NEUTRON ACTIVATION ANALYSIS OF SOILS

BY

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INTEGRI PROCEDAMUS

DEDICATION

This work is dedicated to my mother, Margaret.

DECLARATION

I declare that, except for references to other people's work, this thesis is the result of my own research. It has neither in part nor in whole been presented elsewhere for another degree.

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ABTRACT

Instrumental Neutron Activation Analysis has been applied in the multi-element analysis of five soils from three agro-ecological zones in Ghana, using the Single Relative Standardization Method. The analysis was carried out at the Ghana Atomic Energy Commission Research Reactor-1 (GHARR-1) Centre. Concentrations of 34 elements in deciduous forest, forest and Coastal Savanna soils were obtained. Elemental compositions and their levels in the five soils; Oda ,Bekwai, Toje, Akuse and Ankasa series are related to the nature of parent materials and the degree to which these materials have been altered by weathering. The low isotopic abundance, low thermal and epithermal cross-section together with the low sensitivity of 0.07 counts/µg for the ^{30}Si nuclide with energy 1266KeV made detection of silicon in the five soils impossible. Validation of the analytical technique which was done using a Standard Reference Material SOIL-7 supplied by the International Atomic Energy Agency showed a maximum deviation of 23.9%.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Von Hevesy and Levy (1936) proposed Neutron Activation Analysis (NAA) for the analysis of dysprosium in rare earths using an isotopic neutron source. Since this historical experiment, NAA has been developed as a highly valuable analytical technique, especially with the advent of nuclear reactors. Nuclear reactors offer high neutron fluxes so that extremely small quantities (10^{-10}g) of a large number of elements can be determined at a time (Hoste et al, 1978).

Today NAA is widely applied in biomedical, environmental, industrial, geological and archaeological fields. Due to its sensitivity, precision and accuracy it is considered an ideal method for the determination of a large number of trace elements in several materials (Ehmann and Vance, 1991).

Several methodologies, other than NAA have been developed to determine elemental composition and their levels in soils. Notably among these methodologies are ion chromatography (IC), atomic absorption spectrometry (AAS), emission spectrometry (ES) and X-Ray fluorescence analysis (XRFA). The application of NAA in the multi-element analysis of five Ghanaian soils will provide valuable information to geologists and agronomists about the parent materials and elemental composition of the Ghanaian soils.

1.2 Objective

The objective of this work is the application of Instrumental Neutron Activation Analysis (INAA) in the multi-element analysis of soils at the GHARR-I centre. To this end, five Ghanaian soils namely: Oda and Bekwai series from the deciduous forest agro-ecological zone, Ankasa series from the forest agro-ecological zone, and Toje and Akuse series from the coastal savanna agro-ecological zone were sampled and analyzed. The five soils were chosen from the three ago-ecological zones to give a fairly wide representation of Ghanaian soils.

The analysis, which was done using a miniature neutron source reactor and a PC-based gamma spectroscopy system at the GHARR-1 Centre determined elemental composition and their levels in the soils.

A standard reference material (SRM) supplied by the International Atomic Energy Agency (IAEA) was used to validate the results of the analytical procedure.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nuclear Activation Analysis

Nuclear Activation Analysis techniques include those methods that use nuclear reaction to form product radionuclides or excited states of the target nucleus as the basis for analytical determination.

In this process, an element is bombarded with neutrons charged particles or photons. A nuclear reaction is thus induced and an excited intermediate element is formed. The intermediate element may de-excite by emitting prompt gamma rays due to the fact that they are emitted within less than 10^{-14} s after formation of the excited intermediate. The radioactive product may decay via alpha, beta, delayed neutron emission processes, et cetera. All these may be accompanied by gamma emission. The gamma rays emitted in the delayed neutron emission process may be known as delayed gamma rays. The radiations emitted are measured to obtain both qualitative and quantitative analytical information (Ehmann and Vance, 1991).

When the irradiation is by neutrons, the method is termed Neutron Activation Analysis (NAA) [Briggs-Kamara, 2001]. If energetic photons are used to activate the element(s) the method is termed instrumental Photon Activation Analysis (IPAA). In this process the Bremsstrahlung radiation resulting from the acceleration of electrons in a linear accelerator is used as the photon source. When a variety of charged particles such as protons, deuterons and alpha particles are used to activate the analyte element(s), the process is termed Charged-Particles Activation Analysis (Ehmann and Vance, 1991).

2.2 Neutron Activation Analysis

In NAA, which is the most common form of activation analysis, neutrons are the activating particles. Neutrons induce different kinds of nuclear reactions, depending on their energy. For the normal NAA, it is the delayed gamma radiation from the radioactive product that is detected after activation for qualitative and quantitative information.

The other form of NAA is the prompt gamma neutron activation analysis (PGNAA). In this procedure, it is the prompt gamma rays emitted by the excited intermediate nucleus that are monitored (Ehmann and Vance, 1991).

Neutron activation analysis can be divided into three categories according to the energy of the activating neutrons:

1. Thermal neutron activation analysis (TNAA), the most common, employs neutrons with energy of about 0.025 eV.
2. Epithermal neutron activation analysis (ENAA) employs neutrons with energies between 0.025 eV and 1.0 MeV.
3. Fast neutron activation analysis (FNAA) is NAA with neutron energy greater than 1.0 MeV

Neutron activation analysis can also be classified into another three groups depending on the need for chemical separation and the time of the separation. The three groups are:

1. Instrumental neutron activation analysis (INAA). No chemical treatment is carried out on the sample before or after irradiation.
2. Radiochemical neutron activation analysis (RNAA). Chemical separations are done after irradiation to remove interference or to concentrate the radionuclide of interest.

3. Chemical neutron activation analysis (CNAA). Chemical separations are carried out before irradiation.

2.1.1 Basic Principles of NAA

When a sample is irradiated with neutrons in the nuclear reactor, nuclear reactions take place between the neutrons and the nuclei of the element in the sample:

$$\mathbf{A} + \mathbf{n} \longrightarrow \mathbf{B}^{*} \longrightarrow \mathbf{B} + \gamma_d$$

A is the stable nucleus, which captures a neutron **n** and becomes an excited nucleus **B*** The excited radioactive nucleus **B*** then decays with its inherent half-life ($T_{1/2}$) to a stable nucleus **B**. This is always accompanied by the emission of gamma rays, γ_d. The emitted rays and its intensities are measured with a detector to obtain analytical results.

The energy associated with the gamma radiation is characteristic of the radioactive isotope, and hence it is used for element identification, that is, qualitative analysis. The number of gamma rays emitted correlate to the number of atoms present in the sample, that is, quantitative analysis. This forms the basis of neutron activation analysis.

The net rate of accumulation of the radioactive nucleus is dependent on two factors:

1. The rate of formation of the product nuclei. This is proportional to the number of neutrons per unit time per unit area, or particle flux ϕ, the nuclear reaction cross-section, that is, the probability that the required reaction takes place σ ; and the number of target nuclei n_i.

2. The rate of decay of the product nuclei. This decay posses the property of statistics since radioactive nuclide produced by nuclear reactors decay continuously from the beginning of their production (IAEA-TECDOC-564, 1990).

2.1.2 Theory of Neutron Activation Analysis

Suppose a sample is exposed to a thermal neutron flux, the stable nuclide in the sample can capture a neutron and may produce radioactive isotope of that element. The mass number of the element is increased by one. The radioactive isotope decays with the emission of gamma rays, which are characteristic of the isotope. This can be represented by the equation:

$$^{A}zY + {}^{1}_{0}n \Rightarrow {}^{A+1}zX + \gamma$$

Let n_i be the number of nuclides of a given sample exposed to thermal neutron flux ϕ, σ_i the activation cross-section for the (n, γ) reaction of the i^{th} nuclide and t_i the time that the nuclide has been exposed to the thermal neutrons.

Suppose N_i (t_i) is the number of the i^{th} radionuclide of the i^{th} nuclide formed by time t_i, then the rate of reaction is given by

dN_i (t)/dt = rate of production of N_i rate of radioactive decay of N_i

Production rate $= \phi\sigma_i n_i$

where σ_i is the effective cross-section for the (n, γ) reaction.

Rate of radioactive decay is $\lambda_i N_i(t)$. Hence

$$dN_i(t)/dt = \phi\sigma_i n_i - \lambda_i N_i(t) \qquad (1)$$

λ_i is the decay constant of the i^{th} nuclide formed.

Integrating equation (1) yields

$$N_i(t) = \{\phi\sigma_i n_i (1 - \exp(-\lambda_i t))\} / \lambda_i \qquad (2)$$

$$\lambda_i = 0.693/t_{1/2} \qquad (3)$$

$t_{1/2}$ is the half-life of the radionuclide. The activity at any time t during the irradiation period is given by:

$$A_i(t) = \lambda_i N_i(t) = \phi \sigma_i n_i (1 - \exp (1 - \lambda_i t)) \qquad (4)$$

n_i can be expressed as:

$$n_i = m_i \theta_i N_A / M_i \qquad (5)$$

m_i = mass of the i^{th} nuclide

θ_i = isotopic abundance of nuclide

M_i = chemical atomic weight of nuclide

N_A = Avogadro's number (6.02×10^{23} atoms / mole)

Let T be the end of irradiation period, then activity is given by:

$$A_i(T) = [\phi \sigma_i m_i \theta_i N_A (1 \quad \exp (- \lambda_i T))] / M_i \qquad (6)$$

If counting is delayed for time t_d then the activity at the end of the delay is:

