CHARACTERIZATION OF THE CADMIUM LINED IRRADIATION CHANNEL OF THE NIGERIA RESEARCH REACTOR-1 (NIRR-1) AND ITS APPLICATION FOR ELEMENTAL DETERMINATION IN SOME LEGUMES

BY

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DECLARATION

I declare that this project/thesis entitled **"Characterization of the Cadmium Lined Irradiation Channel of the Nigeria Research Reactor-1(NIRR-1) and its Application for Elemental Determination in Some Legumes "** is my own work and has not been submitted in any form for another degree or diploma to any other University or Institution. Information derived from published or unpublished work of other workers have been acknowledged in the text.

_____ _____

Fidelis Tachio Sheyin Date

CERTIFICATION.

This thesis entitled **" Characterization of the Cadmium Lined Irradiation Channel of the Nigeria Research Reactor-1(NIRR-1) and its Application for Elemental Determination in Some Legumes "** by Fidelis Tachio Sheyin meets the regulations governing the award of the degree of Doctor of Philosophy(Ph.D.) in Physics of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to my late parents who first sent me to school and to all those who taught, guided or supported me at all levels of my education. It is also dedicated to all workers in the world who have undertaken or are presently undertaking research work in the application of neutron activation analysis and related analytical techniques to trace element analysis in medicine and biology.

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ABSTRACT

The epithermal neutron shape factor(α) and the epithermal neutron flux(φ_e) were determined in the permanent cadmium lined irradiation channel of the NIRR-1. The value of α that was determined by the cadmium covered multimonitor method using the monitor set Al-0.1%Au, Zr and Zn thin foils and Mo thin wire using an iterative process with MS Excel was found to be -0.137±0.018. The epithermal neutron flux using the activity of ^{198}Au in the Al-0.1% Au thin foil in the monitor set irradiated for α determination was found to be $(4.51\pm0.01)\times10^9$ n/cm^2.s. The high negative value of α corresponds to a hardened(poorly thermalized) epithermal neutron spectrum in the cadmium lined irradiation channel of the NIRR-1.

The result of the α value was used in the single comparator method of ENAA(k_o-ENAA) for the determination of the concentrations of elements in the SRM NIST 1515 Apple leaves using Al-0.1% Au thin foil as the single comparator. The concentrations of the elements Sm and Br with high Q_o values were determined in the NIST 1515 Apple leaves and are in good agreement with the certified values. Thus, the k_o-ENAA method is a reliable standardization method for the analysis of the samples of legumes in the cadmium lined irradiation channel of the NIRR-1.

The k_o-ENAA and thermal NAA methods were applied to elemental analysis of the food legumes cow peas, soya beans and groundnuts. The standard reference material NIST 1515 Apple leaves was used for quality control. The results show that the elements Se, Br and Rb with high Q_o values in samples of legumes were better analysed by the k_o-ENAA method in the Cd lined irradiation channel. The elements Na, K, Zn, La and Sc with low Q_o values are better analyzed by the relative method of thermal NAA. The elements Br and Sm have high Q_o values and can be determined by the k_o-ENAA and thermal NAA methods.

The established k_o-ENAA method in the cadmium lined irradiation channel of the NIRR-1 using MS Excel can be regarded as a reliable method of neutron activation analysis in the NIRR-1 and can be applied for the elemental analysis of samples of materials in many areas that include human nutrition, human health and diseases, environmental studies, geology and industrial materials.

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LIST OF ABBREVIATIONS AND SYMBOLS

eV	electron volts
keV	kilo electron volts
MeV	mega electron volts
MW	mega watt
NIRR-1	Nigeria Research Reactor -1
MNSR	Miniature Neutron Source Reactor
IAEA	International Atomic Energy Agency
$n/cm^2.s$	neutron per centimeter square per second
NAA	Neutron activation analysis
ENAA	epithermal neutron activation analysis
k_o-ENAA	single comparator method of epithermal neutron activation analysis
k_o-NAA	single comparator method of neutron actvation analysis
TNAA	Thermal neutron activation analysis
rel-TNAA	relative method of thermal neutron activation analysis
Cd	cadmium
B	boron

kW	kilowatt
μg/g	microgram per gram
ppm	parts per million
^{o}C	degrees Celsius
f	thermal to epithermal neutron flux ratio
φ_{th}	thermal neutron flux
φ_{e}	epithermal neutron flux
φ_{f}	fast neutron flux
α	epithermal neutron shape factor
σ_{th}	thermal neutron cross section
^{235}U	isotope of uranium with mass number 235
I_o	resonance integral in 1/E epithermal neutron spectrum
Q_o	resonance integral to thermal neutron cross section ration in the 1/E epithermal neutron spectrum
$I_o(\alpha)$	resonance integral in the $1/E^{1+\alpha}$ epithermal neutron spectrum
$Q_o(\alpha)$	resonance integral to thermal neutron cross section ration in $1/E^{1+\alpha}$ epithermal neutron spectrum
E	neutron energy

CHAPTER ONE

INTRODUCTON

1.1 Neutron Spectrum Parameters in Reactor Irradiation Sites

In most nuclear research reactor irradiation sites, the neutron spectrum with energy of range 0.025 eV–15 MeV or more consists mainly of 90-95% of thermal neutrons, 2% of epithermal neutrons and about 5% of fast neutrons(Glascock, 2004). Fast neutrons have energy above 0.5 MeV. Epithermal neutrons have energy of range 0.5 eV-0.5 MeV. Thermal neutrons consist of low energy neutrons of energy less than 1 eV, with mean energy of 0.0253 eV and a most probable velocity of 2200 m/s at room temperature(20 ^{o}C)(IAEA, 1990).

The distribution of the reactor neutron spectrum varies in the irradiation sites of different research reactors and even in the different irradiation sites within the same reactor. It is therefore important to measure the neutron spectrum parameters such as the thermal neutron flux(φ_{th}), epithermal neutron flux(φ_e), fast neutron flux(φ_f), thermal to epithermal neutron flux ratio(f) and the epithermal neutron shape factor(α) at the irradiation sites of a research reactor such as the Nigeria Research Reactor-1(NIRR-1) to ensure the accuracy of neutron activation analysis(NAA). In epithermal neutron activation analysis(ENAA) especially the single comparator method of ENAA(k_o-ENAA), the most important parameters of interest are the epithermal neutron shape factor(α) and the epithermal neutron flux(φ_e).

1.2 The Epithermal Neutron Shape Factor(α)

When applying the single comparator method of ENAA(k_o-ENAA), we need to take into account the effect of the real or non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron flux distribution in actual reactor irradiation sites (De Corte *et al*., 1982). In thermal reactor theory, the epithermal neutron flux in the ideal $\frac{1}{E}$ epithermal neutron energy region is given by (Benjelloun and Paulus, 1987; Jovanovic *et al*., 1987):

$$\phi_e(E) = \frac{\phi_e}{E} \qquad (1.1)$$

where ϕ_e = epithermal neutron flux per unit of the neutron energy interval

ϕ_e = proportionality constant, independent of energy

=integrated epithermal neutron flux per unit of lnE interval

E = epithermal neutron energy

In the ideal $\frac{1}{E}$ epithermal neutron energy region, the resonance integral I_o for an isotope is given by(Benjelloun and Paulus,1987; Jovanovic *et al*., 1987);

$$I_o = \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E} dE \qquad (1.2)$$

where E = epithermal neutron energy in the ideal epithermal neutron flux distribution

E_{Cd} = cadmium cut-off energy for epithermal neutrons(0.55eV)

$\sigma(E)$ = (n, γ) reaction cross section.

$I_o =$ resonance integral in the ideal $\frac{1}{E}$ epithermal neutron energy region

The resonance integral to thermal neutron cross section ratio for an isotope in the ideal $\frac{1}{E}$ epithermal neutron energy region is given by (Benjelloun and Paulus,1987; Jovanovic *et al*. 1987; De Corte *et al*., 1982):

$$Q_o = \frac{I_o}{\sigma_{th}} = \frac{1}{\sigma_{th}} \int_{E_{Cd}}^{2MeV} \frac{\sigma(E)}{E} dE = \frac{1}{\sigma_{th}} \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E} dE \qquad (1.3)$$

where $Q_o =$ resonance integral to thermal neutron cross section ratio in the ideal $\frac{1}{E}$ epithermal neutron energy region

$\sigma(E) =$ (n, γ) reaction cross section.

$I_o =$ resonance integral in the ideal $\frac{1}{E}$ epithermal neutron energy region

$\sigma_{th} =$ thermal neutron cross section

In practice, the moderation processes of the fission neutrons produced by the nuclear chain reaction in the ^{235}U used as fuel in the research reactor core vary from one research reactor to another and even in different irradiation sites within the same type of research reactor due to factors that include the type of reactor, core configuration, type of and geometry of the moderation materials, fuel distribution in the reactor core, types of reflector materials and geometry of the irradiation sites(De Corte et al., 1979a). Therefore, the epithermal neutron flux distribution in actual irradiation sites may deviate from the ideal $\frac{1}{E}$ law (the neutron spectrum undisturbed by irradiation positions,

absorbent material and reflectors). In actual reactor irradiation sites, the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron flux distribution has been better approximated as (De Corte *et al*., 1979a; De Corte *et al*., 1979b):

$$\phi_e(E) = \frac{\phi_e}{E^{1+\alpha}}.(E_a)^{\alpha} \qquad (\alpha \neq 0) \qquad (1.4)$$

where ϕ_e = epithermal neutron flux per unit of the neutron energy interval

ϕ_e = proportionality constant, independent of energy

= the integrated epithermal neutron flux per unit of $\frac{E^{-\alpha}}{-\alpha}.(E_a)^{\alpha}$ interval

E_a = arbitrary energy(usually 1eV), so that $(E_a)^{\alpha} = ((1eV)^{\alpha} \equiv 1$

α = the epithermal neutron flux shaping factor.

For simplicity,the term $(E_a)^{\alpha} = ((1eV)^{\alpha} \equiv 1$ will be omitted in all following expressions(De Corte *et al*., 1981a).

The epithermal neutron flux shape factor (α) is an experimentally determineable characteristic of the reactor irradiation site which is independent of the epithermal neutron energy range(Benjelloun and Paulus, 1987). It is a measure of the degree of distortion or deviation of the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum from the ideal $\frac{1}{E}$ epithermal neutron flux distribution in the actual reactor irradiation site. Its values can be positive or negative corresponding to a softened (well thermalized) or hardened (poorly thermalized) epithermal neutron spectrum. The α values for reactor irradiation

sites are expected to be constant after long periods of use if no rearrangement of the fuel elements of the reactor has been carried out(Verheijke and Jansen, 1988).

The non-ideality $\frac{1}{E^{1+\alpha}}$ representation of the epithermal neutron flux distribution in actual reactor irradiation sites enables the transformation of the resonance integrals I_o and the resonance integral to thermal neutron cross section ratios $Q_o(\frac{I_o}{\sigma_{th}})$ of isotopes that are valid only in the ideal $\frac{1}{E}$ epithermal neutron energy region to $I_o(\alpha)$ and $Q_o(\alpha)$ in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron energy region to ensure the accuracy of the analysis of samples of materials by the single comparator method of ENAA(k_o-ENAA).

The resonance integral of an isotope in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron flux distribution is given as (De Corte *et al*, 1979b):

$$I_o(\alpha) = \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E^{1+\alpha}} dE \qquad (1.5)$$

where $E =$ epithermal neutron energy in the ideal epithermal neutron flux distribution

$E_{Cd} =$ cadmium cut-off energy for epithermal neutrons(0.55eV)

$\sigma(E) =$ (n, γ) reaction cross section.

$I_o(\alpha)$ = resonance integral in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron energy region

$\alpha =$ the epithermal neutron flux shaping factor.

The concept of the effective resonance energy, $\bar{E}_r$ was first introduced by Ryves(1969). The effective resonance energy $\bar{E}_r$ represents the energy of a single effective or average energy which replaces all the resonance energies of an isotope over the epithermal neutron energy region (Ryves, 1969). It is defined experimentally by an α dependent parameter as (Ryves, 1969; Benjelloun and Paulus, 1987; Jovanovic *et al*., 1987; Moens *et al*., 1979):

$$(\bar{E}_r)^{-\alpha} = \frac{I_o^1(\alpha)}{I_o^1} \qquad (1.6)$$

where I_o^1 and $I_o^1(\alpha)$ are the reduced resonance integrals ($\frac{1}{v}$ tail subtracted) for the $\frac{1}{E}$ and $\frac{1}{E^{1+\alpha}}$ epithermal spectra respectively.

$\bar{E}_r =$ the effective energy of all the resonances averaged over an epithermal neutron spectrum

The reduced resonance integral I_o^1 is given in terms of the resonance integral I_o and the contribution to the resonance by the $\frac{1}{v}$ component $I_{\frac{1}{v}}$ from the cadmium cut-off energy in the ideal $\frac{1}{E}$ epithermal neutron spectrum as (Ryves, 1969; Benjelloun and Paulus, 1987; De Soete *et al*., 1972):

$$I_o^1 = \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E} dE - \int_{E_{Cd}}^{\delta} \frac{\sigma(v)}{E} dE \qquad (1.7)$$

$$= \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E} dE - \int_{E_{Cd}}^{\infty} \frac{\sigma_o v_o}{v} . \frac{dE}{E}$$

$$= I_o - 2\sigma_o \frac{\sqrt{E_o}}{\sqrt{E_{Cd}}}$$

$$= I_o - 0.429\sigma_o \qquad (1.8)$$

The reduced resonance integral $I_o^1(\alpha)$ is given in terms of the resonance integral $I_o(\alpha)$ and the contribution to the resonance by the $\frac{1}{v}$ component $I_{\frac{1}{v}}(\alpha)$ from the cadmium cut-off energy in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum as (Ryves, 1969; Benjelloun and Paulus, 1987; De Soete *et al*., 1972):

$$I_o^1(\alpha) = \int_{E_{Cd}}^{\infty} \frac{\sigma(E)}{E^{1+\alpha}} dE - \int_{E_{Cd}}^{\infty} \frac{\sigma(v)}{E^{1+\alpha}} dE \qquad (1.9)$$

$$= I_o(\alpha) - \int_{E_{Cd}}^{\infty} \frac{\sigma_o v_o}{v} \cdot \frac{dE}{E^{1+\alpha}}$$

$$= I_o(\alpha) - 2\sigma_o \frac{1}{(2\alpha+1)} \left[\frac{E_o^{1/2}}{E_{Cd}^{1/2+\alpha}} \right]$$

$$= I_o(\alpha) - \frac{0.429\sigma_o}{(2\alpha+1)E_{Cd}^{\alpha}} \qquad (1.10)$$

where $E_{Cd} = 0.55$ eV and $E_o = \frac{1}{2} m v_o^{\,2} = 0.0253$ eV

$v_o = 2200\, m/s$, $v =$ neutron velocity

$\sigma_0 = (E_o) =$ neutron capture cross section at v_o

$m =$ mass of neutrons

$\alpha =$ epithermal neutron shape factor

Introducing equations (1.8) and (1.10) into equation (1.6) and after rearrangement, the resonance integral $I_o(\alpha)$ of an isotope in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal energy region is given as (Benjelloun and Paulus,1987; Jovanovic *et al*. 1987; De Corte *et al*., 1981a):

$$I_o(\alpha) = \left[\frac{I_o - 0.429\sigma_o}{\bar{E}_r^{\ \alpha}} + \frac{0.429\sigma_o}{(2\alpha+1)E_{Cd}^{\alpha}} \right] \qquad (1.11)$$

where $\bar{E}_r =$ effective resonance energy,

$E_{Cd} =$ cadmium cut-off energy(0.55eV),

$\alpha =$ value of epithermal neutron shape factor in reactor irradiation site

$\sigma_o = \sigma(E_o) =$ neutron capture cross section

$I_o =$ resonance integral of isotope in the $\frac{1}{E}$ epithermal neutron spectrum

$I_o(\alpha) =$ resonance integral in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

The resonance integral to thermal neutron cross section ratio of an isotope in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron energy region is given by (De Corte *et al*., 1981a; Benjelloun and Paulus, 1987; Jovanovic *et al*., 1987):

$$Q_o(\alpha) = \frac{I_o(\alpha)}{\sigma_o} = \left[\frac{Q_o - 0.429}{\bar{E}_r^{\ \alpha}} + \frac{0.429}{(2\alpha+1)E_{Cd}^{\alpha}} \right] \qquad (1.12)$$

where $\bar{E}_r =$ effective resonance energy,

E_{Cd} = cadmium cut-off energy(0.55eV),

α = value of epithermal neutron shape factor in reactor irradiation site

$I_o(\alpha)$ = resonance integral in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

Q_o = resonance integral to thermal neutron cross section in the ideal $\frac{1}{E}$ epithermal neutron spectrum

$Q_o(\alpha)$ = resonance integral to thermal neutron cross section in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

$\sigma_o = \sigma(E_o)$ = neutron capture cross section

Thus, when determining the concentrations of elements in samples of materials by the k_o-ENAA method, the values of the epithermal neutron shape factors(α) in the reactor irradiation sites should be known to preserve the accuracy of the analysis.

1.3 Epithermal Neutron Activation Analysis(ENAA)

In thermal neutron activation analysis(TNAA), use is usually made of the whole reactor neutron spectrum, although the samples are activated mainly by the thermal neutron component due to their higher fluxes. However, the use of thermal neutron activation analysis(TNAA) has some drawback due to the interfering effects of the high activities induced by thermal neutrons on the major elements such as Na, Cl and Al and the minor elements such as Fe, Mn, Cr, Sc, Co, La with low Q_o values in geological materials and also the major elements such as Na, Cl, K and the minor elements such as Zn, Fe, Mn, Cu, in biological materials. These elements with low Q_o values almost completely mask or hinder the measurement of the trace elements with relatively high Q_o

values such as Ag, As, I, Br, F, Au, Gd, Hf, Ir, Sn,Cd, Mo, Sb, Se, Pt, Sm, Tm, W, U, Th, Rb, Sr,Cs,Ta, Ba, Tb, Re, In and Ga in many types of samples of materials(Brune and Jirlow, 1963;Tian and Ehmann, 1984). These elements with high Q_o values strongly absorb neutrons of specific resonance energies in the epithermal neutron region (0.5 eV-1 MeV)(Bem and Ryan, 1981). Therefore, it is necessary to optimize a reactor neutron activation analysis(NAA) scheme such as that with the NIRR-1 by using epithermal neutron activation analysis where cadmium or boron can be used to filter or lower the thermal neutrons of the reactor neutron spectrum thereby reducing the high activities from the interfering elements with low Q_o values and enhance the measurement of the activities of the trace elements with high Q_o values (Q_o >10) in different types of samples of materials (Brune and Jirlow, 1963; Hou *et al*., 1996; Laul,1979; Lyttle, 2005).

Cadmium(Cd) has been widely used as a thermal neutron filter for ENAA because of its large absorption cross section for thermal neutrons (1.991×10^4 barns) and sharp cut-off energy at about 0.55 eV for 1.00 mm thickness of the material. Cadmium is easier to fabricate. The main disadvantage of the use of Cd as a neutron filter is the low melting point (320.9 $^\circ$C). It can melt and burn up thereby becoming less effective after long periods of use. Also, the resulting high intensity of gamma-rays emitted from the high radioactivity of the long lived isotope of ^{115m}Cd($T_{1/2}$=44.6d) after irradiation may require taking radiation protection measures and this precludes the reuse of Cd shielded vials and measurement of short lived elements($T_{1/2}$ < 20 s). However, this problem can be solved by the installation of a permanent cadmium lined irradiation channel in the reactor irradiation site such as that installed at the large outer irradiation site (A3) of the 30 kW NIRR-1 in March 2011. On the other hand, boron has a thermal neutron cross section of 3.84×10^3 barns and a cut-off energy of range up to approximately 280eV but depends on the thickness of the absorption layer and could form a better shield than cadmium.

Varying the thickness of boron will vary the cut-off energy of the shield over a wide range of energy of neutrons, thus allowing some discrimination among the elements depending upon the energy of the epithermal neutron resonance absorptions. Boron and its compounds (BN, B_4C and B_2O_3) are fragile and are more difficult to fabricate. It does not produce high radioactivity from the (n,γ) reaction making it safer to handle after irradiation in even high neutron fluxes than cadmium. However, boron generates a lot of heat from the $^{10}B(n,\alpha)^7Li$ reaction which if not well cooled could lead to the decomposition of biological samples and the explosion of air tight irradiation capsules due to high pressure that may be generated(Hou *et al*., 1996; Stuart and Ryan, 1981; Lyttle,2005). Boron powders have impurities such as ^{28}Al, ^{56}Mn and ^{38}Cl. However, by combining B+Cd filters together, the intereferences due to the activities of ^{28}Al, ^{56}Mn and ^{38}Cl from the boron powders can be significantly reduced (Lyttle, 2005).

Cadmium as a shielding material for permanent epithermal neutron irradiation site for ENAA has been adopted by many low power research reactor laboratories such as the Reactor laboratory(Triga Mark II Reactor), Technical Research Centre, Finland(IAEA, 1990), the Dalhousie SLOWPOKE reactor, Canada (Acharya and Chatt, 2003), London University Reactor, UK(Parry, 1982), the University of Virginia Reactor, U.S.A. (Williamson *et al*., 1987), the 27kW prototype MNSR, China Institute of Atomic Energy, Beijing, China (Hou *et al*., 1996) and the 30 kW Syrian MNSR, Atomic Energy Commission Syria(Khattab *et al*., 2008).

Rossitto *et al*.(1972) have shown that Cd is the most appropriate neutron filter for measurement of elements in samples when the main resonance energies are located at low energy, say less than about 2eV. For resonance energies from 2 eV up in a wide

range of boron thickness Cd +B is more advantageus than Cd. For resonance energies greater than 15 eV, Cd+B or B are equally effective in the optimum thickness condition.

1.3.1 Cadmium ratio and Advantage factor

The concept of cadmium or boron ratio is used to compare the ability to activate an element in a sample of material by epithermal neutrons to that by thermal neutrons(Lyttle, 2005; Parry,1991). The cadmium ratio of elements of interest in a sample matrix for a specific reactor neutron spectrum is given experimentally as(De Soete *et al*., 1972; IAEA, 1990):

$$R_{Cd} = \frac{A}{A_{Cd}} = \frac{\phi_{th}\sigma_{th} + \phi_e I_o(\alpha)}{\phi_e I_o(\alpha)} = 1 + \frac{f}{Q_o(\alpha)} \tag{1.13}$$

where R_{Cd} = cadmium ratio,

ϕ_{th} = thermal neutron flux,

σ_{th} = thermal neutron cross section,

ϕ_e = epithermal neutron flux,

A = activity of nuclide in sample irradiated without cadmium cover

A_{Cd} = activity of nuclide in sample irradiated under cadmium cover

$I_o(\alpha)$ = resonance integral of element of interest in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron flux distribution.

$Q_o(\alpha) =$ the resonance integral to thermal neutron cross section in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum in the reactor irradiation sites.

$f =$ thermal to epithermal neutron flux ratios in the reactor irradiation sites

$\alpha =$ epithermal neutron shape factors in the reactor irradiation sites

The activity ratio for an infinitely thin gold foil or gold- alloy wire irradiated with and without cadmium covers is a frequently used method for measuring the epithermal neutron flux and as a calibration standard to measure the resonance integrals and also calculate the cadmium ratios of any other elements in samples of materials in a reactor irradiation site. This is because the reaction ^{197}Au(n,γ)^{198}Au which has only a single resonance peak has been investigated and its resonance integral is known to be 1550 barns(IAEA, 1990). Therefore, in comparison with gold(Au) foil, the expected cadmium ratio for any isotope in a reactor irradiation site is given theoretically as (De Soete *et al*., 1972; Lyttle, 2005; IAEA, 1990):

$$R_{Cd} = 1 + \frac{f}{Q_o(\alpha)} = 1 + \frac{(R_{Cd(Au)} - 1)Q_o(\alpha)_{Au}}{Q_o(\alpha)} \qquad (1.14)$$

where $f = (R_{Cd(Au)} - 1)Q_o(\alpha)_{Au} =$ thermal to epithermal neutron flux ratio for gold

$Q_o(\alpha)_{Au} =$ resonance intergral to thermal neutron cross section of gold in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum in the reactor irradiation sites.

$Q_o(\alpha) =$ the resonance integral to thermal neutron cross section in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum in the reactor irradiation sites.

$R_{Cd(Au)}$ = cadmium ratio for gold

The theoretically calculated expected cadmium ratios of elements of interest in comparison with gold foil are useful for comparison with the experimentally determined values of cadmium ratios in reactor irradiation sites. The cadmium ratios of elements of interest and those of the interfering elements can be compared to decide if it would be useful to use epithermal neutron activation analysis to enhance the measurement of the element of interest in a sample of material(Parry, 1991).

The advantage of using epithermal neutron activation analysis(ENAA) over thermal neutron activation analysis(TNAA) is defined by the advantage factor(Brune and Jirlow, 1963). The advantage factor(the effectiveness of ENAA) is a measure of the degree of the relative enhancement of the nuclide of interest with respect to the interfering nuclide when epithermal neutron activations are used with a cadmium or boron neutron filter(Parry, 1991; Nakahara *et al*., 1982 1981). It represents the degree to which the particular interference will be reduced by using a cadmium or boron neutron filter(Stuart and Ryan, 1981). Several methods are used to quantify the advantage factor in epithermal neutron activation analysis.

The advantage factor is defined as (Brune and Jirlow, 1963):

$$F_a = \frac{R_i}{R_x} \qquad (1.15)$$

where R_i = cadmium or boron ratio of the interference radionuclide(usually ^{24}Na

R_x = cadmium or boron ratio of the element of interest

F_a = advantage factor of the element of interest.

The nuclide ^{24}Na (E_γ = 1368.60 keV, 2754.00 keV) is often chosen as the main or standard interfering element in biological materials because it activates well with a short irradiation time and also has high energy gamma-rays thus causing high background in the gamma-ray spectra below a large number of lines from the nuclides of interest (Parry, 1984). Similar properties are shown by ^{38}Cl as well as ^{28}Al and ^{56}Mn, the other common interferences in biological and geological samples respectively (Tian and Ehmann, 1984; Alfassi, 1985; Parry, 1984).

The real advantage factor is based on the improvement in counting statistics or the relative standard deviation of the activity of the radionuclide of interest and gives a truer picture of the potential of ENAA. It is defined as (Bem and Ryan, 1981):

$$F_a^1 = \frac{\sqrt{R_i}}{R_x} \qquad (1.16)$$

where R_i = cadmium or boron ratio of the interference radionuclide(usually ^{24}Na)

R_x = cadmium or boron ratio of the element of interest

F_a^1 = the real advantage factor

Parry(1980) has shown that when the advantage factor is based on the practical improvement of the detection limit or sensitivity of elements of interest in a sample, it is given by the improvement factor as (Parry, 1980):

$$F_i = \frac{\sqrt{R_i}}{R_x} \qquad (1.17)$$

where R_i = cadmium or boron ratio of the interference radionuclide(usually ^{24}Na)

$R_x =$ cadmium or boron ratio of the element of interest

$F_i =$ the improved advantage factor

Tian and Ehmann(1984) introduced a new generalized advantage factor which is based on the practical improvement in the relative standard deviation or detection limit of the element of interest if the sample is activated by epithermal neutrons. In the previous discussions, it was assumed that the activated samples with and without cadmium or boron shielding are counted in the same geometry. However, in practice after epithermal activation of a sample, the gross activity of the sample is highly reduced and the irradiated sample may be placed much closer to the detector and counted earlier than samples activated by thermal neutrons without resulting in the problems associated with high dead time. If the change in counting position increases the counting efficiency by a factor G, the advantage factor is given by (Tian and Ehmann, 1984):

$$F = \frac{\sqrt{G.R_i}}{R_x} \qquad (1.18)$$

where $G =$ counting efficiency. It is essentially the efficiency amplification factor due to change in geometry between bare and shielded irradiations.

