159.7 ±10.9	170.1 ± 10.6	176.6 ± 10.8
V	100 ± 5	91.2 ± 4.5	105 ± 5
Rb	65 ± 4	44.4 ± 1.2	71.2 ± 4
Cr	67 ± 3	69 ± 2.83	64.7 ± 2.97
Nd	59.3 ± 0.2	68.3 ± 2.6	58.4 ± 2.3
Co	16.9 ± 0.4	18.04 ± 0.4	17.12 ± 0.4
Hf	12.7 ± 0.3	13.6 ± 0.3	12.4 ± 0.3
Th	11.3 ± 0.2	11.7 ± 0.2	11.19 ± 0.25
Sc	10.5 ± 0.1	10.95 ± 0.08	10.83 ± 0.08
Br	4.11 ± 0.29	4.9 ± 0.32	5.6 ± 0.34
La	9.1 ± 0.1	8.64 ± 0.13	8.5 ± 0.13
Sm	1.2 ± 0.03	1.2 ± 0.02	1.1 ± 0.02
Yb	6.4 ± 0.18	6.4 ± 0.17	6.4 ± 0.17
Dy	5.3 ± 1.4	12.5 ± 1.0	11.1 ± 1.4
Ta	4.7± 0.3	5.8 ± 0.3	5.3 ± 0.3
EU	3.3 ± 0.2	2.4 ± 0.2	2.7 ± 0.2
Cs	3.04 ± 0.07	3.3 ± 0.04	3.5 ± 0.04
Tm	2.68 ± 0.26	2.5 ± 0.2	2.3 ± 0.2
Tb	2.5 ± 0.15	2.36 ± 0.15	2.4 ± 0.2
Lu	0.93 ± 0.03	1.03 ± 0.03	0.92 ± 0.03
Sb	0.38 ± 0.02	BDL	BDL
U	BDL*	BDL	BDL

* Below Detection Limit.

Table 16: Concentration of elements in the samples of Ewoa.

collected from "Agena" and the lowest concentration is from the sample E.Bole.
It is a key element in the metabolism of almost all living organisms (48). In humans, it is an essential component of hundreds of proteins and enzymes (49). Heme is an iron-containing compound found in a number of biologically important molecules. Hemoglobin and myoglobin are heme-containing proteins. They are involved in the transport and storage of oxygen (50). Cytochromes are heme-containing compounds which are vital in mitochondrial electron transport; therefore, cytochromes are critical to cellular energy production and thus life. They serve as electron carriers during the synthesis of ATP, the primary energy storage compound in cells (50).

Calcium: For the use and function of calcium see section 9:4.

Titanium: Titanium is the ninth most abundant element on earth. Titanium has no known biological role. But it is not toxic (51). In this study it is the fourth most concentrated element in the mineral soil.

Elements sodium, Magnesium,potassium and Manganese were the second group of elements having concentrations in the order of 10^4 ppm, in all of the samples of the mineral soil.
Sodium: Sodium helps to maintain the bodys fluid balance. It is also essential for nerve transmission, muscle contraction and cardiac function (52). Sodium is the primary determinant of extracellular fluid volume, including blood volume, a number of physiological mechanisms that regulate blood volume and blood pressure work by adjusting the body's sodium content. Its retention results in water retention and sodium loss results in water loss (52).
Sodium is the cation in the compound sodium chloride and in some other salts.

Magnesium: The concentration of magnesium ranges from 4067 $\pm$ 862 ppm to 3520 $\pm$ 721 ppm, in the samples E.Bole and E.Agena respectively.

Magnesium is involved in more than 300 essential metabolic reactions (53). For example, the metabolism of carbohydrates and fats to produce energy requires numerous magnesium-dependent chemical reactions (54). Magnesium is required for the active transport of ions like potassium and calcium across cell membranes. Through its role in ion transport systems, magnesium affects the conduction of nerve impulses, muscle contraction, and normal heart rhythm.

Potassium: Potassium is an essential dietary mineral and bodys principal intracellular electrolyte. Normal body function depends on tight regulation of potassium concentrations both inside and outside of cells (55). Potassium is the main positively charged ion (cation) in the fluid inside of cells, Potassium concentrations are about 30 times higher inside than outside cells, while sodium concentrations are more than ten times lower inside than outside cells . Potassium is critical for nerve impulse transmission, muscle contraction, and heart function (52).
In this work the concentration of Potassium is found to be ranged from 1511±181 ppm to 1645±209 ppm, the smallest being from E.Bole and the higher concentration was from E.Shamene. This concentration may be reasonably good for the people and animals using the mineral soil.

Manganese: Essential elements activate enzymes and vitamins hence lack of them can present serious health challenges including clinical and pathological disorders in animals, plants and man. Some essential elements make vitamins work more effectively. For instance, vitamin A works best with Se and Zn while vitamin B are enriched by Se, Zn, Co, Cu, Fe and Mn. For vitamin C, the essential elements found to promote its effectiveness are Co, Cu and Se while vitamin E is activated by Fe, Mn, Se and Zn (56). Hence manganese is used to control Vitamins B and C, its concentration in the mineral soil is essentially acceptable.

Other group of elements Barium, Zinc and Vanadium constitute those elements whose concentration lies in the order of 10^2 ppm in almost all of the mineral soil samples.
Zinc: Zinc is one of the most abundant essential trace metals in animals and human. The highest concentration of Zinc occurs in the eyes, male sex organs, liver and kidneys. It is also present in the plasma, erythrocytes, leukocytes and platelets. Zinc is essential for proteins and synthesis of cells genetic material DNA and RNA (52; 56). It helps the pancreas with its digestive functions, helps metabolize carbohydrate, protein and fat, liberate vitamin A from storage in the liver and dispose of damaging free radicals (56). Adding a little zinc to the diet could reduce the duration of diarrhea attack by 20-30% and could stop up to 38% of cases from ever happening at all (57). Zinc could also reduce respiratory infections such as pneumonia by up to 45% and malaria cases by 35% (57).

Zinc is one of the essential mineral elements that is found in almost every cell, where it stimulates the activity of over 100 enzymes needed for various biochemical reactions (58; 59). In fact, it has been established that the six categories of the international nomenclature are zinc metalloenzymes (60). Important enzymes stimulated by zinc, sup-

port metabolic processes such as the immune system, wound healing, organoleptic abilities of taste and smell, brain development, synthesis of DNA and RNA, normal growth and development during pregnancy, cell division, sexual maturation, storage and release of insulin among others (62). Because of its roles in the biochemical processes of growth and development, zinc is considered as one of the most essential mineral elements in fetal, infant and early childhood development(62).

There were other elements with minor and trace levels as shown in table 5 which has very useful roles in the animals and human development. From all the elements identified in this experiment we didn't find a heavy metal with toxic level of concentration or any other toxicity in all of the samples. Hence we saw that, the mineral soil contains more useful elements in its nature for animals and human.

Chapter Seven

7 Naturally occurring radioactive materials measurement of the mineral soil Ewoa

7.1 Introduction

Natural radioactivity is the major contributor to ionizing radiation in environment, that comes from both natural background and man-made sources (18). Most of these radionuclides are long half-lives which will remain in the environment even after millions of years. Some of these radionuclides and their progenies are emitting gamma rays, which become one of the major sources for external exposure, (16).

Naturally abundant radionuclides (^{226}Ra,^{232}Th and ^{40}K) in the environment and releases from fertilizers, agrochemicals, research and medical facilities forms the bulk of radionuclides in ground and surface water,(65). Therefore presence of radioactivity in contaminated environment can be attributed to naturally occurring and or artificially induced sources. Naturally occurring radioactivity are due to bedrock formations which are weathered, resulting in mineral leaching that leads to contamination, (19). Artificial radioactivity is due to human activities. Contaminations are mainly as a result of agriculture, medicine, research as well as other activities like mining and milling of mineral ore which exposes the earth surface. All this contamination may have health effect (61); that poses great danger to human and other living organism. Early investigations in soil and rock (i.e., components of earths crust) showed that there are measurable amounts of radio nuclides such as Uranium and Thorium. Some of radioactive gaseous isotopes are released to the atmosphere. Radium-226 produces Radon-222 via alpha decay which diffuses from the earth into the atmosphere producing a number of short lived radio nuclides, inhalation of the radiation in larger doses can produce lung cancer (16).

This chapter focuses on the measurement of natural radioactivity of a mineral soil "locally called Ewoa". People using the mineral soil store it in large amount inside their living home for longer durations. Studying the radioactivity of the mineral helps to check if the cough which is common in animals and people in the surrounding, they associate it with a cold weather, "Gheri", has some connection with the radioactive dose emanating from the soil. It also is used as a sample by the researcher to apply the knowledge of nuclear physics and measure radiations emanating from materials in nature.

Because the half-lives of the parent nuclei are so long relative to the other members of each series, all members of each decay series are in secular equilibrium i.e the activities of each member of the chain are equal at equilibrium if the sample has not been chemically fractionated (19).

In gamma-ray spectroscopic studies of these decay series, most frequently decays from the daughter can be observed. For example, in the Thorium (^{232}Th) series gamma-ray decays from $^{228}Ac(338.32, 911.20, 968.97keV$ with relative intensities of $41.127\%, 25.8\%$, and 15.8%, respectively), ^{212}Bi (609.31 and $1120.29keV$ with relative intensity of 44.6%, 14.7%) and $^{208}Tl(2614.53keV$ with 35.64% relative intensity) are observed. Whereas, in the Uranium (^{238}U) series, gamma-ray following the radioactive decays of ^{226}Ra (186.21 keV 3.59%),^{214}Pb (351.93 keV with 35.1% intensity) and ^{214}Bi (609KeV 46.1%, 1.765MeV 15.4%, 1.12MeV 15.1%) can be readily identified (18).

7.2 Materials and Method

The major technique employed in to the analysis of the samples for background activity is the Gamma Spectroscopy using NAI(Tl) detector because the resolution of the detector is not very important as the spectrum contains well separated peaks.

7.2.1 Study Area and Sample Collection

Three samples of the mineral soil were collected from three different markets in the region mentioned in chapter two. The samples were kept opened to dry at ambient temperature at laboratory in a clean environment, which were later carefully packed into polyethylene bags and transported to the Center for Energy Research and Training, Zaria, Nigeria for further preparation, Gamma spectroscopy count and analysis in accordance with IAEA method.

7.2.2 Samples Preparation

The collected samples (i.e Mineral soil samples) brought to the laboratory were left open for a minimum of 24 hrs to dry under ambient temperature if wet, in the NORM preparation laboratory CERT,Ahmadu Bello University, Nigeria, Zaria, similar to in (61). They were grounded to fine powder and packed to fill cylindrical plastic containers of height 7cm by diameter 6cm in order to fit with the sample putting space in the lead shielding of NaI(Tl) detector, figure 9 .