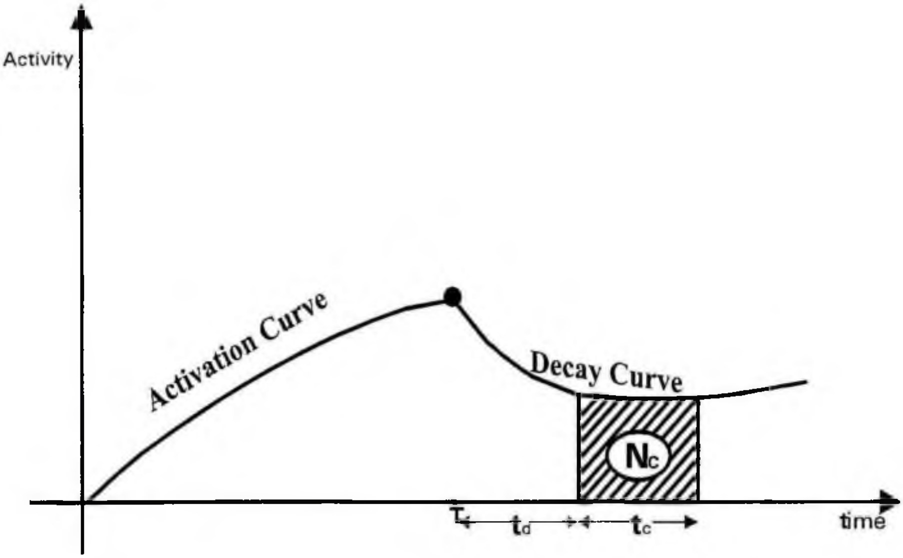
$$A_i(t_d) = A_i(T) \exp (- \lambda_i t_d) \qquad (7)$$

After the delay time (Fig2.1), if the time allowed for counting is t_c then the number of disintegration that occur during the counting period is (Osae,1988);

$$N_c = \int_0^{t_c} A_i(t_d) \exp (- \lambda_i t) dt = A_i(t_d) (1 - \exp (- \lambda_i t_c)) / \lambda_i$$

Substituting the values for $A_i(t_d)$ from equation (7) gives

$$N_c = A_i(T) \exp (- \lambda_i t_d) (1 - \exp (- \lambda_i t_c)) / \lambda_i \qquad (8)$$



T = End of irradiation period
t_c = Counting time after delay period
t_d = Delay period before counting
N_c = Number of disintegrations that occur during the counting period

Fig2.1Graph of Activity versus Time

Suppose $\varepsilon_{(E)}$ is the photo peak detection efficiency for gamma of energy E and C_i total counts recorded by the detector, then N_c is related to G, the sample to detector geometry by (Osae,1978)

$$N_c = C_i / \varepsilon_{(E)} f_i G \tag{9}$$

where f_i is the gamma emission probability

$$C_i / \varepsilon_{(E)} f_i G = A_i (T) \exp(-\lambda_i t_d)(1 - \exp(-\lambda_i t_c)) / \lambda_i \tag{10}$$

Substituting the value of A_i (T) from equation (6) gives

$$m_i = C_i \lambda_i M_i / \phi \sigma_i \theta_i N_A \varepsilon_{(E)} f_i G B_i \tag{11}$$

where $B_i = (1 - \exp(-\lambda_i t_c)) \exp(-\lambda_i t_d) (1 \quad \exp(-\lambda_i T))$.

$$\phi\sigma_i = \phi_t\sigma_{it} + \phi_e\sigma_{ie} \tag{12}$$

where σ_{it} and σ_{ie} are the thermal and epithermal cross-sections, respectively, for the (n,γ) reaction; and ϕ_t and ϕ_e are the thermal and epithermal particle flux, respectively.

If W is the weight of sample used, then the concentration of the element in the sample is given by:

$$m_i / W = C_i \lambda_i M_i / W \phi \sigma_i \theta_i N_A \varepsilon_{(E)} f_i G B_i \tag{13}$$

The amount of an element in a sample can be obtained from equation (13) using either the Absolute method or the comparator method (Hoste, 1988).

2.1.3 Absolute Method

The absolute method uses the basic neutron activation equation and, therefore, relies on the nuclear constants obtained from literature in addition to an accurate knowledge of the efficiency of the gamma detector and the neutron flux at the irradiation position. The accuracy of measurement in this mode depends, therefore, on the accuracy of the nuclear constants, the accurate knowledge of the efficiency of the detector, the neutron flux, the counting statistics and source to detector geometry. For most elements, the errors in nuclear constants are less than 5% (IAEA – TECDOC – 564; 1990).

The nuclear constants in equation (13) are M, f, σ, θ, λ and N_A. Equation (13) may be expressed in a simple form as (Osae et al, 1996):

$$m_i = D_i C_i / \phi \varepsilon_{(E)} B_i \qquad (14)$$

where D_i is $\lambda_i M_i / \sigma_i \theta_i N_A f_i G$

The constant D may be calculated for any element by obtaining the nuclear constants from any current nuclear data book.

Knowing D, ϕ, $\varepsilon_{(E)}$ and B_i and measuring C, the amount m_i of the element in the sample can be calculated using equation (14). To reduce the overall error, the Absolute Method is standardized (Osae et al, 1996).

The Standardization of this procedure is to irradiate known standard reference material (SRM) of the element of interest and then determine the experimentally measured value using equation (14).

The correction factor, F, for the measured value is given by:

$$F = m_e / m_{std}$$

where m_e is the experimentally measured value and m_{std} is the known concentration

2.1.4 Relative (Comparator) Method

Most NAA experts normally use the relative method. In this approach, a standard containing a known amount of the element to be determined is irradiated along with the samples. It is assumed that the neutron flux, cross-sections, irradiation times and all other variables associated with counting are constant for the standard and the sample for a particular sample-to-detector geometry at the irradiation position.

The equation for quantifying the amount of an element in a sample, using the comparator method, is (IAEA – TECDOC – 564, 1993):

$$C_{std} / C_{sam} = m_{std} (\exp - \lambda T_{std}) / m_{sam} (\exp - \lambda T_{sam}) \qquad (15)$$

where C_{std} and C_{sam} are the counting rates for the element in the standard and sample, m_{std} and m_{sam} are the masses of the element in the standard and sample and T is the decay time. If decay times are the same, then equation (15) reduces to:

$$C_{std} / C_{sam} = m_{std} / m_{sam} \qquad (16)$$

2.1.5 Single Relative Standardization Method

For stable neutron sources once the specific activities (sensitivities) of the elements of interest have been determined, samples can be irradiated without standards. As a precaution for unseen changes, it is a good practice to monitor the neutron flux within a series of experiments to check if the neutron flux is indeed stable. If conditions do not change with time, then the standardization can be done once.

Equation (16) can be written as:

$$C_{sam} / m_{sam} = C_{std} / m_{std} = S.A \qquad (17)$$

where S.A is the specific activity or sensitivity of the element with regards to INAA.

From equation (17), $S.A = C_{sam} / m_{sam}$ (18)

Knowing the number of counts under a photo peak area and the specific activity of the element, the amount of the element in the sample can be calculated using equation (18).

Neutron activation analysis has some advantages and disadvantages.

Advantages

(i) *Sensitivity*:- The method is highly sensitive for many elements. In some instances sensitivity is as high as10^{-10}g.

(ii) *Matrix effect* :- The chemical or physical nature of the matrix is unimportant. Thus, samples and standards do not need to have similar bulk composition.

(iii) *Contamination*:- As the only operations performed on environmental samples prior to irradiation are usually collection and preparation, there is no reagent blank and the possibility of contamination from apparatus or reagents is minimized or eliminated completely.

(iv) *Multi-element technique*:- For many applications, the method is non-destructive and multi-element. For example, as many as twenty-eight (28) elements may be determined in air particulate (Soete et al, 1978). Even where radiochemical separations are necessary, groups of elements can often be separated rather than individual elements.

Disadvantages

(i) Not all elements possess suitable radioactive nuclides; either formation cross-sections are low or half-lives are very long or very short, resulting in poor sensitivity.

(ii) In NAA methods for environmental samples, decay periods of up to one month may be necessary to allow the determination of some long-lived nuclides. Hence, the method will have a time lag for some results.

(iii) No direct information on the chemical state of the element is obtained.

(iv) The average analytical laboratory may not have access to a nuclear reactor.

(v) Initial equipment cost for semiconductor spectrometry and irradiation facilities is high.

(vi) Long counting times may limit the number of samples that can be processed (Kruger, 1971).

2.3 Gamma-Ray Spectrometry

The main objective in gamma – ray spectroscopy is to detect the gamma – rays being emitted by a radioactive source, classify them according to their energies and calculate their activities.

Gamma-ray spectroscopy system consists essentially of:

a) Radiation detector in which the radiating energy is converted into electrical pulses, and
b) Electrical, electronic and other transducers by means of which the magnitude of these pulses may be determined.

Fig 2.2 shows the schematic set-up of gamma – ray spectrometer for INAA use (Osae, 2000). The set-up consists of:

I Gamma detector for the conversion of gamma energy into electrical pulses
II. Pre – amplifier for the amplification of the pulses and to provide impedance matching of the detector to the main amplifier
III. Amplifier for further amplification of the signals
IV. High voltage source to the detector which provides the necessary potential difference to bias the detector and create the needed depletion region
V. Multi-Channel Analyzer (MCA) to convert the analog signals to digital and sort them according to their incoming energies.

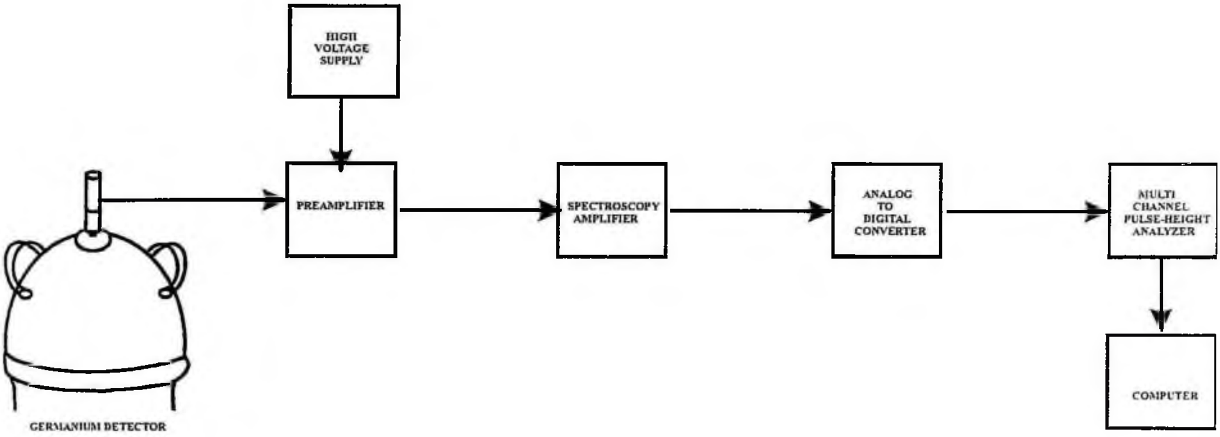


FIG 2.2 **Schematic set-up of gamma ray spectrometer for use in INAA (Osae, 1988)**

These digital signals are presented on the display unit in energy channels according to their pulse - heights

2.4 Interaction Mechanism of Gamma-Rays

When gamma – rays interact with matter they do so through three main mechanisms (processes):

a) Photoelectric Effect
b) Compton Scattering (Effect), and
c) Pair Production.