$R_i =$ cadmium or boron ratio of the interference radionuclide(usually ^{24}Na)

$R_x =$ cadmium or boron ratio of the element of interest in the sample of material

$F =$ advantage factor based on counting efficiency

If the samples are counted in the same position then G=1 and $F = F_a^1$ which is the definition of the advantage factor by Bem and Ryan(1981). However, if the counting efficiency for the sample from ENAA can be increased by placing the sample closer to

the detector such that the total sample counting rate which is largely due to the interference activity is approximately equal to that for thermal neutron activation analysis(TNAA), then $G = R_i$ and $F = F_a$ which is the definition of the advantage factor by Brune and Jirlow(1964). The new generalized advantage factor given in equation (1.18) above defines a practical improvement in the relative standard deviation, counting statistics or limit of detection for which the real advantage factor defined by Bem and Ryan(1981) and the advantage factor defined by Brune and Jirlow (1964) are special cases. It gives the widely used advantage factor of Brune and Jirlow(1964) a firm statistical basis as a limiting case(Tian and Ehmann, 1984).

Nikahara *et al*.(1982) have shown that the actual improvement in sensitivity in epithermal neutron activation analysis can be expressed experimentally as:

$$IS = \frac{(S/\sqrt{N})_{Cd}}{(S/\sqrt{N})_O} \qquad (1.19)$$

where S =photopeak area falling within plus-minus one standard deviation from the peak position corresponding to 0.68 of the total photopeak area if it has a Gaussian shape.

N =total background area beneath the photopeak corresponding to the area S

The subscripts Cd and O denote the irradiation with and without cadmium filter respectively.

If a single interfering nuclide contributes to the background, the actual improvement in sensitivity (IS) in equation 1.19 is given as (Nikahara *et al*., 1982):

$$IS = \frac{\sqrt{R_i}}{R_x} \qquad (1.20)$$

where R_i = cadmium or boron ratio of the interference radionuclide(usually ^{24}Na)

R_x = cadmium or boron ratio of the element of interest

which is equivalent to the improvement factor proposed by Parry(1980) or the real advantage factor defined by Bem and Ryan(1981).

1.4 Dependence of Neutron Absorption Cross Sections on Reactor Neutron Energy

Reactor neutrons that are involved in nuclear reactions can be classified conveniently according to the behaviour of the cross sections. For a considerable number of nuclides of moderately high or high mass numbers, the variation of the absorption cross sections with the incident reactor neutron energy reveals the existence of three regions on a curve of absorption cross section versus reactor neutron energy as illustrated in figure 1.1 below. In the thermal neutron energy region, the cross section decreases steadily with increasing neutron energy. In this region the absorption cross section of nuclides which is often high is inversely proportional to the neutron velocity(the 1/v law). Following the 1/v region is the resonance(epithermal neutron) region. In this region the cross sections rise sharply to high values called resonance peaks and then fall again for certain energies called resonance energies. These resonance energies are due to the affinity of the nucleus for neutrons whose energies closely match its discrete quantum energy levels. That is, resonance absorption occurs when the binding energy plus the kinetic energy of the neutron are exactly equal to the amount of energy required to raise a compound nucleus from its ground state to an excited state. For higher neutron energies, the absorption cross section steadily decreases with increasing neutron energy.

This is the fast neutron region in which the (n, p) and (n, α) reactions predominate(especially for low Z or light nuclides) and the absorption cross sections are usually low (less than 10 barns) or neglible.

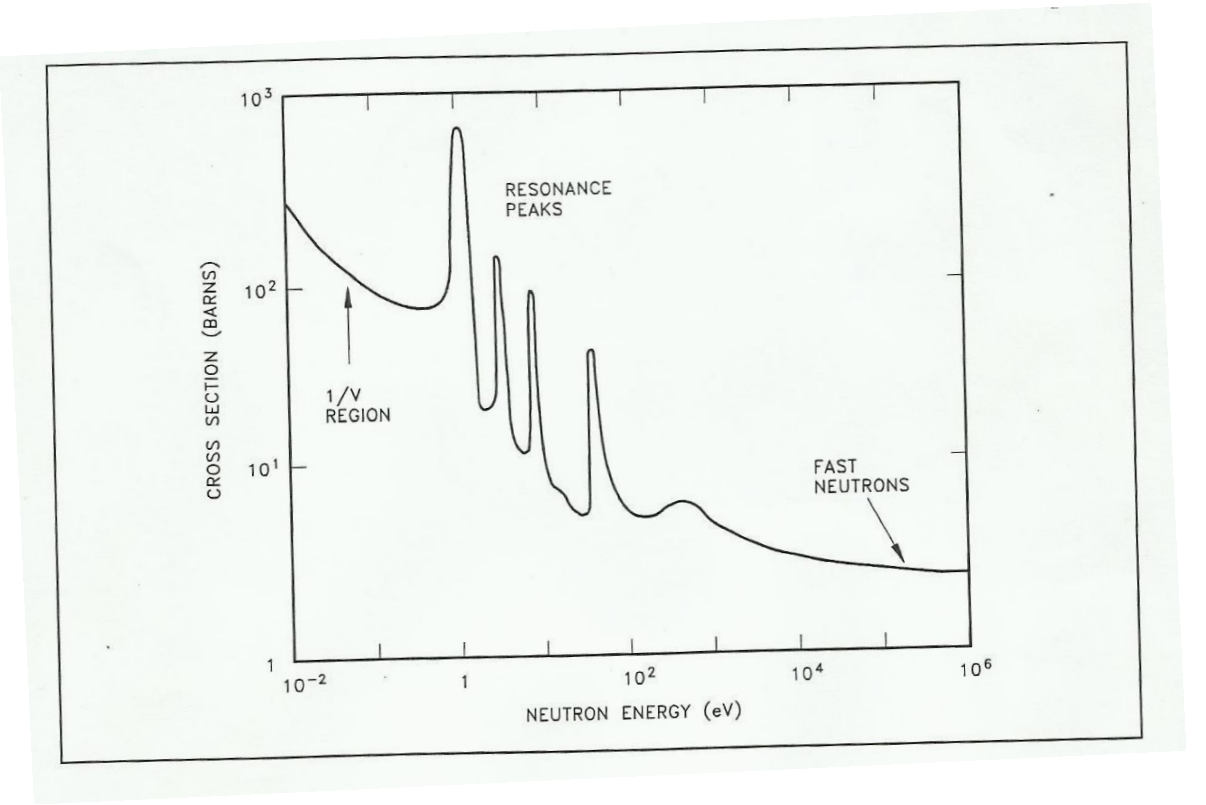


Figure 1.1 Typical Neutron Absorption Cross Section Versus Reactor Neutron Energy

1.5 Applications of Epithermal Neutron Activation Analysis(ENAA)

The epithermal neutron activation analysis (ENAA) method using cadmium or boron as thermal neutron filters has been used by several research workers to enhance the relative sensivities for several trace elements in a wide variety of samples such as :

(i) geological materials like standard reference materials(Parry, 1991; Glascock *et al*., 1985), soils, rocks and sediments(Hou *et al*., 1996; Stuart and Ryan, 1981), granite and phosphate rocks (Zaghoul, 1987; Zaghoul *et al*. 1987).

(ii) biological materials such as biological reference materials(Glascock et al., 1985), plants(Hou *et al*., 1996), human foodstuffs(Zikovsky and Soliman, 1999; Stroube *et al*.,1987) and human diet(Hou *et al*., 1997)

(iii) Human health and disease :- human fingernails(Chaudhary *et al*., 1995), human urine(Mason *et al*., 1993), human head hair(Akamine *et al*., 2007).

(iv) Environmental studies:- air pollution(Landsberger and Wu, 1993; Gladney *et al*., 1983).

(v) Industrial materials:- rubbers and plastics (Parry *et al*., 2000), pure Al, Al alloy , Al_2O_3 materials and Ni, (Hou *et al*., 1996).

(vi) Art and Archaeology(Oddone *et al*., 1997; Ochsenkohn *et al*., 1999).

1.6 Mineral Elements in Plant Foodstuffs

The bioavailability of mineral elements in plant foodstuffs (including legumes) is widely varied and depends on the soils they are grown. The mineral elements in plant foodstuffs consist mainly of the macronutrients and the trace elements (Underwood, 1977; Shacklette et al., 1978). The macronutrients are essential for not only plants but all living organisms. They comprise of carbon (C), hydrogen (H), oxygen (0_2), nitrogen (N_2) as major components (about 95% of dry weight) and sodium (Na), calcium (Ca), phosphorus (P), potassium (K), magnesium (Mg), sulphur (S) and chlorine (Cl) as minor

components (they constitute the rest of the percentage). The trace elements include all the naturally occurring elements in organisms except the macronutrients. They are in small quantities and constitute less than 1% of plant foodstuffs. The trace elements generally accepted as essential for the growth of plant crops are B, Cu, Fe, Mn, Mo, Zn and Cl (Underwood, 1977).

According to Underwood (1977), the trace elements can be divided from a dietary point of view into three groups:-the essential trace elements (micronutrients),the possibly essential trace elements and the non-essential trace elements.

1.6.1 The Essential Trace Elements

The essential trace elements (microelements) in addition to the macronutrients are presently known to be important for many vital functions in all living organisms. They are constituents of hormones, vitamins and catalysts for the enzyme systems for the metabolic processes in the cells and other biological molecules. The essential trace elements have a common property in which they normally occur and function in living tissues in low concentrations. These normal tissue concentrations vary greatly in magnitude and are characteristic for each element. Their concentrations are usually expressed in parts per million (ppm) or parts per billion (ppb). The trace elements generally accepted as essential to mammals are Cr, Co, Cu, Fe, I, Mn, Zn, F, Se and Mo.

1.6.2 The Possible Essential Trace Elements

The group of trace elements possibly essential to mammals include: Ni, V, Sr, As, Cd, Ba, Sn and Si. Some evidence exists but is not completely convincing that these elements are essential to mammals.

1.6.3 The Non -essential Trace Elements

About 20 – 30 or more trace elements do not meet the requirement of the essential trace elements and are called the non-essential trace elements. It is either because they do not contribute to the vital function of the tissues of living organisms or their presence in the tissues is toxic (harmful) to the tissues. The non-essential trace elements consist of the non-toxic and toxic elements.The non-toxic elements which include Li, Ti, Zr, Nb, Sr, Sm, La, Sc and Al have no known metabolic functions in either man, plants or animals. They have no recognized toxic properties at concentrations usually found in natural organic materials. The toxic elements which include Pb, As, Hg, Cd, Sb, have no known metabolic functions and are usually considered as toxic (harmful) to living tissues so that they are undesirable at any level of concentrations in foods or mammals.

In general, all chemical elements are potentially toxic to all living organisms at some excess levels of concentrations.

1.7 Trace Elements in Humans

Plant foodstuffs are major sources of the total daily intake of the essential and non-essential trace elements by man. The elemental concentrations of plant foodstuffs

reflect those of the surrounding soils or environment they are grown. Water also contributes to the total daily intake of the essential and non-ssential trace elements by man. It can be a significant source of trace elements supply in some areas. Trace elements in water may or may not reflect those of the surrounding soils or environment as the water supplies may not be related in origin to the local soils. Insignificant quantities of trace elements are normally contributed by the atmosphere except in areas with significant air pollution. Pollution of agricultural soils on which food crops are grown either directly or indirectly through water and air can also pose a health hazard to man because of the possible contamination of foods.

The essential trace elements for human health include Fe, Zn, Cu, Mn, Cr, Mo, Co, Se, I and F. The deficiency or excesses of the essential trace elements in the human body could cause ill health. The roles of the essential trace elements in human health and diseases have been documented in the literature (Garrison and Somer,1995; Underwood, 1977; Schroeder, 1976; WHO, 1996).

1.8 Analysis of Plant Foodstuffs

The analysis of seeds of crops including legumes has been useful as a method of nutritional survey in populations. Several recent developments indicate that marginal deficiencies of some trace element nutrients are fairly common in all the countries of the world. There is therefore increasing interest world wide on the evaluation of the concentrations of mineral element nutrients in human foodstuffs of which a greater percentage is derived from the seeds of plant foodstuffs.

The problem faced is whether or not the dietary intake of plant foodstuffs including legumes do meet the human requirement of the mineral element nutrients. But according to Schroeder (1976), a diet suitable for an omnivore obtainable from unrefined foods would contain adequate amounts of the mineral element nutrients such as Mn, Cr, Zn, Cu, Co, Fe, and Mo for the metabolism of foods in the human body. Apart from refinement, other factors that affect the mineral element nutrient composition of plant foodstuffs including legumes include:- soil composition, growing and environmental conditions, maturity of the crops at the time of harvest, inherent characteristics (genetic constitution) of the plant crops, use of fertilizers, pesticides such as fungicides and insecticides, effects of processing and cooking (Underwood, 1977).

A way of assessing the adequacy of the amounts of mineral element nutrients intake from foodstuffs including grains is to analyse the amounts of the foodstuffs consumed daily in domestic homes. The daily intake of the mineral element nutrients is then computed from the results of the analysis of the foodstuffs consumed per person per day. But the daily intake of mineral element nutrients from plant foodstuffs including legumes by individuals is better obtained by the analysis of actually prepared human diets in domestic homes. This is because plant foodstuffs including legumes suffer from the loss of mineral element contents when processed or cooked.

There are yet no national legislations (regulations governing the mineral element composition in foods) in Nigeria on the maximum permissible concentrations of the mineral element nutrients and the toxic elements in Nigerian foodstuffs for human consumption. Such information has however been provided for the toxic elements in foodstuffs for human consumption by Reilly (1980) which is presented in Table 1.1 below.

Table 1.1 Summary of the maximum permissible concentrations of some of the toxic elements in foodstuffs for human consumption .

Element	Foods (mg/kg or mg/l)
As	1
Cd	1
Cr	-
Hg	-
Pb	1-5
Se	2
Cu	20-50
Sb	1
Zn	40-50

Foods in general, excluding fish, vegetables and beverages

1.9 Legumes

Legumes belong to the family Leguminosae or Fabaceae which is probably the second most important source of food next only to the cereal grains, the monocot family Gramineae or Poaceae which includes rice, wheat, barley, millet, maize, and guinea corn (Elegbede, 1998). They are a major source of dietary proteins next to amimal meat and their products. They are also a source of other nutrients such as vitamins, carbohydrates, fat, oils, the essential elements(macroelements and trace elements) and fibre for human health.They also contain the non-essential trace elements. Several types of legumes with each type of legume having several species are cultivated in Nigeria(Elegbede, 1998). In this work, the types of legumes that are of main interest are cowpeas, soya beans and groundnuts.

Legumes such as cowpeas, soya beans and groundnuts having several species are widely cultivated in Nigeria especially in the northern states of Nigeria. The main source of all the mineral elements in these legumes is the soil, pollutants from the environment

and use of fertilizers and pesticides such as fungicides and insecticides. The legumes:- cowpeas, soya beans and groundnuts form about 40-50% of the daily dietary intake in not only the northern states but also in other states of Nigeria. They are therefore representative of the daily dietary intake in Nigeria.

1.10 Statement of the Research Problem

1.10.1 Epithermal neutron activation analysis with the NIRR-1

The Nigeria Research Reactor-1(NIRR-1) has been used mainly for thermal neutron activation analysis (TNAA) of the major and trace elements with low Q_o values in a wide variety of samples of materials such as geological and biological materials (Jonah et al., 2006). It is necessary to use epithermal neutron activation analysis in the NIRR-1 to enhance the measurement of the trace elements with high Q_o values(>10) in the presence of the high activities of the interfering elements with low Q_o values in different types of samples of materials(Laul, 1979;Parry,1991; IAEA. 1990;Lyttle, 2005).

1.10.2 Determination of α in the Cadmium Lined Irradiation Channel of the NIRR-1

A permanent cadmium lined irradiation channel with the cadmium lining of length 250.00 mm and thickness 1.00 mm has been installed at the large outer irradiation site A3 of the NIRR-1 for epithermal neutron activation analysis(ENAA). It is necessary to characterize it for the precise values of the epithermal neutron shape factor (α) and

the epithermal neutron flux(φ_e) for the single comparator method of ENAA (k_o-ENAA).

1.11 Aims and Objectives of the Research Work

The main aims of the research work are as follows:

(a) To characterize the permanent Cd lined irradiation channel of the NIRR-1 for the precise values of the epithermal neutron shape factor(α) and the epithermal neutron flux(φ_e).

(b) To use the the single comparator method of ENAA(k_o-ENAA) in the cadmium lined irradiation channel (A_3) for elemental determination in some food legumes.

The main objectives of this research work are as follows:

(a) To measure the full energy peak efficiency of the P-type GEM 30195 HPGe detector using the IAEA standard sources at distances 2cm and 15cm and plot the full energy peak efficiency versus energy curves in the normal and Ln-Ln scales.

(b) To fit the measured experimental data of the full energy peak efficiency curves with a mathematical or theoretical function from which the efficiency at any energy within and outside the energy range of interest can be calculated.

(c) To determine the value of the epithermal neutron shape factor(α) in the Cd lined irradiation channel of the NIRR-1 by the cadmium covered multimonitor method using the set of monitors Al-0.1% Au, Zr and Zn thin foils and Mo thin wire.

(d) To test the accuracy of the k_o-ENAA method in the Cd lined irradiation channel by the determination of the concentrations of elements in some standard reference materials(SRMs) using the Al-0.1% Au thin foil to be co-irradiated with samples of SRMs as the single comparator.

(e) To use the single comparator method of epithermal neutron activation analysis(k_o-ENAA) for the determination of the concentrations of the essential and non-essential trace elements in some samples of legumes such as cowpeas, soya beans and groundnuts in the Cd lined irradiation channel of the NIRR-1

1.12 Justification of the Research Work

The justification of this research work is as follows:

(a) The determination of the epithermal neutron shape factor(α) by the Cd covered multimonitor method and the use of the single comparator method of ENAA(k_o-ENAA) in a reactor irradiation site require accurate knowledge of the efficiency of the detector system for the source-detector geometry. It is therefore necessary to measure the full energy peak efficiency of the P-type GEM 30195 HPGe detector at the geometries 2 cm using the IAEA standard sources. It is also necessary to fit a theoretical function to the experimental data of the full energy peak efficiency curves from which the efficiency of gamma-ray energies of the nuclides involved in the α determination method and the k_o-ENAA method can be calculated to ensure the accuracy of the methods in the Cd lined irradiation channel of the NIRR-1.

(b) The neutron spectrum parameters in research reactors vary from one reactor to the other and even in different irradiation sites within the same reactor. It is necessary to

determine the precise value of the epithermal neutron shape factor (α)(as well as the epithermal neutron flux(φ_e)) in the cadmium lined irradiation channel of the NIRR-1. Knowledge of the value of the epithermal neutron shape factor (α) in the Cd lined irradiation channel is important in order to transform the I_o and Q_o values of isotopes in the ideal $\frac{1}{E}$ epithermal neutron spectrum to $I_o(\alpha)$ and $Q_o(\alpha)$ in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum using literature values of I_o, Q_o and $\bar{E}_r$ to ensure the accuracy of the analysis of samples of materials by the k_o-ENAA method·

(c) Legume foodstuffs (cowpeas, soya beans and groundnuts) are a major source of macronutrients such Na, K, Ca, P, Ma, S and Cl, the essential trace elements such as Cr, Co, Cu, Fe, I, Mn, Zn, Se, F and Mo for human health as well as the non-essential elements such as As, Cd, Ba, Sn, V, Sr, Sm, Rb, Sc, La and Br.

There is the need to use the single comparator method of ENAA in the Cd lined irradiation channel of the NIRR-1 for the determination of the essential trace elements for human health such as I, Se, F and Mo as well as the non-essential elements with high Q_o values in samples of legumes to avoid errors that may be caused by the use of the relative method of ENAA that relies on the use of standard reference materials (SRMs) that can be subjected to many errors such as the unavailability of sufficient or suitable standarad reference materials(SRMs) and the inability to determine the concentrations of some elements in a sample of material due to the absence of those elements in the standard reference material and optimize the use of the neutron activation analysis(NAA) method in the NIRR-1.

(d) The results of the analysis of legumes(cowpeas, soya beans and groundnuts) by the k_o-ENAA method are needed to provide necessary data from the Zaria environment needed as base line data in studies on the elemental composition of foodstuffs in Nigeria.

1.13 Scope of the Research Work

The scope of this research work is as follows :

(a) The measurement of the full energy peak efficiency of the P-type GEM 3015 HPGe detector at the distance 2 cm from the detector in the energy range 59.54 keV to 1408 keV using the IAEA standard sources ^{241}Am, ^{152}Eu ^{226}Ra, ^{137}Cs, ^{60}Co and ^{22}Na and the plotting of the measured full energy peak efficiencies versus energy curves in the normal and ln-ln scales using the Microsoft Excel Spreadsheet 2007 .

(b) The interpolation of the experimental data of the efficiency curves of the P-type GEM 30195 HPGe detector using a mathematical or theoretical function of third degree order polynomial in the ln-ln scale and use of the established fitting theoretical function for the calculation of the efficiency of the gamma-ray energies of the nuclides involved in the α determination in the Cd lined irradiation channel of the NIRR-1 by the Cd covered multimonitor method and the k_o-ENAA method using the Microsoft Excel Spreadsheet 2007.

(c) The determination of the value of the epithermal neutron shape factor (α) in the Cd lined irradiation channel of the NIRR-1 by the cadmium covered multimonitor method using the four monitors Al-0.1% Au, Zn and Zr thin foils and Mo thin wire. An iterative procedure using the Microsoft Excel Spreadsheet 2007 will be used for the determination of the final value of α by the Cd covered multimonitor method.

(d) The determination of the epithermal neutron flux (φ_e) in the Cd lined irradiation channel of the NIRR-1 using the activity of ^{198}Au in the Al-0.1%Au thin foil to be irradiated along with the monitor set for α determination .

(e) The determination of the concentrations of elements in some standard reference materials by the k_o-ENAA method in the Cd lined irradiation channel of the NIRR-1 with the Microsoft Excel Spreadsheet 2007 using the activity of ^{198}Au in the Al-0.1% Au thin foil to be co-irradiated with the standard reference material as the single comparator in order to test the accuracy or applicability of the single comparator method of epithermal neutron activation analysis (k_o-ENAA) in the Cd lined irradiation channel of the NIRR-1.

(f) The determination of the concentrations of the essential and non-essential trace elements in some samples of legumes (cow peas, soya beans and groundnuts) by the k_o-ENAA method in the Cd lined irradiation channel of the NIRR-1 with the Microsoft Excel Spreadsheet 2007 using the activity of ^{198}Au in the Al-0.1% Au thin foil to be co-irradiated with the samples of legumes and standard reference materials.

1.14 Previous work

1.14.1 The determination of α

The effect of the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron flux distribution on the accuracy of the single comparator standardization method of epithermal neutron activation analysis (ENAA) in (n, γ) activation analysis has been studied by several research workers(Bereznal and Macmahon, 1978; De Corte *et al*., 1982; De Corte *et al*., 1986). De Corte *et al*.(1982) have shown for some isotopes at a typical channel of the

250kW Thetis reactor that if α is neglected, errors of 4-18% can be introduced in ENAA. Therefore, when applying the single comparator method of ENAA($k_o - ENAA$) in the NIRR-1, the values of α in the irradiation sites should not be neglected.

De Corte *et al*.(1979b) determined the value of α in channel 15 of the 250kW Thesis reactor, Gent by the generalized multi-resonance detector(cadmium covered multimonitor) method using ^{115}In, ^{197}Au, ^{152}Sm, ^{186}W, ^{99}Mo, ^{96}Zr and ^{94}Zr. They found the value of α to be 0.084±0.011.

Dung and Sasajima(2003) determined the values of α at the PN-2 and PN-3 irradiation sites of the 20MW JJR-3M pool type Research Reactor, Tokai, Japan by the cadmium covered multimonitor method using ^{197}Au, ^{59}Co, ^{64}Zn, ^{96}Zr and ^{94}Zr. The values of α at the two irradiation sites were found to be 0.15±0.01 and 0.05±0.01 respectively.

Dung and Cho(2003) determined the value of α by the cadmium covered multimonitor method using ^{197}Au, ^{59}Co, ^{64}Zn, ^{96}Zr and ^{94}Zr in the NAA number 1 irradiation channel of the HANARO Research reactor(KAERI), Korea. The value of α was found to be 0.137±0.008.

Jonah *et al*.(2005) determined the values of the thermal to epithermal neutron flux ratios (f) and α in the small inner irradiation site B_2 and the outer irradiation site B_4 of the NIRR-1 using the Cadmium ratio for multimonitor method for the $k_o - NAA$ method. The f and α values in the irradiation sites B_2 were found to be 19.2±0.02 and -0.052±0.002 respectively while those in the irradiation site B_4 were found to be 48.3±3.3 and +0.029±0.003 respctively. The neutron spectrum parameters were found to be compatible with those of other reactor facilities which have similar configuration (Jonah *et al*., 2005).

Hamidatou and Ramdhane(2008) determined the value of α in the Es-Salam Research Reactor, Algeria by the cadmium covered multimonitor method using the monitors Au, Co, Zr, Zn and Lu. They found the value of α to be 0.024±0.010 .

Sadiq *et al*.(2010) determined the f and α values in the small inner irradiation site (A_1) and the large outer irradiation sites (A_2) of the NIRR-1 by the Cadmium ratio for multimonitor method for the $k_o - NAA$ method. The f and α values in the irradiation sites A_1 were found to be 18.4±0.34 and -0.046±0.005 respectively while those in the irradiation site (A_2) were found to be 49.5±0.96 and +0.024±0.002 respctively. The results obtained are in good agreement with the values obtained for the irradiation channels B_2 and B_4 reported earlier by Jonah et al.(2005) which is an indication of the stability of the neutron flux of the NIRR-1.

Njinga(2012) determined the value of α in the Cd lined irradiation channel of the NIRR-1 by the Cd covered multimonitor method. The value of α was found to be

-1.274±0.016

1.14.2 The Single Comparator method of ENAA(k_o-ENAA)

The single comparator method of epithermal neutron activation analysis (k_o-ENAA) under cadmium cover is an extension of the single comparator method of neutron activation analysis(k_o-NAA) that relies on the use of a single element as a comparator or standard and an experimentally determined composite nuclear constant called k_o – factors that are independent of the reactor neutron spectrum, irradiation and counting conditions and of the detector characteristics (Simonits *et al*., 1975). The method has been applied by several laboratories.

El NIMR *et al*.(1981) determined the concentrations of elements in synthetic and geological multielement standards by the k_o-ENAA method under cadmium cover.