This satisfies the selection of optimal sample container height (63; 64). Each container were containing approximately 295.0 - 300.g of the sample. They were carefully sealed (using Vaseline, candle wax and masking tape) to prevent radon escape as shown in figure 43, and store for a minimum of 30 days to allow the natural radioactivity attain secular equilibrium, (64).

Figure 43: Sealed samples for measurement of NORM.

Measurement of the three radionuclides , (^{226}Ra,^{232}Th and ^{40}K), were carried using NaI(Tl) gamma spectrometer. Gamma ray spectrometry technique was employed in the spectra collection of the prepared samples using the higher energy region of the gamma line as indicated in the table 7, so that the concentration of the radioactive materials can be calculated.

The measurement system consists of a 7.62 cm X 7.62 cm NaI(Tl) detector housed in a 6 cm thick lead - shield and lined with a cadmium and copper sheets. The shield assisted in the reduction of the background radiation.

IAEA NORM standards (IAEA/RGK-1, IAEA/RGU-1 and IAEA/RGTh-1) containing known amount of the radioactive elements were used for the purpose of quality assurance.

Counting of the activity concentration of (IAEA-RGK-1) was made in the same procedure and geometry as the sample and background, from which the potassium concentration was analyzed. The obtained concentration of potassium in the standard was, finally compared with the value given in the certificate of the standard (34).

With the same procedure explained for (IAEA-RGK-1) for the analysis of potassium, the standard reference material (IAEA-RGU-1) was analysed for the quality control of Uranium and a reference material (IAEA-RGTh-1) was used for the analysis validation of Thorium. The spectrum obtained during the counting of the reference materials were as shown in figure 28, 29 and 30.

All the obtained raw data were converted to conventional units using calibration factors to determine the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th (20).

7.2.3 Technique of Activity Acquisition and Analysis

The prepared samples were mounted on the detector surface and each was counted for 29,000 seconds in reproducible sample-detector geometry. The configuration and geometry was maintained throughout the analysis. A computer program MAESTRO was used for data acquisitions and save the spectrum of the activities.

The 1764 keV -line of ^{214}Bi was used in assessment of the activity concentration of ^{226}Ra while 2614.5 keV -line of ^{208}Tl was used to measure the activity concentrations of ^{232}Th. The single 1460 keV -line of ^{40}K was used in evaluation of ^{40}K. The activity concentrations in the samples were obtained using Eq. 29.

$$C(BqKg^{-1}) = KC_0 \tag{29}$$

Where $K = \frac{1}{\epsilon P_\gamma M_s}$, C is the activity concentration of the radionuclide in the sample given in $Bqkg^{-1}$, C_0 is the count rate under the corresponding peak, ϵ is the detector efficiency at the specific gamma ray energy, P_γ is the absolute transition probability of the specific γ-ray and M_s is the mass of the sample (kg). The below detection limit (BDL) of a measuring system describes its operating capability without the influence of the samples.

The BDL given in $Bqkg^{-1}$ which is required to estimate the minimum detectable activity in samples was obtained using Eq.30, (16; 20).

$$DL(Bqkg^{-1}) = 4.65\frac{\sqrt{C_b}}{t_b}K \tag{30}$$

where C_b is the net background count in the corresponding peak, t_b is the background counting time (s) and k is the factor that converts counts per second (cps) to activity concentration ($Bqkg^{-1}$) as given in Eq.29 (18).

All the obtained raw data were converted to convectional units using conversion factors of $8.632x10^{-4}$, $8.768x10^{-4}$ and $6.431x10^{-4}$ for ^{40}K, ^{226}Ra and ^{232}Th respectively to determine their activity concentrations (64). With the counting time of 29,000 seconds for each sample, the environmental γ-ray background of the laboratory site was determined using an empty container under identical measured conditions. This was subtracted from the measured gamma ray activity concentration of each sample (20).

Calculation of Absorbed Dose Rate from Measured Activity Concentrations of the mineral soil:

Radiation emitted by a radioactive substance is absorbed by any material it encounters. Different literatures have given the dose conversion factors for converting the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K into dose ($nGyh^{-1}perBq(kg)^{-1}$) as 0.427, 0.662 and 0.043, respectively (63). Using these factors, the total absorbed dose rate in air is calculated by the Eq.31 (64).

$$D = (0.427C_{Ra} + 0.043C_K + 0.662C_{Th})nGyh^{-1} \tag{31}$$

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

Calculation of Annual effective dose:

The estimation of the annual effective dose rates, depended on conversion coefficient from absorbed dose to effective dose, 0.7 $nGyh^{-1}$ and outdoor occupancy factor of 0.2 as proposed by (UNSCEAR, 2000) (63). The effective dose rate in units of $mSvGy^{-1}$ was calculated using Eq.32.

$$Effective\ dose\ rate\ (mSvGy^{-1}) = D(nGyh^{-1})\ x\ 8760h\ x\ 0.2\ x\ 0.7SvGy^{-1}\ x\ 10^{-6} \tag{32}$$

External Hazard Index (Hex):
Radiation exposure due to ^{226}Ra, ^{232}Th and ^{40}K may be external. This hazard, defined in terms of external hazard index or outdoor radiation hazard index and denoted by "H''_{ex}, can be calculated using the Eq.33, (64):

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \tag{33}$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations ($Bqkg^{-1}$) of radium, thorium and potassium, respectively as obtained in the analyzed samples. The value of this index should be less than 1 $mSvy^{-1}$ in order for the radiation hazard to be considered acceptable to the public(18).

Internal Hazard Index (H_{in}):
The internal hazard index (Hin) gives the internal exposure to carcinogenic radon and is given by Eq.34, (64):

$$H_{int} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{299} + \frac{C_K}{4810} \tag{34}$$

The value of this index should be less than 1 mSvy^{-1} in order for the radiation hazard to have negligible hazardous effects to the respiratory organs of the public (64).

7.3 Result and Discussion

7.3.1 Concentrations of the Activities of ^{40}K, ^{226}Ra, and ^{232}Th in the Mineral Soil

For the purpose of checking the quality of the experimental detection of activities and analysis the three IAEA standards were measured and analyzed in this work. The result obtained by the analysis were compared with the values in their certificate which are given with 95% confidence of interval (95%C.I) (34), as shown in the table 17.

As can be seen from the table 17, the activity concentration of the reference materials obtained during the experiment in this work lies with in the 95% interval of confidence of the activity concentrations given in the certificate of the standard reference materials (34). This shows that the result of the activity concentrations measured in the lab background as well as in the mineral soil samples were acceptable.

Analyte	IAEA standard	Recommended Activity(Bq/Kg)	95% C.I (Bq/Kg)	This work Activity(Bq/Kg)
^{40}K	RGK-1	14000	13600 - 14400	13950±30.48
^{226}Ra	RGU-1	4940	4910 - 4970	4941.95±4.9
^{232}Th	RGTh-1	3250	3160 - 3340	3279.8±28.2

Table 17: Activity concentration of radioactive nuclides in IAEA reference materials obtained during the experimental work compared with the values in the certificate.

Three samples of the mineral soil each were taken from three different markets coded SS1, SS3 and SS5,shown in figure 43, (from "Bozebar", "Shamene" and "Bole" respectively) were measured. The spectra that were generated from samples during spectrometric analysis were used in identification of the radionuclides in the samples and analyzing the concentration of the radioactive materials, one of such spectrum was shown in the figure 44. This has made it possible to have a comprehensive activity concentration in (Bqkg^{-1}) of ^{40}K, ^{226}Ra, and ^{232}Th for the mineral soils collected at various locations.

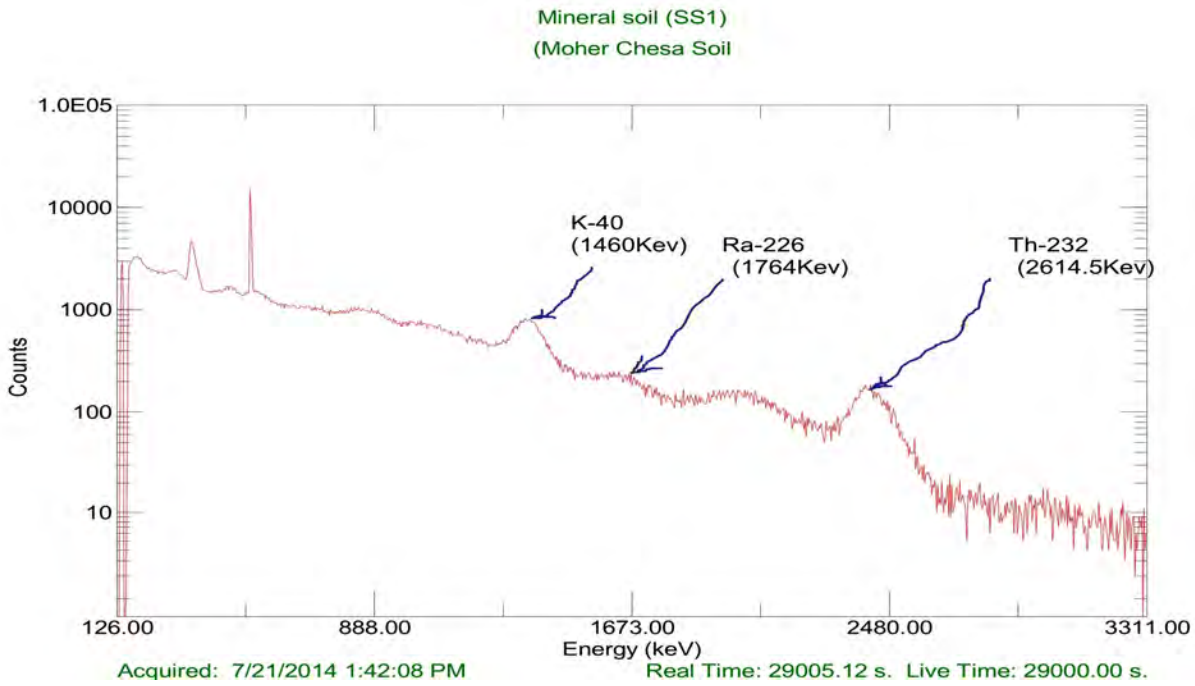

Figure 44: Spectrum of one of the samples of the mineral soil.

The results of analysis of activity concentration of ^{40}K, ^{226}Ra, and ^{232}Th radionuclides in the mineral soils for different locations of the study area are presented in Tables 18.

sample ID	K-40 (cps)	K-40 (Bq/Kg)
SS01	0.281±0.002	437.01±3.11
SS03	0.282±0.0018	438.57±2.80
SS05	0.279±0.0021	433.90±3.26

Table 18: Concentration of radioactive element K-40 in the three samples of Ewoa.