2.4.1 Photoelectric Effect

In photoelectric effect the gamma – ray collides with the electronic cloud of the atom as a whole. The atom absorbs the gamma – ray and transfers its energy to one of the bound electrons, usually those in the innermost shell. This is ejected with the kinetic energy

$$k.e = hv - E_b \tag{19}$$

where hv = energy of the gamma ray (photon) and

E_b = binding energy of the orbital electron.

2.4.2 Compton Scattering

In Compton Scattering a gamma –ray of energy hv interacts with one of the loosely bound electrons of the atom (outer electron). For conservation of both momentum and energy the electron is considered as a free electron. Thus the interaction is considered as an elastic collision between the gamma- ray and the electron. In the interaction the gamma – ray of energy hv collides with an electron, the gamma – ray moves with a reduced energy hv' and the electron now recoils with kinetic energy

$$k.e = h(v-v') \qquad (20)$$

2.4.3 Pair Production

In pair production, the gamma – ray comes into the nuclear field of the atom. It is annihilated, and in its place an electron and a positron pair is created. For this interaction to take place, the gamma – ray energy must be greater than the total mass energy of the electron and positron. This means the kinetic energy of the created electron must be

$$k.e = hv - 1.02 \text{ MeV} \qquad (21)$$

Thus this reaction is only feasible when gamma – ray energy is greater than 1.02 MeV

CHAPTER THREE

NEUTRON SOURCES

3.1 Nuclear Reactors

Nuclear reactors produce neutrons from uranium fission processes occurring within the reactor core. Large reactors used for electrical power generation are not used by researchers as neutron sources. Instead, smaller reactors called Research Reactors have been designed to provide neutrons needed for physics research and applications such as nuclear activation analysis (IAEA – TECDOC – 564, 1990).

Nuclear reactors are devices in which controlled nuclear fission occurs. The fission that takes place in a reactor is largely not spontaneous but is neutron-induced. In neutron-induced fission a neutron is captured by a high-mass nucleus which subsequently splits into two small nuclei with the release of about 200 MeV of energy and the production of fast neutrons (mean energy ≈ 22.5 MeV) as shown below:

$$^{235}\mathrm{U} + {}^{1}_{0}\mathrm{n} \Rightarrow {}^{147}\mathrm{La} + {}^{87}\mathrm{Br} + 2\,{}^{1}_{0}\mathrm{n}$$

Moderation of these fast neutrons produces a mixture of thermal neutrons and epithermal neutrons at the available NAA irradiation positions. There are two competing forces at work in the target nucleus namely: binding force that holds the nucleons together and the coulomb force that tends to push them apart. In a stable nucleus, the binding force is stronger. For low-mass nuclide, the binding force is much larger than the repulsive force whiles for heavier nuclide, the two forces are more equal in magnitude and it is possible to shift the balance in favour of the repulsive forces by addition of a neutron. The added neutron provides internal excitation energy that deforms the nucleus into a transition state and consequently splits into two or more fragments if the deformation is severe enough. The fission fragments are repelled away from each other with considerable kinetic energy due to the coulomb repulsive force. The fragments are neutron-rich, so they will decay by negatron emission and often followed by a gamma transition; until a favourable neutron/proton ratio is attained and stable products are formed. All these occur in an extremely short time. The neutrons produced are a by-product of the uranium fission process.

3.2 Isotopic Neutron Sources

Three main types of isotopic neutron sources can be distinguished namely, alpha – emitters, which produce neutrons through an (α, n) reaction, gamma-emitters, through (γ, n) reaction and isotopes of heavy elements, which undergo spontaneous fission (De Sorte et al, 1978).

3.2.1 Alpha (α, n) – Sources

Radioactive alpha emitters can be used in neutron sources as they induce (α, n) reaction on a number of target nuclides. Usually, beryllium is used as a target material through the reaction:

$$^{9}Be\ (\alpha, n)\ ^{12}C$$

that has a Q-value of 5.20 MeV. Other nuclides can also be used as target materials but with neutron yields that are substantially lower than beryllium.

3.2.2 Photoneutron Sources

When the gamma energy exceeds the binding energy of the neutron in the nucleus (γ, n) reaction can take place. Only beryllium (Q = 1.66 MeV) and deuterium (Q = 2.225 MeV) need be considered here since most nuclei have a neutron binding energy above 8 MeV. In practice only ^{124}Sb is used as a gamma source. This isotope has a half-life of 60.2 days, gamma energies of 1.69 MeV and 2.091 MeV with intensities 49% and 6% respectively. The ^{124}Sb is produced by neutron activation of natural antimony in a nuclear reactor. Since the half-life is only 60 days, reactivating is required 2 or 3 times a year.

3.2.3 Fission Sources

A number of transuranium elements not only disintegrate by alpha decay but also by spontaneous fission releasing several neutrons in the process. Among these only Californium-252 is widely applied.

3.3 Accelerator Neutron Sources

In recent times, accelerator produced neutrons have played an important role in nuclear physics research and neutron activation analysis. Accelerators have been used to produce either charged particles or energetic neutrons as a result of nuclear reaction. The most used neutron generator is the Cockroft-Walton accelerator (Ehmann-Vance, 1991). Other neutron generators are Van der Graaf and linear accelerators. The latter generators are large and expensive devices hence are primarily constructed for nuclear physics research. A typical research neutron generator produces analytically useful flux density of 10^9 n $cm^{-2}s^{-1}$ at the sample irradiation position and energy of 14.7 MeV. The research neutron generator usually consists of deuterium ions accelerating towards a tritium-containing target. The nuclear reaction that takes place is:

$$^{3}H\ (^{2}H,\ ^{1}n\ )\ ^{4}He$$

The application of neutron generators has one main of advantage:

(i) Ability to turn the neutron beam off by simply de-exciting the acceleration high voltage.

However, there are some inherent problems as well, such as:

(i) Difficulty in determining accurately the flux of the primary neutron emitted from the target.

(ii) Inhomogeneity of the neutron flux.

(iii) Short life span of the target material for the neutron generator, meaning frequent replacement (Nargolwall et al, 1973).

CHAPTER FOUR

EXPERIMENTAL MATERIALS AND METHODS

4.1 Description of GHARR-1

The Miniature Neutron Source Reactor (MNSR) known in Ghana as GHARR-1, is a SLOWPOKE type of a reactor, developed and constructed by China Institute of Atomic Energy (CIAE). It is a simple, small, reliable and safe reactor. GHARR-1 adopts the pool-tank structure, and employs highly enriched uranium as fuel, light water as moderator and coolant, and metal beryllium as reflectors. The reactor is cooled by natural convection. The rated thermal power of GHARR-1 is 30KW; the corresponding thermal neutron flux is 1.0×10^{12} n/cm^2 s. Since the small excess reactivity of GHARR-1 cannot compensate the negative reactivity temperature effect of the moderator and equilibrium xenon poisoning, it cannot be operated continuously at the rated neutron flux for a long time, but can be continuously operated at 5.0×10^{11} n cm^{-2} s^{-1} of flux level for a long time. The GHARR-1 facility consists of the reactor core, metal beryllium reflectors, the reactor vessel, the pool, the control system, the gamma-radiation monitoring system, the thermal hydraulics monitoring system and the auxiliary systems (fig. 4.1). The main parameters of GHARR-1 are listed in Table 4.1 (Wang, 1992).

The heart of the reactor facility is the reactor core, which is located at the bottom of the lower section of the reactor vessel.

The core consists of a fuel cage, control rod guide tube, 344 fuel elements, 6 dummy elements and 4 tie rods. Figure 4.2 and Figure 4.3 show the core configuration of GHARR-1 and location of start-up detectors, respectively. The circles of holes are concentrically arranged in the upper and lower gird plates to form a lattice with 355 positions in the grill. The central one is the control guide tube position. The meat of fuel element is a thin rod of Uranium-Aluminium alloy with a length of 23 cm, diameter 0.43 cm, and average density 3.45 g/cm^3 The total mass of each fuel meat is 11.53g; uranium content is 27.6%, enrichment of 90.2% and U-235 mass of 2.87g (Wang, 1992).

4.1.1 Applications of GHARR-1

GHARR-1 has many applications. The main applications are: Neutron Activation Analysis, Preparation of Short-lived Radioisotopes, Education and Training. GHARR-1 has many advantages. Firstly, it can be installed in densely populated cities. Secondly, the reactor is easy to start, shutdown, operate at any power level and is suitable for activation analysis of medium-lived and short-lived radionuclides. Thirdly, the burn up of the reactor is low and the neutron flux is stable and is therefore ideal for NAA methods, which utilise single standardisation procedures. The fourth advantage is the low temperature in the irradiation sites, which is good for analysis of biological and liquid samples, which cannot be irradiated, in large reactors (Wang, 1992).

4.1.2 Reactor Control System

The control system of GHARR-1 includes the main control console, neutron detectors, a control rod and its drive mechanism (figure 4.4). GHARR-1 uses only one control rod, which serves as shim rod, regulating rod and safety rod. The control rod controls the reactor start-up, shutdown and power regulation. The main control console is used to monitor operating conditions by means of manipulations so that the functions of control and protection of the reactor can be fulfilled.

The main control console provides two kinds of control modes: one in the automatic control mode which responds to the signals from the neutron detectors; the other, manual control mode which responds to manual operations. The main functions of the control console are to start-up, shutdown and operate the reactor manually or in automatic mode, to monitor the operating parameters of the reactor, to display signals of normal and abnormal operating conditions, to provide audible and optical alarm and emergency shutdown and protection under severe abnormal conditions, and to provide power supply for the various control and monitoring instruments (Yougchen and Yuchwen, 1992).