De Corte *et al*.(2005) used the k_o-ENAA method to determine the concentrations of K, U and Th in wind blown sediments of loess(an aeolian unstratified loamy deposit) and sand under cadmium cover using Al-0.1% Au foil as the single comparator. The results were found to be satisfactory for evaluating the annual radiation dose in thermoluminescence or optically stimulated luminescence (TL/OSL) dating.

Njinga (2012) determined the concentrations of Th, U and K in archaeological samples by the k_o-ENAA method in the Cd lined irradiation channel of the NIRR-1. The results of the concentrations of these elements in the archaeological samples were found to be satisfactory.

The main aim of this research work is to determine the epithermal neutron shape factor(α) in the Cd lined irradiation channel of the NIRR-1 by the multimonitor method and apply the result of the α value in the single comparator method of ENAA(k_o-ENAA) for the determination of the concentrations of elements in some samples of standard reference materials(SRMs) and food legumes using Al-0.1% Au thin foil as the single comparator.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nuclear Research Reactors for Neutron Activation Analysis(NAA)

2.1.1 Nuclear Research Reactors

The main groups of neutron sources that have been introduced in neutron activation analysis(NAA) are :- isotopic neutron sources such as ^{241}Am-Be^{9}, ^{239}Pu-Be^{9}, ^{210}Po-Be^{9}, ^{226}Ra-Be^{9}, ^{124}Sb-Be^{9} and ^{252}Cf, neutron generators, accelerators and nuclear research reactors. However, the nuclear research reactor is the most important source of neutrons for NAA because of the availability of abundant and high thermal neutron fluxes of the order of 1×10^{11}-1×10^{18} n.cm^{-2}.s^{-1} (IAEA, 1998; IAEA, 2001; IAEA, 1990).

All nuclear reactors are based on the principle of the nuclear fission chain reaction. The fissionable material is usually enriched ^{235}U. The ^{235}U fuel in a nuclear research reactor will undergo fission with thermal neutrons producing two fission fragments of about equal masses, two to three neutrons and energy 200 MeV thus initiating a fission chain reaction of the type(Liverhant , 1960)

$$^{235}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{140}\mathrm{Ba} + {}^{94}\mathrm{Kr} + {}^{1}_{0}n + 200\ \mathrm{MeV} \qquad (2.1)$$

Through elastic collision with the nuclei of the moderation materials(light water, heavy water, graphite or beryllium) which surround the reactor core, the fission neutrons rapidly become thermalized creating a broad continuous neutron spectrum of energy 0.025eV – 15MeV or more that consists mainly of thermal, epithermal and fast neutrons.

The fast neutrons constituting about 5% of the total neutron flux are of energy above 0.5Mev and consists of primary fission neutrons which still have much of their original energy following fission.

The epithermal neutrons have energy of range 0.5eV-0.5MeV and are those neutrons that have only been partially moderated by the reactor moderator material surrounding the reactor core. Their distribution can be approximately described by a $\frac{1}{E}$ slope beginning above the cadmium threshold and ranging up to about 1 MeV. The epithermal neutron flux in a typical research reactor is usually about 2% of the total neutron flux.

The thermal neutrons(≈90-95% of the neutrons) consist of low energy neutrons below 1eV in thermal equilibrium with the atoms of the reactor moderator. For neutrons in thermal equilibrium with the moderator, the energy distribution of the neutrons can be given by the Maxwell- Boltzmann expression (Liverhant, 1960)

$$n(E)dE = \frac{2\pi n_o}{(\pi kT)^{3/2}} E^{1/2} \exp(\frac{-E}{kT})dE \qquad (2.2)$$

where n_o = number of neutrons per cm^3

$E = kT$ = neutron energy

T = temperature

$k = \frac{R}{N_A} =$ Boltzmann constant=1.360658×10^{-23} J/K

R = universal gas constant=8.314J/mol.K,

N_A = Avogadro's number=6.022×10^{23} atoms/mol

A typical neutron spectrum showing the various components used to describe the neutron energy regions is shown in figure 2.1 below.

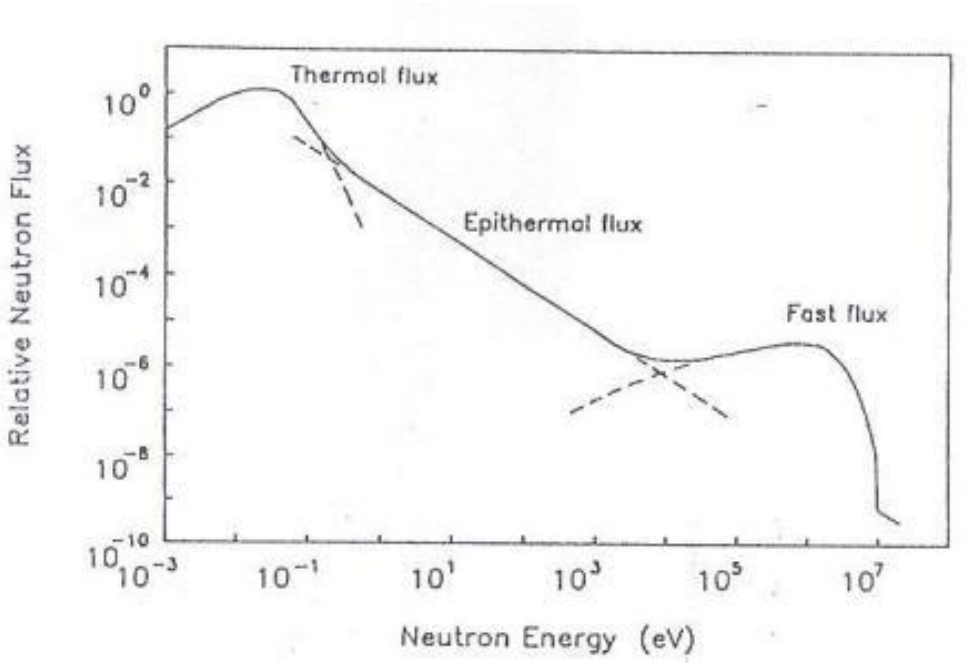


Figure 2.1 A typical reactor neutron spectrum showing the various components used to describe neutron energy regions

The main advantages of nuclear research reactors for neutron activation analysis(NAA) include the availability of abundant and high thermal neutron fluxes ($1\times10^{11}-1\times10^{18}\,n/cm^{2}.s$) (IAEA, 1998; IAEA, 2001; IAEA, 1990). Also, multielement analysis of a wide variety of samples of materials by thermal and epithermal neutron activation is possible with nuclear research reactors. The main disadvantages of nuclear research reactors are their high cost, complex structure and high cost of maintenance.

2.1.2 Classification of Nuclear Research Reactors for NAA

Nuclear research reactors for NAA can be classified in terms of their maximum thermal neutron fluxes and operating powers as follows:- high power research reactors(HPRR)($1\times10^{14}-1\times10^{18} n/cm^2.s$, 10-26MW or more); medium power research reactors(MPRR)($1\times10^{13}-1\times10^{14} n/cm^2.s$, 1-10MW) and low power research reactors(LPRR)($1\times10^{11}-1\times10^{13} n/cm^2.s$, 10 kW-1 MW)(IAEA,1998;IAEA,2001; IAEA,1990; Parry, 1991). Heavy water and Tank type(WWR) reactors are examples of high power research reactors; some swimming pool type and Triga reactors are examples of medium power research reactors while some Triga reactors, Argonaut, Canadian Slowpokes and Chinese Miniature Neutron Source Reactors are examples of low power research reactors(IAEA, 1990; IAEA, 1998; IAEA, 2001). The 30 kW Nigeria Research Reactor-1(NIRR-1), installed at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria is a low power commercial type Chinese Miniature Neutron Source Reactor(MNSR) and will be described in more detail.

2.1.3 Description of the Nigeria Research Reactor-1(NIRR-1)

The 30 kW Nigeria Research Reactor-1(NIRR-1) is an undermoderated tank-in-pool commercial type Chinese Miniature Neutron Source Reactor(MNSR) with the reactor core having highly enriched uranium (90.2%) as fuel. The loading of ^{235}U fuel in the reactor core is $\approx 1kg$ (995.89g) and the ratio of the number of hydrogen to uranium atoms ($\frac{H}{U^{235}}$) is 197. There are 355 lattices in the fuel cage which are arranged in ten concentric rows or circles. The central one is used for the control rod guide tube and four for the tie rods. About 347 lattices are for the fuel elements cladded with aluminium alloy

while the rest of the 3 lattices are for dummy fuel elements which are solid aluminium rods with the same shape and size as the fuel elements(Yongchun et al.,1992; Yuewen, 2003). The radial pitch between the two adjacent rows is 10.95mm(Yuewen, 2003). The NIRR-1 has light water as the coolant and moderator and metallic beryllium reflector which surrounds the reactor core as side annulus and bottom reflector. The reactor core is suspended at the bottom of a water pool made of reinforced concrete and covered with stainless steel of height 6.5m and diameter 2.7m with 30 litres of water located below the ground level. The pool water serves as a neutron moderator, heat cooling system and biological shield. The fission heat from the reactor core is removed from the pool water into the environment by natural convection. The NIRR-1 has negative temperature coefficient of 0.1mk/^{o}C and a very small excess reactivity of 3.77mk. The NIRR-1 has a single control rod made of cadmium for the control of neutrons in the reactor core during reactor operation. The start up and shut down of the NIRR-1 is controlled automatically by the microcomputer closed loop system and manually by the main control console.

The NIRR-1 can be operated at the full operating power for 2.5 hours daily with the same fuel loading for over 10 years. It has a relatively low fuel burn up of less than 1% during the life time of the core (Jonah *et al*., 2005; Jonah *et al*., 2009; Yongchun *et al.*, 1992). The loss of the reactivity due to temperature effect, fuel burnup and poisoning mainly from ^{149}Sm and ^{135}Xe can be compensated by adding available beryllium shims loaded inside the aluminium tray with four different kinds of thicknesses on top of the beryllium reflector(Yongchun *et al*., 1992; Yuewen, 1992; 2003).

The NIRR-1 has 10 irradiation sites (5 small inner, 3 small outer and 2 large outer). However, only six irradiation sites are connected to the pneumatic transfer systems types A and B control desks:- 4 small inner(B1, B2, B3 and A1), 1 small

outer(B4) and 1 large outer(A3). The rabbit system type B is used for the pneumatic transfer of samples into and out of the irradiation sites B1, B2, B3 and B4. A permanent cadmium(Cd) lined irradiation channel of thickness 1.00mm and length 250.00mm was installed at the second large outer channel A3 in March 2011. The rabbit system type A is used for pneumatic transfer of samples into and out of the irradiation sites A1 and the Cd lined irradiation channel A3. There are air routes in the irradiation sections which are made up of thimble with two layers .At full operating power, the maximum thermal neutron fluxes in the inner and outer irradiation sites (excluding the Cd lined irradiation channel A3) are $\approx 1\times10^{12} n/cm^2.s$ and $\approx 5\times10^{11} n/cm^2.s$, respectively. The variation in neutron flux in the irradiation sites is $\pm 3\%$. The useable neutron flux range is $5\times10^{10} - 1\times10^{12} n/cm^2.s$. The Schematic Diagram of the Top View of the Reactor Complex of the NIRR-1 is shown in Fig. 2.2(Abubakar, 2014).

The 30kW Nigeria Research Reactor-1(NIRR-1) with other low power research reactors such as the Canadian Slowpoke, and the Chinese MNSRs which run on the same fuel loading over ten years are kown to exhibit stable neutron flux characteristics which make them suitable for the k_o-standardization method (Kennedy *et al*., 2000; Kennedy and St. Pierre, 1999; Acharya and Chat, 2003; Akaho and Nyarko, 2002; Jonah *et al*., 2005). The thermal neutron flux distribution in the inner and outer irradiation sites of the NIRR-1 have been shown to remain stable even after the installation of the permanent Cd lined irradiation channel of the NIRR-1(Njinga, 2012). The main parameters of the Nigeria Research Reactor-1(NIRR-1) are shown in Table 2.1 below.

Table 2.1 The Main Parameters of the NIRR-1

Parameters	Description
Reactor type	Tank-in-pool
Rated thermal power	30kW
Fuel	UAl_4 dispersed in Al base material
Fuel shape	Thin rod
^{235}U enrichment	90.2%
Number of fuel elements in core	347
Total fuel loading in reactor core	995.89g
Core shape	Cylinder
Core diameter	23cm
Core height	23cm
Height of core inlet orifice	5.5 mm
Height of core outlet orifice	7.0mm
Fuel element	Length 248mm, diameter 5.5mm
Fuel meat	Length 230mm, diameter 4.3mm
Reactor continous operating time (at rated power)	$\geq$ 2.5 hours
Refuel period	> 10 years
Burn up	$\approx$ 1%
Excess reactivity	3.77mk
Temperature coefficient	-0.1mk/^{o}C
$\frac{H}{U^{235}}$ ratio	197
Number of Control rods	1(Cd absorber, length 230 mm)
Number of irradiation sites	10(5 small inner, 3 small outer and 2 large outer)
Number of irradiation sites connected	6(4 small inner, 1 small outer and 1 large outer)
Thermal neutron flux	Inner irradiation sites, 1×10^{12}n/cm^2.s Outer irradiation sites, 5×10^{11} n/cm^2.s
Number of Cd lined irradiation channels	1(1 large outer, A_3)
Dimension of Cd lining	Length 250mm and thickness 1mm
Reactor cooling mode	Natural convection

Table 2.2 The Lattices of the Reactor Core

Row No.	Lattice No.	Diameter of Row (mm)	Radial pitch (mm)
0	1	0	0
1	6	21.9	11.47
2	12	43.8	10.47
3	19	65.7	10.86
4	26	87.6	10.98
5	32	109.5	10.75
6	39	131.4	10.58
7	45	153.3	10.70
8	52	175.2	10.58
9	58	197.1	10.68
10	65	219.0	10.58

2.1.4 Safety Features of the Nigeria Research Reactor-1(NIRR-1)

The design features of the NIRR-1 enables it to have inherent safety characteristics. The NIRR-1 is a 30 kW low power tank-in-pool type reactor which is small and compact. The NIRR-1 core is designed to ensure that it has an undermoderated core with the ratio of number of hydrogen to uranium atoms equal to 197 and a large negative temperature effect due to its large negative temperature coefficient of moderation of -0.1mk/^{o}C. The large negative temperature feedback of the NIRR-1 makes it to possess inherent safety.

The NIRR-1 uses highly enriched ^{235}U(total loading ≈1kg) as fuel. The total excess reactivity is 3.77mk. Therefore, even if the control rod is stuck or ejected out of the reactor releasing all the excess reactivity, the reactor can be drawn back automatically to the safe state by its negative temperature effect. The heat at the peak power can be transferred out of the reactor safely and reliably by natural convection(Yongchun *et al.*,

1992). The NIRR-1 has low fuel burnup of $\approx$ 1% and therefore very small total amount of fission products of mainly ^{149}Sm and ^{135}Xe poisons to absorb the excess reactivity significantly. The prevention of the fission products from getting out of the reactor core is by cladding of the fuel rods with aluminium alloy and the reactor vessel that forms the tank. In order to compensate for the reactivity losses during operation due to temperature effect, fuel burnup and poisoning mainly from ^{149}Sm and ^{135}Xe, top beryllium shims reflectors loaded inside the aluminium tray with four different kinds of thicknesses are added on the top of the annulus beryllium reflectors surrounding the reactor core once in two years or whenever necessary so that the life span of the reactor core can be elongated (Yongchun *et al*., 1992; Yuewen, 1992; 2003). All these features also contribute to the inherent safety nature of the NIRR-1(Yongchun *et al*., 1992).

The NIRR-1 has a single control rod made of cadmium absorber which acts as a shim, regulating and safety rod, making the drive mechanism of the control rod simple, reliable and safe. In the event of an accident such as power supply failure or malfunction of the reactor components during reactor operation, the control rod can easily be scrammed or droped to the reactor core flow by its own weight, thus shutting down the reactor(Yongchun *et al*., 1992).

The NIRR-1 is designed not to attend very high temperatures that might lead to the reactor water reaching boiling point. This situation is not allowed because when the temperature increases, the excess reactivity in the reactor core decreases and without sufficient excess reactivity, the reactor can not be started. During reactor operation, the maximum temperatures in the inner and outer irradiation sites are less than $50^{o}C$ and $45^{o}C$, respectively. The NIRR-1 is therefore suitable for the analysis of liquids, fluids

and wet biological samples directly without fear of vapourization, burning or explosion which is not possible in reactors with higher operating powers (Wang, 1992).

The safety features in the NIRR-1 make it a very safe and reliable facility for many purposes such as NAA, production of radioisotopes, reactor physics experiments, education and training.

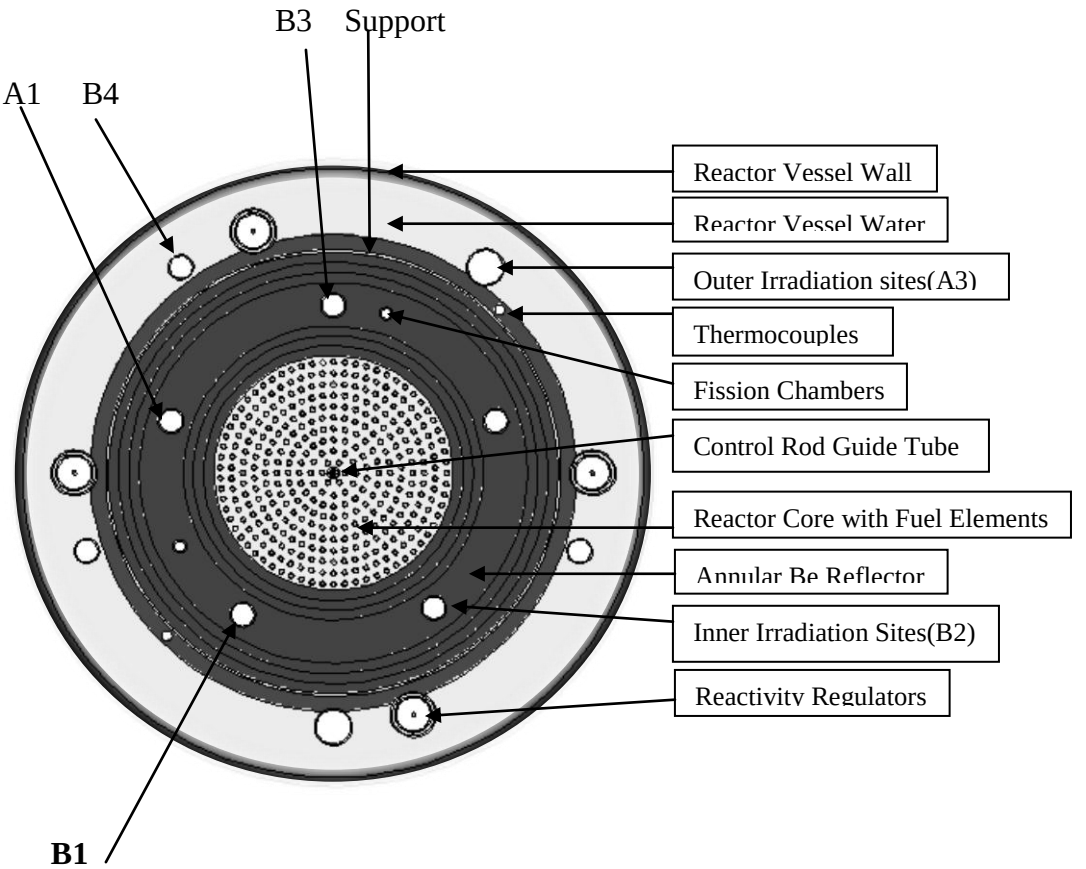


Fig. 2.2 The Schematic Diagram of the Top View of the Reactor Complex of the NIRR-1

A3- cadmium lined irradiation channel, A1- small inner irradiation channel, B1- small inner irradiation channel, B2- small inner irradiation channel, B3-small inner irradiation channel, B4-small outer irradiation channel

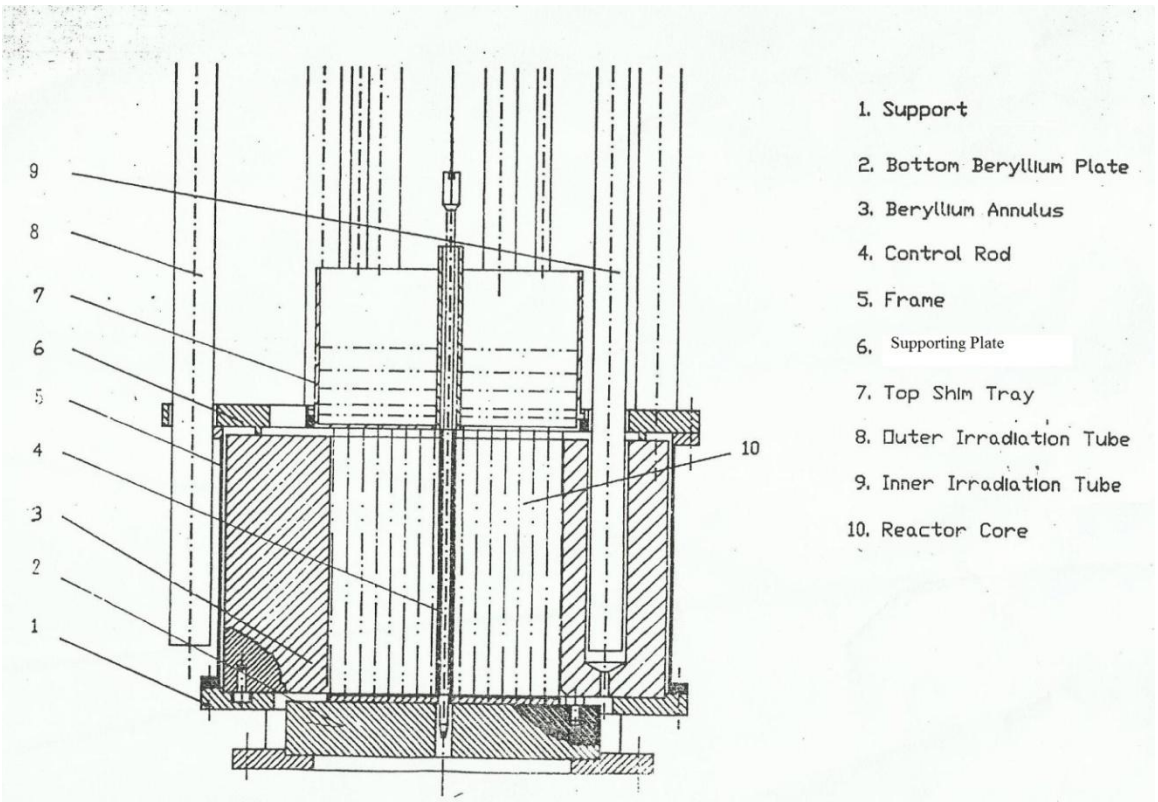


Figure 2.3 Schematic diagram of the Reactor Critical Assembly of the NIRR-1

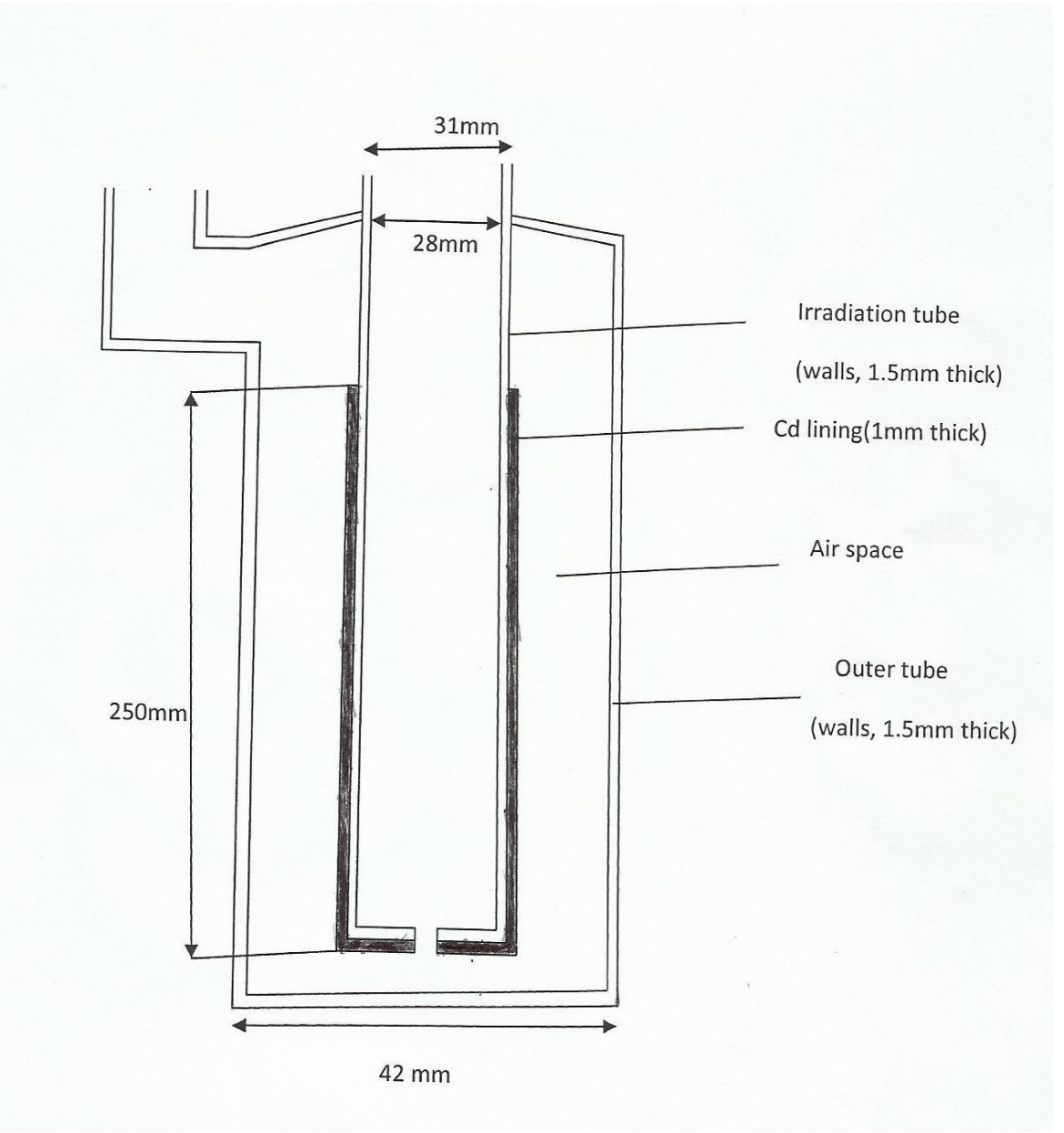


Figure 2.4 Schematic diagram of the cross section of the Cd lined irradiation channel A3 of the NIRR-1

2.2 Theory of the Methods

2.2.1 The Determination of α

The determination of the α parameter is based on the types of and response of the selected activation nuclei (or set of monitors) having resonance peaks for neutron capture of different energies in the epithermal neutron region (Dias *et al*., 2010). The methods widely used for the simultaneous determination of the thermal to epithermal neutron flux ratio (f) and epithermal neutron shape factor(α) in reactor irradiation sites are the bare triple monitor, the cadmium-ratio and the cadmium-ratio for multi-monitor methods. The cadmium covered multimonitor method is widely used for the determination of only α.