The activity is reported in Bqkg^{-1} on the basis of the sediments dry weight, calculated using the conversion factors as shown in Eq. 35, 36 and 37 (64).

$$C(Bq/Kg)\ of\ ^{40}K = \frac{C(c/s)\ of\ ^{40}K}{0.000643} \tag{35}$$

$$C(Bq/Kg)\ of\ ^{226}Ra = \frac{C(c/s)\ of\ ^{226}Ra}{0.000863} \tag{36}$$

$$C(Bq/Kg)\ of\ ^{232}Th = \frac{C(c/s)\ of\ ^{232}Th}{0.000877} \tag{37}$$

Where $C(Bq/Kg)$ and $C(c/s)$ are concentrations in *Bequrel per kilogram* and in *counts per second* respectively.

The concentration of K-40 activity ranges from $433.9 \pm 3.26 Bqkg^{-1}$ to $438.57 \pm 2.8 Bqkg^{-1}$. K-40 activity concentration in the mineral soils in Bqkg^{-1} are, 437.01 ± 3.11 Bqkg^{-1} obtained from SS01 ("Bozebar" mineral soil), 438.57 ± 2.8 Bqkg^{-1} measured from SS03 ("Shamene" mineral soil) and 433.9 ± 3.26 Bqkg^{-1} measured from SS05, ("Bole" mineral soil), which shows that there is no significant difference between the K-40 activity concentration of the mineral soil samples collected from different locations of the study area. These obtained activity concentration of ^{40}K is slightly higher when compared to the world average values for sediments, 32Bqkg^{-1}, 45 Bqkg^{-1} and 420 Bqkg^{-1} ^{226}Ra, ^{232}Th and ^{40}K respectively, (16).

As shown in table 19, the measured activity concentrations for ^{226}Ra range from $0.019 \pm 0.0003 cps$ to $0.024 \pm 0.0004 cps$.

sample ID	Ra-226 (cps)	Ra-226 (Bq/Kg)
SS01	0.021±0.0004	24.33±0.46
SS03	0.019±0.0003	22.02±0.35
SS05	0.024±0.0004	27.80±0.46

Table 19: Concentration of radioactive element Ra-226 in the samples of Ewoa.

The activity concentration of the mineral soils in $BqKg^{-1}$ as presented in the table 19 are, 24.33 ± 0.46 obtained from SS01 ("Bozebar" mineral soil), 22.02 ± 0.35 measured from SS03 ("Shamene" mineral soil) and 27.80 ± 0.46 measured from SS05, ("Bole" mineral soil), which shows that there is slight difference between SS03 and SS05 in the activity concentration of ^{226}Ra, i.e the mineral soil obtained from "Bole" has activity concentration approximately 5.4Bqkg^{-1} higher than the activity concentration of ^{226}Ra in the "Shamene" mineral soil.

These obtained activity concentration of ^{226}Ra is smaller when compared to the world average values for sediments, 32Bqkg^{-1}, 45 Bqkg^{-1} and 420 Bqkg^{-1} ^{226}Ra, ^{232}Th and ^{40}K respectively, (17).

From table 20, one can see that the measured activity concentrations for ^{232}Th range from $0.028 \pm 0.0001cps$ to $0.067 \pm 0.0002cps$.

sample ID	Th-232 (cps)	Th-232 (Bq/Kg)
SS01	0.064±0.0001	72.9±0.11
SS03	0.028±0.0001	31.93±0.11
SS05	0.067±0.0002	76.39±0.23

Table 20: Concentration of radioactive element Th-232 in the samples.

The concentration values of ^{232}Th in Bqkg^{-1} are, 72.9 ± 0.11 obtained from SS01 ("Bozebar" mineral soil), 31.93 ± 0.11 measured from SS03 ("Shamene" mineral soil) and 76.39 ± 0.23 measured from SS05, ("Bole" mineral soil), which shows that there is difference between SS03 and SS05 in the activity concentration of ^{232}Th, i.e the mineral soil obtained from "Bole" has activity concentration higher than the activity concentration of ^{232}Th in the "Shamene" mineral soil by a factor of about 2.4.

The obtained activity concentration of ^{232}Th in Shamene mineral soil is smaller than the world average values for sediments 32Bqkg^{-1}, 45 Bqkg^{-1} and 420 Bqkg^{-1} ^{226}Ra, ^{232}Th and ^{40}K respectively, (17), while the result of concentrations in SS01 and SS05 is higher.

7.3.2 Absorbed Dose Rate, Annual Effective Dose Equivalent, External Hazard and Internal Hazard Index for the Mineral soil

The absorbed dose rates due to the emitted gamma rays at 1m above the ground for the activity concentration from ^{226}Ra, ^{232}Th and ^{40}K in the samples of the mineral soil were calculated using Eq.31. Table 21 present the dose rate, effective dose equivalent and external and internal hazard indexes form all the sediments. The absorbed dose values ranges from 50.34±0.358 nGyh^{-1} to 82.29±0.509 nGyh^{-1} with a rough average of 70.4 nGyh^{-1} as shown in the table 21. This is within the worldwide value range which is from 18 nGyh^{-1} to 93 nGyh^{-1} of sediments.

No	sample ID	Absorbed dose rate(nGyh^{-1})	Effective dose rate ($10^{-3}mSvy^{-1}$)	External hazard index (H_{ex}) in $10^{-3}mSvy^{-1}$	Internal hazard index(H_{in}) in $10^{-3}mSvy^{-1}$
1	SS01	78.49±0.423	96±0.52	400±2.31	466±3.5
2	SS03	50.34±0.358	62±0.44	274±1.95	317±3.07
3	SS05	82.29±0.509	101±0.62	460±2.81	496±3.93

Table 21: Experimentally determined hazard indexes and dose rates due to Ewoa samples.

The effective annual dose rate due to these radionuclides in the mineral soil was also obtained from Eq.32 and the values ranges from 0.062±0.0004 mSvy^{-1} to 0.101±0.0006 mSvy^{-1} with an average value of 0.082 mSvy^{-1}. This is also less than the average annual dose limit set for radiological assessment which is 1mSvy^{-1} (17).

The external (H_{ex}) and internal (H_{in}) hazard indexes, which represent the risk associated from exposure to a radiation, for the radionuclides in the samples of the mineral soil was calculated using equations, (Eq.33 and Eq.34), the results were as presented in the table 21. From the table 21, it had been shown that the minimum value of (H_{ex}) was 0.274±0.00195 mSvy^{-1} and the maximum value 0.460±0.0028 mSvy^{-1} with over all rough average of 0.378 mSvy^{-1} which is far less than the limit for radiological exposure

protection to the public which is 1 $mSvy^{-1}$ (63).

The analysis of the samples SS01, SS03, and SS05 for their internal hazard index (H_{in}) gives the minimum value 0.317±0.003 $mSvy^{-1}$ from the analysis of the sample SS03 and a Maximum value of 0.496±0.0039 $mSvy^{-1}$ from the analysis of SS05. The sample SS01 analysis resulted in a value of 0.466±0.0035 $mSvy^{-1}$ which lies between the two mineral soil samples and less than the limiting value of radiological exposure protection 1 $mSvy^{-1}$. If the overall average value of the indexes (H_{ex}) and (H_{in}) of the mineral samples were considered, (0.378 ± 0.00236 $mSvy^{-1}$ and 0.426 ± 0.0035 $mSvy^{-1}$ respectively), they have a value less than 1 $mSvy^{-1}$.

This indicated that the risk associated with the mineral soil samples is quite below the limit for radiological exposure protection to the public (63). The activity concentration value obtained for the mineral soils in this study were found to be within the acceptable limits. Most of the activities obtained were lower than the worlds average values. The calculated effective absorbed dose rate, the average hazard indexes obtained for both external and internal exposure do not exceeded the limits set by UNSCEAR (63). Therefore the mineral soil does not pose much or any threat to the public. However care has to be taken since it is believed that radiation at any given level poses a risk.

Chapter Eight

8 Multi-Elemental Analysis of "Atmet, or Bulla" (local food) by Instrumental Neutron Activation Analysis

8.1 Introduction

The research area in this work is predominantly agricultural. A common local food in this area is called "Wusa" in some other parts of Ethiopia also known as "Kocho" which is well known food that the peoples in the surrounding eat every day of a year. It is prepared from a green plant locally called "Enset" (scientific name Ventricosum). The bread form of Kocho presented to be consumed with "kitfo" produced from beef, cabbage and cheese is seen in the figure 45 and its bread is shown in the figure 46.

Figure 45: A dish containing Kocho bread.

Figure 46: Kocho bread.

In this research, samples of higher quality of the family of the food "Kocho" namely called "Atmet" in the research area and called "Bulla" in other part of Ethiopia were considered. The food "Atmet" is mostly prepared in the form of porridge to be consumed by any member of the society in the region of interest. The multi- elemental determination of the food is of great importance for the determination of its nutritional value as well as potentially toxic effects. "Atmet" is a staple food for a large part of the Population in the surrounding, making it among the most consumed food of the region. Ventricosum "Enset" which is the source of "Atmet" is belongs to the family of steam and root edible plants. There are a number of species of "Enset" which are grown as plants.

In recent years, there has been increasing implementation of multi-elemental techniques for the analysis of food items to establish limits for human exposure to contaminants from the food. The study of elements in "Atmet" is important in searching for contamination or leftover toxic elements because foods might be contaminated by chemical compounds, particularly heavy metals, during cultivation. For example, cadmium contamination in agriculture products was discovered (57), (66). Plant product foods have long been regarded as valuable sources of essentials nutrients. They provide energy, protein, minerals, and vitamins in the human diet (37).

Different research projects have been conducted to develop methods to measure elements in foods which are of interest because of their effect on human health (49; 58; 60). Neutron activation analysis (NAA) has the potential to determine multi-elements in all types of samples including "Atmet".

Multi-elemental studies have recently become a reality and with the development of sensitive and sophisticated instrumentation like the NAA, most elements can be determined in a routine manner. Because of the interactive nature of some elements, their determination is essential to provide data on their pattern of association and their composition in food stuffs. There is therefore, a need to know their levels in samples drawn from different chemical environments of the world (49).

The concept of specification applies not only to metals of nutritional importance, but also to potentially toxic elements, such as selenium, arsenic, cadmium, mercury and lead (58). A better understanding of the predominant chemical forms of such contaminants in food would, therefore, seem to be essential for those who have to make decision concerning dietary requirements and related legislation. The study of human nutrition and health requires more information about trace elements species in food (58).

Proper dissemination of accurate information gives consumers with scientifically verified choices, allows industry to make the best use of foods, supplements and processing (which might affect chemical species), and provides governments with the basis for good advice and legislation. Both essential minerals and heavy metals would be useful for the assessment of safety in the consumption of these foods (67). It may be that one day essential trace element species will be listed on food composition labels or that legislation for potentially toxic elements will be based on chemical species present.

The purpose of this chapter is to determine the elemental concentrations in local food called "Atmet" by instrumental neutron activation analysis (INAA) obtained from Welkite zone, Eja of Ethiopia.