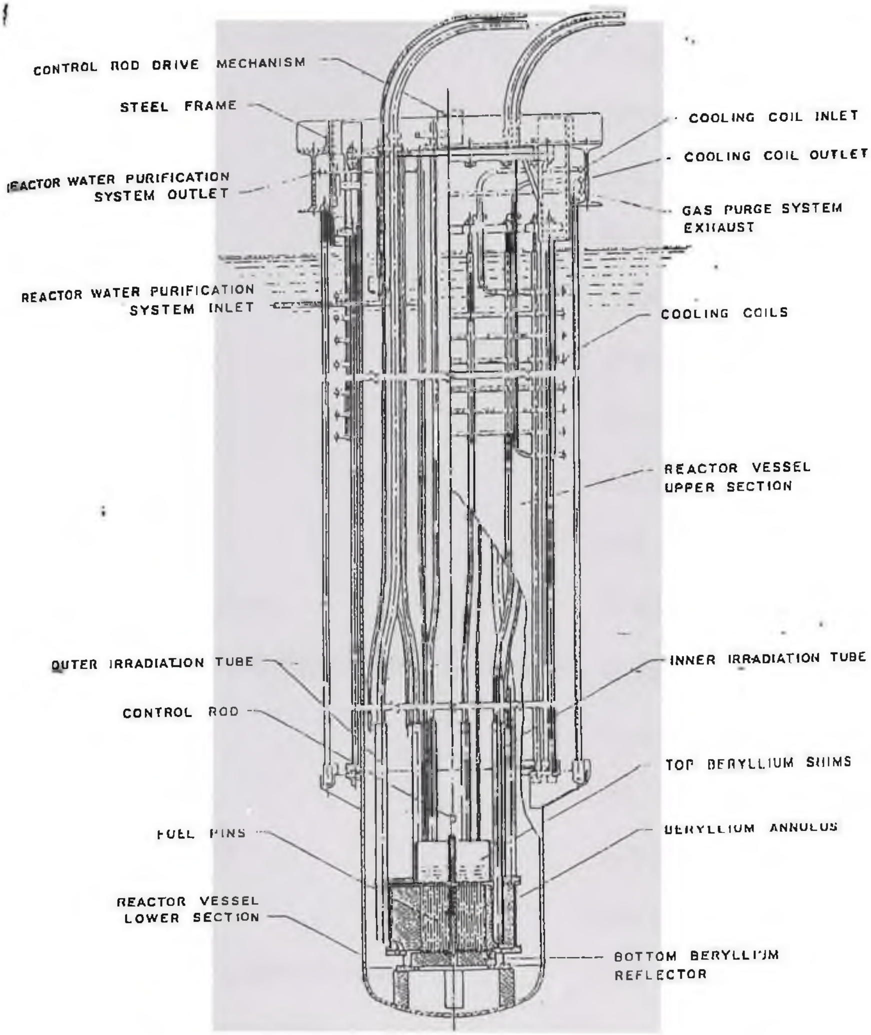


FIG 4.1 Longitudinal cross section through the reactor vessel

Table 4.1 GHARR-1 CHARACTERISTICS

No	Parameter	Description
1	Reactor type	Pool-tank
2	Rated Thermal Power	30KW
3	Fuel	UAl_4 dispersed in Al base Material
4	U-235 enrichment	90.2%
5	Core Shape	Cylindrical
6	Core diameter	23cm
7	Active Core height	23cm
8	Fuel element shape	thin rod / cylindrical
9	Fuel element in core	344
10	Total U-235 loading in core	<1.0Kg
11	Reactor continuous operating time (at rated power)	>2.5hours
12	Refuel period	more than ten years
13	Burn up	1%
14	Temperature coefficient	0.01 Milli Kelvin per Celsius
15	Control rod (Cd)	One at centre of the core
16	Total number of inner irradiation sites	10
17	Number of inner irradiation sites	5
18	Thermal neutron flux (at rated Power) at inner sites	5.0×10^{12} n/cm^2.s
19	Number of outer irradiation sites	4 (2 larger, 3 smaller)
20	Thermal neutron flux (at rated power) in outer sites	5.0×10^{11} n/cm^{2}s
21	Reactor cooling	natural convection