From error propagation studies, De Corte *et al*.(1981a) have shown that the Cadmium covered multimonitor method is one of the most accurate methods for α-determination in reactor irradiation sites on the condition that a set of suitable α monitors is used and that the reactor neutron flux characteristics is constant or stable over a long period. The NIRR-1 is a low power research Chinese Miniature Neutron Source Reactor(MNSR) with stable neutron flux characteristics(Kennedy *et al*., 2000; Kennedy and St. Pierre, 1999; Jonah *et al*., 2005; Njinga, 2012). The cadmium covered multimonitor method will be used for the determination of only α in the Cd lined irradiation channel of the NIRR-1 and is described below.

2.2.1.1 The Cadmium Covered Multimonitor Method

In the cadmium covered multimonitor method, a set of N suitable α monitors(minimum 2) are coirradiated under cadmium cover and the induced activities measured on an efficiency calibrated high purity germanium(HPGe) detector system.

For elements having a cross section $\sigma(v) \propto 1/v$ in the range up to $\approx 1.5ev$, α can be found using the Hogdhal convention by plotting the graph of(De Corte *et al*., 1981a):

$$\log \frac{\bar{E}_{r,i}^{-\alpha} .(A_{sp,i})_{Cd}}{k_{o,Au(i)} F_{Cd,i} Q_o(\alpha),i\varepsilon_{d,i}} \quad \text{versus} \quad \log \bar{E}_{r,i}$$

which gives a straight line with the slope$(-\alpha)$.

where $k_{o,Au(i)} = k_o$ – factors for the ith monitor with respect to Au

$\bar{E}_{r,i} =$ average resonance energy of the ith monitor

$(A_{sp,i})_{Cd} =$ specific activity of the ith monitor under Cd cover

$F_{Cd,i} =$ cadmium epithermal neutron transmission factors for the ith nuclide

$Q_o(\alpha),i$ resonance integral to thermal neutron cross section ratio of the ith nuclide in the reactor irradiation site

$\varepsilon_{d,i} =$ detector efficiency of the ith nuclide

i=1,2……N= number of nuclides

The left hand term is itself a function of α, and thus an iterative procedure can be applied with a least square regression analysis to fit the experimental data to the straight

lines for every iterative step. The parameter α is initially set equal to 0, followed by the iterative procedure until the sequence of the values α_o, $\alpha_1,\alpha_2,\alpha_3$ ……..α_n becomes convergent or no significant variation of the α value is observed thus yielding the final value of α (De Corte et al., 1981a).

Mathematically, the final α result of this iteration procedure is identical with solving for the value of α from the equation(De Corte *et al*., 1981a):

$$\alpha + \frac{\sum_{i=1}^{N}\left\{\left[\log \bar{E}_{r,i} - \frac{\sum_{i=1}^{N}\log \bar{E}_{r,i}}{N}\right]\left[\log T_i - \frac{\sum_{i=1}^{N}\log T_i}{N}\right]\right\}}{\sum_{i=1}^{N}\left[\log \bar{E}_{r,i} - \frac{\sum_{i=1}^{N}\log \bar{E}_{r,i}}{N}\right]^2} = 0 \qquad (2.3)$$

where $T_i = \frac{\bar{E}_{r,i}^{-\alpha}.(A_{sp,i})_{Cd}}{k_{o,Au(i)}F_{Cd,i}Q_o(\alpha),i\varepsilon_{d,i}}$

$k_{o,Au(i)} = k_o$ – factors for the ith monitor with respect to Au

$\bar{E}_{r,i}$ = average resonance energy of the ith monitor

i=1,2……N= number of product nuclides

A summary of the list of combination of suitable monitors used in the Cadmium covered multimonitor method for α determination is shown in Table 2.3 below.

Table 2.3 Summary of suitable monitors for only α determination

Method	Activation detectors
Cd covered multimonitor	^{197}Au-^{94}Zr-^{96}Zr
	^{197}Au-^{59}Co-^{94}Zr-^{96}Zr
	^{197}Au-^{152}Sm-^{186}W-^{98}Mo-^{96}Zr-^{94}Zr
	^{115}In-^{197}Au-^{152}Sm-^{186}W-^{98}Mo-^{96}Zr-^{94}Zr

According to De Corte *et al*.(1981a), the choice of the set of suitable monitors for the determination of only α by the Cd covered multimonitor method must fulfill the following conditions:

(i)The values of the Q_o values must be sufficiently large in order to get sufficient epithermal neutron activation with respect to the thermal neutron activation.

(ii)The values of $\bar{E}_{r,i}$ must spread over the whole epithermal neutron energy region.

(iii)The nuclear data needed for the calculations must be known with sufficient accuracy.

(iv) The set of monitors should have uniformly distributed $\bar{E}_{r,i}$ values ranging from low to high which offer the possibility of checking the linearity of the curve thus proving

that α is a constant over the whole epithermal neutron energy region in the reactor irradiation position under consideration.

2.3 The Basic Principles of Neutron Activation Analysis.

The nuclear research reactor is the most important source of neutrons for neutron activation analysis(NAA) because of the availability of abundant and high thermal neutron fluxes in the order of $1\times10^{11}-1\times10^{18} n/cm^2.s$ (IAEA, 1998; IAEA, 2001; IAEA, 1990).

When a neutron interacts with the stable target nucleus in the sample of material, a compound nucleus is formed in a highly excited state. The high excitation energy of the compound nucleus (8 MeV) on the average is due to the high binding energy of the neutron with the nucleus. The life time of the compound nucleus is typically $1\times10^{-16}-1\times10^{-14} s$ (IAEA, 1990). The compound nucleus formed undergoes a rapid de-excitation to a more stable form in a number of different ways usually involving the emission of nuclear particles or prompt $\gamma-$rays. In most cases, a majority (≈90%) of the new nuclei are radioactive and will further de-excite or decay with a characteristic half life after undergoing for example beta (β^-) decay with the emission of one or more delayed γ-rays (Laul, 1979). The radionuclide formed may also decay to a daughter (usually stable) product in various ways or processes. The characteristic prompt or delayed $\gamma-$rays are measured for identification and determination of the concentrations of the elements present in the samples of materials irradiated with the reactor neutrons. In normal neutron activation analysis, the delayed γ-rays from the radioactive product are employed. About 70% of the elements have nuclides possessing properties suitable for

neutron activation analysis(NAA) (IAEA, 1990). The schematic diagram illustrating the sequence of events for a typical (n, γ) reaction is shown in figure 2.5 below.

The most commonly occurring nuclear reaction with reactor neutrons is the radiative capture (n, γ) reaction with thermal and epithermal neutrons. Thus, thermal and epithermal neutrons are most widely used for neutron activation analysis because their (n, γ) reaction cross sections are the largest. Fast neurons induce mainly threshold reactions such as (n, n^1), (n, p) and (n, α) reactions.

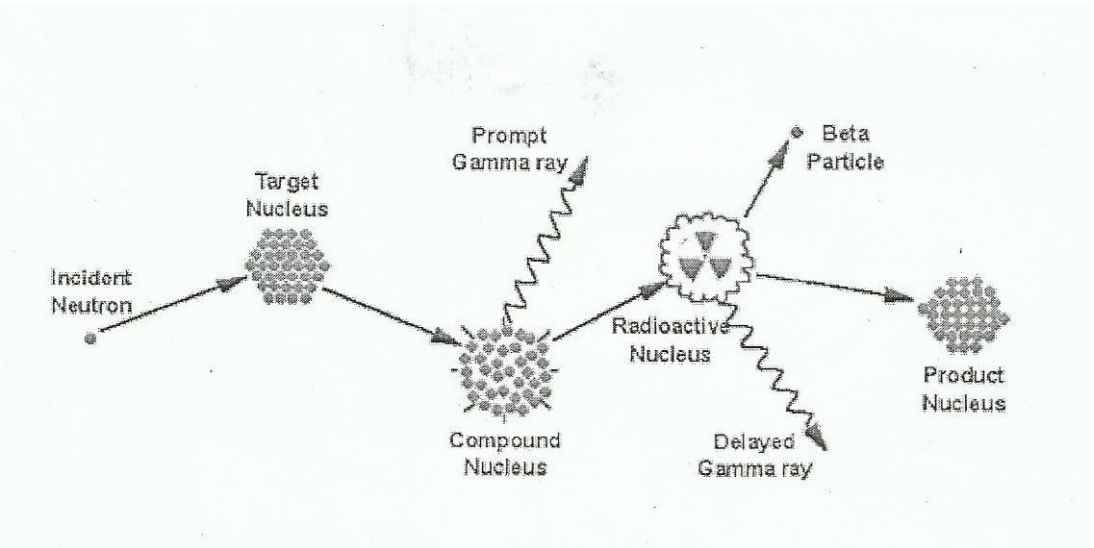


Figure 2.5 Schematic diagram illustrating the sequence of events for a typical (n,γ) reaction

In practice, when a sample of material is irradiated in the whole reactor neutron spectrum, it is activated mainly by thermal and epithermal neutrons. Following the

Hogdhal convention,the basic equation for neutron activation analysis(NAA) is given as (De Soete *et al*., 1972)

$$A_s = \frac{N_p}{t_c} = N.(G_{th}\phi_{th}\sigma_{th} + G_e\phi_e I_o(\alpha)).SDC\varepsilon_d \qquad (2.4)$$

where $A_s =$ activity of elements in sample in whole reactor neutron spectrum

$N_p =$ net photopeak counts of elements of interest in sample in whole reactor neutron spectrum

$N = \frac{N_A w_s \theta I_\gamma}{M} =$ total number of nuclei/atom

$N_A = 6.023 \times 10^{23}$ atoms/mol= Avogadro's number

$\theta =$ isotopic abundance of element of interest

$w_s =$ unknown weight of element of interest in sample irradiated

$M =$ atomic weight of element of interest,

$\phi_{th} =$ thermal neutron flux, $\sigma_{th} =$ thermal neutron cross section for elements of interest

$\phi_e =$ epithermal neutron flux

$G_{th} =$ correction factor for thermal neutron self shielding

$G_e =$ correction factor for epithermal neutron self shielding

$I_o(\alpha) =$ resonance integrals of elements of interest in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

α= epithermal neutron shape factor in the reactor irradiation site

$S = (1 - e^{-\lambda t_i})$ = saturation factor for element of interest in sample irradiated

$D = e^{-\lambda t_d}$ = decay factor for element of interest in sample

$C = \left(\frac{1 - e^{-\lambda t_c}}{\lambda t_c} \right)$ = correction factor for decay of element of interest during counting

ε_d = detector efficiency

$I_\gamma = \gamma -$ ray intensity

λ = decay constant of element of interest

t_i = irradiation time, t_d = decay time, t_c = counting time

When the sample of material is irradiated with the whole reactor neutron spectrum under cadmium cover, the thermal neutrons are absorbed or filtered by the cadmium cover and the sample is activated mainly by epithermal neutrons. Following the Hogdhal convention, the basic equation for ENAA is given as (De Soete *et al*., 1972):

$$A_{s(Cd)} = \left(\frac{N_p}{t_c} \right)_{Cd} = N.\phi_e I_o(\alpha) F_{Cd} G_e SDC\varepsilon_d \qquad (2.5)$$

where $A_{s(Cd)}$ = activity of elements in sample under cadmium cover

$N = \frac{N_A w_s \theta I_\gamma}{M}$ = total number of nuclei/atom

$N_A = 6.023 \times 10^{23}$ atom/mol= Avogadro's number

$\theta =$ isotopic abundance of element of interest

$w_s =$ unknown weight of element of interest in sample irradiated

$M =$ atomic weight of element of interest,

$N_p =$ net photopeak counts of elements of interest in sample under cadmium cover.

$\phi_e =$ epithermal neutron flux

$F_{Cd} =$ Cd transmission factor for epithermal neutrons

$G_e =$ correction factor for epithermal neutron self factor

$I_o(\alpha) =$ resonance integrals of elements of interest in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

α= epithermal neutron shape factor

$S = (1 - e^{-\lambda t_i}) =$ saturation factor for element of interest in sample irradiated

$D = e^{-\lambda t_d} =$ decay factor for element of interest in sample

$C = \left(\frac{1 - e^{-\lambda t_c}}{\lambda t_c} \right) =$ correction factor for decay of element of interest during counting

$\varepsilon_d =$ detector efficiency

$I_\gamma = \gamma -$ ray intensity

$\lambda =$ decay constant of element of interest

$t_i =$ irradiation time, $t_d =$ decay time, $t_c =$ counting time

2.4 Standardization Methods in Epithermal Neutron Activation Analysis(ENAA)

The main standardization methods that are used for the determination of the concentrations of elements in samples of materials activated with epithermal neutrons are the relative method of epithermal neutron activation analysis(rel- ENAA) and the single comparator method of epithermal neutron activation analysis(k_o-ENAA).

2.4.1 The Relative method of ENAA (rel-ENAA)

In the relative method of epithermal neutron activation analysis(rel-ENAA), both the samples and standard reference material (SRMs) are irradiated under the same irradiation conditions. They are irradiated together under cadmium or boron covers for the medium and long lived nuclides and separately under cadmium or boron covers for the short lived nuclides. After irradiation of samples and standard reference materials, the cadmium or boron covers are removed and both samples and standard reference materials are measured exactly under the same counting conditions on the same high purity germanium (HPGe) detector system. The use of the relative method in ENAA helps to eliminate uncertainties in nuclear parameters such as resonance integrals, epithermal neutron flux, detector efficiency and decay constants.

For the relative method of ENAA(rel-ENAA), the concentrations of the unknown elements in the sample irradiated under cadmium cover is given by (Kucera *et al*., 2000; IAEA, 1990):

$$C_{s(Cd)} = \left[\frac{w}{W}\right]_{Cd} = \left[\frac{N_s w_{st} D_{st}}{N_{st} DW}\right]_{Cd} \qquad (2.6)$$

where $w =$ unknown weight of element of interest in sample irradiated under cadmium cover.

$W =$ weight of sample irradiated under Cd cover

$w_{st} =$ weight of element in standard irradiated under Cd cover

$N_s =$ Net photopeak area of radionuclide of interest in sample under Cd cover

$N_{st} =$ Net photopeak area of radionuclide of interest in standard under Cd cover.

$D =$ decay factor for elements in the sample irradiated under Cd cover

$D_{st} =$ decay factor for elements in the standard irradiated under Cd cover

It should be noted that if boron is used as the thermal neutron filter or shield, all the parameters used in equation 2.6 will apply to boron. In the relative method ENAA(rel-ENAA), the elemental composition of the standard reference materials(SRMs) used should be similar to those of the actual samples analysed.

2.4.2 The Single Comparator Method of ENAA(k_o-ENAA)

It has been shown by several authors that the concept of the single comparator method of NAA($k_o - NAA$) originally developed by Simonits *et al.*(1975) for the standardization in reactor (n, γ) activation analysis for multielement analysis of samples of materials can also be applied to epithermal neutron activation analysis(ENAA) which makes use of cadmium as the thermal neutron filter (El NIMR *et al.*, 1981; De Corte *et al*., 1981b; De Corte *et al*., 2005). The single comparator method of ENAA ($k_o - ENAA$) is based on the co-irradiation of a sample of material with a single element (usually a

thin gold foil) as the comparator or standard under a cadmium cover and using an experimentally determined composite nuclear constant called k_o – factors that are independent of the reactor neutron spectrum, the irradiation and counting conditions and the detector characteristics. Use of the method obviates inconveniences or errors that could be caused by the use of the relative method of ENAA that relies on the use of standard reference materials (SRMs) that can be subjected to many errors such as the labour involved in the preparation of standard reference materials, the unavailability of sufficient or suitable standard reference materials and the inability to determine the concentrations of some elements in a sample of material due to the absence of those elements in the standard reference material(Simonits *et al*.1975). The method also avoids the errors that can be caused by use of the single comparator standardization (k-method) that depends mainly on experimentally determined k-factors which was first developed by Girardi *et al*.(1965), namely its dependence on the reactor neutron spectrum, irradiation and counting conditions, the detector characteristics and the uncertainties and inaccuracies associated with nuclear data.

In the single comparator method of ENAA(k_o-ENAA), both the samples of materials and the single comparator are irradiated simultaneously under the same Cd cover in the reactor neutron spectrum at the same irradiation site under the same irradiation condition. The induced activities are measured on an efficiency calibrated HPGe detector system. If a $\frac{1}{v}$ single comparator with well known I_o value such as gold (Al-0.1%Au) foil is used, the concentrations of the unknown elements in the known amount of samples of materials irradiated is obtained by the single comparator method of ENAA from the expression (EL NIMR *et al*., 1981; De Corte *et al*., 1981b):

$$C_{s(Cd)} = \frac{w_s}{W} = \left[\frac{\left(\frac{N_{p,s}/t_c}{SDCW} \right)_s}{\left(\frac{N_{p,Au}/t_c}{SDCw_{Au}} \right)_{Au}} \right]_{Cd} \cdot \left[\frac{F_{Cd,Au}.Q_o(\alpha)_{Au}.\varepsilon_{d,Au}}{k_{o(Au)}F_{Cd,s}Q_o(\alpha)_s\varepsilon_{d,s}} \right] \qquad (2.7)$$

The $k_{o(Au)}$ factor is a compound nuclear constant of the nuclide in the sample of material with respect to Au which is independent of the irradiation and counting conditions and is defined theoretically in the $k_o - ENAA$ method as (Simonits *et al*., 1975):

$$k_{o(Au)} = \frac{M_{Au}\theta_s\varepsilon_{\gamma,s}\sigma_{o,s}}{M_s\theta_{Au}\varepsilon_{\gamma,Au}\sigma_{o,Au}} \qquad (2.8)$$

In equations 2.7 and 2.8

$M_{Au} =$ atomic mass of gold,

$M_s =$ atomic mass of the element of interest in the sample matrix

$\theta_s =$ isotopic abundance of the element of interest in the sample matrix

$\theta_{Au} =$ isotopic abundance of gold

$\varepsilon_{\gamma,s} = \gamma -$ ray intensity of the element of interest in the sample matrix

$\varepsilon_{\gamma,Au} = \gamma -$ ray intensity of gold

$\sigma_{o,s} =$ thermal neutron cross section of elements of interest in the sample matrix

$\sigma_{o,Au} =$ thermal neutron cross section for Au

$F_{Cd,Au} =$ the cadmium epithermal neutron transmission factor for gold

$F_{Cd,s}$ = the cadmium epithermal neutron transmission factor for elements in sample matrix

$Q_o(\alpha)_{Au}$ = the resonance integral to the thermal neutron cross sections for gold in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

$Q_o(\alpha)_s$ = the resonance integral to the thermal neutron cross sections for the elements in sample matrix in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

α = measured epithermal neutron shape factor in reactor irradiation site

$\varepsilon_{d,s}$ = detector efficiency for γ-ray energy of nuclide in sample matrix

$\varepsilon_{d,Au}$ = detector efficiency for γ-ray energy of ^{198}Au

W_s = total amount of sample irradiated under cadmium cover

C_s = concentration of the unknown element in samples under cadmium cover(ppm).

w_s = calculated unknown weight of element in samples under cadmium cover.

w_{Au} = weight of the sample of gold foil irradiated under Cd cover

$N_{p,s}$ = Net photopeak area of radionuclide of interest in samples under Cd cover

$N_{p,Au}$ = Net photopeak area of ^{198}Au under Cd cover

$S = (1 - e^{-\lambda t_i})$ = saturation factor for gold or elements of interest in samples under Cd cover

$D = e^{-\lambda t_d} =$ decay factor for gold or elements of interest in the samples under Cd cover

$C = \frac{(1 - e^{-\lambda t_c})}{\lambda t_c} =$ correction factor for decay during counting for gold or elements in samples

$\lambda =$ decay constant, $t_i =$ irradiation time , $t_d =$ decay time, $t_c =$ counting time

The single comtarator method of ENAA(k_o-ENAA) will be used for the elemental analysis of some samples of standard reference materials(SRMs) and food legumes in this work. However, the relative method of thermal NAA(rel-TNAA) will also be used to complement the results of the trace element composition of the food legumes under investigation.

2.5 Gamma-ray Spectrometer for Measurements in NAA

The basic set-up of any gamma-ray spectrometer for NAA is shown in figure 2.6 below.

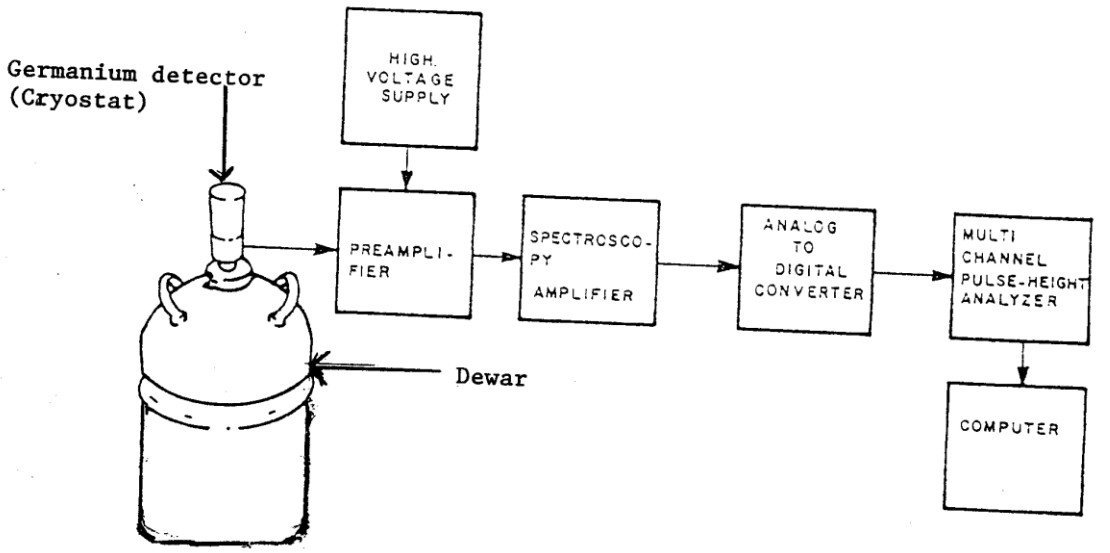


Figure 2.6 Schematic set-up of a gamma ray spectrometer for use in NAA.

Figure 2.6 consists of a semiconductor detector with associated preamplifier, high voltage power supply, spectroscopy amplifier, analog-to- digital converter (ADC), multi-channel pulse height analyzer (MCA) and a computer system with input/output facilities (IAEA, 1990).

2.5.1 The HPGe Semiconductor Detector

The semiconductor detectors more widely used in NAA today are mainly high purity germanium (HPGe) detectors. HPGe detectors are operated at liquid nitrogen(LN_2) temperature (77^o K) using liquid nitrogen(LN_2) in a dewar in order to minimize thermal noise to the detector. The advantages of HPGe detectors for NAA measurements include the non requirement of liquid nitrogen for cooling at room temperature during storage(when not in use) without damaging the crystals provided the high voltage bias supply is removed and their ability to be repaired when damaged by radiation. The cooling of HPGe detectors is with a copper rod dipstick in contact with a dewar of liquid nitrogen. The HPGe crystal is mounted in a vacuum cryostat that has an aluminium casing with a beryllium window and is thermally connected to the copper rod. The copper rod transfers the dissipated heat from the HPGe crystal to the cooling medium.

2.5.2 Cryostat and Dewar

In figure 2.6, the cryostat mounted on the liquid nitrogen dewar is a vertical dipstick cryostat with in-built pulse shaping preamplifier which suits specific shielding or other application requirements. Vertical dipstick cryostats have the additional advantage of samples being placed on the top of the end cap.

2.5.3 Pulse Shaping Preamplifier.

The pulses produced in the semiconductor detector are very small. The preamplifier which is in-built in the detector cryostat amplifies or maximizes the signal to noise ratio, serves as impedance matcher, converts an input charge pulse into an output

voltage pulse and amplifies with gain of about 2VpC-1 to ≈0.1VmeV-1 (in the charge sensitive preamplifier).

Simple pulse shaping in the pulse shaping preamplifier involves the use of CR (differentiator), then followed by RC (integrator) circuits to produce a unipolar pulse. Combining two CR differentiators with one RC integrator circuit produces bipolar pulses. Bipolar pulses are useful for the minimization of baseline shifts with varying count rates.

2.5.4 High Voltage Supply

The high voltage(HV) bias supply provides voltages for the operation of the HPGe detectors. The Ortec 659 high voltage bias supply in the nuclear instrumentation modules(NIM) of the P-type GEM 30195 HPGe coaxial detector system in the NIRR-1 NAA laboratory has output characteristics of 0 – 5 kV at low currents and low noise level. The optimum operating voltage of the P-type GEM 30195 HPGe coaxial detector is 1.50kV. The HV filter model 138 with built in HV time constants varying from 5 – 10 seconds is directly connected to the 237P preamplifier.

2.5.5 Spectroscopy Amplifier

The main functions of the main spectroscopy amplifier are as follows:-linear amplification of the small signal pulses from the preamplifier to levels suitable for pulse height analysis (0-10V), improvement of signal to noise ratio by shaping of the signal pulses and DC power supply to the pulse shaping preamplifier.

2.5.6 Pole Zero Cancellation.

In the CR – RC circuits an undershoot or over shoot may be observed. This undershoot or over shoot needs removal otherwise it will lead to a distortion of the spectrum. The cancellation of the undershoot is carried out with a variable resistor (because the actual value of the undershoot is not well known) added across the capacitance of the differentiator which cancels the undershoot. When pole zero cancellation has been done, the set up becomes stable and should not be disturbed.

2.5.7 Baseline Restoration(BLR).

A shift in the baseline level will affect the amplitude of the signal out put from the preamplifier measured relative to a zero base line. The non restoration of the base line level will lead to distortion of the spectrum. A base line restorer circuit is usually used to reduce the base line to zero. Base line restorers are commonly found at the output stage of linear amplifiers which are intended to supply pulses directly to the analog – to – digital converter (ADC) of a multi-channel analyzer (MCA).

2.5.8 Pulse Pile Up.

Pulses of γ-rays from radiation detector are randomly spaced in time. Some γ-rays could be incident on a radiation detector at a time the pulses from another γ-ray are being processed. These lead to interference effects between pulses called pile up. Pulse pile up occur at high count rates. Due to pulse pile up in a system, dead time increases, spectrum distortation occurs (introduction of unwanted peaks and peak shifts) and energy resolution degrades.

Two types of pulse pile up are tail and peak pile ups. Tail pile up involves the superposition of pulses in the long duration tail or undershoot from a preceeding pulse. Tails or undershoots can persist for a relatively long period of time so that tail pile up can be significant at relatively low counting rates. Tail pile up worsens the resolution by adding wings to the recorded peaks in the pulse height spectra. Tail pile up can be removed using pole zero cancellation and base line restoration techniques. Peak pile up occurs when two pulses are sufficiently close together so that they are treated as a single pulse by the analysis system.