8.2 Materials and Method

8.2.1 Collecting and Preparing Samples for Irradiation

A total of three samples were collected of which all were directly from the farmers.
Individual food samples were obtained from local markets in three markets of the surrounding of the research area.

The samples from the markets were labeled as in the table 22.

No	sample label	description
1	ABU	Atmet from Agena
2	BBU	Atmet from Bole
3	SBU	Atmet from Shamene

Table 22: Description of Atmet samples.

The samples were oven dried at a temperature of $40C^0$ for 48 hours using a Heat regulating oven shown in the figure 12. The dried samples were weighed directly into pre-cleaned polyethylene bags which were capped and heat-sealed. The amount of materials taken varied between 200 mg - 250 mg. The heat sealed polythene bags containing samples, were then placed in 7.0-ml irradiation vials which were again capped and heat-sealed. The vials were pre- cleaned by washing them first with distilled water and then soaked in ultra pure HNO3 (acetone) for 24 hours. They were then rinsed thoroughly with distilled deionized water DDW and air- dried in a clean fume hood. The moisture content of the samples was removed using the conventional oven drying method (3).

A similar procedure was adopted for Standard Reference Material NIST 1515, Apple leaves, which were also weighted and packed together with the samples for both regime of irradiation. The purpose of the SRM is for quality control of the experimental procedure.

Irradiation and counting of the samples as well as the facilities used were as described in the section 5.2.3.

8.3 Result and Discussion

The precision and trueness of the method were checked by analyzing SRM (standard reference material), namely NIST 1515, Apple leaves, under the same experimental conditions as the samples and comparing results with the certificate values.

The result of the analysis of the standard reference material, NIST1515, compared to the values in its certificate, Certified and non certified, was as shown in the table 23. This standard reference material is intended primarily for the use in evaluating the reliability of analytical methods for the determination of major, minor, and trace elements in botanical materials, agricultural food products, and materials of similar matrix. A unit of SRM 1515 consists of 500g of dried apple leaves of the Golden Delicious and Rome varieties (68).

The certified concentrations of the constituent elements are given in table 23. These concentrations are based on the agreement of results from at least two independent analytical methods or results from a method of known accuracy but the non certified (NC) values are given as information, they are not cross checked with different methods (68). Table 23 shows the results obtained experimentally during this work were quite agrees with the recommended values, this shows that the results of the analysis of the samples of Atmet were acceptable and correct.

Element	Eγ (Kev)	$T_{1/2}$ (second)	certified value (ppm)	Experimental (ppm)
Mg	1014.4	567.6	2710 ± 80	2710±85
Al	1779	134.4	286±9	286±5
Cl	2167.7	2232	579±23	579±20
Ca	3084.5	523.2	15260±150	15260±143
Mn	2113.1	$9.288 * 10^3$	54±3	54±1
Na	2754	$5.4 * 10^4$	24.4±1.2	24.4±0.5
K	1524.6	$4.464 * 10^4$	16100±200	16100±161
Br	776.5	$1.271 * 10^5$	1.8 NC	1.8
La	1596.2	$1.45 * 10^5$	20 NC	20
Sm	103.2	$1.667 * 10^5$	3 NC	3
Sc	889.3	$1.197 * 10^6$	0.03 NC	0.03
Fe	1291.6	$43.845 * 10^6$	83±5	83±28
Zn	1115.6	$2.9722 * 10^7$	12.5±0.3	125±0.7
Rb	1076.6	$1.6157 * 10^6$	10.2±1.5	10.2±0.3
Ba	496.3	$1.0195 * 10^6$	49±2	49±1
Nd	91.1	$9.504 * 10^5$	17 NC	17

NC = non certified values.

Table 23: Gamma Energy, half life including the concentration in the certificate of NIST1515, (68), compared with experimentally obtained concentration of elements used during analysis.

After the irradiated samples were counted, the spectrum were acquired by the software MAESTRO, and analysed using the analysis software WINSPAN, the elements and their concentration analysed were given as in the table 24. The table shows that Cl, Na, K, Ca, Mn, Sm, and Al were detected during the experimental analysis of the samples.
Elements Sc, Fe, Zn, Rb and Ba are below detection limit (BDL). The part of the spectrum of Atmet which contains Ca, Cl and Na is shown in the figure 47, and the part of the spectrum containing Mn is shown in the figure 48.

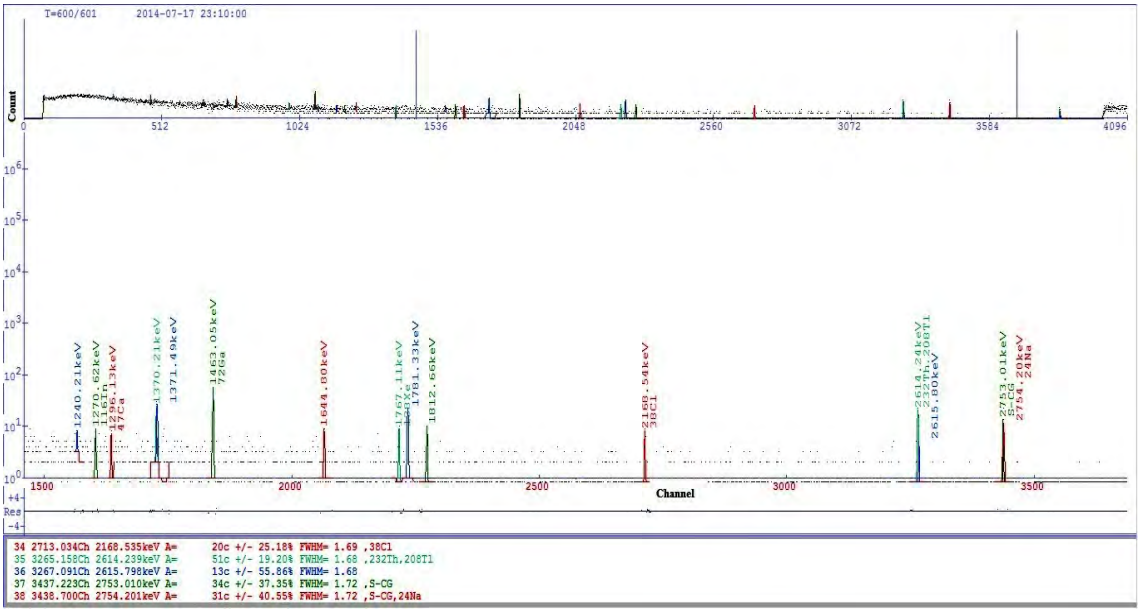

Figure 47: Ca, Cl and Na peak containing spectrum of Atmet.

In general, no significant differences were found among the three samples; however, some considerations can be made as regards a few elements such as “sm” which is BDL in one of the samples and detected in other samples, Ca, Cl, Al, Mn, Na , K and Br, which appear to reach slightly higher concentrations in one of the samples and lower in other. But the concentration difference may be considered very small and negligible.

Calcium from daily and other foods is important for bone strength and cell health. Calcium is an important mineral for a body. It primarily takes three forms in the body. First, it is part of the molecular composition of bone, forming a complex with other molecules. second it exists in bond to proteins and other molecules, and the third as free electrically charged particles (48). Since Atmet is relatively rich in calcium, eating Atmet helps to get the benefits that one get from all forms of calcium.

potassium is an essential mineral for the human body and is needed for the body to function normally. It helps maintain acidity levels and blood pressure with in the body and is also required for electrical signals to go between nerves and cells. Potassium also helps to regulate the water balance in the body and control muscle contractions. it is

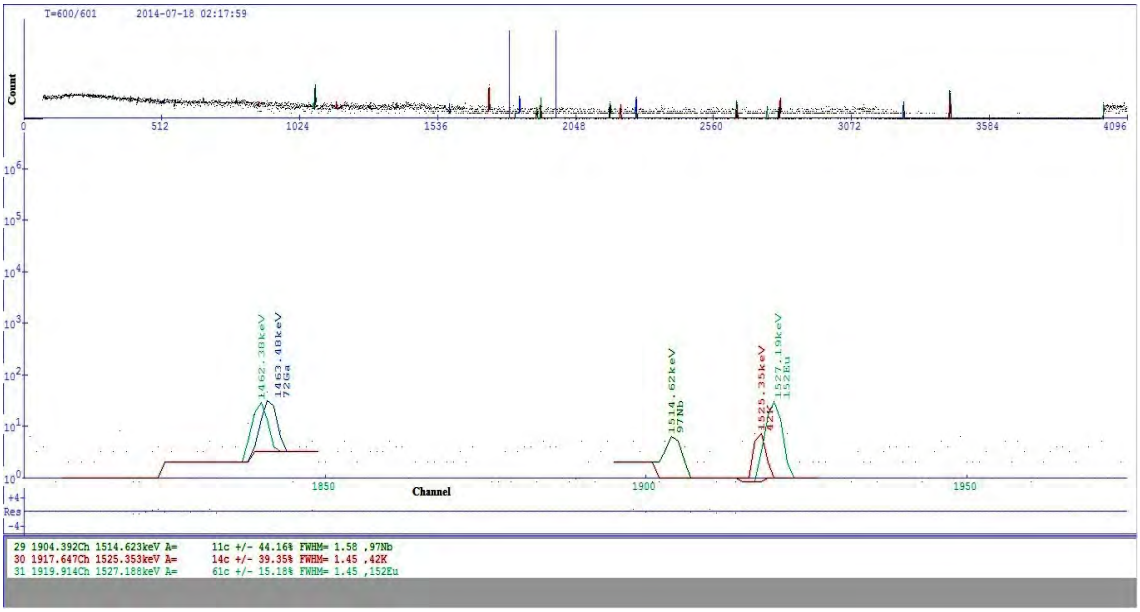

Figure 48: Potassium (K) peak containing spectrum of Atmet.

extremely important that the human body has a good balance of potassium since too little and too much can cause serious health issues.
In this regard eating Atmet helps to get potassium with all of its uses (37).

Aluminum, though it is not very toxic in normal levels, neither has it been found to be essential. Aluminum is very abundant in the earth and in the sea. It is present only in small amounts in animal and plant tissue (60). However, it is commonly ingested in foods and in medicines. Many scientists feel that, because of its prevalence in the earth and its common uses, it is not actually very toxic(58).
Aluminum is not really a heavy metal that is it is low in molecular weight so it does behave differently from metals such as lead or mercury. The evidence of aluminum's toxicity or essentiality is not conclusive as yet (48).

Sodium is an important component in the human body. Controlled levels of sodium are highly significant to our nervous system. It also helps our brain to work. The human diet has a requirement of 1.5 grams of sodium intake everyday.

Chlorine is important for the regulation of osmotic pressure,. Chloride help to maintain the water balance and PH balances. It activate salivary amylase. Chloride provides the acid medium for the activation of the gastric enzymes and digestion in the stomach(52). The other elements Cl, Mn,Br, La and sm are available in a trace level, these elements are not toxic rather useful for life.