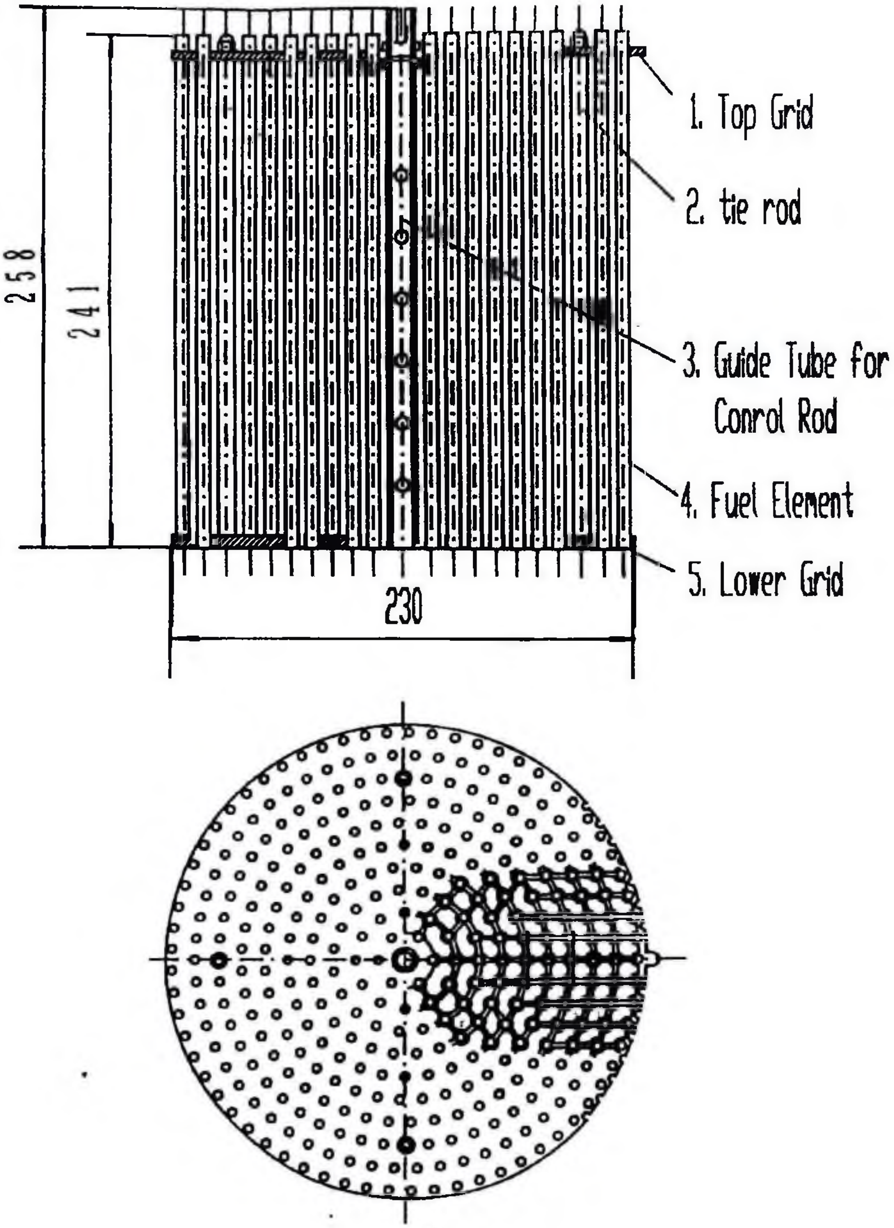


FIG 4.2 Fuel Cage Of GHARR-1

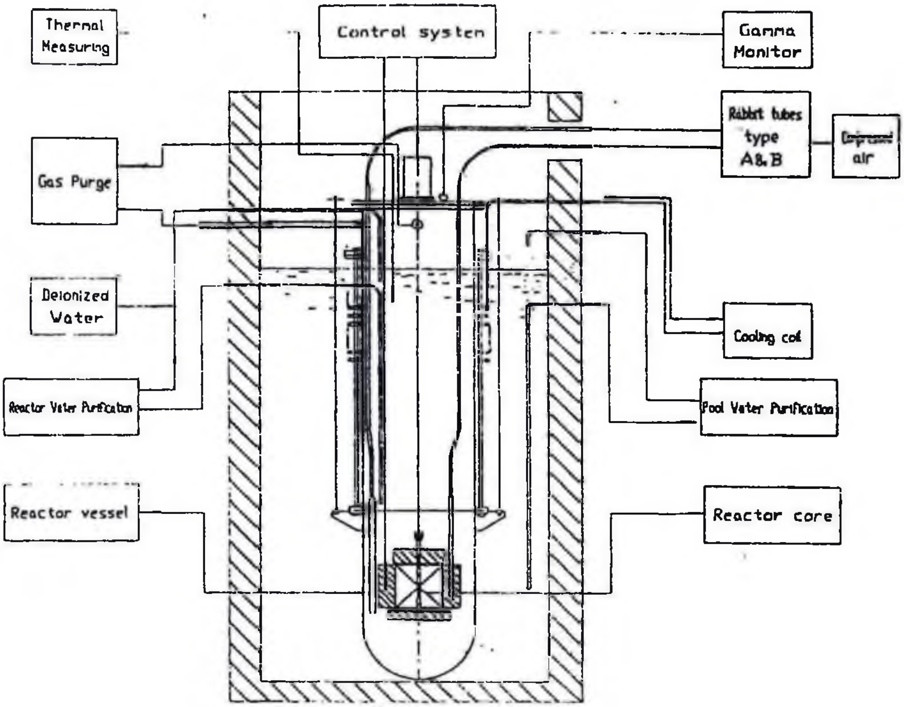
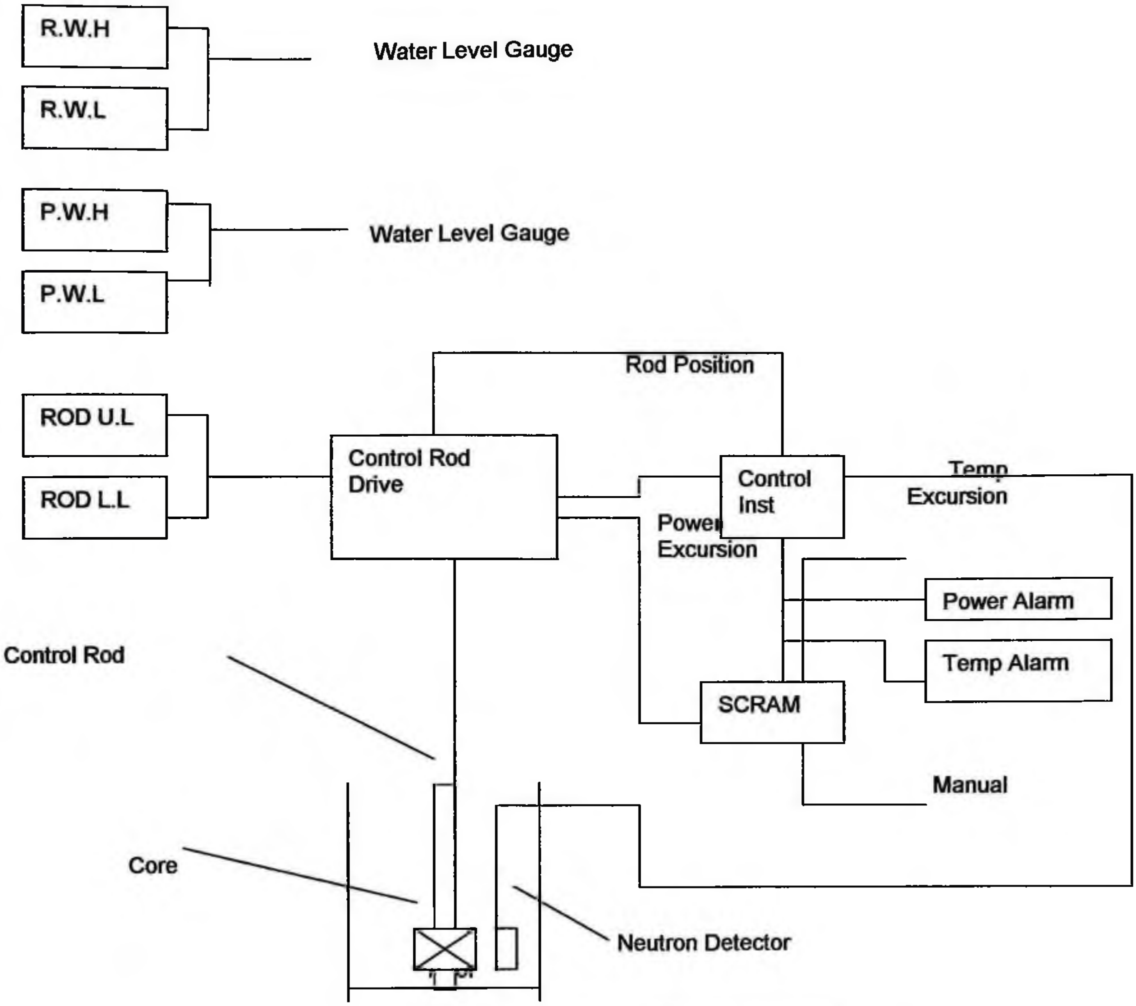


FIG 4.3 MNSR Reactor and Its System



R.W.H: Reactor water level high
R.W.L : Reactor water level low
P.W.H : Pool water level high
P.W.L : Pool water level low
ROD L.L: Control rod low limit
ROD U.L : Control rod upper limit

FIG 4.4 Control System Of Main Control Console

4.2 Sample Irradiation and Transfer Systems

The GHARR-1 facility has two types of sample irradiation and transfer systems: pneumatic capsule transfer system (rabbit type A) and multiple function capsule transfer system (rabbit type B). Both systems were used for the transfer and irradiation of samples.

4.2.1 Pneumatic Capsule Transfer System Type A

The rabbit type A system has one large rabbit loop and a small rabbit loop. In this work, the smaller rabbit loop was used for the sample transfer and irradiation. The two sections of tubes are connected at the reactor top cover plate. At each connection location, a photoelectric cell is mounted to monitor the sample capsule entering and leaving the reactor. On the reactor top cover plate, the polythene pipe of the large rabbit loop is connected to an aluminium alloy pipe in the outer irradiation site. The outer end of the polythene pipe is connected to the receiving lead chamber by polythene pipe. The smaller one has the same features as that of the large one except that it is connected to a small rabbit pipe in the inner irradiation site. The sample travelling time in or out of the reactor is about 1 to 3 seconds depending on the pressure of the compressed air circuit and total mass of the sample capsule. The pressure used in this work was 0.25 MPa (Yougchen and Yuchwen, 1992).

4.2.2 Multiple Function Capsule Transfer System (Rabbit Type B)

The type B rabbit system is basically the same as type A rabbit system but its sample irradiation and transport are provided with much more selection mechanism than those of type A. It can, therefore, conduct multiple function sample transfer and irradiation. The type B system is made up of a control desk, a glore box, a large shielded lead chamber, four polythene pipes from the control desk connecting to four small rabbit pipes (aluminium irradiation pipes) of which three are inserted into three inner irradiation sites while one is inserted in a small outer site. Only the inner irradiation sites were used for irradiations in this work. The sample capsules were transferred by compressed air pressure of 0.25 MPa (Yougchen and Yuchwen, 1992).

4.3 Sampling Sites

Five soil samples were taken from three agro-ecological zones in Ghana namely; forest, deciduous forest and coastal savanna zones. The Ankasa soil series was taken from the forest zone, Oda and Bekwai soil series were taken from the deciduous forest zone, and Toje and Akuse soil series were sampled in the coastal savanna zone. Sampling areas were chosen to give a fairly wide variety of Ghanaian soils.

4.3.1 Oda & Bekwai Series (Deciduous Forest Soils)

The study site for Oda and Bekwai soil series is at the University of Ghana Agricultural Research Station, Kade (6^{o} 05'N: 0^{o} 05'W) in the moist semi-deciduous forest zone of Ghana, approximately 175 km North East of Accra, and 150 m above sea level (Fig 4.6).

The climate of the area is humid tropical. Average annual temperature is 28°C, with the maximum temperature in March and the minimum temperature in August. The monthly average temperature varies less than 5°C during the year. The rainfall pattern is bimodal and the average annual rainfall during the period 1978-98 amounted to1179 mm with about 80 percent falling from March to mid-July and from September to November. Annual potential evapotranspiration is about 1400 mm.

Oda and Bekwai series are located down-slope and upslope, respectively, in a gently rolling part of the Birim basin with soil parent materials being exclusively Precambrian rocks, predominantly phyllites, schists and gneisses. A tributary of the Kadewa, a small seasonal stream drains the site. Drainage is good on the uplands but becomes poor down-slope towards the streambed. Up to a depth of 24 centimetres, sand, silt and clay fractions of the soil are 42%, 26.8% and 31.2 % respectively for Bekwai series while sand, silt and clay fractions of the soil are 16.4%, 55.5% and 28.1% respectively for Oda series. Clay mineral of Oda and Bekwai series is largely kaolinite (Edem, 2000).

4.3.2 Toje Series (Coastal Savanna Soil)

The study site for Toje soil series is at the University of Ghana farm at Legon-Accra (5°39'N: long 0°11'W), in the Coastal Savanna zone and in the Greater Accra region of Ghana. The site has an elevation of 30 m above sea level and experiences two rainfall and two dry seasons in a year. The major rainy season starts from March to June while the minor rainy season starts from September and ends in November (Fig 4.6). Toje is well drained and hence contains a large amount of Fe^{3+}, which explains its reddish colour (Stephen, 1994).

4.3.3 Akuse Series (Coastal Savanna Soil)

Akuse soil series is located at the University of Ghana, Agricultural Research Station at Kpong in the Coastal Savanna zone of Ghana. The site has less than two per cent slope. The parent material is derived from weathered garnetiferrous hornblende gneiss. The drainage is class 3, that is, moderately well drained.

The major rainy season starts from March and lasts until July, then a short dry spell that runs until the end of August. The minor rainy season starts from early September and ends in mid-September. Average annual temperature is 27°C. The vegetation of the area is generally savanna grassland with scattered Coppice shoots and trees (Fig 4.6). For a depth of 24 centimetres, composition of soil clay, sand and silt is 38.32%, 60.03% and 16.65% respectively (Stephen, 1994). The soil is dark-coloured, with the clay mineral being predominantly montmorillonite (Agbemabiese, 2000).

4.3.4 Ankasa Series (Forest Soil)

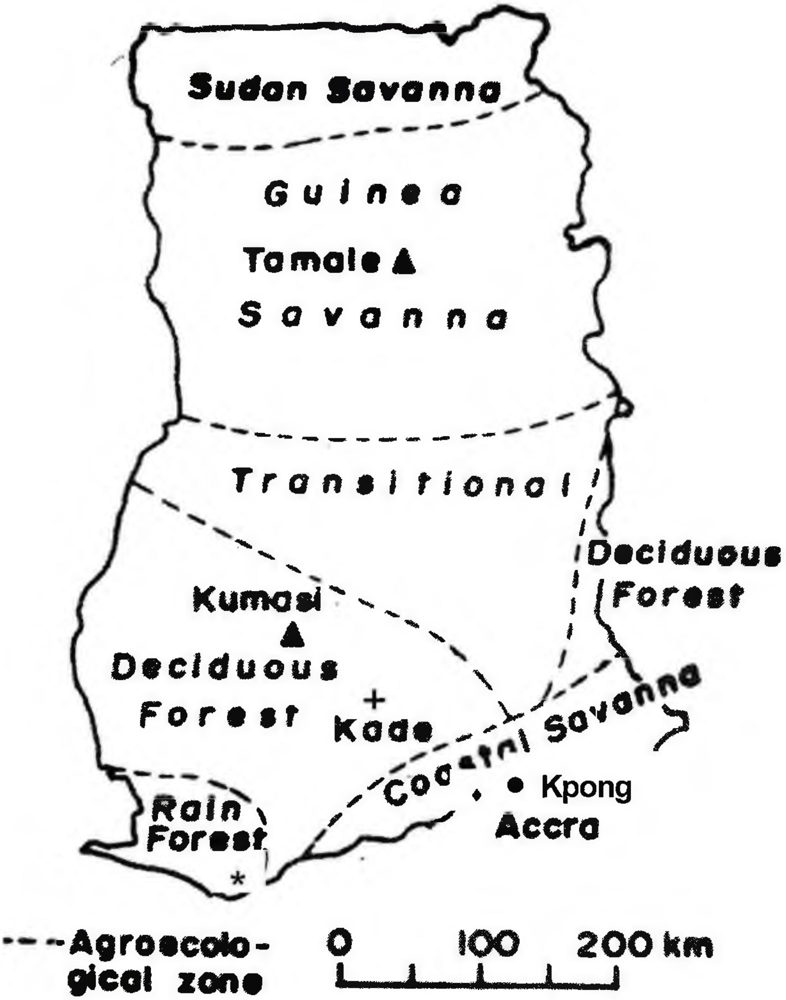
The Ankasa soil series occurs in the evergreen rain forest of the Western region in Ghana, with rainfall amounts greater than 1750 mm and mean annual temperatures of 25°C. Parent material of Ankasa is biotite granite schist (fig 4.6). The sand, silt and clay composition of the soil at a depth of 24 centimetres is 67.5% 5.4% and 27.1% respectively (Haruna, 1994).