2.5.9 Pile Up Rejection.

The problem of pulse pile up is presently solved by the use of amplifiers with pileup rejection circuits. In the pile up rejection (PUR) circuit, the amplifier output is followed by a fast amplifier which detects the incoming pulse. The fast pulses are fed to a discriminator whose output triggers an inspect interval device. When the inspect interval circuit is triggered, the fast discriminator output pulse generates an inhibit pulse. This inhibit pulse disables or gates off the ADC with the result that no counts are added in the spectrum.

2.5.10 Dead Time.

Two pulses can be recorded separately in a γ-ray detector system. For this to happen, there must be a minimum amount of time separating the two events. The limiting time is sometimes set by the processes in the detector and associated electronics, for example the amplifier and the ADC. The minimum time separation between two pulses in a counting system is known as dead time. To estimate the true average dead

time (DT), a timer is usually installed in the γ-ray counting system to yield clock time. A life timer is an electronic current which stops the timer during the pulse height analysis and memory storage and which automatically corrects for count losses. The dead time(DT) in a detector system is given by

$$DT = CT - LT \qquad (2.9)$$

where CT = clock time or true time, LT=Live time and DT=dead time

The average fractional dead time is given in percentage as

$$DT(\%) = \frac{(CT - LT)}{CT}.100 \qquad (2.10)$$

The best acceptable range of dead time is 0 – 5%. This helps to prevent significant loss of pulses during counting.

2.5.11 The Analog to digital Converter (ADC)

The Analog–to-digital converters(ADCs) convert the pulse height of the amplifier output signal (0-10v) into a digital signal proportional to the pulse height for storage as counts in the appropriate address or channel number in a memory of the multichannel analyzer(MCA) buffer. Conversion gains of 2048, 4096, 8192 or 16384 channels for multielement analysis in NAA are normally used. Most present day ADCs often form an integral part of MCAs inserted into the computer in the form of a card or board.

The Wilkinson type ADC is more generally used in MCAs. In the Wilkinson type ADC or linear ramp converter, high frequency clock pulses such as 50, 100, 200 or even 450 MHz are employed. The higher the clock frequency, the faster the analog signals are

digitized and the lower the dead time per channel. A discrete number of digitized periodic pulses are counted by the address register. This happens during the discharging time of the capacitor. The total number of pulses counted in the address register is proportional to the input pulse amplitude.The time required for conversion in the Wilkinson type ADC is directly proportional to the number of pulses accumulated in the register. Clock frequencies of 100 MHz are commonly used in present day commercial ADC designs.

2.5.12 Multichannel Analyzer (MCA)

The multichannel analyzer(MCA) consists of three main parts, the analog-to-digital converter(ADC), the MCA buffer and the computer.The ADC has already been discussed. All the multichannel analyzer (MCA) buffers include a microprocessor and memory enabling an independent functioning of the MCA during data acquisitions. The memory section of the MCA has one addressable location for every channel. Once a pulse has been processed by the ADC, the analyzer controlled circuit seeks out the memory location corresponding to the digitized amplitude stored in the address registers and the content of that location is incremented by one count. The data memory available in the MCA memory vary from 4K to 32K channels. The count per channel capacity is always high from 8×10^6 counts/channel upwards usually more than what is needed in NAA. For the P-type GEM 30195 HPGe coaxial detector system, the ADC and MCA are in the form of cards inserted in the computer.

2.5.13 Nuclear Instrumentation Modules (NIM) – BIN and Power Supply.

The BIN and power supply is the supporting rack for the nuclear instrumentation modules(NIMs) in the NIM standard. The power supply provides necessary DC voltages to the connectors for the nuclear instrumentation modules(NIMs) in the bin. The 4001M Mini Bin and power supply for the P-type GEM 30195 HPGe coaxial detector system has a supporting rack for 6 NIMs. It supplies the standard DC voltages of $\pm$12V and $\pm$ 24 V with currents of 1A and 0.5A respectively. The 4001M Mini Bin and power supply has a front panel control indicator and monitoring position for the DC output.

2.5.14 Cables.

Impedance matching of cables and input-output connections is of importance to avoid reflections of signals and oscillations resulting in peak-shape distortion and attenuation. Doubly shielded coaxial cables are used to minimize pick up of noise from stray electric and electromagnetic fields. For most routine NAA applications, single shielded cables provide entirely satisfactory insulation from unwanted signal pick up. Cables are made from insulating materials such as polyethylene or teflon.The cables between the preamplifier and the main amplifier should be relatively short and connectors properly attached to reduce capacitance and interferences.

2.5.15 Computers

The computer is used to visually show the results and to do calculations on the acquired gamma-ray spectrum. The data transfer for the computer is by the MCA buffer. The gamma-ray acquisition system used in the NIRR-1 NAA laboratory consists of the P-type GEM 30195 HPGe coaxial detector, an IBM compartible computer of the type

Compaq (DESKPr0) Pentium 4 computer with a HP L1706 video. The ADC and the MCA buffer are in the form of cards inserted in the computer. The gamma-ray acquisition system of the P-type GEM 30195 HPGe coaxial detector system consists of the Maestro Multicannel Annalyser(MCA) emulation software card coupled to the detector via electronic nuclear instrumentation modules(NIM). The photopeak analysis (identification and evaluation) and NAA calculations are carried out with the software WINSPAN 2004 (Liyu, 2004) in a Pentium 4 HP Compaq computer with a HPL1706 video. The Epson LQ 300k printer is used to print the results of all peak analysis and NAA calculations.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Full Energy Peak Efficiency Calibration of the GEM 30195 HPGe detector

The full energy peak efficiency calibration of the P-type GEM 30195 HPGe coaxial detector was performed over the energy range 59.54 keV to 1408 keV using the standard sources ^{241}Am, ^{152}Eu ^{226}Ra, ^{137}Cs, ^{60}Co and ^{22}Na that were obtained from the International Atomic Energy Agency(IAEA), Vienna, Austria. The initial activities of the standard sources ^{241}Am and ^{226}Ra were measured on the 1st July 2004 while those for the standard sources ^{60}Co, ^{152}Eu, ^{137}Cs and ^{22}Na were measured on the 15th July 2004. The standard sources were counted at the distance of 2 cm from the detector for one hour. The present activities of the standard sources were calculated using the Microsoft Excel Spreadsheet 2007 from the equation (Debertin and Helmer, 1988):

$$A = A_o e^{-\lambda t_d} \qquad (3.1)$$

where A_o = initial activity (in Bq)

A = present activity(activity on the date of measurement) (in Bq)

$\lambda = \frac{0.693}{T_{1/2}}$ = decay constant, $T_{1/2}$ = half life, t_d = decay time

The full energy peak efficiency of the P-type GEM 30195 HPGe coaxial detector for a particular standard source was calculated using the Microsoft Excel Spreadsheet 2007 from the equation (Debertin and Helmer, 1988):

$$\varepsilon = \frac{N_p}{T_c A I_\gamma} \qquad (3.2)$$

where $\varepsilon =$ efficiency of the detector

$N_p =$ net peak area under the photopeak of energy of interest (in counts)

$T_c =$ counting time of standard souces

$I_\gamma =$ probability of emission of the particular $\gamma-$ray being measured($\gamma-$ray abundance or intensity)

$A =$ present activity(in Bq) calculated from equation 3.1

The experimental full energy peak efficiencies were plotted against the gamma-ray energies over the energy range of interest on normal scale using the Microsoft Excel Spreadsheet 2007. The natural logarithm of the full energy peak efficiency was also plotted against the natural logarithm of the gamma-ray energy using Microsoft Excel Spreadsheet 2007 to relate the detection efficiency of the P-type GEM 30195 HPGe coaxial detector as a function of energy.

A mathematical or theoretical function of third degree order polynomial on ln-ln scale was fitted to the experimental data from which the efficiency at any energy within or outside the range 59.54 -1408 keV can be obtained by calculation. This theoretical function is given as (Debertin and Helmer, 1988):

$$\ln \varepsilon(E) = a_o + a_1 \ln E + a_2 (\ln E)^2 + a_3 (\ln E)^3 \qquad (3.3)$$

where a_o, a_1, a_2 and a_3 are the coefficients of the energy polynomial

$\varepsilon =$ efficiency of the detector, $E =$ energy

The coefficients of the energy polynomial or fitted parameters a_o, a_1, a_2 and a_3 were obtained from the full energy peak efficiency versus energy curves on the ln-ln scale for the source to detector distance of 2 cm from the P-type GEM 30195 HPGe coaxial detector using the Microsoft Excel Spreadsheet 2007.

The full energy peak efficiencies of the standard sources measured at the distance 2 cm from the detector were theoretically calculated for the energy range 59.54-1408 keV from the expression (Debertin and Helmer, 1988):

$$\varepsilon(E) = \exp(a_o + a_1 \ln E + a_2 (\ln E)^2 + a_3 (\ln E)^3) \qquad (3.4)$$

where a_o, a_1, a_2 and a_3 are the determined coefficients of the polynomial

$\varepsilon =$ efficiency of the detector, $E =$ energy

The percentage deviation of the theoretically calculated full energy peak efficiency of the gamma-ray energies of the standard sources from the experimental values at the distance 2 cm from the P-type GEM 30195 HPGe coaxial detector were calculated from the expression:

$$D(\%) = \left(\frac{E_e - C_e}{E_e} \right).100 \qquad (3.5)$$

where $E_e =$ experimental full energy peak efficiency of γ-ray energies of nuclides

$C_e =$ theoretically calculated full energy peak efficiency of γ-ray energies of nuclides

$D(\%) =$ percentage deviation of calculated from experimental full energy peak efficiency of γ-ray energies of nuclides

3.2 Characterization of the Cadmium Lined Irradiation Channel of the NIRR-1

3.2.1 Determination of Epithermal Neutron Shape Factor(α) by the Cadmium Covered Multimonitor Method

The cadmium covered multi-monitor method was used for the determination of the epithermal neutron shape factor(α) in the cadmium lined irradiation channel A3 of the NIRR-1. One set of four monitors comprising of high purity Al-0.1%Au , Zr and Zn thin foils and Mo thin wire were cleaned with acetone to remove all traces of sodium and other sources of contamination. They were weighed using the electronic balance Mettler AE 240 and then arranged in a small pre-cleaned polyethylene thin film bag and put inside a pre-cleaned 25 cm^3 polyethylene vial. They were covered with cotton wool and the top of the polyethylene vial properly sealed with a celotape. Thin foils and wires were used to avoid or minimize epithermal neutron self shielding effects(Jovanovic *et al*., 1989). The characteristics of the detector foils and wire used are shown in Table 3.1 below(Jonah *et al*., 2005).

. Table 3.1 Description of the activation detector foils and wire for α determination

Element	Material description	mass (g)
Au	Al-0.1%Au thin foil, 0.1mm thick, IRMM-530	0.0132
Zn	99.95% Zn foil, 0.025 mm thick, Goodfellow	0.0083
Zr	99.8% Zr foils, 0.125 mm thick, Goodfellow	0.0446
Mo	Thin wire	0.0168

The polyethylene vial containing the set of monitors was lowered manually into the cadmium lined irradiation channel of the NIRR-1 through the open end of the pneumatic transfer tube at the reactor top using a light strong string attached at the top of the polyethylene vial. The Al-0.1%Au, Zr and Zn thin foils and the Mo thin wire in the 25 cm^3 polyethylene vial were irradiated simultaneously in the Cd lined irradiation channel of the NIRR-1 at a thermal neutron flux of $5\times10^{11} n/cm^3.s$ for 3 hours. A stop watch was used to measure the time between the beginning and end of the irradiation of the set of monitors. At the end of the irradiation period, the polyethylene vial containing the irradiated set of monitors was brought out of the cadmium lined irradiation channel manually using the light strong string attached at the top of the polyethylene vial. The polyethylene vial containing the irradiated set of monitors was put inside a small lead shield, kept in the fumed chamber and allowed to cool before the irradiated monitors were counted.

The induced activities on the irradiated set of monitors were measured using the full energy peak efficiency calibrated P-type GEM 30195 HPGe coaxial detector system at the distance of 2cm from the detector. The photopeak areas of the radionuclides found in the spectra were obtained from the gamma-ray acquisition system of the P-type GEM 30195 HPGe coaxial detector system that consists of the Maestro Multicannel Annalyser (MCA) emulation software card coupled to the detector via electronic nuclear instrumentation modules(NIM) manufactured by Ortec. The optimum conditions employed for the measurement of the product nuclides of the 4 monitors irradiated for α determination are shown in Table 3.2 below.

Table 3.2 Optimum Conditions used for the Measurement of the product nuclides of the 4 monitors irradiated for α determination at 2cm from the detector.

Element	Half life	γ-ray energy (keV)	Irradiation time(hours)	Decay time (seconds)	Counting time (seconds)
^{97}Zr	16.74h	743.4	3	77313	3600
^{69m}Zn	13.76h	438.6	3	81813	3600
^{198}Au	2.7d	411.8	3	86493	3600
^{99}Mo	65.9h	140.51	3	90333	3600
		739.58	3		
^{95}Zr	64.02d	724.2		1288113	7200
		756.7	3	1288113	
^{65}Zn	243.9d	1115.5	3	1295493	7200

The nuclear reactions that produced the nuclides shown in Table 3.2 above are ^{197}Au(n, γ)^{198}Au, ^{64}Zn(n, γ)^{65}Zn, ^{68}Zn(n, γ)^{69m}Zn, ^{64}Zr(n, γ)^{65}Zr, ^{96}Zr(n, γ)^{97}Zr and ^{98}Mo(n, γ)^{99}Mo .

The iterative linear regression approach for the calculation of α by the Cd covered multimonitor method was performed as follows:

The specific activity for each of the product nuclides of the four monitors was calculated using the Microsoft Excel Spreadsheet 2007 from the expression(Simonits *et al.*, 1976):

$$A_{sp(Cd)} = \left(\frac{A}{SDWw}\right)_{Cd} = \left(\frac{N_p / t_c}{SDCw}\right)_{Cd} \qquad (3.6)$$

where $A_{Cd} = N_p / t_c =$ measured activity of each monitor irradiated in Cd lined channel

$A_{sp(Cd)} =$ specific activity of each monitor irradiated in Cd lined channel(counts/s.g)

N_p = Net photopeak area (counts) of each monitor irradiated in Cd lined channel

w = W×C= actual mass of element in sample of thin foil or wire irradiated(g),

W= mass of sample of thin foil or wire irradiated

C= percentage of element in sample of thin foil or wire irradiated

$S = (1 - e^{-\lambda t_i})$ = saturation factor for each monitor

$D = e^{-\lambda t_d}$ = decay factor for each monitor

$C = \left(\frac{1 - e^{-\lambda t_c}}{\lambda t_c} \right)$ =correction factor for decay during counting for each monitor

λ = decay constant, t_i = irradiation time , t_d = decay time, t_c = counting time

The efficiencies ε of the gamma-ray energies for the product nuclides of the 4 monitors(^{198}Au, ^{69m}Zn. ^{65}Zn, ^{99}Mo, ^{95}Zr and ^{97}Zr) were calculated using the mathematical fitting function in equation 3.4 and the coefficients of energy polynomials in Table 4.3. The relevant nuclear data $\bar{E}_r$, Q_o, F_{Cd} and $k_{o,Au}$-factors obtained from the literature were introduced(Jovanovic *et al*., 1987; De Corte and Simonits, 2003; De Corte and Simonits, 1989; De Corte *et al*., 1989; Simonits *et al*., 1984; EL NIMR *et al*. 1981; IAEA, 1990). The experimental and relevant nuclear data obtained from the literature are shown in Table 3.3 below.

Table 3.3 Nuclear data for the product nuclides of 4 monitors irradiated for α determination in the Cd lined irradiation channel

Target Nucleus	Product Nucleus	Half life	E_r (keV)	$\bar{E}_r$ (eV)	Q_o	$k_{o,Au}$ factors	$A_{sp(Cd)}$ (C/s.g)	ε	$\mathbf{F_{Cd}}$
^{197}Au	^{198}Au	2.70d	411.8	5.65	15.71	1	5.43×10^{8}	0.0212	0.991
^{64}Zn	^{65}Zn	243.9d	1115.5	2560	1.908	5.72×10^{-3}	5.02×10^{5}	0.00784	1
^{68}Zn	^{69m}Zn	13.76h	438.6	590	3.19	3.98×10^{-4}	8.49×10^{4}	0.0197	1
^{94}Zr	^{95}Zr	64.02d	724.2, 756.7	6260	5.88	9.32×10^{-5} 1.15×10^{-4}	1.27×10^{4} 1.53×10^{4}	0.0110 0.0105	1
^{96}Zr	^{97}Zr	16.74h	743.4	338	282	1.30×10^{-5}	4.06×10^{4}	0.0107	1
^{98}Mo	^{99}Mo	65.94h	140.51	241	53.1	5.27×10^{-4}	1.73×10^{6}	0.0336	1

The value of α was obtained using the Hogdhal convention by plotting the graph of (De Corte *et al*., 1981a):

$$\log \frac{\bar{E}_{r,i}^{-\alpha}.(A_{sp,i})_{Cd}}{k_{o,Au(i)}F_{Cd,i}Q_o(\alpha),i\varepsilon_{d,i}} \quad \text{versus} \quad \log \bar{E}_{r,i}$$

which gives a straight line with the slope$(-\alpha)$.

where $k_{o,Au(i)} = k_o$ – factors for the ith monitor with respect to Au

$\bar{E}_{r,i}$ = average resonance energy of the ith monitor

$(A_{sp,i})_{Cd}$ = specific activity of the ith monitor

$F_{Cd,i}$ = cadmium epithermal neutron transmission factors for the ith nuclide

$Q_o(\alpha),i$ resonance integral to thermal neutron cross section ratio of the ith nuclide in the Cd lined irradiation channel

$\varepsilon_{d,i}$ = detector efficiency of the ith nuclide,

i=1,2……N= number of nuclides

The Microsoft Excel Spreadsheet 2007 was used for the iterative procedure and least square regression analysis for the determination of the final value of α in the cadmium lined irradiation channel of the NIRR-1. As a first approximation in the iterative procedure, the initial value of α was set equal to 0 in order to calculate the $Q_o(\alpha)$ and Log(Yi) values. The $Q_0(\alpha)$ values were calculated using equation 1.12. The Log(Yi) represents the left hand term for the product nuclides of the 4 monitors. The graph of Log(Yi) versus Log $\bar{E}_r$ was plotted for the product nuclides of the 4 monitors. The slope of the straight line ($-\alpha_1$) resulted in the value of α_1= -0.123±0.020. This resulting α_1 value was used as a starting point for the next iteration. It was substituted into equation 1.12 for the $Q_o(\alpha)$ and then the Log(Yi) values for a second approximation for the next iteration. The iterative procedure was carried out four times until a constant value of α was obtained for two successive iterations. The third and fourth iterations both led to α_3 and α_4 equal to -0.137±0.018. Thus, the final value of α was -0.137±0.018.

3.2.2 Precision on α by the Cd covered multimonitor method.

The precision on the α determination by the Cd covered multimonitor method is due mainly to random errors. Random errors are mainly due to counting statistics of the activities of the product nuclides of the irradiated monitors for the α determination.

Using the error propagation theory described by De Corte *et al*.(1981a), the precision on the α value by the Cd covered multimonitor method was calculated from the expression (De Corte *et al*., 1981a):

$$S_{\alpha,R} = \left(\sum_{i=1}^{N} \left[Z_{\alpha}(A_{sp,i}).s(A_{sp,i}) \right]^2 \right)^{1/2} \qquad (3.7)$$

where $Z_{\alpha}(A_{sp}) =$ error propagation factor on A_{sp} for each of the nuclides

$s(A_{sp}) =$ relative error on the A_{sp} parameter for each of the nuclides

$i = 1.....N =$ number of nuclides

The relative errors on the A_{sp} values of each of the nuclides of the four monitors were calculated from the measured photopeak areas and the associated uncertainties of the nuclides from the equation:

$$\frac{\sigma^2_{A_{sp}}}{A^2_{sp}} = \frac{\sigma^2_{N_p}}{N^2_p} \qquad (3.8)$$

where A_{sp}= calculated specific activity of nuclide

σ_{Asp}= calculated relative error in specific activity of nuclide

N_p= net peak area of nuclide

σ_{Np}= relative error in net peak area of nuclide

The error propagation factor on the A_{sp} value of each of the nuclides, $Z_{\alpha,j}(A_{sp})$ was calculated from the equation (De Corte *et al*., 1981a):

$$Z_{\alpha}(A_{sp}) = 0.434 \left| \frac{1}{\alpha}. \left[\frac{1}{\frac{1}{Q_o(\alpha)}. \left(\frac{(Q_o - 0.429)}{\bar{E}_r{}^{\alpha}}. \log \bar{E}_r + \frac{0.112}{(2\alpha+1)E^{\alpha}_{Cd}}. \left(\frac{1.67}{\alpha + 1/2} - 1 \right) \right)} \right] \right| \qquad (3.9)$$

where $Q_o(\alpha) =$ corrected resonance integral to thermal neutron cross section ratios of nuclides in the Cd lined irradiation channel

$Q_o =$ resonance integral to thermal neutron cross section ratio of nuclies in the $\frac{1}{E}$ law

$\bar{E}_r =$ mean resonance energy of each nuclide

$E_{Cd} =$ Cd cut- off energy(0.55 eV)

$\alpha =$ measured epithermal neutron shape factor in Cd lined irradiation channel

$A_{sp} =$ specific activity of each nuclide

$Z_\alpha(A_{sp}) =$ error propagation factors on the A_{sp} value of each of the nuclides

3.2.3 Determination of the epithermal neutron flux(φ_e) in Cd lined Irradiation Channel

The activity of the nuclide ^{198}Au in the Al-0.1%Au thin foil irradiated along with the monitor set for the determination of α by the Cd covered multimonitor method in the Cd lined irradiation channel was used for the calculation of the epithermal neutron flux(φ_e). The activity of the ^{198}Au is given as (De Soete *et al*.,1972):

$$A_{Cd} = \frac{N_p}{t_c} = N\phi_e I_o(\alpha) F_{Cd} SDC\varepsilon_d \qquad (3.10)$$

The epithermal neutron flux in the Cd lined irradiation channel of the NIRR-1 was obtained from the activity of ^{198}Au using the expression (De Soete *et al*, 1972):

$$\phi_e = \left(\frac{N_p / t_c}{SDCw}\right).\frac{M}{N_A \theta I_\gamma I_o(\alpha) F_{Cd} \varepsilon_d} \qquad (3.11)$$

where $A_{Cd} = N_p / t_c =$ measured activity of ^{198}Au in Cd lined irradiation channel

$N_p =$ Net photopeak area (counts) of ^{198}Au

$S = (1 - e^{-\lambda t_i}) =$ saturation factor,

$D = e^{-\lambda t_d} =$ decay factor

$C = \left(\frac{1 - e^{-\lambda t_c}}{\lambda t_c}\right) =$ correction factor for decay during counting for ^{198}Au

$N = \frac{N_A \theta w I_\gamma}{M} =$ total number of nuclei/atom in ^{197}Au

$N_A =$ Avogadro's number=6.023×10^{23} atoms/mol

$I_o(\alpha) =$ corrected resonance integral for gold in the Cd lined irradiation channel(in barns)

$F_{Cd} =$ Cadmium epithermal neutron transmission factor for Au=0.991

$\alpha =$ measured epithermal neutron shape factor in the Cd lined irradiation channel

$w =$ W×C= actual mass of gold in the sample of Al-0.1% Au foil irradiated(g),

W= mass of Al-0.1%Au thin foil irradiated

C= percentage of Au present in Al-0.1% Au thin foil

M= atomic weight of gold

$\theta =$ isotopic abundance for gold,

$I_\gamma =$ the abundance of γ-ray energy of ^{198}Au

ε_d= photopeak efficiency of the detector for ^{198}Au

$\lambda =$decay constant, $t_i =$ irradiation time , $t_d =$decay time , $t_c =$counting time

The α value determined in cadmium lined irradiation channel was used to correct the value of the resonance integral for gold using equation 1.11. The efficiency of the gamma-ray energy for ^{198}Au measured at the distance 2 cm from the detector was calculated using equation 3.4 and the coefficients of energy polynomials in Table 4.3.

3.2.4 Precision in the epithermal neutron flux(φ_e) in the cadmium lined irradiation channel

The precision in the value of the epithermal neutron flux in the Cd lined irradiation channel is affected mainly by random errors due to counting statistics of the activity of the ^{198}Au nuclide in the Al-0.1%Au thin foil irradiated along with the monitors for α determination. Since only a single determination of the epithermal neutron flux was done, the precision in the value of the epithermal neutron flux was calculated from the error propagation equation (Taylor, 1997; De Soete *et al*., 1972):

$$\frac{\sigma_{\phi_e}^2}{\phi_e^2} = \frac{\sigma_{N_p}^2}{N_p^2} \qquad (3.12)$$

where $\phi_e =$ calculated epithermal neutron flux=4.51×10^9 n/cm^2.s

$\sigma_{\phi_e} =$ precision in epithermal neutron flux

$N_p =$measured net photopeak area of 411.8 keV energy of ^{198}Au=622576 counts

σ_{N_p} = standard deviation in measured net peak area of 411.8 keV energy of ^{198}Au =800 counts

The calculated precision in the value of the epithermal neutron flux in the cadmium lined irradiation channel of the NIRR-1 using the activity of ^{198}Au in the Al-0.1%Au thin foil irradiated along with the monitor set for α determination was found to be 0.01×10^{9} n/cm^2.s.

3.2.5 Epithermal Neutron Fluxes in other Irradiation Sites of the NIRR-1.

The epithermal neutron fluxes in the inner irradiation sites B_1 and A_1 and the outer irradiation sites B_4 and A_2 of the NIRR-1 were calculated using already determined values of the thermal neutron fluxes and thermal to epithermal neutron flux ratios in these inner and outer irradiation sites from the equation(Jonah *et al*., 2005; Sadiq *et al.*, 2010):

$$\phi_e = \frac{\phi_{th}}{f} \qquad (3.13)$$

where f = thermal to epithermal neutron flux ratio

ϕ_{th} = thermal neutron flux

ϕ_e = epithermal neutron flux

3.3 Application of the Single Comparator Method of Epithermal Neutron Activation Analysis for Elemental Determination in Some Legumes.

In section 3.2, the values of the epithermal neutron shape factor(α) by the Cd covered multimonitor method and the epithermal neutron flux in the Cd lined irradiation channel were determined. In this section, the value of α obtained was used in the single comparator method of ENAA(k_o-ENAA) in the Cd lined irradiation channel of the NIRR-1 for the determination of the concentrations of elements in some samples of legumes and the SRM NIST 1515 Apple leaves using Al-0.1% Au thin foil as the single comparator

3.3.1 Sampling of the Legumes

A total of twenty samples of some legumes:- Cowpeas, Soya beans and groundnuts were sampled at four rural villages around Zaria. The sampling of the legumes was carried out manually using the Simple Random Sampling Method. The rural villages at which the samples of legumes were purchased are as follows:- Tudun Sarki, Unguwa Rafin Magaji, Kufena and Unguwa Goruba. The quantities of cow peas, soya beans and groundnuts purchased were 1 tiya each. Some of the samples of groundnuts of quantities about 3-4 tiyas were purchased with the husk so that after removing the husk, the quantities obtained were about one tiya. A tiya is the standard container used for measurement of foodstuffs in Zaria.