Element	Conc.ABU (ppm)	Conc,BBU (ppm)	Conc.SBU (ppm)
Mg	BDL	BDL	BDL
Al	54.5±8.3	65±10	61.3±6.2
Cl	24.5±5.2	29±5	23.3±4.8
Ca	476±10.6	824±14.6	626±11.2
Mn	1.34±0.25	1.43±0.05	1.51±0.25
Na	44±3	26±0.2	41±0.8
K	262±27	132±6	223±38
Br	0.18±0.02	0.19±0.02	0.143±0.02
La	0.09	0.06	0.076
Sm	BDL	0.0057	0.0071
Sc	BDL	BDL	BDL
Fe	BDL	BDL	BDL
Zn	BDL	BDL	BDL
Rb	BDL	BDL	BDL
Ba	BDL	BDL	BDL

Table 24: Concentration of elements in the samples of Atmet obtained during the experiment.

Other elements which are obtained during the experiment in a trace level are Mn, Br, La, and Sm.

From the result of the experiment, the number of elements identified in major, minor and trace levels have no concentrations which is in a toxic level. Bromine concentration is trace so that the possible toxicity of the food due to bromine is not probable.

In sight of the identified elements and their concentrations, the local food Atmet is acceptable and useful type of food.

Chapter Nine

9 Application of NAA to compare elemental concentrations in two medicinal foods locally called "Astara" and "Guariye"

9.1 Introduction

Herbal medicines are the staple of medical treatment in many civilizations in the world (43; 69). Herbal medicines are considered as natures pharmacy and form a major component in all indigenous traditional medicines (70). The sophistication of herbal remedies used around the world varies with the technological advancement of the countries that produce and use them.
These two medicinal plants "Astara and Guariye" are specious of the plant Ventricosum (locally called "Enset"). Both of the plants can be prepared for food in two different ways. One is directly eating the root of the plants by cooking. The second is preparing two parts of the plant including its root and steam by cutting in to small fine parts and mixing to homogenize the parts and keeping compactly packed for about a minimum of fifteen days before it is prepared like a pasty called "Kocho" to be consumed as a food.

Astara as a Medicine: The plant "Astara" can be differentiated from other specious of the plat Ventricosum by its color. Its steam is reddish green and purple near the top of the steam where its branches begin, as shown in the figure 49. Other Ventricosum plants are not dark green near their branches hence it can be easily identified with this color.

People in the research area prepare and cook the root of the plant "Astara" and eat for a minimum of one meal time, either for dinner, or lunch, or both with yogurt when they get a disease which brings a swelling on the part of their body like abscess and they like the swelling (abscess) on their body to burst in to pus and finally cure from it. With a minimum of one or two days the swelling get pierced and give pus which is the sign of getting cure.

When a person gets bone related problems due to unknown reasons since there are no such modern health centers which can identify such disease causes and the economy of the people doesn't allow to go urban regions for medication, there are cultural physiother-

apists who massage the affected bone parts and order the patients to eat Astara at one period of time and eat Guariye at another period of time. Finally most of such patients get cured from the disease.
A maternal mother who gave birth in recent days eat the cooked root of Astara with milk products for two or three days. In the next days her breast carries a lot of milk for the infant so that the infant gets sufficient amount of breast milk to become healthy and strong.

When milk producing animal like cow, goat, etc.. give birth, the farmers in the research area want the animal yield better amount of milk per day. For this reason the animal eats cooked Astara steam and root mixed with a mineral soil called "Ewoa" studied in chapter five. The animals milk product per day will be increased for longer period of time.

Figure 49: Ripened Ventricosum plant specious called "Astara"

But eating Astara during the period of pregnancy is strictly not allowed in the society, because it brings abortion of the pregnancy in some cases and inconvenient health condition of the pregnant most of the time. Even when people like to abort a pregnancy they

do not eat Astara, because it can not do the assignment effectively, rather it makes the fetus grow not healthy and affects the mother's health negatively.

Guariye as a Medicine. The medicinal plant which is the specious of Ventricosum, also can be prepared in two ways as mentioned above in preparing Astara. This plant can be easily identified from other specious by its color. It is yellowish green, from bottom to top, as shown in the figures 50.

Figure 50: Young Guariye plant the specious of Ventricosum.

The plant helps the people in the surrounding as a medicine for healing from bone fracture or bone break. When a person gets such incidence, there are local doctors who can treat, massage and bandage the fractured or broken bone forcing the pieces back in to the original place. According to a belief in the society, these bone massaging doctors get the skill by nature, or inherited from their family ancestors. Except some one who is the member of these family, no one is allowed in the society to carryout the task.

After a patient get tied with the bandage by the local doctors, he/she will be ordered

to continuously consume the cooked root of Guariye plant till he/she gets cure. The cure may take a period of one month to three months depending up on the amount of the damage. It is not allowed to eat Astara to this person for about one to two years, because the bone fractured place of the body starts to spoil making a pus like fluid.

9.2 Sample Collection and Preparation

Astara and Guariye are the most used plants in traditional herbal medicine in the rural part of Gurage zone, Shamene, of Ethiopia. The root samples used in the experiment were collected from the local farmers randomly. Ten Astara plant roots were collected and prepared to be homogenized in to two parts (five of them in one from "Gebteder" and the rest five from "Egrema" region of the surrounding), depending up on the weather condition of the region which grows the plants. Similar procedure was used to collect the sample of Guariye. Surface contaminants of the roots were removed by scratching first from the surface then washing with distilled water repeatedly.

The useful parts of the samples were air dried in a clean drying chamber and then dried at $60C^0$ for 12 h in an oven. The dried samples were then crushed into a homogeneous fine powder of uniform particle size using an agate mortar. Two samples from each of the medicinal plants, a total of four samples, were prepared and transported to CERT, Zaria, Nigeria for irradiation facilities.

The dried samples were further crushed in to fine powder using agate mortar and oven dried until constant mass in the sample preparation laboratory of CERT. A mass in the range of 200 mg - 250 mg were measured from each of the four samples, coded, encapsulated and sealed using polythene vials for irradiation together with a multi elemental standard (Apple leaves, National Institute for Standards and Technology (NIST) 1515), which was prepared in the same manner as the samples.
The purpose of preparing the multi elemental standard was for analytical quality control.

9.3 Experiment

The facilities used, Irradiation, counting and measurement of samples were similar to the one that have been thoroughly described in the chapter five section 5.2.3. Four subsamples of each of the medicinal plants were prepared to allow quadruplicate analysis by instrumental neutron activation. Some of the part of the spectrum obtained during counting were as shown in the figures 51 and 52.

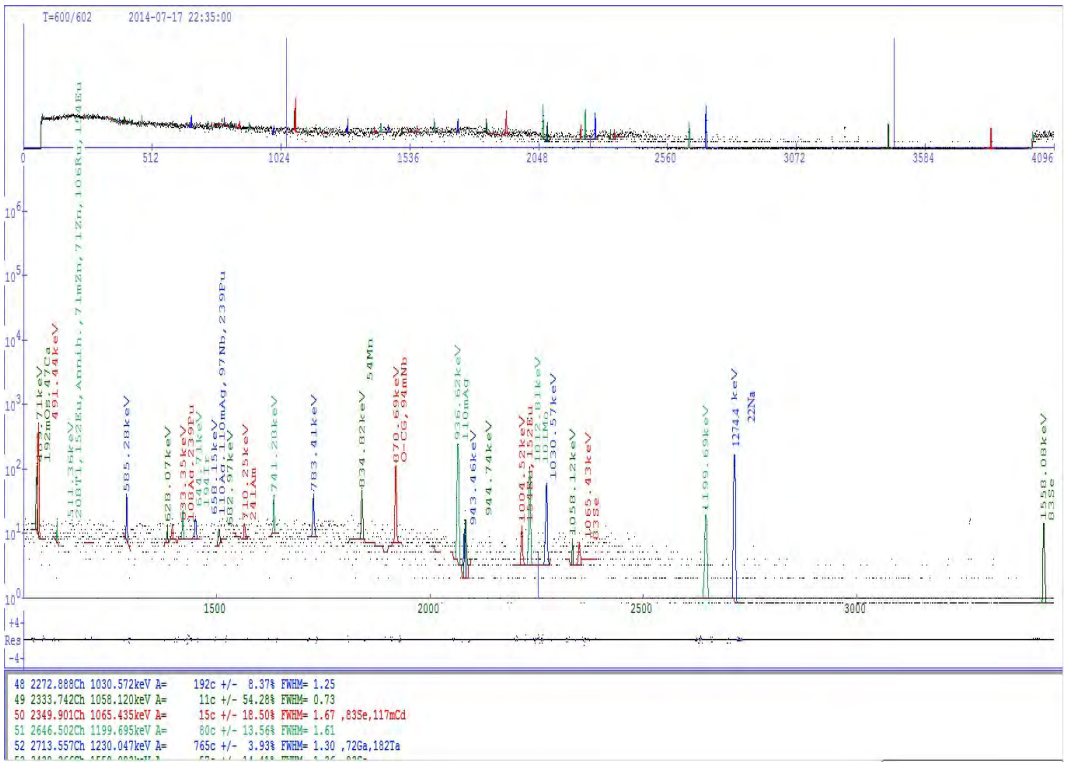

Figure 51: Part of first short spectrum of Astara.

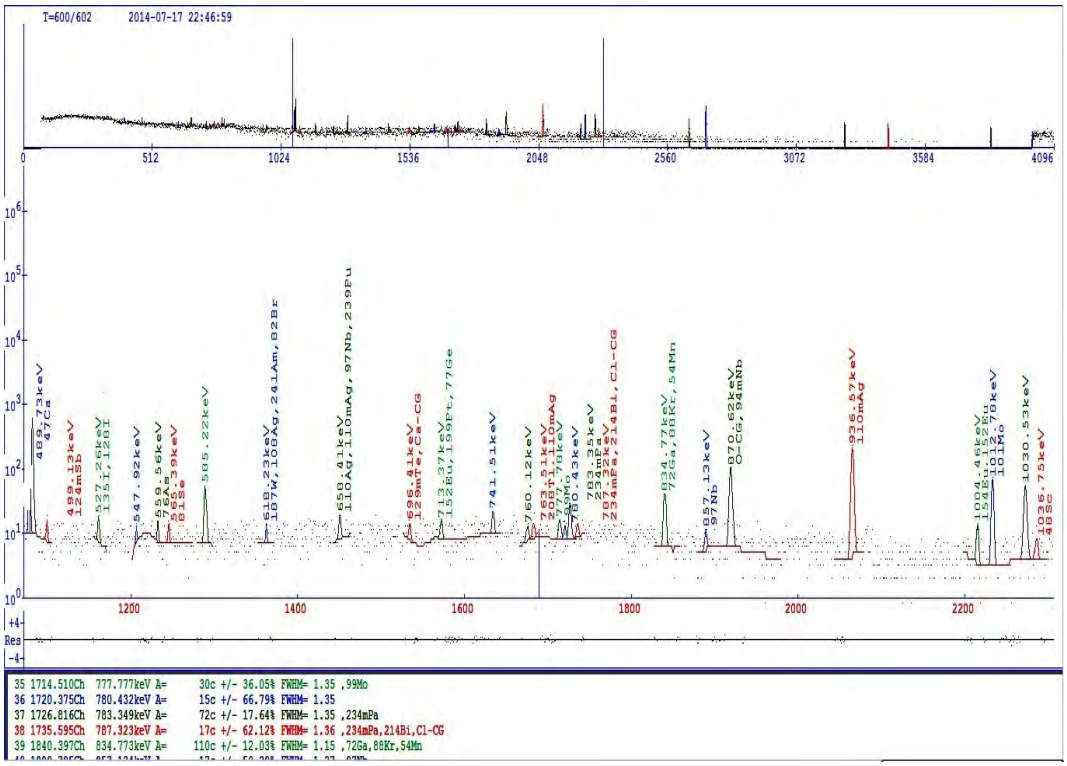

Figure 52: Part of second short spectrum of Guariye.