4.4 Sampling

Soil samples were taken from pits in agricultural stations at the respective locations from the 0 – 24 cm layer. Samples were taken from one location or zone for each of the sampling sites. Soil samples were put into polythene bags, labelled and transported to the NAA Laboratory at Kwabenya - Accra.

4.5 Sample Preparation

Representative samples of the five soils namely; Ankasa, Oda, Bekwai, Toje and Akuse series were dried, ground, sieved with a 500 μm mesh and homogenised. Thirty-six analyte samples of each soil were prepared, twelve for short irradiation, twelve for medium irradiation and twelve for long irradiation. The mass of each analyte sample determined using a mettler electronic balance was between 100 mg and 150 mg. The analyte samples were wrapped in thin polythene foils. For the short irradiations, each of the wrapped analyte samples was put into a separate polyethylene capsule and heat-sealed using a hot soldering iron.



- * Ankasa soil series sampling site
- + Bekwai & Oda soil series sampling site
- ◆ Toje soil series sampling site
- • Akuse soil series sampling site

Fig 4.6 Ghana Map Showing Sampling Sites

For the medium and long irradiations the twelve previously individually wrapped analyte samples were put into two polyethylene capsules, that is, six in each capsule and also heat-sealed. The difference in irradiation methodology is to account for differences in the half-lives of possible radionuclei, which will be produced by the irradiation. A standard reference material, soil-7, from the International Atomic Energy Agency (IAEA) was analysed to evaluate the accuracy of the analytical technique. Three analyte samples of the standard reference material (SRM) each weighing 100 mg was wrapped in thin polyethylene foil. Each of the three SRM materials was put into a separate polyethylene capsule and heat-sealed, for short, medium and long irradiation.

4.6 Irradiation and Counting

The irradiation time was chosen according to the half-lives of the elements of interest. For short-lived elements with half-lives up to 20 minutes, irradiation time of 30 seconds was chosen. For the medium-lived elements, that is, those with half-lives between 20 minutes and 3 days the irradiation times were between 10 and 60 minutes. For the long-lived elements, that is, those with half-lives greater than 3 days, the irradiation time was 6 hours. Irradiation of the samples and standard materials was carried out in the GHARR-1 reactor operating at 15 KW with neutron flux of 5.0×10^{11} n $cm^{-2}s^{-1}$. The samples were sent into the reactor by means of the pneumatic transfer system.

At the end of each irradiation the capsule was returned from the reactor and allowed to cool down (decay) until the level of activity was within the acceptable limit for handling. The analyte samples were then removed from the capsule for counting. Each of the analyte samples was placed at the appropriate position on the detector and the counts were accumulated for a pre-selected time to obtain the spectra intensities. For short irradiation counting time of 600 s was found to be adequate. For the medium and long irradiation, counting times were1800 s and 3600 s, respectively.

4.7 Qualitative and Quantitative Analyses

A PC-based gamma-ray spectroscopy system was used for qualitative and quantitative analysis (Fig 4.7). The spectroscopy system consisted of an N-Type High Purity Germanium (HPGe) detector model GR2518, a High Voltage Power Supply Model 3103, a Spectroscopy Amplifier Model 2020 (all manufactured by Canberra Industries Inc.), a Silena ACCUSPEC Multi-Channel Analyzer (MCA) Emulation Software Card and a 486 Microcomputer. The efficiency of the detector is 25%. It operates on a bias voltage of 3000 V and has a resolution of 0.85 KeV and 1.8 KeV respectively, for Co-57 and Co-60 gamma-ray energies of 122 KeV and 1332 KeV respectively. The spectra intensities for the samples were obtained by means of the MCA Card. The qualitative analyses were performed by means of a Gamma Ray spectrum Analysis Software SPAN (Wang,1995). The photo peak Counts for the identified elements in the sample were calculated by the software (Fig 4.7). The counts were then converted into concentrations using equation (18).

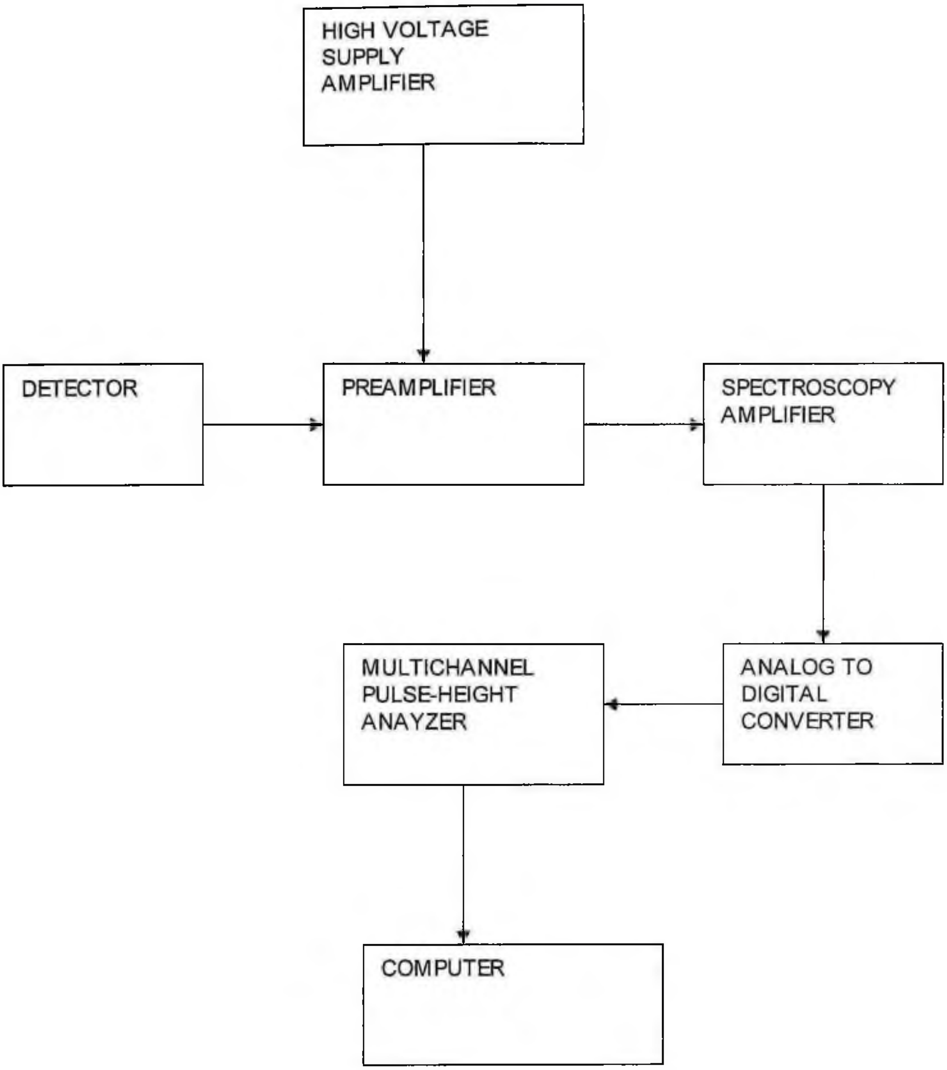


FIG 4.7 Block diagram of the gamma spectrometry system at the GHARR-1 Centre

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 RESULTS

Table 5.1 to 5.3 show the three categories of irradiation times used in identifying elements in the Standard Reference Material, SOIL-7. Table 5.4 shows the known concentration and measured concentration of identified elements in the Standard Reference Material, SOIL-7. Tables 5.5 to 5.7 show the three categories of irradiation times used for the application of INAA in the multi-element analysis of the five Ghanaian soils. Table 5.8 shows a full scan of identified elements and their concentrations in the five soils following INAA analytical technique. Figures 5.1 to 5.9 show graphs of identified elements and their concentrations in the five soils. Figure 5.10 shows graph of deviation of measured values following INAA of SOIL-7.