A visual inspection on the levels of healthiness and relative purity of the samples of legumes was made before they were purchased from the rural farmers. All the samples of legumes purchased were put into separate strong polyethylene bags, labeled

appropriately and then transported to the Centre for Energy Research and Training, Ahmadu Bello University, Zaria where they were weighed with a balance(Hana, the Big Boss balance) and the preservative phostoxin inserted in envelopes to protect especially the cow peas from infection by insects. The sampling locations are shown in figure 3.1 below which is the map of Zaria obtained from the Zaria Map, 2nd edition, Sheet 102, published by the Northern Nigerian Survey (NNS), Kaduna, 1965. The locations on the map abbreviated TS, KF and GR represent the villages Tudun Sarki, Kufena and Unguwa Goruba respectively. A description of the types of legumes purchased from the rural farmers at the four rural villages around Zaria with their code numbers is shown in Table 3.4 below. The botanical (Scientific) names of the samples of legumes are shown in Table 3.5 below.

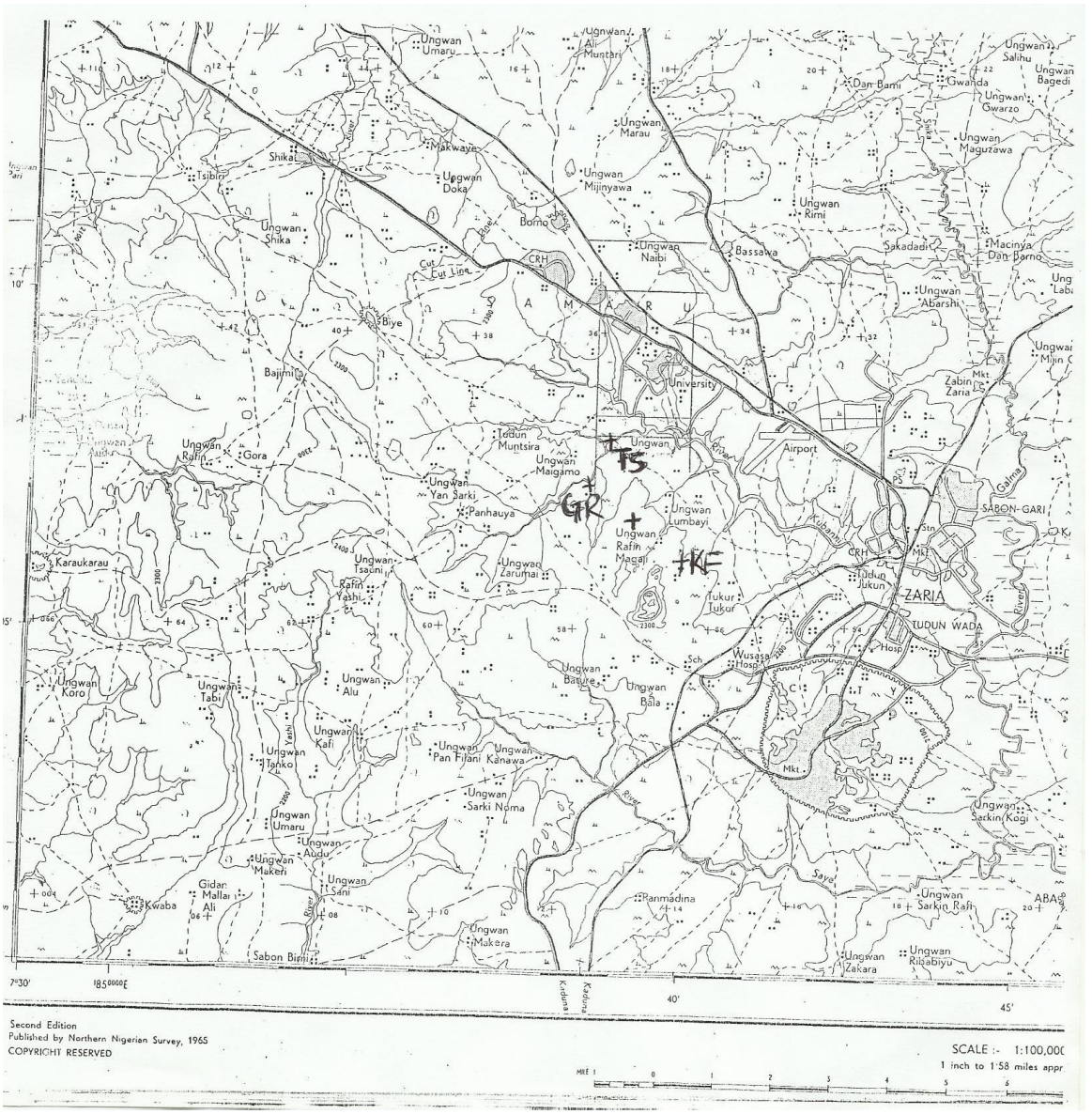


Figure 3.1 Zaria map: (Source:- Zaria Map, 2nd edition, Sheet 102, NNS, Kaduna, 1965)

Table 3.4 Description of the Types of Legumes sampled according to the Sampling locations and Sources.

Locations	Type of Samples	Code numbers	Source	Weight (kg)
Tudun Sarki	Cow pea	CPTS2	Farmer	2.40
	Cow pea	CPTS3	Farmer	2.70
	Cow pea	CPTS4	Farmer	2.50
	Soya beans	SbTS1	Farmer	2.66
	Soya beans	SbTS2	Farmer	2.50
	Groundnuts	GNTS1	Farmer	2.55
	Groundnuts	GNTS2	Farmer	3.00
Unguwa Rafin Magaji	Cow pea	CPRM1	Farmer	2.30
	Cow pea	CPRM2	Farmer	2.18
	Groundnuts	GNRM1	Farmer	2.58
Kufena	Cow pea	CPKF1	Farmer	2.35
	Cow pea	CPKF2	Farmer	2.48
	Soya beans	SbKF1	Farmer	2.38
	Soya beans	SbKF2	Farmer	2.75
	Soya beans	SbKF3	Farmer	2.65
Unguwa Goruba	Cow pea	CPGR1	Farmer	2.45
	Cow pea	CPGR2	Farmer	2.53
	Cow pea	CPGR3	Farmer	2.45
	Groundnuts	GNGR1	Farmer	2.55
	Groundnuts	GNGR2	Farmer	2.48

Table 3.5 Scientific names of the legumes.

Common names	Botanical(Scientific) names
Cow peas	Vigna unguiculata
Soya beans	Glycine max
Groundnuts	Arachis hypogaea

3.3.2 The Homogenization of the Samples

All the samples of legumes in the polyethylene bags were turned into different new strong polyethylene bags, mixed manually for 1-2 minutes by closing the ends of the polyethylene bags and shaking them vigorously. The samples of legumes were turned onto a large flat polyethylene sheet on a flat table and homogenized using the quartering technique. In the quartering technique, the samples of legumes were made into cones. Unbiased division of the samples of legumes in the form of cones into quadrants was made using pieces of ply-wood and the samples in each quadrant put into new strong polyethylene bags. The samples in each quadrant were mixed manually again and the process of the quartering technique continued until a total of sixteen sub-samples were obtained and stored in small polyethylene bags. All the sixteen sub-samples of each homogenized field sample of legume in small polyethyne bags were put in one strong polyethylene bag. Only one sub-sample was taken at random from the total of sixteen sub-samples in each of the homogenized field samples of legumes for grinding and drying for analysis.

3.3.3 The Grinding of Samples

All the sub-samples of legumes selected for grinding were weighed in pre-cleaned aluminium pans using a triple beam balance and then put into pre-cleaned plastic containers for grinding. The range of the masses of the sub-samples of legumes selected for grinding was 77.40-173.05g.

The grinding of the homogenized samples of legumes was carried out at the Department of Food Science and Technology, Institute for Agricultural Research, Ahmadu Bello University, Zaria. All the samples of legumes in the pre-cleaned plastic

containers were ground whole using the Thomas Wiley Laboratotry Mill Model 4 made of stainless steel to a size so that the grounded whole samples of legumes passed through a sieve with 1 mm diameter openings inserted in the Thomas Wiley laboratory mill. The ground whole samples of legumes were transfered back into their respective pre-cleaned plastic containers and covered tightly for drying.

3.3.4 Drying of the Samples

All the samples of ground whole legumes were put into pre-cleaned and already weighed aluminium pans. The aluminium pans with the undried samples of legumes were weighed using a triple beam balance and the masses of the undried samples of legumes found. All the undried samples of legumes were dried in the air oven Memmert Oven dryer type UM 200 with power 1100W and maximum temperature of 220 C. All the samples of ground whole cow peas and soya beans were dried at 101±5°C for 7 hours until constant weight was achieved. The samples of ground whole groundnuts were dried at 101 ± 5^{o}C for 5 hours until constant weight was achieved. The aluminium drying pans with the dried samples of ground whole legumes were always covered with their covers before removal from the oven. After removal of the aluminium pans with the dried samples of ground whole legumes from the air oven, they were allowed to cool for about 25-30 minutes, weighed using a triple beam balance to find the masses of the dried samples of the legumes and quickly transferred into their respective pre-cleaned plastic containers with sizes of about 1 litre and covered tightly.

The percentage moisture content in the samples of legumes was calculated from the expression (Bradley, 2002):

$$M_c(\%) = \frac{W_{H_2O}}{W}.100 \qquad (3.14)$$

where $M_c(\%) =$ percentage moisture content

$W_{H_2O} =$ weight of water in the samples= weight of undried samples- weight of dried samples

$W =$ weight of undried samples

The ranges of the percentage moisture content found in all the varieties of the dried samples of legumes are as follows: -cow peas, 5.78-9.56%; soya beans, 5.74-6.50% and groundnuts, 2.94-3.87%.

The dried ground whole samples of legumes were homogenized manually again by shaking vigorously and rotating the plastic containers with the samples for about 3-5 minutes. Small quantities of the dried homogenized ground whole samples of legumes were taken at random using small pre- cleaned plastic vials for analysis.

3.3.5 Preparation of Samples of legumes for Analysis

Twenty samples of the ground whole legumes consisting of cow peas, soya beans and groundnuts were weighed in pre-cleaned polyethylene films using the five digit electronic balance Mettler AE 240. The pre-cleaned polyethylene films with the weighed samples of ground whole legumes were heat sealed.

The total of twenty samples of legumes were divided into three sets. The first set of samples consisted of five samples of legumes weighing between 0.2593-0.2970 g and two prepared samples of standard reference materials(SRMs) NIST 1573a Tomato

leaves and NIST 1548a typical diet which were equally weighed. The second set of samples consisted of twelve samples of legumes weighing between 0.2527-0.2728 g and two prepared standard reference materials NIST 1515 Apple leaves and NIST 1573a Tomato leaves weighing 0.2573g and 0.1256g respectively. The third set of samples consisted of three samples of legumes weighing between 0.2571-0.2658 g, three SRMs NIST 1573a Tomato leaves, NIST 1515 Apple leaves and NIST 1547 Peach leaves weighing 0.1420g, 0.2510g and 0.2755g repsctively and Al-0.1%Au thin foil weighing 0.0132g. Each set of the samples of legumes and SRMs were put into different pre-cleaned 25 cm^3 polyethylene vials, covered with cotton wool and the tops sealed with a celotape for analysis by the k_o-ENAA method.

To complement the results of the analysis of the samples of legumes by the single comparator method of ENAA(k_o-ENAA) , another set of twenty samples of the ground whole legumes were also weighed in pre-cleaned polyethylene films using the five digit electronic balance Mettler AE 240 for analysis by the relative method of thermal neutron activation analysis. The pre-cleaned polyethylene films with the weighed samples of ground whole legumes were heat sealed. The total of twenty samples of legumes in the heat sealed pre-cleaned polyethylene films were divided into three sets. The first set of samples consisted of six samples of legumes weighing between 0.2539- 0.2728 g and one standard reference material(SRM) NIST 1515 Apple leaves weighing 0.2535g. The second set of samples consisted of six samples of legumes weighing between 0.2570-0.2667g and one SRM NIST 1573a Tomato leaves weighing 0.1561g. The third set of samples consisted of eight samples of legumes weighing between 0.2543-0.2724g and NIST 1515 Apple leaves. All the sets of samples were put into different pre-cleaned 7 cm^3 polyethylene vials, covered with cotton wool and the tops sealed with a celotape for analysis by the relative method of thermal neutron activation analysis(rel-TNAA).

3.3.6 Irradiation of Samples of Legumes for Analysis by the Single Comparator Method of ENAA(k_o-ENAA)

The first and second sets of samples of legumes and SRMs in the 25 cm^3 polyethylene vials were separately lowered manually into the cadmium lined irradiation channel of the NIRR-1 through the open end of the pneumatic transfer tube at the reactor top using a light strong strings attached at the top of the polyethylene vials. They were irradiated separately with epithermal neutrons of the Cd lined irradiation channel at a thermal neutron flux of $5\times10^{11} n/cm^2.s$ of the NIRR-1 for 6 hours. At the end of the irradiation periods, the samples of legumes and SRMs were brought out of the cadmium lined irradiation channel. The third set of samples of legumes and SRMs together with the Al-0.1% Au thin foil in the 25 cm^3 polyethylene vials was sent into the Cd lined irradiation channel using the pneumatic transfer system of the rabbit system type A and co-irradiated with epithermal neutrons at a thermal neutron flux of $5\times10^{11} n/cm^2.s$ of the NIRR-1 for 6 hours. After irradiation, they were brought out of the Cd lined irradiation channel. A stop watch was used to measure the time between the beginning and end of irradiation of the sets of samples of legumes and SRMs.The 25 cm^3 polyethylene vials containing each irradiated set of samples were put inside a small lead shield, kept in the fumed chamber and allowed to cool before counting.

The induced activities on the elements of interest in the samples of legumes, SRMs and Al-0.1%Au thin foil were measured under the same counting conditions at the distance of 2 cm from the efficiency calibrated P-type GEM 30195 HPGe coaxial detector system after appropriate decay and counting periods. The photopeak areas of the radionuclides found in the spectra were obtained from the gamma-ray acquisition system of the P-type GEM 30195 HPGe coaxial detector system that consists of the Maestro

Multicannel Annalyser (MCA) emulation software card coupled to the detector via electronic nuclear instrumentation modules(NIM) manufactured by Ortec. The analysis scheme employed for the elements measured in the samples of legumes and NIST 1515 Apple leaves irradiated in the Cd lined irradiation channel for analysis by k_o-ENAA is shown in Table 3.6 below.

Table 3.6 Analysis Scheme for Elements measured in Samples of legumes and NIST 1515Apple leaves for k_o-ENAA

ϕ_{th} ($n/cm^2.s$)	Irradiation time(hours)	Decay time	Counting time (seconds)	Product nuclides
$5x10^{11}$	6h	1.68-3.74d	1800	^{24}Na ^{42}K, ^{82}Br, ^{140}La
		8.76-12.96d	3600	^{46}Sc,^{86}Rb, ^{152}Eu,^{75}Se

3.3.7 Irradiation of Samples of Legumes for the Relative Method of Thermal NAA(rel-TNAA)

The first, second and third sets of samples of legumes and SRMs were irradiated separately with thermal neutrons in the irradiation sites B2 and B3 of the NIRR-1. All the 7 cm^3 polyethylene vials containing each set of samples of legumes and SRMs were sent to the irradiation sites B2 and B3 of the NIRR-1 separately using the pneumatic transfer system of the rabbit system type B. All sets of samples of legumes and SRMs were irradiated at a thermal neutron flux of $5\times10^{11} n/cm^2.s$ of the NIRR-1 for 6 hours. A stop watch was used to measure the time between the beginning and end of irradiation of the sets of samples of legumes and SRMs. At the end of the irradiation period, the 7

cm^3 polyethylene vials containing each set of samples of legumes and SRMs were brought out of the irradiation sites using the pneumatic transfer system of the rabbit system type B and put inside a small lead shield, kept in the fumed chamber and allowed to cool before counting.

The induced activities on the elements of interest in the samples of legumes and SRMs were measured under the same counting conditions at the distance of 2cm from the efficiency calibrated P-type GEM 30195 HPGe coaxial detector system after appropriate decay and counting periods. The P-type GEM 30195 HPGe coaxial detector system has a gamma-ray acquisition system that consists of the Maestro Multicannel Annalyser(MCA) emulation software card coupled to the detector via electronic nuclear instrumentation modules(NIM) manufactured by Ortec. The analysis scheme employed for the elements measured in the samples of legumes and NIST 1515 Apple leaves irradiated in the irradiation sites B2 and B3 of the NIRR-1 for analysis by the relative method of thermal NAA is shown in Table 3.7 below.

Table 3.7 Analysis Scheme for Elements Measured in Samples and NIST 1515 Apple leaves for Thermal NAA

ϕ_{th} ($n/cm^2.s$)	Irradiation time(hours)	Decay time	Counting time (seconds)	Product nuclides
$5x10^{11}$	6h	2.751-5.784d	1800	^{24}Na, ^{42}K, ^{82}Br, ^{140}La,^{153}Sm, ^{99}Mo,^{122}Sb
		10.819-13.04d	3600	^{86}Rb,^{65}Zn,^{131}Ba, ^{152}Eu,^{60}Co, ^{175}Yb, ^{59}Fe, ^{46}Sc,

3.3.8 Calculation of the Concentrations of the Elements Measured in the Samples of Legumes by the Single Comparator Method of ENAA

The unknown concentrations of elements measured in the samples of legumes and NIST 1515 Apple leaves were calculated by the single comparator method of ENAA using the activity of ^{198}Au in Al-0.1% Au thin foil co-irradiated with the samples of legumes and standard reference materials in the Cd lined irradiation channel of the

NIRR-1 as the comparator with the MS Excel spreadsheet 2007 from the expression (Simonits *et al*., 1980; EL NIMR *et al*., 1981; De Corte *et al*., 1981b):

$$C_{s(Cd)} = \frac{w_s}{W} = \left[\frac{\left(\frac{N_{p,s}/t_c}{SDCW} \right)_s}{\left(\frac{N_{p,Au}/t_c}{SDCw_{Au}} \right)_{Au}} \right]_{Cd} . \left[\frac{F_{Cd,Au}.Q_o(\alpha)_{Au}.\varepsilon_{d,Au}}{k_{o(Au)}F_{Cd,s}Q_o(\alpha)_s\varepsilon_{d,s}} \right]$$

$$= \left[\frac{\left(\frac{N_{p,s}/t_c}{SDCW} \right)_s}{A_{sp,Au}} \right]_{Cd} . \left[\frac{F_{Cd,Au}.Q_o(\alpha)_{Au}.\varepsilon_{d,Au}}{k_{o(Au)}F_{Cd,s}Q_o(\alpha)_s\varepsilon_{d,s}} \right] \qquad (3.15)$$

The $k_{o(Au)}$ factor is a compound nuclear constant of the nuclide in the sample of material with respect to Au which is independent of the irradiation and counting conditions and is defined theoretically in the $k_o - ENAA$ method as (Simonits *et al*., 1975):

$$k_{o(Au)} = \frac{M_{Au}\theta_s\varepsilon_{\gamma,s}\sigma_{o,s}}{M_s\theta_{Au}\varepsilon_{\gamma,Au}\sigma_{o,Au}} \qquad (3.16)$$

In equations 3.15 and 3.16

M_{Au} = atomic mass of gold,

$M_s =$ atomic mass of the element of interest in the sample

$\theta_s =$ isotopic abundance of the element of interest in the sample

$\theta_{Au} =$ isotopic abundance of gold

$\varepsilon_{\gamma,s} = \gamma -$ ray intensity of the element of interest in the sample

$\varepsilon_{\gamma,Au} = \gamma -$ ray intensity of gold

$\sigma_{o,s} =$ thermal neutron cross section of elements of interest in the sample

$\sigma_{o,Au} =$ thermal neutron cross section for Au

$F_{Cd,Au} =$ the cadmium epithermal neutron transmission factor for gold

$F_{Cd,s} =$ the cadmium epithermal neutron transmission factor for elements in sample

$Q_o(\alpha)_{Au} =$ the resonance integral to the thermal neutron cross sections for gold in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

$Q_o(\alpha)_s =$ the resonance integral to the thermal neutron cross sections for the elements in sample in the non-ideal $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum

$\alpha =$ measured epithermal neutron shape factor in the Cd lined irradiation channel

$\varepsilon_{d,s} =$ detector efficiency for γ-ray energy of nuclide in sample

$\varepsilon_{d,Au} =$ detector efficiency for γ-ray energy of ^{198}Au

$W_s =$ total amount of sample irradiated

$C_s =$ concentration of the unknown element in samples (ppm).

$w_s =$ calculated unknown weight of element in samples

$w_{Au} =$ weight of the sample of gold foil irradiated

$N_{p,s} =$ Net photopeak area of radionuclide of interest in samples

$N_{p,Au} =$ Net photopeak area of ^{198}Au

$A_{sp,Au} =$ specific activity for ^{198}Au

$S = (1 - e^{-\lambda t_i}) =$ saturation factor for gold or elements of interest in samples

$D = e^{-\lambda t_d} =$ decay factor for gold or elements of interest in the samples

$C = \frac{(1 - e^{-\lambda t_c})}{\lambda t_c} =$ correction factor for decay during counting for gold or elements in samples

$\lambda =$ decay constant, $t_i =$ irradiation time , $t_d =$ decay time, $t_c =$ counting time

The value of the epithermal neutron shape factor(α) determined in the $\frac{1}{E^{1+\alpha}}$ epithermal neutron spectrum of the Cd lined irradiation channel by the cadmium covered multimonitor method using the four monitors Al-0.1%Au, Zn, and Zr thin foils and Mo thin wire was used to correct the Q_o values for ^{198}Au and the nuclides determined in samples of legumes(as well as for the NIST 1515 Apple leaves). The corrected $Q_o(\alpha)$ values for the elements of interest measured in the samples of legumes (as well as for

the NIST 1515 Apple leaves) were calculated with the MS Excel spreadsheet 2007 using equation 1.12. The nuclear data k_o, $Q_{o,}$and $\bar{E}_r$ and the cadmium epithermal neutron transmission factor, F_{Cd} for ^{198}Au and the elements measured in the samples of legumes (as well as for the NIST 1515 Apple leaves) were obtained from the literature ((IAEA, 1990; De Corte and Simonits, 1989; De Corte and Simonits, 2003; EL NIMR *et al*. 1981; De Corte *et al*, 1989).

The specific activity of the nuclide ^{198}Au in the Al-0.1% Au thin foil co-irradiated with the samples of standard reference materials and legumes was calculated with the Microsoft Excel Spreadsheet 2007 using equation 3.5. The value of the specific activity of ^{198}Au was found to be 4.47×10^{8} counts/s.g.

The efficiencies of the gamma-ray energies of ^{198}Au and the nuclides measured in the samples of legumes and the SRM NIST 1515 Apple leaves were theoretically calculated with the MS Excel spreadsheet 2007 using equation 3.4 and the coefficients of energy polynomials in Table 4.3. The nuclear data for the ^{198}Au in the Al-0.1% Au thin foil and the nuclides measured in samples of legumes and SRM NIST 1515 Apple leaves were important for the calculation of the concentrations of the elements measured in the samples of legumes and the SRM NIST 1515 Apple leaves by the k_o-ENAA method.

3.3.9 Precision in the Concentrations of Elements in Samples of legumes by the k_o-ENAA Method

The precision in the the concentrations of elements found in the samples of legumes by k_o-ENAA is due mainly to random errors. Random errors are due mainly to

counting statistics of ^{198}Au and the nuclides measured in the samples of legumes. They affect the precision of measurements of each element in the samples of legumes and the ^{198}Au in the Al-0.1% Au thin foil (De Corte *et al*., 1981a).

Only single samples of the legumes were irradiated by epithermal neutrons in the Cd lined irradiation channel of the NIRR-1. The precision of the concentrations of each element in each of the samples of legumes was calculated from the error propagation equation (Kafala and MacMahon, 2007; Taylor, 1997; De Soete *et al*., 1972):

$$\frac{\sigma_{C_e}^2}{C_e^2} = \frac{\sigma_{N_{p,Au}}^2}{N_{p.Au}^2} + \frac{\sigma_{N_{p,s}}^2}{N_{p,s}^2} \qquad (3.17)$$

where C_e = concentration of elements in samples of legumes by k_o-ENAA

σ_{C_e} = standard deviation in concentrations of elements in samples of legumes by k_o-ENAA

$N_{p,Au}$ = measured net photopeak area of 411.8 keV γ-ray energy of ^{198}Au

$\sigma_{N_{p,Au}}$ = standard deviation in measured net peak area of 411.8 keV γ-ray energy of ^{198}Au

$N_{p,s}$ = measured net photopeak area of γ-ray energy of nuclide in the legume samples

$\sigma_{N_{p,s}}$ = standard deviation in measured photopeak area of γ-ray energy of nuclide in the legume samples

3.3.10 Quality Control for the k_o-ENAA Method

The accuracy or applicability of the single comparator method of ENAA in the Cd lined irradiation channel of the NIRR-1 was assessed by the determination of the

concentrations of elements in the SRM NIST 1515 Apple leaves using the activity of the nuclide ^{198}Au in the Al-0.1%Au thin foil irradiated along with the SRMs from equation 3.15. The concentrations of elements measured in the SRM NIST 1515 Apple leaves using the same set up as the one used to measure the legumes were compared with the certified values.

3.3.11 Calculation of the Concentrations of Elements in the Irradiated Samples of legumes by the Relative Method of TNAA

The unknown concentrations of the elements in the samples of legumes were calculated by the relative method of thermal NAAA (rel-TNAA) using the SRM NIST 1515 Apple leaves irradiated along with the samples of legumes as the comparator from the expression (Kucera *et al*., 2000; IAEA, 1990)

$$C_s = \left[\frac{w}{W}\right] = \left[\frac{N_s w_{st} D_{st}}{N_{st} DW}\right] \qquad (3.18)$$

where $w =$ unknown weight of element of interest in sample irradiated

$W =$ weight of sample irradiated

$w_{st} =$ weight of element in standard irradiated

$N_s =$ Net photopeak area of radionuclide of interest in sample

$N_{st} =$ Net photopeak area of radionuclide of interest in standard

$D =$ decay factor for elements in the sample irradiated

$D_{st} =$ decay factor for elements in the standard irradiated

C = concentrations of elements in the samples in μg/g.

$w_{st} = M_{st} C_{st}$ = known weight of element in the amount of standard irradiated.

C_{st} = certified values of the concentrations of elements in the standard (μ g/g)

M_{st} = actual mass of standard irradiated (g)

The photopeak analysis and neutron activation analysis calculations of the radionuclides found in the spectra were carried out using the software WINSPAN 2004(Liyu, 2004).

3.3.12 Quality Control for the Relative Method of TNAA

The accuracy of the relative method of thermal NAA was assessed by the analysis of the SRM NIST 1515 Apple leaves irradiated along with the legumes using the software WINSPAN 2004(Liyu, 2004). The concentrations of the elements measured in the SRM NIST 1515 Apple leaves using the same set up as the one used to measure the legumes were compared with the certified values.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1.0 Introduction

In this chapter, the results of the full energy peak efficiency calibration of the GEM 30195 HPGe detector with IAEA standard sources, the neutron spectrum parameters such as the epithermal neutron shape factor(α) and epithermal neutron flux(φ_e) and the elemental analysis of some samples of legumes and the standard reference material NIST 1515 Apple leaves by the k_o-ENAA method in the cadmium lined irradiation channel have been presented. The results of the elemental anaylysis of the legume samples and the NIST 1515 Apple leaves by the relative method of thermal neutron activation analysis have also been presented.