9.4 Results and discussion

The accuracy of the method based on the analysis of NIST 1515 (apple Leaves) proved to be for most of the elements within 10% of the certified values (the certified values were as in (68)). The result of analyzing the multi standard reference material NIST 1515, was displayed in the table 25. The table contains the kind of elements in the standard, the concentration of the elements experimentally obtained in the CERT INAA lab, Nigeria, the certified concentration of the elements and non certified (information) values are as given in its certificate(68).

From the table it can be concluded that the procedures and all the works including the stages of sample preparation, irradiation, activity acquiring, and analysis were amenable and correct, in agreement with other literatures (43). This is because the experimentally obtained type of elements were the same as the certified elements listed in the certificate of the standard and the experimental concentration is in a high precision with the certified concentration of the elements.

The elements obtained in the samples of Astara and Guariye which were also available in the standard were analyzed, since the quality of the work is assured correct for these elements only, according to the common method used in INAA laboratories and IAEA procedures (45; 3). The result of the analysis were displayed in table 26 in the unit of mg/Kg.

There were 16 Elements in the samples of Astara and Guariye detected by the experiment during the work. Elements Na, Cl, K and mg were detected as a major concentrated elements, Al, Fe, and Ca were detected in a minor concentration and the rest Mn, Br, La, Sm, Sc, Co, Zn, Rb, Se were detected in a trace level.

Sample code names A_{sh}, A_{ag}, G_{sh}, G_{ag} were used during the experiment to differentiate which of the samples were Astara samples and which were Guariye samples including from which particular place of the research area the samples were collected. A_{sh} refers to Astara from shamene region, "which was called Gibteder" in the sample collection stage". From this region of the research area a sample of Guariye was prepared and it was coded as G_{sh}.
In the other region of the research area, "Egrema region", sample of Guariye was coded G_{ag} and sample of Astara was coded as A_{ag}.

Element	$E_\gamma(Kev)$	$T_{1/2}(Sec)$	present work (ppm)*	certified (ppm)	information values(ppm)
K	1524.6	$4.464x10^4$	16100±190	16100±200	
Mg	1014.4	567.6	2710 ± 85	2710±80	
Al	1779	134.4	286 ± 7	286±9	
Cl	2167.7	2232	579 ± 21	579±23	
Ca	3084.5	523.2	15260 ± 143	15260±150	
V	1434.1	289.02	0.26 ± 0.05	0.26±0.03	
Mn	2113.1	$9.288x10^3$	54 ± 2	54±3	
Na	2754.0	$5.4x10^4$	24.4 ± 1.5	24.4±1.2	
Br	776.5	$1.271x10^5$	1.8 ± 0.12		1.8
La	1596.2	$1.451x10^5$	20 ± 0.03		20
Sm	103.2	$1.667x10^5$	3 ± 0.01		3
Sc	889.3	$7.197x10^6$	0.03 ± 0.01		0.03
Cr	320.1	$2.3933x10^6$	0.3±0.008		0.3
Fe	1291.6	$3.845x10^6$	83 ± 8	83±5	
Co	1332.5	$1.663x10^8$	0.09±0.007		0.09
Zn	1115.6	$2.9722x10^7$	12.5 ± 2.5	12.5±0.3	
Rb	1076.6	$1.6157x10^6$	10.2 ± 1.2	10.2±1.5	
Ba	496.3	$1.0195x10^6$	49 ± 11	49±2	
Nd	91.1	$9.504x10^5$	17 ± 0.01		17
Eu	91.1	$9.504x10^5$	0.2 ± 0.03		0.2
Tb	879.4	$6.2467x10^6$	0.4 ± 0.015		0.4
Yb	396.3	$3.6202x10^5$	0.3 ± 0.06		0.3
Th	312	$2.333x10^6$	0.03 ±0.1		0.03

*ppm=parts per million.

Table 25: Nist1515, certified and information values compared with the present work.

The elements Ca, Cl, K, Mg and Na were generally found to be present at the major element concentration levels. As can be seen from table 26, the concentration of potassium were A_{sh} = (26560±212 ppm), A_{ag} = (26440±211 ppm), G_{sh} = (8660±121 ppm) and G_{ag} = (8650±121 ppm).

It was observed, (table 26 and figure 53) that Astara samples both exhibited a very high value of K (proximately 2.6% of its dry weight), So as Potassium may be attributed to an intrinsic characteristic of the plant. The natural color of the plant dark green is due to potassium manganate (K_2MnO_4) and the purple color is due to the presence of per manganate ($KMnO_4$) (71)

The presence of potassium in Astara explains it is effective against some disease causing agents. High levels of potassium in Astara may make it be good sources of natural mineral

Element	A_{sh} (ppm)	A_{ag} (ppm)	G_{sh} (ppm)	G_{ag} (ppm)
K	26560 ±212	26440±211	8660±121	8650±121
Mg	1320±213	1776±190	BDL	870±106
Al	128±17	148±6	55±3	47±4
Cl	4122±49	3421±43	704±19	666±19
Ca	626±98	678±105	1801±200	1336±143
Mn	21.77±0.17	20.8±0.1	9.01±0.12	8.6±0.1
Na	1030±10	1110±10	37.7 ± 0.1	37.7±0.5
Br	30.9±0.2	30.1±0.15	2.25±0.17	3.74±0.06
La	0.29±0.02	0.32±0.22	3.73±0.06	0.15±0.01
Sm	0.041±0.004	0.043±0.004	0.17±0.003	0.027±0.004
Sc	0.23±0.01	BDL	BDL	BDL
Fe	146±28	119±27	114 ± 29	BDL
Co	0.091±0.017	0.07±0.01	BDL	BDL
Zn	46±3	46±3	53±3	63±3
Rb	17.2±1.7	14.6±1.6	5.62±1.64	BDL
Se	0.05±0.01	BDL	BDL	BDL

*ppm = mg/Kg

Table 26: Elements and their concentrations analysed in the samples of Guariye and Astara.

supplements. According to World Health Organization an average adult human should take 5.1mg/day to be healthy (54). According to the use of potassium as reported from different literatures and the concentration contained in it, Astara may be used as a special diet to protect high blood pressure, stroke, cancer and digestive disorder. But the proportional ratio of potassium and sodium is necessary, excess of potassium with out sodium or vice versa is not good (72).

It is known that potassium is necessary for muscle contraction (especially cardiac fiber), for the synthesis of some proteins and as an enzymatic cofactor. The action of potassium depends on the presence of sodium (58).

Compared to other plants content of potassium reported in literatures the concentration of potassium in Guariye plant also be is high, so that Guariye also has comparable advantages as the advantage that can be obtained from Astara plant.

The sodium content of Astara samples were very high compared to the concentration of sodium in Guariye. As can be seen from figure 54 and table 26, the sodium concentration of the samples were obtained as A_{sh} = (1030±10 ppm), A_{ag} = (1110±10 ppm), G_{sh} = (37.7± 0.1 ppm) and G_{ag} = (37.7±0.5 ppm), the concentration of both samples of

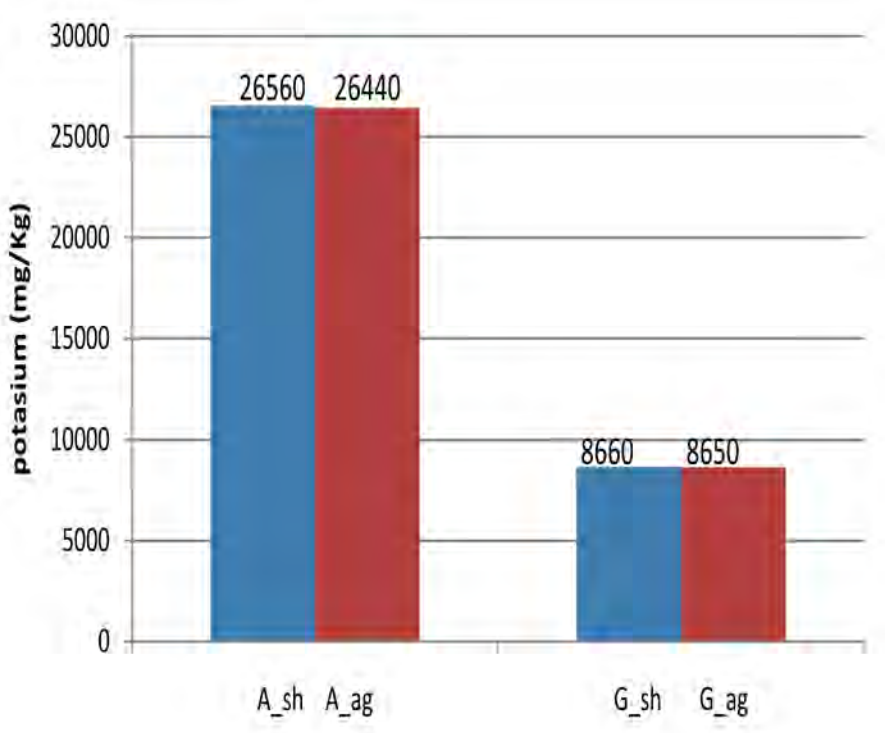

Figure 53: Potassium content of the samples of Astara and Guariye.