Table 5.1 elements identified after short irradiation of IAEA SOIL-7. Irradiation time t_i = 30 s

Element	Nuclide	Half-life/ min	Energy
Aluminium	^{28}Al	2.27	1778.9
Vanadium	^{52}V	3.76	1434
Calcium	^{49}Ca	8.7	3084.54
Titanium	^{51}Ti	5.8	320.1
Manganese	^{56}Mn	154.8	846.7
Manganese	^{56}Mn	154.8	1811
Magnesium	^{27}Mg	9.45	843.8
Magnesium	^{27}Mg	9.45	1014

Table 5.2 Elements Identified after medium irradiation of IAEA SOIL-7. Irradiation time t_i = 1 Hr

Element	Nuclide	Half-life/ Hrs	Energy / KeV
Arsenic	^{76}As	26.3	156.5
Lanthanium	^{140}La	40.23	1596
Potassium	^{42}K	12.36	152.7
Potassium	^{42}K	12.36	2754
Sodium	^{24}Na	15.02	1368.5

Table 5.3 Elements Identified after long irradiation of IAEA SOIL-7. Irradiation time t_i = 6 Hrs

Element	Nuclide	Half-life/ days	Energy/ KeV
Chromium	^{51}Cr	27.72	320
Cobalt	^{60}Co	1923	288
Scandium	^{46}Sc	83.8	889
Iron	^{59}Fe	44.5	1099

Table 5.4 Elements and their concentrations detected in IAEA SOIL-7

ELEMENT	SYMBOL	CONCENTRATION (PPM)*		ERROR
		CERTIFIED VALUE	THIS WORK	%
Aluminium	Al (%)	4.7	5.00 ± 0.30	-6.4
Arsenic	As	13.4	16.6 ± 2.00	-23.9
Chromium	Cr	60	62.3 ± 4.00	-3.8
Cobalt	Co	8.9	10.9 ± 1.30	-22.5
Europium	Eu	1	0.90 ± 0.22	10
Lanthanium	La	28	31.0 ± 2.30	-10.7
Manganese	Mn	631	637 ± 10.6	-1
Magnesium	Mg (%)	1.13	1.20 ± 0.14	-6.2
Scandium	Sc	8.3	9.20 ± 0.40	-10.1
Uranium	U	2.6	2.50 ± 0.04	3.8
Vanadium	V	66	64.0 ± 2.80	3
Calcium	Ca (%)	16.3	17.5 ± 2.60	-7.4
Potassium	K (%)	1.21	1.24 ± 0.07	-2.5
Sodium	Na (%)	0.24	0.23 ± 0.04	4.16
Titanium	Ti (%)	0.3	0.37 ± 0.01	-23.3
Iron	Fe (%)	2.57	2.70 ± 0.20	-5.1

* Unit applies to all elements except those with other units indicated against them

Table 5.5 Elements Identified after short irradiation of soil samples. Irradiation time t_i = 30 s

Element	Nuclide	Half-life/min	Energy/KeV
Bromine	^{80}Br	17.7	617.2
Chlorine	^{38}Cl	37.24	1642
Iodine	^{128}I	25	443
Indium	^{116}In	54.2	1293.54
Indium	^{116}In	54.2	1097
Manganese	^{56}Mn	154.8	846.7
Manganese	^{56}Mn	154.8	1811
Tantalum	^{182}Ta	15.84	171.6
Tantalum	^{182}Ta	15.84	146.8
Tantalum	^{182}Ta	15.84	184.9
Uranium	^{239}U	23.5	75
Vanadium	^{52}V	3.76	1434.1
Aluminium	^{28}Al	2.27	1779
Magnesium	^{27}Mg	9.45	843.8
Magnesium	^{27}Mg	9.45	1014
Titanium	^{51}Ti	5.8	320.1
Calcium	^{49}Ca	8.7	3084.54

Table 5.6 Elements Identified after medium irradiation of soil samples. Irradiation time t_i = 1 Hr

Element	Nuclide	Half-life/Hrs	Energy/KeV
Arsenic	^{76}As	26.3	559
Gallium	^{72}Ga	14.1	834
Sodium	^{24}Na	15.02	1368.5
Sodium	^{24}Na	15.02	2754
Sodium	^{24}Na	15.02	685.74
Tungsten	^{187}W	23.9	479.59
Potassium	^{42}K	12.36	1524.7

Table 5.7 Elements Identified after long irradiation of soil samples. Irradiation time t_i = 6 Hrs

Element	Nuclide	Half-life/days	Energy
Cerium	^{141}Ce	32.5	145
Cobalt	^{60}Co	1923	1173
Chromium	^{51}Cr	27.72	96
Caesium	^{134}Cs	751.9	661.66
Europium	^{154}Eu	8.59	1274
Hafnium	^{181}Hf	42.4	482.2
Lutetium	^{177}Lu	160	208
Rubidium	^{86}Rb	18.7	1076.6
Antimony	^{122}Sb	2.72	564
Scandium	^{46}Sc	83.8	889
Zinc	^{65}Zn	243.9	1116
Terbium	^{160}Tb	72.1	879.4
Thorium	^{233}Th	27	311.9
Ytterbium	^{175}Yb	4.19	396.3
Zirconium	^{97}Zr	16.7	743.33

Table 5.8 Elements and their concentrations detected in the five soils.

		Concentration (PPM)*				
Identified Element	Element Symbol	Deciduous Forest Soil		Forest Soil	Coastal Savanna Soil	
		Oda	Bekwai	Ankasa	Toje	Akuse
Arsenic	As	15.9	4.8	2.4	3.44	
Bromine	Br	4.27	12.7	5.8	5.34	
Cerium	Ce	13.8	33.1	19.4	56.6	31.4
Chlorine	Cl		115	29	667	
Cobalt	Co	5.23	7.33	5.55	11.4	34.7
Chromium	Cr	23.3			26.5	45.3
Caesium	Cs			2.98		
Europium	Eu	0.31	1.15	0.19	0.6	0.54
Gallium	Ga	5.69	15.1	17.1	14.5	11.2
Hafnium	Hf	8.14	7.5	5.86	12.9	11.8
Iodine	I		27.7	21.2	37.5	
Indium	In					96.1
Lanthanium	La	6.14	10.9	13.5	26.3	12.3
Lutetium	Lu	0.83	0.94	301		1.16
Manganese	Mn	31.9	472	34.7	205	2800
Sodium	Na	216	472	220	208	5200
Rubidium	Rb		86.2			
Antimony	Sb	0.41		2.31		
Scandium	Sc	3.4	14.8	2.48	9.23	16.8
Tantalum	Ta	32.6	152	28.7	2.07	
Terbium	Tb	1.04	1.51		2.01	1.36
Thorium	Th	3.17	7.41		8.5	2.21
Uranium	U		3.06	2.76	24.6	
Vanadium	V	37.5	124	24.8	57.3	127
Tungsten	W			16.3		
Ytterbium	Yb	2.16		3.8	1.58	3.33
Zinc	Zn			3.78		
Zirconium	Zr			6.14		
Aluminium	Al (%)	1.83	7.09	4.4	4.47	6.22
Iron	Fe (%)	0.6	4.59	0.98	1.72	5.66
Potassium	K (%)	0.15	0.77	0.18	0.12	0.07
Magnesium	Mg (%)	0.41	1.62	1.8	1.09	2.5
Titanium	Ti (%)	0.96	0.83	0.32	6.55	0.85
Calcium	Ca(%)		0.18			1.80