Fitting the measured full energy peak efficiency curves of the P-type GEM 30195 HPGe coaxial detector with a theoretical function of third degree order polynomial in ln-ln scale enabled the theoretical calculation of the efficiencies of the full energy peak efficiencies of the P-type GEM 30195 HPGe coaxial detector at the distance 2 cm from the detector for the energy range of 59.54-1408 keV which were in satisfactory agreement with the experimental values. This established theoretical function was used to calculate the efficiencies of the γ-ray energies of the product radionuclides involved in the α determination by the Cd covered multimonitor method and the k_o-ENAA method. This ensured the accuracy of the results of the epithermal neutron shape factor(α) and and the concentrations of elements determined in the samples of legumes and the standard reference material NIST 1515 Apple leaves by the k_o-ENAA method in the cadmium lined irradiation channel. The result of the value of α obtained ensured the

accuracy of the k_o-ENAA method in the cadmium lined irradiation channel of the NIRR-1.

4.1.1 Results of the Full Energy Peak Efficiency Calibration of the GEM 30195 HPGe detector with IAEA standard sources

Table 4.1 Specification of IAEA standard sources and present activities measured at 2 cm from the P-type GEM 30195 HPGe coaxial detector

Sources	Initial activity (Bq)	Half life (s)	Decay constant (s^{-1})	Decay time (s)	Present activity (Bq) (9.11.2011)
^{241}Am	36500	1.36×10^{10}	5.08×10^{-11}	2.32×10^{8}	36071.98
^{60}Co	38400	1.66×10^{8}	4.17×10^{-9}	2.31×10^{8}	14655.74
^{152}Eu	38000	4.20×10^{8}	1.65×10^{-9}	2.31×10^{8}	25956.87
^{226}Ra	37400	5.05×10^{10}	1.37×10^{-11}	2.32×10^{8}	37281.02
^{137}Cs	36900	9.51×108	7.28×10^{-10}	2.31×10^{8}	31185.66
^{22}Na	36900	8.21×10^{7}	8.45×10^{-9}	2.31×10^{8}	5245.28

^{22}Na was measured on the 11.11.2011

The initial activities of ^{241}Am and ^{226}Ra were measured on the 01.07.2004 while those for ^{60}C0, ^{152}Eu, ^{137}Cs and ^{22}Na were measured on the 15.07.2004.

Table 4.1 above shows the specifications and the calculated present activities of the IAEA standard sources counted on the dates shown at the geometries 2 cm from the P-type GEM 30195 HPGe coaxial detector surface. The calculation of the present

activities of the IAEA standard sources enabled the correction of the initial activities of the standard sources for decay from the date of preparation. This ensured the accurate full energy peak efficiency calibration of the P-type GEM 30195 HPGe coaxial detector at the time this experimental work was carried out.

Table 4.2 Full energy peak efficiencies for standard sources at 2 cm from P-type GEM 30195 HPGe coaxial detector

Source	Present Activity (Bq)	Energy (keV)	γ-ray intensity (%)	Net peak areas (counts)	Count time(s)	Count rate (counts/s)	γ-ray emission rate(γ/s)	Efficiency $\times 10^{-3}$
^{241}Am	36071.98	59.54	35.70	193504	3600	53.75	12877.70	4.17
^{152}Eu	25956.87	121.78	28.37	1067512	3600	296.53	7363.96	40.27
^{226}Ra	37281.02	186.10	3.50	190052	3600	52.79	1304.84	40.46
^{152}Eu	25956.87	244.69	7.51	213570	3600	59.33	1949.36	30.43
^{152}Eu	25956.87	344.29	26.58	604517	3600	167.92	6899.34	24.34
^{137}Cs	31185.66	661.66	85.21	1521850	3600	422.74	26573.30	15.91
^{152}Eu	25956.87	778.92	12.96	150182	3600	41.72	3364.01	12.40
^{152}Eu	25956.87	964.11	14.62	149886	3600	41.64	3794.89	10.97
^{152}Eu	25956.87	1112.08	13.50	128084	3600	35.58	3504.18	10.15
^{60}Co	14655.74	1173.20	99.90	515541	3600	143.21	14641.08	9.78
^{22}Na	5245.28	1274.53	99.94	163055	3600	45.29	5242.13	8.64
^{60}Co	14655.74	1132.50	99.98	466717	3600	129.64	14652.81	8.85
^{152}Eu	25956.87	1408.00	20.85	163553	3600	45.43	5412.01	8.40

Table 4.2 above shows the measured full energy peak efficiencies of the P-type GEM 30195 HPGe coaxial detector at the distance 2 cm from the detector surface. The gamma-ray emission rate from the nuclides were calculated by multiplying the present activities of the standard sources shown in Table 4.1 by their respective gamma-ray abundances or intensities (probability of emission of the particular $\gamma-$ray being measured) that were obtained from the literature. The measured count rates were obtained

by dividing the measured net peak areas under the photopeaks of energies of interest (in counts) by the counting times of the standard sources. The full energy peak efficiencies of the standard sources were calculated by dividing the counting rates by the gamma-ray emission rates.

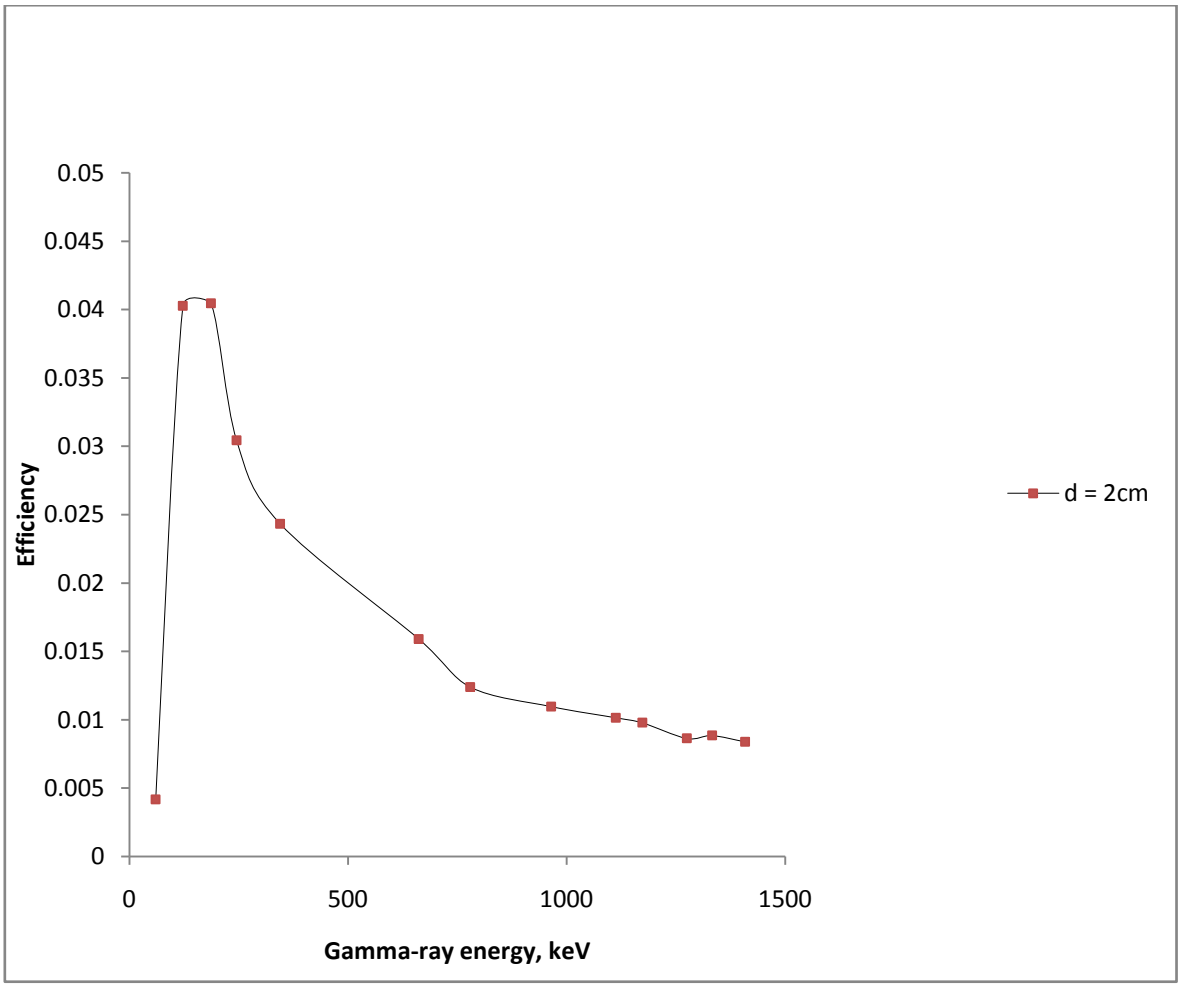


Figure 4.1 Full Energy Peak Efficiency Curves for the P-type GEM 30195 HPGe coaxial detector at the distance 2 cm from the detector

Figure 4.1 above shows the full energy peak efficiency curves of the P-type GEM 30195 HPGe coaxial detector on normal scale for the distance 2 cm from the detector surface for the energy range 59.54-1408.00 keV. The full energy peak efficiency of the P-type GEM 30195 HPGe coaxial detector depends on factors that include, the physical size of the crystal, the source to detector distance, gamma-ray energy incident on the detector and the interactions of the incident gamma-rays with the sensitive or active volume of the HPGe crystal, the detector aluminium end cap or window and dead layers. For the P-type GEM 301595 HPGe coaxial detectors, the thickness of the lithium contact represents a dead layer around the outer surface of the crystal with which energy depositions do not result in detector signals.

From Figure 4.1, it can be observed that at the low energy region where the photoelectric interactions or absorptions which are used to measure the energy of the γ-ray in a HPGe detector are dominant, the full energy peak efficiency rises rapidly to the energy peak of 121.78 keV because of abrupt reduction in the attenuation in detector aluminium cap or dead layer. A maximum is reached for the energy value at 186.10 keV and this depends on the detector characteristics. Beyond the energy value of 186.10 keV, the full energy peak efficiencies decreases exponentially. The full energy peak efficiencies in the gamma-ray energy range from 186.10 eV to 964.11 eV are due to the interactions of the gamma-rays by Compton scattering while those in the gamma-ray energy range 1112.08 keV to 1408 keV are due to interactions by pair production. It should be noted that the threshold energy for pair production is 1022 keV, which is about twice the energy corresponding to the rest mass of the electron. The decreasing nature of the full energy peak efficiencies in the energy range from 186.10 keV to 1408 keV is due to the fact that in both the Compton scattering and pair production interactions which dominate in this energy region, the original total energies of the incident gamma-rays are

not deposited at the locations of the first interactions(Debertin and Helmer, 1988; Gilmore and Hemingway, 1995).

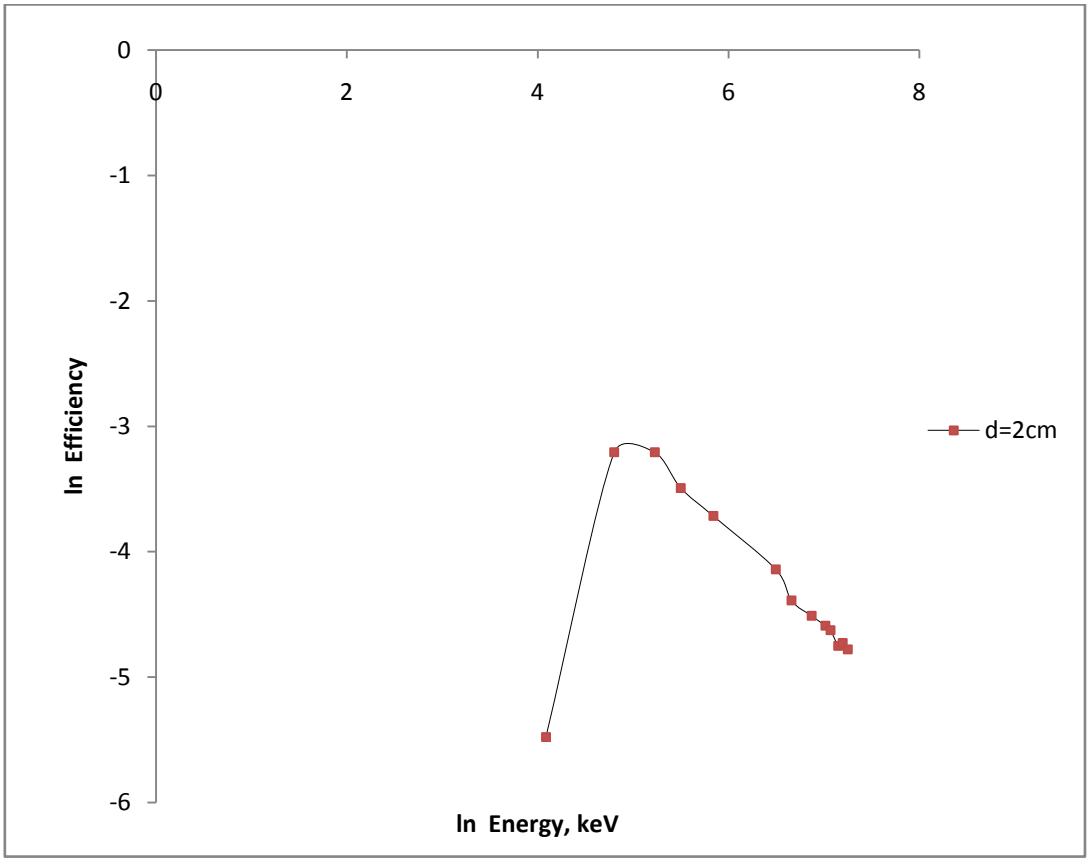


Figure 4.2 Full energy peak efficiency curves for the P-type GEM 30195 HPGe coaxial detector on ln-ln Scale at the distance 2 cm to the detector

Figure 4.2 above shows the full energy peak efficiency curve of the gamma-ray energies of the standard sources on ln-ln scale at the distance 2 cm from the P-type GEM 30195 HPGe coaxial detector. The efficiency curve on ln-ln scale was fitted with a theoretical function of third degree order polynomial on ln-ln scale for the energy range of 59.54-1408 keV using equation 3.3 at the distance 2 cm from the P-type GEM 30195

HPGe coaxial detector. The facilities in the MS Excel spreadsheet 2007 were used for the calculation of the coefficients of energy polynomial that are shown in Table 4.5 below.

Table 4.3 Coefficients of energy polynomial

Source to detector distance (cm)	Coefficients of energy polynomial			
	$59.54 \leq E \leq 1408$ keV			
	a_0	a_1	a_2	a_3
2	-93.23	45.38	-7.49	0.40

Table 4.3 above shows the coefficients of energy polynomial of the fitting function of third degree order polynomial onl ln-ln scale at the distance 2 cm from the P-type GEM 30195 HPGe coaxial detector for the energy range of 59.54-1408 keV. These coefficients of energy polynomial were used to calculate theoretically the full energy peak efficiencies of the HPGe detector with the theoretical function of third degree order polynomial in the ln-ln scale at the distance 2 cm from the P-ype GEM 30195 HPGe coaxial detector using equation 3.4.

Table 4.4 Comparison of the Experimental and Calculated Efficiencies at 2 cm from the P-type GEM 30195 HPGe Coaxial Detector

Energy (keV)	Detector efficiency(ε)×10^{-3} d= 2cm		
	Experimental d= 2cm	Calculated (using equ. 3.4)	Deviation (%) (using equ. 3.5)
59.54	4.17	4.38	5.04
121.78	40.27	29.22	27.44
186.1	40.46	37.22	8.01
244.69	30.43	34.21	-12.42
344.29	24.34	25.81	-6.04
661.66	15.91	12.12	23.82
778.92	12.40	10.21	17.66
964.11	10.97	8.52	22.33
1112.08	10.15	7.85	22.66
1173.2	9.78	7.68	21.47
1274.53	8.64	7.52	12.96
1132.5	8.85	7.48	15.48
1408	8.40	7.48	10.95

From Table 4.4 above, it can be observed that the theoretical function of third degree order polynomial on ln-ln scale fits or describes satisfactorily the experimental data of the full energy peak efficiency curves of the P-type GEM 30195 HPGe coaxial detector at the distance 2 cm from the detector for energies of nuclides within or outside the energy range of 59.54-1408 keV. The results of the theoretically calculated full energy peak efficiencies of the P-type GEM 30195 HPGe coaxial detector using equation 3.4 are in satisfactory agreement with the experimental values measured at the distance 2 cm from the detector in the energy range 59.54-1408 keV using the IAEA standard sources ^{241}Am, ^{152}Eu ^{226}Ra, ^{137}Cs, ^{60}Co and ^{22}Na. Thus, by means of the

established theoretical function, the efficiencies of the γ-ray energies of the product radionuclides involved in α determination by the Cd covered multimonitor method and the k_o-ENAA method were calculated.

4.1.2 Results of Neutron Spectrum Parameters in the Cadmium Lined Irradiation Channel

Table 4.5 Result of α parameter in the Cd lined irradiation channel calculated by iterative linear regression method

Monitors	Ēr (eV)	Log(Ēr)	Step 1		Step 4	
			Qo(α=0)	Log(Y_0)	Qo(α_4)	Log(Y_4)
^{198}Au	5.65	0.7520	15.71	9.2165	19.92	9.2165
^{97}Zr	338	2.3820	248	9.0706	550.29	9.0710
^{99}Mo	241	2.5289	53.1	9.2631	112.21	9.2645
^{69m}Zn	590	2.7709	3.19	9.5309	7.16	9.5593
^{65}Zn	2560	3.4082	1.908	9.7684	4.88	9.8276
^{95}Zr	6260	3.7966	5.05	9.3802	15.85	9.4035
			-0.123 ± 0.020		-0.137 ± 0.018	

Table 4.5 above shows part of the first and fourth steps of the iterative linear regression methods extracted from the Microsoft Excel Spreadsheet 2007 calculation in the determination of α by the Cd covered multimonitor method. Starting with step 1 when setting α=0 resulted in the value of α_1= -0.123±0.020 from the slope of the straight line (-α). This resulting α_1 value was used as a starting point for the next iteration. The

iterative procedure was carried out four times. The third and fourth iterations both led to α_3 and α_4 equal to -0.137±0.018 Thus, the final value of α is -0.137±0.018.

Table 4.6 Results of the resonance integral $I_o(\alpha)$ and the epithermal neutron flux for Au in the Cd lined irradiation channel of the NIRR-1

Reaction	$^{197}Au(n, \gamma)^{198}Au$
Gamma-ray energy and abundance	411.8 keV(95.5%)
Efficiency of γ-ray energy of ^{198}Au	0.0212
Half life of ^{198}Au	2.7 days
Thermal neutron cross section	98.65 barns
Resonance integral in $\frac{1}{E}$ epithermal spectrum	1550 barns
Epithermal neutron shape factor(α) in Cd lined irradiation Channel	-0.137
Cd cut-off energy	0.55 eV
Cadmium epithermal neutron transmission factor for ^{198}Au	0.991
Relative atomic mass of Au	196.967
Isotopic abundance of ^{198}Au	100%
Avogadro's constant	6.023×10^{23} mol^{-1}
Specific activity for ^{198}Au	5.43×10^{8} (C/s.g)
Effective resonance energy for ^{198}Au	5.65 eV
Calculated resonance integral in Cadmium lined irradiation channel($I_o(\alpha)$)	1965.056 barns
Epithermal neutron flux	4.51×10^{9} ($n/cm^2.s$)

Table 4.6 above shows the nuclear data for gold used for the calculation of the resonance integral $I_o(\alpha)$ and the epithermal neutron flux(φ_e) in the Cd lined irradiation channel of the NIRR-1 using equations 3.11. From Table 4.6, it should be noted that the

efficiency of the gamma-ray energy for ^{198}Au and the epithermal neutron shape factor(α) in the Cd lined irradiation channel were calculated by the author. All other nuclear data were obtained from the literature(IAEA, 1990; De Corte and Simonits, 1989; De Corte and Simonits, 2003; EL NIMR *et al*. 1981; De Corte *et al*, 1989; Daindith, 2008).

The value of the epithermal neutron flux calculated in the Cd lined irradiation channel using the activity of ^{198}Au in Al-0.1% Au thin foil irradiated along with the monitor set for α determination using equation 3.12 is shown in Table 4.7 below.

Table 4.7 Results of neutron spectrum parameters in the Cd lined irradiation channel

Irradiation channel	α	Φ_e (n/cm^2.s)
Cd lined (A3)	-0.137±0.018	(4.51 ±0.01)×10^9

Table 4.7 above shows the values of α and epithermal neutron flux and their associated errors in the Cd lined irradiation channel. From Table 4.11, it can be observed that the value of epithermal neutron shape factor(α) is negative. The negative value of α indicates a hardened (poorly thermalized) epithermal neutron spectrum in the cadmium lined irradiation channel of the NIRR-1

Table 4.8 Comparison of the α values in Cd lined irradiation channel with results in other irradiation sites of the NIRR-1, other MNS and Slowpoke reactors

Facility	**Inner Channel**		**Outer Channel**		**References**
	f ratio	α	f ratio	A	
Slowpoke-2, Ecole Polytecnique,Montreal, Canada,20kW, 20%^{235}U(Sites: **Inner and outer)**	20.9±0.4	-0.048±0.004	64.1±3.0	-0.016±0.01	Kenndy et al., 2000
Slowpoke-2,DUSR,Halifax, Canada, 20kW,20%^{235}U(**Sites :3-inner, 10-outer)** (Sites:**Inner and outer**)	18.9±0.4	-0.0422±0.0053	57.1±2.2	-0.0098±0.0045	Acharya and Chatt,2003
Prototype MNSR, Beijing, China,27kW,90.2% ^{235}U(**Sites: Inner and oute**r)	19.8±0.4	-0.009±0.004	58.5±3	+0.023±0.010	Kennedy et al.,2000
GHARR-1 MNSR, Accra, Ghana, 30kW, 90.2% ^{235}U(**Sites:1-inner, 10-outer**)	18.8	-0.104	49.0	-0.0261	Akaho and Nyako,2002
GHARR-1 MNSR, Accra Ghana, 30kW, 90.2% 235U(**Sites: 5-inner, 7-outer**)	17.28	-0.107±0.001	40.38	-0.173±0.0001	Ahmed, 2004
NIRR-1 MNSR, Zaria, Nigeria, 90.2% ^{235}U (**Sites: B2-inner, B4-outer**)	19.2±0.5	-0.052±0.002	48.3±3.3	+0.029±0.003	Jonah et al.,2005
NIRR-1 MNSR, Zaria, Nigeria, 30kW, 90.2% ^{235}U(**Sites: A1-inner, A2-outer**)	18.4±0.34	-0.046±0.005	49.5±0.96	+0.024±0.002	Sadiq et al., 2010
NIRR-1 MNSR, Zaria, Nigeria, 30kW, 90.2% ^{235}U(**Sites: A3(Cd Lined Channel**))				-0.137±0.018	This work

Table 4.8 above shows a comparison of the result of the α value in Cd lined irradtion channel with the results of the neutron spectrum parameters in other irradiation sites of the NIRR-1, other Chinese Minature Neutron Source Reactors(MNSRs) and Slowpoke reactors. From Table 4.8, it can be observed that due to the installation of the Cd liner in one of the outer irradiation channels, the α value is different from the old data

in similar outer irradiation sites of the NIRR-1 (Sadiq *et al*., 2010; Jonah *et al*., 2005). The high negative value of α in the cadmium lined irradiation channel indicates a hardened (poorly thermalized) epithermal neutron spectrum in the cadmium lined irradiation channel(A3) of the NIRR-1. This is to be expected because the thermal neutron component of the reactor neutron spectrum has been cut-off by the 1.00 mm thick cadmium of the cadmium lined irradiation channel causing the neutron spectrum to be shifted to higher energies in the epithermal region.

Table 4.9 Epithermal neutron Flux in Cd Lined Irradiation Channel and other Irradiation Sites of the NIRR-1

Irradiation site	f	α	ϕ_{th} n/cm^2.s	ϕ_e n/cm^2.s	References
Inner					
B1	19.2±0.5	-0.052±0.002	5×10^{11}	2.60×10^{10}	Jonal *et al*.,2005
A1	18.4±0.96	-0.046±0.005	5×10^{11}	2.72×10^{10}	Sadiq *et al*., 2010
Outer					
B4	48.3±3.3	0.029±0.003	2.5×10^{11}	5.18×10^{9}	Jonah *et al*. 2005
A2	49.5±0.96	0.024±.002	2.5×10^{11}	5.05×10^{9}	Sadiq *et al*., 2010
Cd lined irradiation channel,A3	-	-0.137±0.018	-	$(4.51\pm0.01)\times10^{9}$	This work

From Table 4.9, the value of the epithermal neutron flux calculated using the activity of ^{198}Au in Al-0.1% Au thin foil in the monitor set irradiated for α determination

in the cadmium lined irradiation channel of the NIRR-1 is $(4.51\pm0.09)\times10^{9}$ $n.cm^{-2}.s^{-1}$. This value is comparable to the theoretical values of 5.05×10^{9} $n.cm^{-2}.s^{-1}$ and 5.18×10^{9} $n.cm^{-2}.s^{-1}$ in the outer irradiation site A2 and B4 of the NIRR-1 respectively based on the assumption that the thermal neutron flux values in the outer irradiation sites are 50% of the values in the inner irradiation sites(Sadiq *et al*., 2010; Jonah *et al*., 2005). The thermal to epithermal neutron flux ratios in the outer irradiation sites A2 and B4 of the NIRR-1 have been found to be approximately 49.5±0.96 and 48.3±3.3 respectively (Sadiq *et al*., 2010; Jonah *et al*., 2005) as shown in Table 4.9. It should be noted that the irradiation site A2 is now the channel A3 that has been lined with the 1.0 mm thick Cd-liner.

4.1.3 Results of Analysis of Samples of Legumes by the k_o-ENAA and INAA Methods

Table 4.10 Nuclear Data for Nuclides Measured in Samples of Legumes and NIST 1515 Apple leaves for k_o-ENAA

Nuclide	Half life	Er (keV)	Ēr (eV)	k_o	Qo	Qo(α)	ε_d $\times10^{-3}$	F_{Cd}
^{198}Au	2.7d	411.80	5.65	1	15.71	19.92	21.20	0.991
^{24}Na	14.96h	1368.60	3380.00	4.68×10^{-2}	0.59	1.03	74.70	1
^{42}K	12.36	1524.58	2960	9.46×10^{-4}	0.87	1.86	7.58	1
^{46}Sc	83.81d	889.28	5130.00	1.22	0.43	0.55	0.91	1
^{75}Se	119.77d	264.66	29.40	7.11×10^{-3}	10.8	17.03	32.50	
^{82}Br	35.3h	776.52	152.00	2.76×10^{-2}	19.3	38.10	10.20	1
^{86}Rb	18.66d	1076.60	839.00	7.65×10^{-4}	14.8	36.69	7.97	
^{140}La	40.27h	1596.21	76.00	1.34×10^{-1}	1.24	2.01	7.70	1
^{153}Sm	46.27h	103.18	8.53	2.31×10^{-1}	14.4	19.28	22.70	1
^{152}Eu	13.33y	1408.00	0.448	9.36	0.943	1.00	7.48	1

Table 4.10 above shows the nuclear data for the nuclides measured in samples of legumes and SRMs for the k_o-ENAA method. The $Q_o(\alpha)$ and ε_d values were calculated by the author while the $\bar{E}_r$, Q_o, k_o and F_{Cd} values were obtained from the literature (IAEA,1990, De Corte and Simonits, 1989 ; De Corte and Simonits, 2003 ; El NIMR et al., 1981 ; De Corte et al., 1989). This nuclear data was important for the calculation of the concentrations of the elements found in the sample of the standard reference material (SRM) NIST 1515 Apple leaves and samples of legumes that are shown below in Tables 4.14 and Table 4.15 respectively.