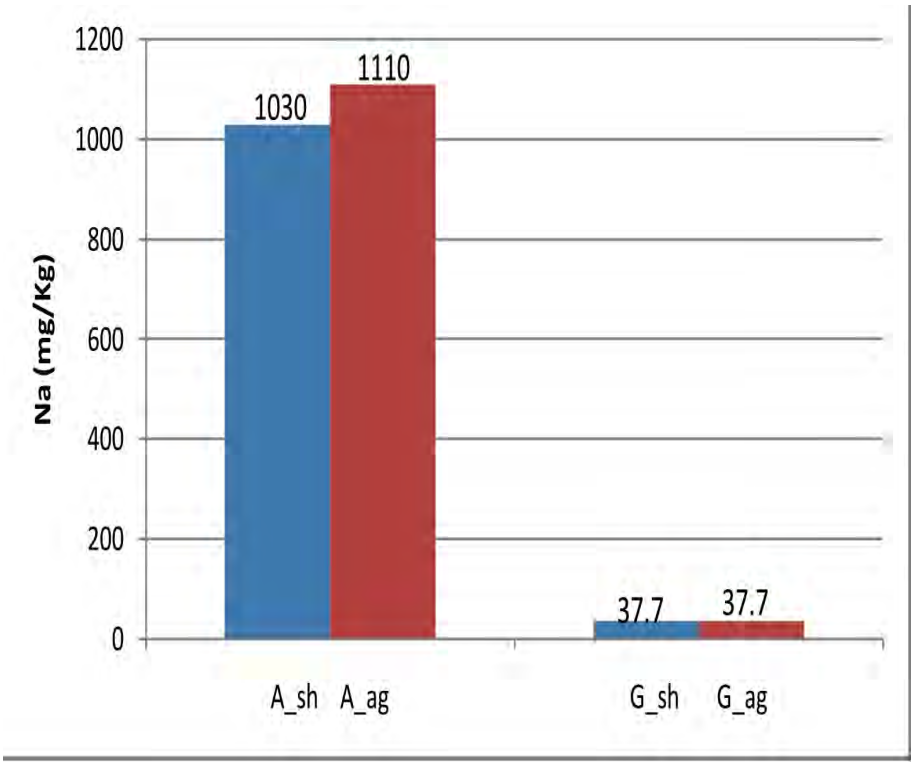

Figure 54: Differences in the sodium content of the samples of Astara and Guariye.

Astara contains relatively equal and higher concentrations i,e the variation between the sodium contents of Astara from Agena and from Shamene region of the research area is insignificant.

Both samples of Guariye contains sodium in a minor amount and there is no difference in the sodium content of both samples of the plant.

Sodium is the cation in the compound sodium chloride and in some other salts. Sodium (Na^+) and chloride (Cl^-) are the principal ions in the fluid outside of cells (extracellular fluid), which includes blood plasma. As such, they play critical roles in a number of life sustaining processes (72). Sodium helps to maintain the bodys fluid balance. It is also essential for nerve transmission, muscle contraction and cardiac function (37). Sodium is the primary determinant of extracellular fluid volume, including blood volume, a number of physiological mechanisms that regulate blood volume and blood pressure work by adjusting the body's sodium content. Its retention results in water retention and sodium loss results in water loss (52; 72).

Na and K act as electrolytes in the human body (52). Na is the principal cation in the extracellular fluids and modulates the maintenance of the intracellular and interstitial volumes. Sodium is essential for regulation of osmotic pressure of the body and helps to maintain acid base and water balance of the body. Its deficiency causes loss of body weight and nerves disorder (58).

In response to a significant decrease in blood volume or pressure (such as serious blood loss or dehydration), the kidneys release enzymes which act to increase the re absorption of sodium and the excretion of potassium. Retention of sodium by the kidneys increases the retention of water, resulting in increased blood volume and blood pressure(52).

From the above function of sodium, the use of Astara by the people in the research area for the purpose of curing from body swellings is because it contains higher concentration of sodium. Eating Astara gives a chance to get higher sodium so that it increases the body fluid content to make a swelling on the body gets pierced to give pus. But taking high amount of sodium has a disadvantage that it causes higher blood pressure making the blood volume higher, to control such an effect potassium has to be taken sufficiently (52; 72). This potassium itself is obtained in Astara in higher concentration so that the food Astara is complete and useful by itself.

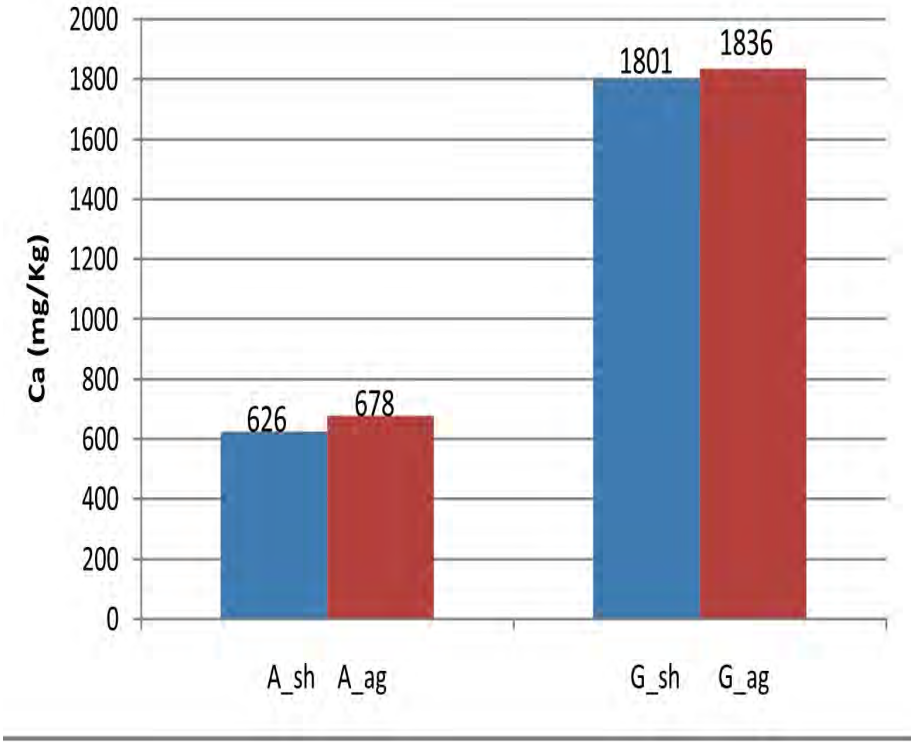

Figure 55: Calcium content of the samples of Astara and Guariye.

The levels of Ca in these medicinal plants were relatively low in Astara compared to its level in Guariye samples. As can be seen fro the table 26 and figure 55 the calcium analysis of the samples gave, A_{sh} = (626±98 ppm), A_{ag} = (678±105 ppm), G_{sh} = (1801±200 ppm) and G_{ag} = (1836±143 ppm). These data shows that calcium concentration differences between two Astara samples and between two Guariye samples were very small. Thus the samples of Astara have no significant differences in their content of calcium and also the samples of Guariye. As mentioned in the section 8.3, and in (73; 74), calcium has health advantages related to bones and teeth.

When we see the cross calcium concentrations between samples of Astara and Guariye, Guariye samples contain much more calcium than samples of Astara. The availability of Calcium in the Guariye as a major concentration may be explaining why it is used by the people of the research area in treating bone related ailments such as, bone break, bone fracture, swollen joints, paining joints and arthritis.
Calcium is needed in the development of bone and teeth and it regulate heart rhythm, helps in normal blood clothing, maintain proper nerve and muscle functions (40; 73; 74; 75).

Calcium is among the most widely distributed heavy metals in terrestrial and aquatic environment. Calcium is the most common mineral in the human body. About 99% of the calcium in the body is found in bones and teeth, while the other 1% is found in the blood and soft tissue (67; 74).
The mineral component of bone consists mainly of calcium and phosphate (73). Thus, adequate dietary calcium is a critical factor in maintaining a healthy skeleton (67; 73).

Magnesium (Mg) plays an important role in regulating muscular activity of heart rhythm and also Magnesium is important cofactor to convert blood glucose into energy. Levels of Mg in medicinal plants were determined and the result is given in the table 26 and in the figure 56. This study shows that magnesium content of the samples of the medicinal plant, Astara samples, were in agreement with a report by (37).

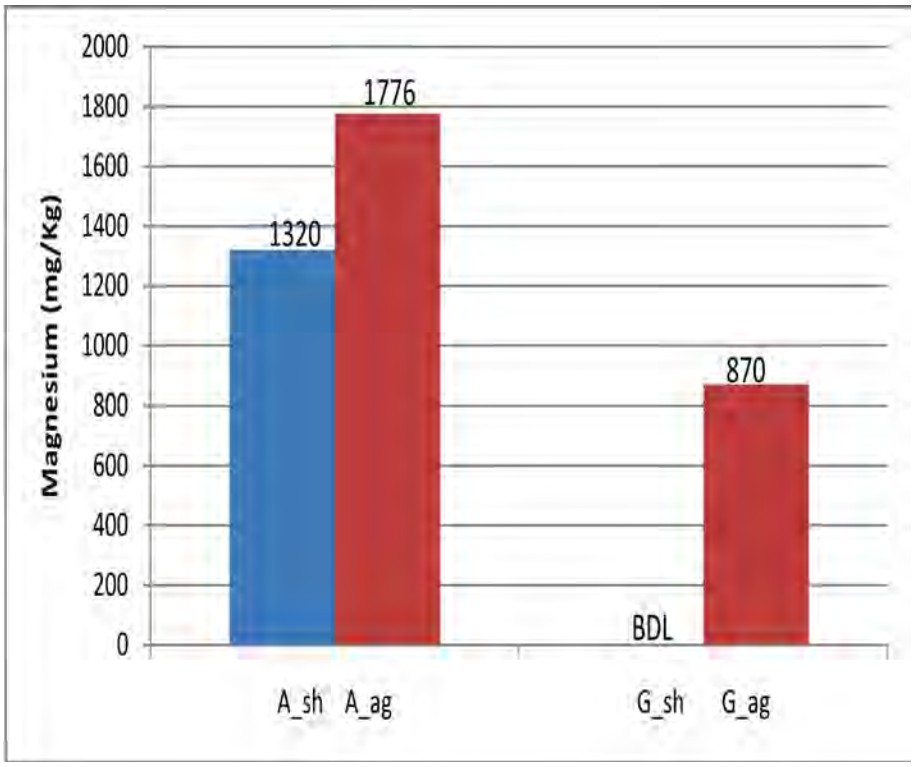

Figure 56: Comparing the magnesium content of the samples of Astara and Guariye.

The concentration of magnesium in the Astara samples show minor difference which may be due to geo-climatic conditions and anthropogenic activities. As can be seen from table 26 the concentration of magnesium in the Astara plant samples were A_{sh} = (1320±213 ppm) and A_{ag} = (1776±190 ppm) the concentration level of magnesium is higher in Agena sample than its level in a sample collected from shamene region.

The availability of magnesium in medicinal plants may be correlated with the use of the medicinal plants in wound healing, malaria treatment and coughs and chest pains as reported in (37). This explains the use of Astara in treating body swellings and healing from the wound left by the bursts of abscess.
The high levels of magnesium in particular in Astara may make it good sources of natural magnesium supplement for the people in the research area.

The magnesium level in Guariye plant samples, as displayed in figure 56 and in the table 26, shows that it is very low in the G_{sh} sample that it is below detection limit i.e it is available but the concentration is below the lowest detectable level by the experiment. But the other sample of Guariye from Agena region of the research area contains better concentration of Magnesium, G_{ag} (870±106 ppm). Both of the concentrations in Astara and Guariye plant samples show that the samples from shamene region of the area contains less magnesium mineral than the samples from Agena region.

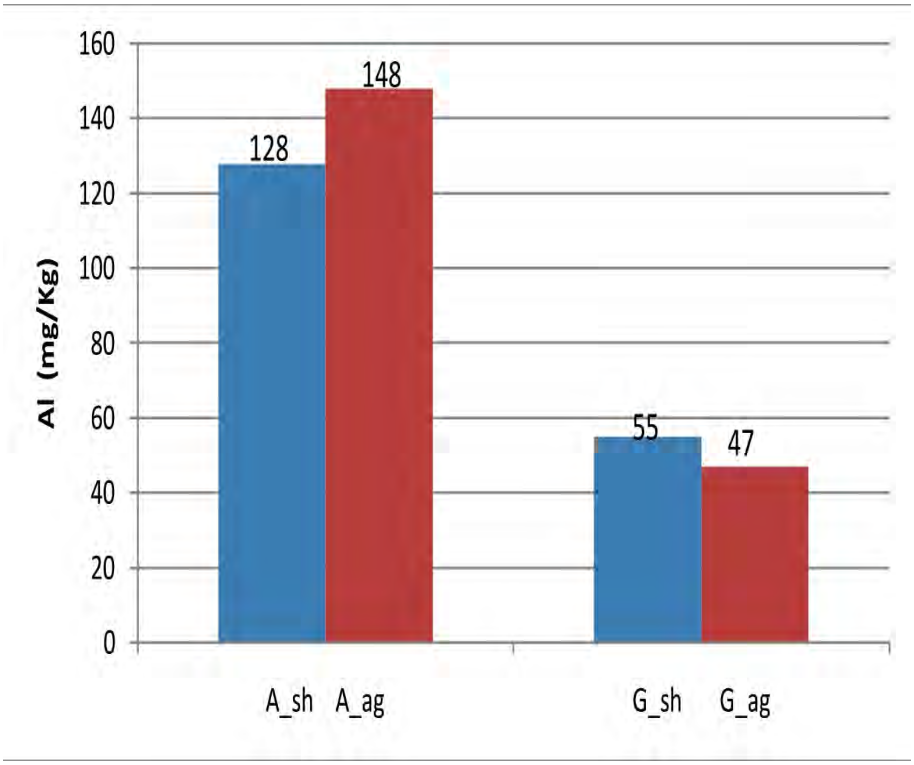

Figure 57: block diagram comparing Aluminum content of Astara and Guariye.

The concentration of aluminum in the samples as displayed in the table 26 and shown

in the figure 57, were A_{sh} = 128±17 ppm, A_{ag} = 148±6 ppm, G_{sh} = 55±3 ppm and G_{ag} = 47±4 ppm. The data shows that Astara samples contain better more concentrations of aluminum than Guariye samples. It was not found a report of dietary aluminum toxicity to healthy individuals in the literature.

Chlorine concentration in the Astara samples were very high compared to the concentrations in the Guariye plant samples. It can be observed from table 26 that the chlorine concentration in the samples were 4122±49 ppm in A_{sh} Astara sample, 3421±43 ppm in A_{ag} sample of Astara, 704±19 ppm in G_{sh} Guariye sample and 666±19 ppm in G_{ag} sample of Guariye. Chlorine has a disinfectant property which kills germs and bacterias, and forms salt compound using sodium (52). Chloride works with sodium and potassium carry an electrical charge when dissolved in body fluids and uses to regulate the pH in the body. Chloride is also important to digest the food properly and absorb many elements that we need them to survive (75).

Al, Fe, and Ca were detected in a minor concentration and the rest Mn, Br, La, Sm, Sc, Co, Zn, Rb, Se were detected in a trace level. Similar observations of variation in elemental concentrations in plant medicines and plants have been reported (70). The difference in the concentration of these elements within the different plant medicines may be attributed to factors such as the preferential uptake of a particular plant for certain elements. Other important factors to consider include ambient climatic conditions as well as the mineral composition of the soil in which the plant grows.

These and other essential elements perform various complimentary vital functions in the body to keep the people using them healthy. Zinc has concentrations 46±3 ppm in A_{sh}, 46±3 ppm in A_{ag}, 53±3 ppm in G_{sh} and 63±3 ppm in G_{ag}. It is known to be a working part of many enzymes, it is present in the hormone insulin and is involved in the working of genetic materials, proteins, immune reactions, wound healing, development of the fetus and sperm production. Normal levels of Zn can also prevent diarrhea.

Cobalt is known to be part of vitamin B_{12} and, therefore, involved in the nerve cell formation and in the process of blood formation. The element was detected in the Astara samples only with concentrations A_{sh} (0.091±0.017 ppm) and A_{ag} (0.07±0.01 ppm) while it is below detection limit in the Guariye samples.

The main use of Iron is the formation of hemoglobin, part of many enzymes, and helps in the formation of protective covering around the nerves, for more see section 5.4. Iron was

detected in both Astara and Guariye samples except in the sample G_{ag} which is below the detection limit. The concentration of iron in the other samples were, given in the table 26, obtained in a minor level as $A_{sh} = 146 \pm 28$ ppm, $A_{ag} = 119 \pm 27$ ppm and $G_{sh} = 114 \pm 2$ ppm.

Manganese concentrations were detected in all of the samples, its concentration is relatively greater in the Astara samples than in the Guariye samples. It is an activator and form part of several enzymes. It has some controlling nature for vitamins C and B, see section 6.4.

From the elements Samarium(Sm), Selenium(Se), Rubidium(Rb), Bromine(Br), scandium(Sc), Lanthanum(La), were elements detected. Samarium is used to help relieve the bone pain that may occur with certain kinds of cancer. Selenium is a mineral that is needed in small amounts by the body to help regulate the thyroid hormones and support a healthy immune system. There are currently no known essential function of rubidium. The only legitimate diet which contains bromine is a diet which destroys parasites, otherwise bromine is toxic, see section 5.4. Scandium is a toxic mineral which is a threat to the liver when it accumulates in the human body. The concentration of these toxic and useful minerals in the Astara and Guariye are in a trace level, so that the harm expected from the toxicity of the minerals is negligible. From the general information of the experiment, the medicinal plant foods are useful and recommended good for health.

Chapter Ten

10 Conclusion and Recomendation

10.1 Conclusions

From the result of Instrumental Neutron Activation Analysis using the (n, γ) nuclear reaction, the sample of "Chima" analysis gives More than twenty elements, from which Bromine was identified as toxic which is used to kill parasites in the human intestine, it was seen as the main element associated with the anti parasitic nature of the plant medicine Hygenya Abyssinia.

In the mineral soil sample Ewoa, there were 30 elements identified and from all the elements identified there were no heavy metals with toxic level of concentration or any other toxicity in all of the samples. Hence it was seen that, the mineral soil contains more useful elements in its nature for animals and human.
Due to the high concentrations of Fe and Ca the mineral soil can be considered as a useful additive for human food and cattle. It can provide hemoglobin and blood oxygen correcting advantages and useful for bone and teeth strength related issues of health. It is also a useful mineral for maintaining the body fluid balance due to its high concentration of sodium.

In sight of the identified sixteen elements and their concentrations, the local food *Atmet* is seen acceptable and useful type of human food. There are no toxic elements and heavy metal contaminations identified in the samples of the food. The food Atmet can be consumed by human and other animals with the advantages that can be obtained from elements like potassium and calcium.

Different concentration of elements were identified in the samples of medicinal plants, Astara and Guariye. From the elements and their concentrations analyzed in the samples of medicinal Astara and Guariye plants, the elements Sodium and Calcium respectively may take a major role in their medicinal aspects. The concentration of toxic or harmful minerals in the Astara and Guariye plants were in a trace level and the harm expected from the toxicity of the minerals is negligible. Even more the plants are not regular food types they only are used when needed as a medicine. In General from the result of the experiment, the medicinal plants Astara and Guariye are useful and recommended good for health.

The use of Astara by the people in the research area for the purpose of curing from body swellings like abscess is because it contains higher concentration of sodium. Eating Astara gives a chance to get higher sodium so that it increases the body fluid content and makes a swelling on the body turgid and burst. But taking high amount of sodium has a disadvantage in that, it causes higher blood pressure making the blood volume higher, to control such an effect potassium has to be taken sufficiently. This potassium itself is obtained in Astara in higher concentration comparable to the concentration of sodium which makes the plant Astara is complete and useful source of medicine.

The mineral component of bone consists mainly of calcium, thus adequate dietary calcium is a critical factor in maintaining a healthy skeleton. The element calcium concentration of Guariye plant makes it useful medicine for bone related diseases by the population.

Using the result of NaI(Tl)-gamma spectroscopy the NORM measurement of the samples of the mineral soil were found to be within the acceptable limits. Most of the values obtained were lower than the worlds average values. The calculated average absorbed dose rate in air due to gamma ray from the mineral soil activity, likewise the average hazard indexes obtained for both external and internal exposure do not exceeded the limits set by United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), (63). Therefore the mineral soil does not pose a threat to the public.

10.2 Recommendation

Scientific data should be available about every environment of Ethiopia regarding exposure to ionizing radiation emanating from the soil and building materials. The sum of effective radiation dose(s) to individual members of the public from exposure to controllable sources with the exception of occupational exposure, accidental release and in door radon exposure, normally should be limited to 1mSv in any year. Thus Ethiopia needs a radioactive mapping of natural radioactivity using NaI(Tl) gamma spectroscopy, which needs extensive experiment on the rocks and soils of different region.

The mineral content of soil and rocks, should be studied in depth because trace-element concentration data is an important geochemical tool for mineral prospecting, and in the quest for understanding the origin of rocks of different types.

The toxicity and the dietary use of different foods commonly used by the community

should be tested. The analysis of mineral contents in foods is needed to obtain an information on a comprehensive elemental composition as well as the investigation on the effects of human nutrition and health based on the dietary intake of mineral elements.

To carry out experiments to provide sufficient scientific data for all environments of Ethiopia, it is difficult and not cost effective to transport samples abroad where a research reactor is available. To be capable of collecting all such informations from environments of Ethiopia, a well facilitated research center which contains all type of radiation (X-ray, gamma ray, alpha) detectors and a research reactor is essential. Therefore the build up of such research center is highly recommended.

In the use of medicinal plants like "Chima" which contains trace concentration of toxic elements, reasonable dose for children and adults should be set, otherwise excessive use of the medicine is recommended not good for health..

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DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other University. All sources of material used for the thesis have been duly acknowledged.

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