Table 4.11 Results of Concentrations of Elements in NIST 1515 Apple leaves by k_o-ENAA in μg/g (ppm)

Elements	Certified values(ppm)	This work(ppm)
Sm	3.00	2.44±0.04
Br	1.80	1.80±0.27
Na	24.4±1.20	4.96±0.18
K	16100±3.22	52400 ±542.03
La	20.00	38.90±0.98
Eu	0.2	20.8±3.57

From Table 4.11 above, the concentrations of the elements Sm and Br are better determined in the NIST 1515 Apple leaves by the k_o-ENAA method. This is because these elements strongly absorb neutrons of specific resonance energies in the epithermal neutron energy region. These elements Sm and Br have high resonance activation integrals compared to their thermal neutron cross sections in the epithermal neutron

region. The concentrations of Sm and Br in the NIST 1515 Apple leaves are in good agreement with the certified values. The elements Na, K, La and Eu are not favourably determined by the k_o-ENAA method because they do not have strong resonance peaks in the epithermal neutron energy region. The elements Na, K, La and Eu have lower resonance activation integrals compared to their thermal neutron cross sections in the epithermal neutron region. The presence of the elements Na, K, La and Eu in the NIST 1515 Apple leaves may be due to the leakage of few thermal neutrons into the cadmium lined irradiation volume and some thermalization of epithermal neutrons by the polyethylene vials. Also from Table 4.11 above, it can be observed that the concentrations of Sm and Br in the NIST 1515 Apple leaves by the k_o-ENAA method compare well with the concentrations of Sm and Br determined in the NIST 1515 Apple leaves by thermal NAA shown in Table 4.13 below even though the irradiation sites are different. This shows that the k_o-ENAA method is a reliable method in the cadmium lined irradiation channel of the NIRR-1.

The use of the k_o-ENAA method for the determination of bromine at trace level will help the country to control the illegal use of potassium bromate ($KBrO_3$) in bread making in the bakery industry. The use of potassium bromate ($KBrO_3$) as a food additive to improve the quality of bread by bread makers was baned by the government of Nigeria in 1993 (Oloyede and Sunmonu,2009).

Table 4.12 Results of the concentrations of elements in the samples of legumes by k_o-ENAA in μg/g (ppm)

Samples	Codes	Essential Major Element (ppm)		Essential Trace Element(ppm)	Non Essential Trace Element(ppm)		
		Na	K	Se	Br	Rb	Sc
Cow pea	CPTS2	41.50±7.02	1.16×10^4±36.22	BDL	0.33±0.08	21.80±6.31	0.01±0.002
Cow pea	CPTS3	173.00±11.29	2.92×10^4±921.39	7.90±2.36	0.16±0.02	BDL	BDL
Cow pea	CPTS4	65.67±8.39	1.45×10^4±757.65	12.29±2.70	0.34±0.08	BDL	BDL
Cow pea	CPKF1	209.00±7.79	3.36×10^4±548.29	BDL	0.63±0.08	23.20±5.66	3.20±0.82
Cow pea	CPKF2	228.04±8.29	2.72×10^4±514.77	BDL	0.28±0.06	BDL	BDL
Cow pea	CPRM1	492.00±10.23	2.62×10^4±388.30	BDL	0.82±0.09	BDL	BDL
Cow pea	CPRM2	151±11.62	1.75×10^4±716.38	BDL	0.68±0.10	BDL	BDL
Cow pea	CPGR1	127.00±5.13	1.93×10^4±354.23	BDL	0.63±0.08	26.40±8.80	BDL
Cow pea	CPGR2	63.41±8.85	1.36×10^4±734.17	15.70±3.17	0.36±0.07	BDL	BDL
Cow pea	CPGR3	205.00±15.29	4.78×10^4±1278.94	13.3±3.15	0.38±0.14	BDL	1.88±0.54
Soya beans	SBTS1	38.63±6.03	2.99×10^4±931.71	BDL	0.18±0.04	BDL	BDL
Soya beans	SBTS2	1910.00±336.54	7.71×10^4±241.48	BDL	0.46±0.08	BDL	BDL
Soya beans	SBKF1	0.23±0.03	1.90×10^4±440.70	BDL	0.51±0.07	BDL	BDL
Soya beans	SBKF2	27.21±3.63	3.19×10^4±522.71	13.7±5.75	0.11±0.01	17.20±4.59	3.25±0.83
Soya beans	SBKF3	31.13±6.79	5.66×10^4±1227.73	BDL	0.74±0.11	BDL	4.26±1.24
Groundnuts	GNTS1	31.28±3.47	9.31×10^3±286.58	BDL	0.27±0.04	BDL	BDL
Groundnuts	GNTS2	33.72±7.43	1.01×10^4±518.69	BDL	0.56±0.09	BDL	BDL
Groundnuts	GNRM1	28.78±3.31	1.03×10^3±25.36	BDL	0.23±0.05	BDL	BDL
Groundnuts	GNGR1	27.06±6.94	8.67×10^3±656.86	14.00±3.07	0.25±0.08	BDL	3.22±1.04
Groundnuts	GNGR2	21.25±5.67	1.09×10^4±674.25	9.54±2.12		25.60±6.56	BDL

BDL-Below detection limit

From Table 4.12 above, the elements Br, Se and Rb are better determined in the samples of legumes by the k_o-ENAA method. This is because these elements strongly absorb neutrons of specific resonance energies in the epithermal neutron region. The elements Br, Se and Rb have high resonance activation integrals compared to their thermal neutron cross sections in the epithermal neutron region. The elements Na, K and

Sc are not favourably determined by the k_o-ENAA method because they do not have strong resonance absorption peaks in the epithermal neutron energy region. The elements Na, K and Sc have resonance activation integrals which are lower compared to their thermal neutron cross sections in the epithermal neutron energy region. The presence of the elements Na, K and Sc in the legume samples may be due to the leakage of few thermal neutrons into the cadmium lined irradiation volume and some thermalization of epithermal neutrons by the polyethylene vials.

Table 4.13 Results of the Concentrations of Elements in NIST 1515 Apple leaves for rel-TNAA in μg/g(ppm)

Element	Certified value (ppm)	This work(ppm)
Na	24.4±1.20	28.91±0.35
K	16100±3.22	16490±82.45
Br	1.80	1.62±0.07
Sm	3.00	3.72±0.02
La	20.00	23.09±0.09
Zn	12.5±0.30	9.55±1.75
Sc	0.03	0.033±0.007
Ba	49.00±2.00	40.48±9.88
Yb	0.30	0.20±0.04

From Table 4.13 above, it can be observed that the concentrations of the elements measured in the SRM NIST 1515 Apple leaves by the relative method of thermal NAA are in good agreement with the certified values. This shows that the relative method of thermal NAA is a reliable method for the analysis of the legume samples in the NIRR-1.

Table 4.14 Results of concentrations of elements in samples of legumes by rel-TNAA in μg/g (ppm)

Sample	Code	Essential major element		Essential trace element	Non essential trace element			
		Na	K	Zn	Br	La	Sm	Sc
Cow pea	CPTS2	31.40±0.25	1.40×10^4±69.80	32.18±2.67	0.54±0.058	0.069±0.013	BDL	0.012±0.003
Cow pea	CPTS3	34.80±0.35	1.54×10^4±76.85	31.68±2.85	0.63±0.045	0.044±0.013	0.01±0.003	0.014±0.004
Cow pea	CPTS4	24.81±0.24	1.62×10^4±81.00	31.11±2.36	0.83±0.036	0.023±0.007	BDL	BDL
Cow pea	CPKF1	44.84±0.36	1.50×10^4±74.85	26.50±2.78	1.46±0.038	0.054±0.012	BDL	BDL
Cow pea	CPKF2	58.04±0.41	1.44×10^4±71.80	32.75±2.33	0.98±0.037	BDL	BDL	BDL
Cow pea	CPRM1	97.00±0.58	1.58×10^4±79.20	41.46±3.23	1.49±0.068	0.33±0.021	0.038±0.004	0.019±0.004
Cow pea	CPRM2	34.75±0.52	1.33×10^4±133.3	27.95±2.93	1.64±0.049	0.039±0.009	BDL	BDL
Cow pea	CPGR1	40.45±0.32	1.51×10^4±75.40	32.57±2.51	1.24±0.036	0.10±0.02	0.019±0.004	BDL
Cow pea	CPGR2	23.02±0.25	1.48×10^4±74.15	29.04±3.17	0.97±0.037	0.044±0.008	0.01±0.003	BDL
Cow pea	CPGR3	30.68±0.28	1.49×10^4±149.6	32.51±2.50	0.76±0.041	0.045±0.009	BDL	0.014±0.004
Soya beans	SBTS1	5.17±0.13	1.88×10^4±75.08	29.58±2.87	0.63±0.036	0.046±0.007	BDL	BDL
Soya beans	SBTS2	4.41±0.13	1.79×10^4±71.72	25.84±2.27	0.71±0.033	0.055±0.007	BDL	BDL
Soya beans	SBKF1	5.12±0.14	1.85×10^4±92.50	27.67±2.79	2.02±0.042	0.038±0.009	BDL	0.016±0.006
Soya beans	SBKF2	3.10±0.12	1.92×10^4±96.00	40.21±0.04	1.83±0.042	0.034±0.01	BDL	BDL
Soya beans	SBKF3	9.00±0.28	1.87×10^4±149.76	32.21±2.71	1.96±0.05	BDL	BDL	BDL
Groundnuts	GNTS1	5.20±0.15	1.02×10^4±61.32	21.11±2.49	0.63±0.028	0.039±0.009	BDL	BDL
Groundnuts	GNTS2	5.87±0.13	8.93×10^3±53.57	11.46±2.80	0.47±0.025	BDL	BDL	0.011±0.004
Groundnuts	GNRM1	9.50±0.16	8.19×10^3±57.34	21.71±2.71	0.60±0.042	0.051±0.007	BDL	BDL
Groundnuts	GNGR1	5.15±0.13	1.04×10^4±62.40	16.70±2.69	0.38±0.03	0.023±0.006	BDL	BDL
Groundnuts	GNGR2	8.44±0.17	9.95×10^3±69.67	21.17±2.16	0.38±0.03	0.055±0.008	0.015±0.004	BDL

BDL- Below detection limit

Table 4.14 above shows the concentrations of elements determined in the samples of legumes by the relative method of TNAA. A comparison of the results of the analysis of samples of legumes by k_o-ENAA in Table 4. 12 above and the relative method of TNAA in Table 4.14 above shows that the k_o-ENAA method in the Cd lined irradiation channel is a favourable method for the determination of the elements Se, Rb and Br

because they strongly absorb neutrons of specific resonance energies in the epithermal neutron region. They have high resonance activation integrals compared to their thermal neutron cross sections in the epithermal neutron region. The elements are Na, K, Zn, La and Sc are more favourably determined by the relative method of TNAA because they have relatively high thermal neutron cross sections compared to their resonace activation integrals in the reactor neutron spectrum. The elements Br and Sm have high Q_o values and can be determined by both k_o-ENAA and thermal NAA. They can be determined by thermal NAA because of their relatively high thermal neutron cross sections

A comparison of the concentrations of elements of interest in the legumes by k_o-ENAA and thermal NAA was made with the results of other authors from Nigeria and other countries. The ranges of the concentrations of the elements of interest in legumes by other authors from Nigeria and other countries are shown in Table 4.15 below.

Table 4.15 Ranges of Concentrations of Elements in Legumes by other Authors from Nigeria and other Countries

Type of legume	Element determined	Concentrations of elements determined in legumes by authors in Nigeria and other countries(ppm)				
		Umar, 2004(Nigeria)	Elegbede,1998 (Nigeria)	Leelhaphunt *et al*., 1988 (Thailand)	Surtipanti *et al*., 1989 (Indonesia)	Santos *et al*., 2006 Brazil)
Cow pea	Na	22.40-30.8(3)	61.0-178.0(2)			
	K	1.14×10^4-1.22×10^4(3)	1.27×10^4-1.32×10^4(2)			1.23×10^4-1.43×10^4(10)
	Zn	6.84-31.60(3)	38.3-49.1(4)	20.85(1)		36.2-46.1(10)
	Se			1.366(1)		
	Br	0.224-0.596(3)		49.59		0.55-1.14(10)
	Rb	10.30-62.20(3)				36.1-47.7(10)
Soya beans	Na	3.02-3.07(2)				
	K	1.55×10^4-1.71×10^4(2)				
	Zn	34.30-50.20(2)		44.11(1)	21.4-34.88(21)	
	Se	0.743-1.05(2)		0.405(1)	0.11-0.29(21)	
	Br	33.30-36.70(2)		3.781(1)		
	Rb					
Groundnuts	Na	3.08-6.91(2)				
	K	9.44×10^3-9.93×10^3(2)				
	Zn	22.20-24.70(2)				
	Se					
	Br	0.248-0.965(2)				
	Rb	27.70-34.30(2)				

Table 4.15 above shows the ranges of the concentrations of the elements of interest in legumes reported by other authors from the Nigeria and other countries. The numbers in the brackets indicate the number of samples analysed by each of the authors. From Table 4.18 above, it can be observed that the concentrations of Br and Rb in samples of cow peas by k_o-ENAA in this work are in general agreement with the ranges of the concentrations of Br and Rb in cow pea from Nigeria(Umar, 2004).The concentrations of Na, K and Zn by thermal NAA are in general agreement with the ranges of the concentrations of these elements in cow pea reported by Umar(2004). While the concentrations of Br in some of the samples of cow pea by thermal NAA are in

general agreement with some of the values reported by Umar(2004), the concentrations in some of the samples of cow pea are lower than some of the concentrations of Br in the cow pea reported by the same author. The concentrations of K and Zn in cow pea by thermal NAA in this work are in general agreement with the ranges of the concentrations of K and Zn from Nigeria reported by Elegbede(1998). The concentrations of Na in cow pea by thermal NAA in this work are lower than the values in cow pea reported by Elegbede(1998). The concentrations of K, Zn and Br by thermal NAA and of Rb by k_o-ENAA in cow pea in this work are in general agreement with the ranges of the concentrations of these elements in beans from Brazil reported by Santos *et al*.(2006). The concentrations of Zn in cow pea by thermal NAA in this work are higher than the results for cow peas from Thailand ((Leelhaphunt *et al*., 1988). The Se content in cow peas in this work are much higher than the Se content in beans from Thailand (Leelhaphunt *et al*., 1988). The concentrations of Br in cow peas in this work are much lower than the results for cow peas from Thailand(Leelhaphunt *et al*., 1988). The concentrations of Na, K, Zn and Br in soya beans by thermal NAA are in general agreement with the ranges of the concentrations of these elements in soya beans from Nigeria reported by Umar(2004). The concentrations of Rb in only one sample of soya beans by k_o-ENAA in this work is lower than the range of the concentrations of Rb in soya beans reported by Umar(2004). While the concentrations of Br in some of the samples of soya beans by k_o-ENAA are in general agreement with some of the values in soya beans reported by Umar(2004), some are lower than some of the values in soya beans reported by the same author. The concentrations of Zn in soya beans in this work are in general agreement with the results for soya beans from Thailand(Leelhaphunt *et al*., 1988) and Indonesia(Surtipanti *et al*., 1989).The concentrations of Se in soya beans in this work are much higher than the results for soya beans from Thailand (Leelhaphunt *et*

al., 1988) and Indonesia(Surtipanti *et al*., 1989). The concentrations of Br in soya beans in this work are lower than the results for soya beans from Thailand(Leelhaphunt *et al*., 1988). The concentrations of Br and Rb by k_o-ENAA and of Na, K, Zn and Br by thermal NAA in the samples of groundnuts in this work are in general agreement with the results of the ranges of the concentrations of these elements in groundnuts reported by Umar(2004).

There are yet no Nigerian national guidelines(regulations governing the mineral compositions in foods) on the maximum permissible concentrations (MPCs) of mineral elements in Nigerian foodstuffs for human consumption. However, with the exception of Se by k_o-ENAA which showed higher concentrations in all the samples, the concentrations of Br and Rb by k_o-ENAA and of Na, K, Zn and Br by thermal NAA in the samples of legumes generally compare favourably with the results of other authors from Nigeria. No Br containing chemicals such as methyl bromide were used as pesticides during the growing period of the legume samples or for the control of pests during storage. This suggests that the main source of Br found in the legume samples in this study is from the naturally occurring Br in the soils they were grown. The concentrations of Se found in the legumes in this work are higher than the maximum permissible concentrations (MPCs) in foodstuffs for human consumption that has been recommended by Reilly(1980) which from Table 1.1 is 2 ppm. The concentrations of Zn found in all the legumes are lower than the maximum permissible concentrations (MPCs) in foodstuffs for human consumption that has been recommended by Reilly(1980) which from Table 1.1 is 40-50 ppm.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

The full energy peak efficiency of the P-type GEM 30195 HPGe coaxial detector was measured at the distance 2 cm from the detector over the energy range 59.54 -1408 keV using the set IAEA standard sources ^{241}Am, ^{152}Eu ^{226}Ra, ^{137}Cs, ^{60}Co and ^{22}Na. The experimental full energy peak efficiencies were plotted against the gamma-ray energies over the energy range 59.54 -1408 keV on normal and ln-ln scales using Microsoft Excel Spreadsheet 2007.

A theoretical function of third degree order polynomial in ln-ln scale fitted or described satisfactorily the experimental data of the full energy peak efficiency curves of the P-type GEM 30195 HPGe coaxial detector at the distance 2 cm for energies of nuclides within or outside the energy range of 59.54-1408 keV. The results of the theoretically calculated efficiencies of the full energy peak efficiencies of the P-type GEM 30195 HPGe coaxial detector are in satisfactory agreement with the experimental values measured at the distances 2cm from the detector. Thus, by means of the established theoretical function, the efficiencies of the γ-ray energies of the product radionuclides involved in α determination by the Cd covered multimonitor method and the k_o-ENAA methods were calculated.

A set of four high purity monitors comprising of high purity Al-0.1%Au , Zr and Zn thin foils and Mo thin wire was irradiated simultaneously with epithermal neutrons in the Cd lined irradiation channel of the NIRR-1 at a preset thermal neutron flux of $5\times10^{11} n/cm^2.s$ for 3 hours. The activities of the product nuclides ^{198}Au, ^{65}Zn, ^{69m}Zn, ^{65}Zr, ^{97}Zr and ^{99}Mo were measured using the full energy peak efficiency calibrated P-

type GEM 30195 HPGe coaxial detector system at the distance of 2 cm from the detector. The MS Excel spreadsheet 2007 was used for the iterative procedure and least square regression analysis to determine the final value of α by the cadmium covered multimonitor method in the cadmium lined irradiation channel of the NIRR-1. The iterative procedure was carried out four times starting with step 1 when setting α=0 which resulted in the value of α_1= -0.123±0.020. This resulting value of α was used for the next iteration. The third and fourth iterations both led to α_3 and α_4 equal to -0.137±0.020. The final value of α with the assossiated precision of determination was found to be -0.137±0.018.

The α value is highly negative and is different from the old data in similar outer irradiation sites of the NIRR-1(Sadiq *et a*l., 2010; Jonah *et al*., 2005). This indicates a hardened (poorly thermalized) epithermal neutron spectrum in the cadmium lined irradiation channel(A3) of the NIRR-1.

The epithermal neutron flux in the Cd lined irradiation channel using the activity of ^{198}Au in the Al-0.1% Au thin foil irradiated with the monitor set for α determination was found to be (4.51±0.01)×10^9 n/cm^2.s and is in satisfactory agreement with the values obtained in the outer irradiation sites B_4 (Jonah *et al*., 2005) and A_2(Sadiq *et al*., 2010) of the NIRR-1.

The α value obtained was used in the single comparator method of ENAA(k_o-ENAA) for the determination of the concentrations of elements in the SRM NIST 1515 Apple leaves using Al-0.1% Au thin foil as the single comparator. The concentrations of the elements Sm and Br are better determined in the NIST 1515 Apple leaves by k_o-ENAA because they strongly absorb neutrons of specific resonance energies in the epithermal neutron energy region. The concentrations of Sm and Br in the NIST 1515 Apple leaves are in good agreement with the certified values. Thus, the k_o-ENAA

method is a reliable method in the cadmium lined irradiation channel of the NIRR-1. The k_o-ENAA method can be used for the determination of bromine at trace level to control the illegal addition of potassium bromate ($KBrO_3$) in bread in the bakery industry.

The k_o-ENAA and thermal NAA methods were used for elemental analysis ofsome legumes. The standard reference material(SRM) NIST 1515 Apple leaves was used for quality control. The results show that the elements Se, Br and Rb with high Q_o values in the legumes are better analysed by the k_o-ENAA method because they strongly absorb neutrons of specific resonance energies in the epithermal neutron region. They have high resonance activation integrals compared to their thermal neutron cross sections in the epithermal neutron energy region. The elements Na, K, La, Hf and Sc with low Q_o values in the legumes are better analysed by thermal NAA because they have relatively large thermal neutron cross sections compared to their reosonance activation integrals in the reactor neutron spectrum. The elements Br and Sm have high Q_o values and can be determined both by thermal NAA and k_o-ENAA. They can be detrmined by thermal NAA because they have relatively large thermal neutron cross sections in the reactor neutron spectrum.

The concentrations of the elements of interest analysed in the legumes are in general agreement with the values normally found in foodstuffs for human consumption except for Se which showed higher concentrations in all the samples.

5.2 Conclusion

A permanent cadmium lined irradiation channel installed in the large outer irradiation site of the NIRR-1 has been characterized to determine the value of the epithermal neutron shape factor(α). The data was determined by the cadmium covered multimonitor method using the monitors Al-0.1% Au, Zr and Zn thin foils and Mo thin wire and was found to be -0.137±0.018. The high negative value of α indicates a hardened (poorly thermalized) epithermal neutron spectrum in the cadmium lined irradiation channel of the NIRR-1. The epithermal neutron flux using the activity of ^{198}Au in the Al-0.1% Au thin foil irradiated with the monitor set for α determination was found to be $(4.51\pm0.01)\times10^{9}$ n.cm^{-2}.s.

The α value was used in the single comparator method of ENAA(k_o-ENAA) for the determination of the concentrations of elements in the SRM NIST 1515 Apple leaves using Al-0.1% Au thin foil as the single comparator. The concentrations of the elements Sm and Br in the NIST 1515 Apple leaves were better determined by k_o-ENAA and are in good agreement with the certified values. This is an important evidence of the reliability of the result for the α value obtained. Thus, the k_o-ENAA method is a reliable method for the analysis of Br and Sm in the samples of NIST 1515 Apple leaves using the cadmium lined irradiation channel of the NIRR-1. The method can be integrated into the routine neutron activation analysis(NAA) scheme of the NIRR-1.

The k_o-ENAA and thermal NAA methods were successfully employed to analyse some samples of legumes. The standard reference material NIST 1515 Apple leaves was used as the quality control material in this work. The results show that the elements Se, Br and Rb with high Q_o values in samples of legumes are better analyzed by the k_o-ENAA method in the Cd lined irradiation channel. The elements Na, K, Zn, La and Sc

with low Q_o values in the samples of legumes are better analysed by thermal NAA. The elements Br and Sm have high Q_o values and can be determined by both thermal NAA and k_o-ENAA.

The concentrations of the elements of interest analysed in samples of legumes are in general agreement with the values normally found in foodstuffs for human consumption except for Se which showed higher concentrations in all the samples.

The single comparator of ENAA(k_o-ENAA) method established in the Cd lined irradiation channel of the NIRR-1 using MS Excel can be considered as a reliable method of neutron activation analysis in the NIRR-1. It has practical applications for the determination of elements with high Q_o values in many areas such as human foodstuffs and diet, the analysis of human hair, finger and toe nails and human fluids like whole blood, blood serum and urine in human health and disease, in environmental studies such as air and water pollution, the analysis of geological materials such as ores, rocks and soils and also the analysis of industrial materials. The k_o-ENAA method can be used for the determination of Iodine in table salt and other types of foods. It can also be used for the determination of Br in bread to control the illegal addition of potassium bromate ($KBrO_3$) in bread in the bakery industry. The toxic health effects of potassium bromate ($KBrO_3$) in bread include:- cancer, tumors, hearing loss, abdominal pain, diarrhea, vomiting, liver and kidney damage (Kurokawa *et al*., 1990; Oloyede and Sunmonu, 2009; Emeje *et al*., 2010).

5.3 Reommendations

The following recommendations are being made to improve this work.

(i) It is suggested that more and different types of set of monitors be made available to reinvestigate the value of the epithermal neutron shape factor(α) by the cadmium covered multimonitor method in the Cd lined irradiation channel of the NIRR-1.

(ii) To optimize the k_o-ENAA method, it is suggested that boron shielded vials with cut-off energy of range up to 280 eV depending on thickness should be used for epithermal activation of samples of materials in the Cd lined irradiation channel of the NIRR-1.

Boron absorbs neutrons with higher energy than does cadmium. Therefore, a combination of cadmium and boron (Cd+B) for epithermal activation of samples of materials will raise up the cut-off energy compared to cadmium alone, thus providing additional filtering of thermal neutrons and the lower epithermal neutron region(1-10 eV). This will provide greater reduction of the high activities of the interfering major and minor elements with low Q_o values such as Na, K, Mn, Cu, Zn, La, Sc and Fe and improve the detection limits of the trace elements such as Se, Br, Rb, I, Mo, Sm, Cd, Ag, , As, Sb, Sn, W,Sr, Ba, Th and U with strong resonance absorption peaks in the higher epithermal neutron region above 10 eV.

The elements Se, I and Mo are essential trace elements for human health. The main role of Se in human health is the prevention of cancer,tumor, cardiomyopathy (cardiac disorder), liver and muscle damages. Iodine is important for the control of human goiter and cretinism. Molybdenum is important for the control of stunted growth, reduced food consumption and life expectancy in humans (Garrison and Somer, 1995).The elements As, Sb and Cd are toxic elements to humans while the roles of the non essential trace elements Br, Rb, Sn, W,Sr, Ba, Th and U in human health are not yet known.

(iii) Selenium is both an essential and a toxic element to humans. It is suggested that further investigation be carried out on the status of the Se concentrations in legumes and other types of foodstuffs in the rural areas where the samples of legumes were obtained for this work.

CHAPTER SIX

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