*Unit applies to all elements, except those with units indicated against them

FIG 5.1 Concentration Of Elements In ODA

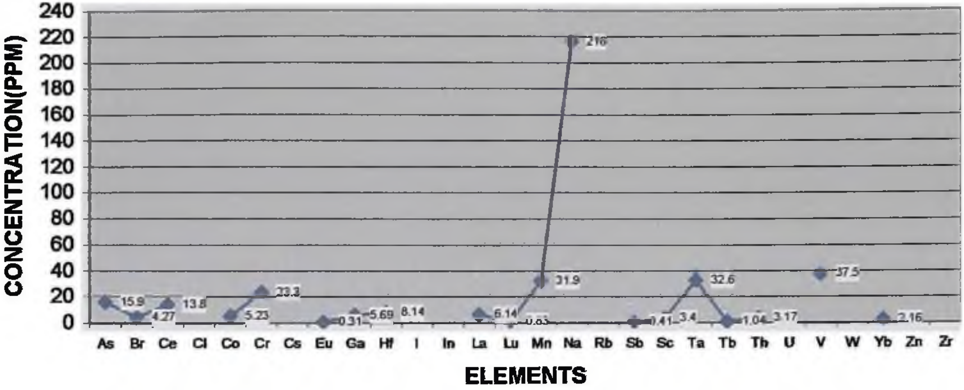


FIG 5.2 **Concentration Of Elements In Bekwai**

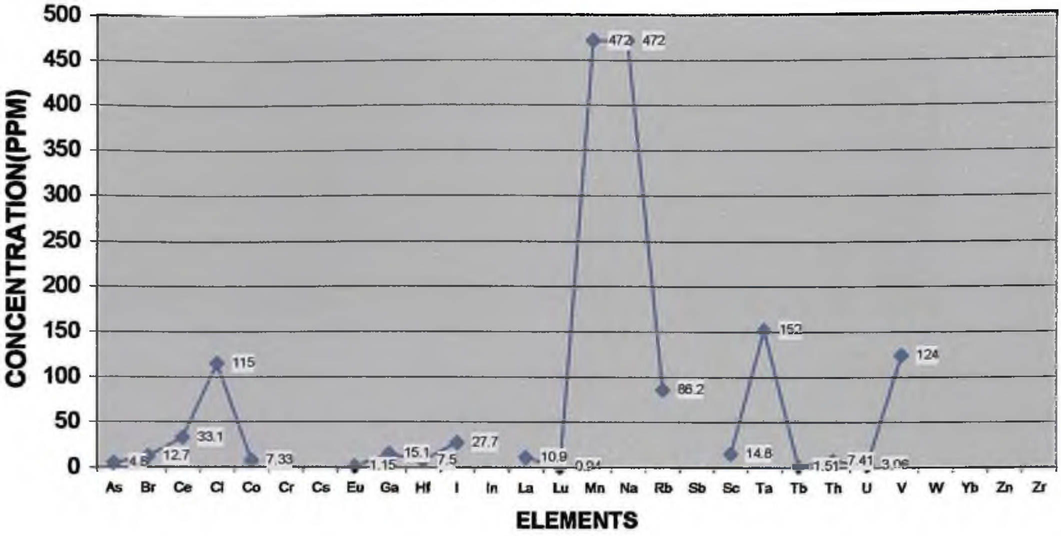


FIG 5.3 **Concentration Of Elements In Oda And Bekwai (PPM)**

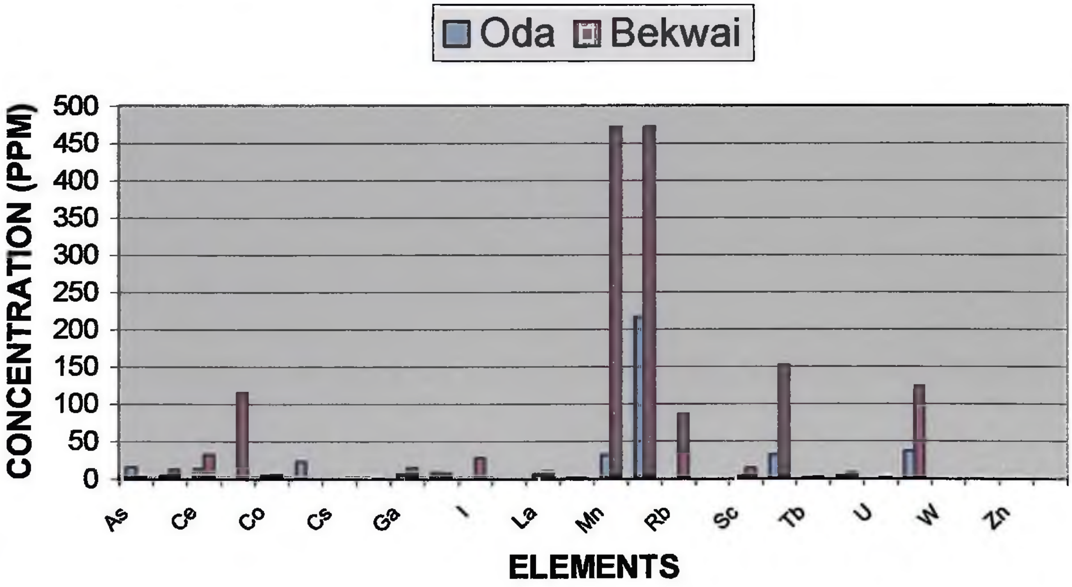


FIG 5.4 Concentration Of Elements In Oda And Bekwai (Continued)

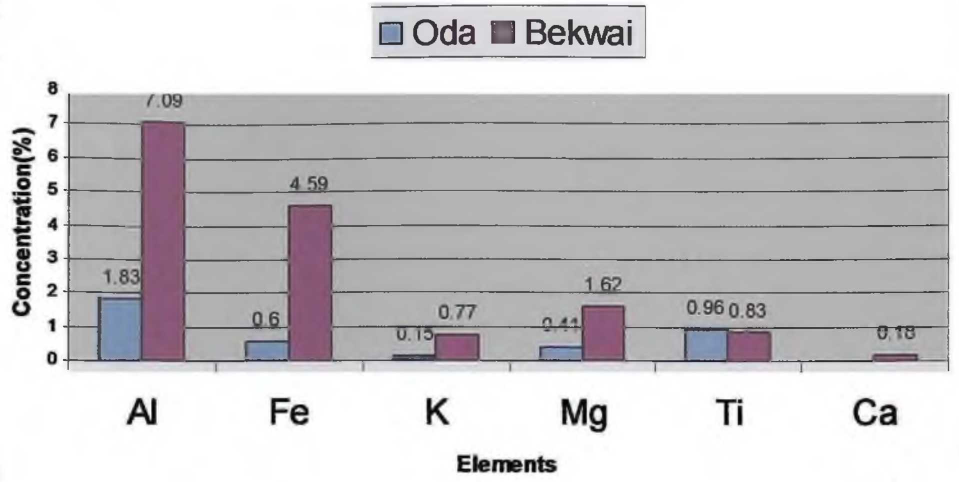


FIG 5.5 Concentration Of Elements In Toje

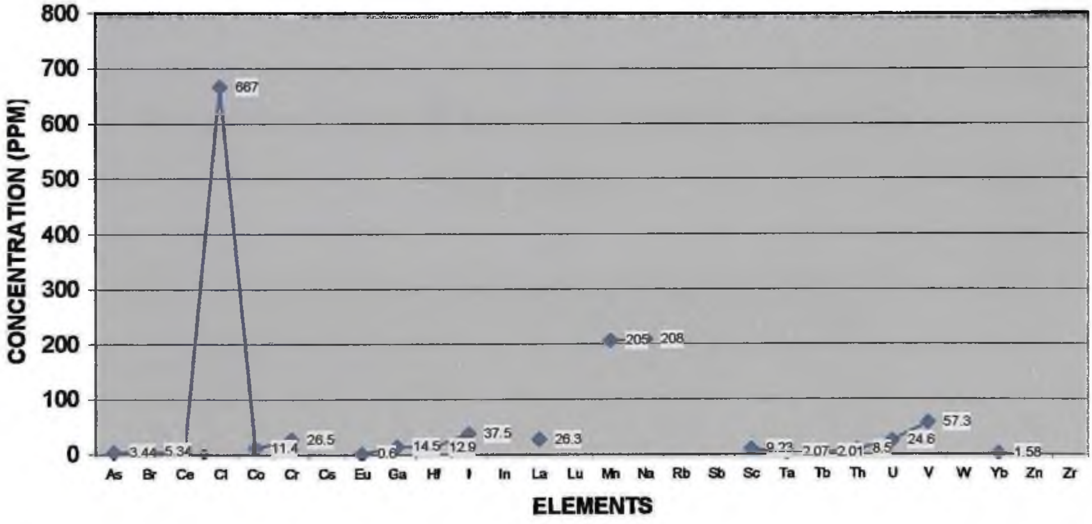


FIG 5.6 Concentration Of Elements In Akuse

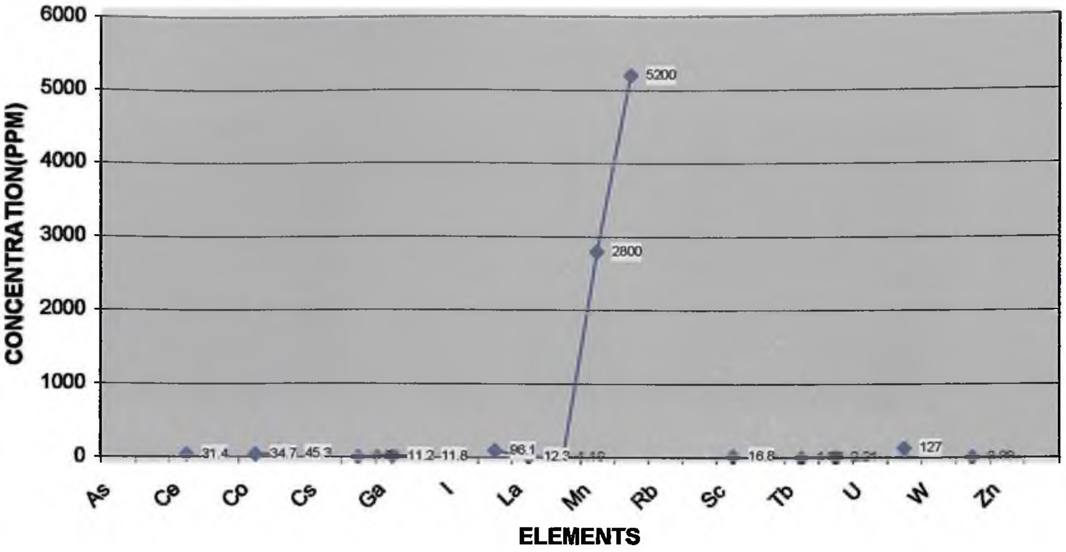


FIG 5.7 Concentration Of Elements In Toje And Akuse (PPM)

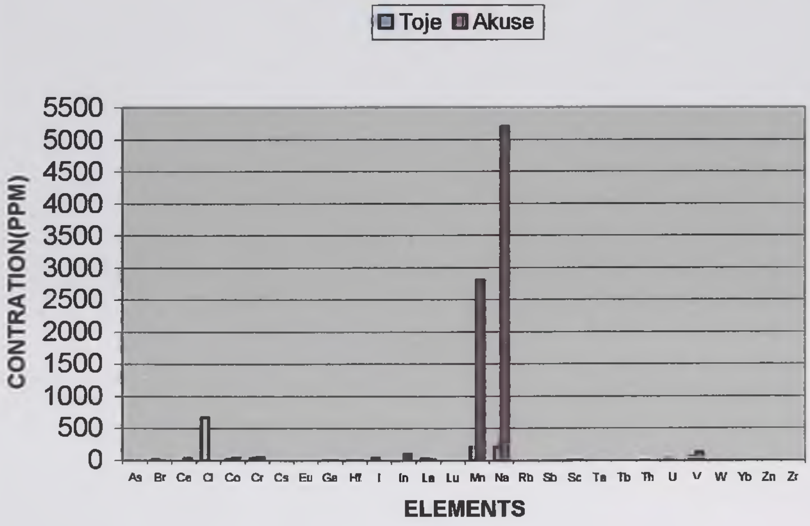


FIG 5.8 Concentration Of Elements in Toje And Akuse (Continued)

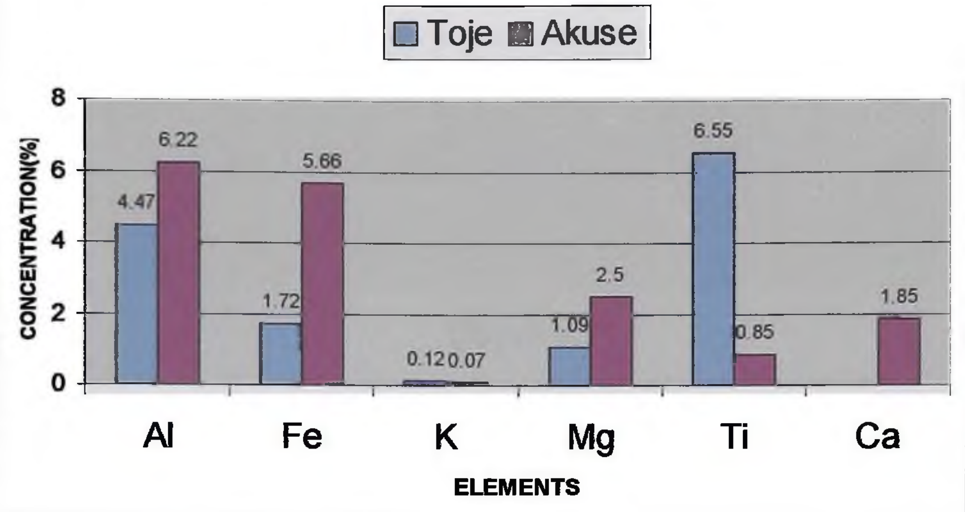


FIG 5.9 Concentration Of Elements In Ankasa

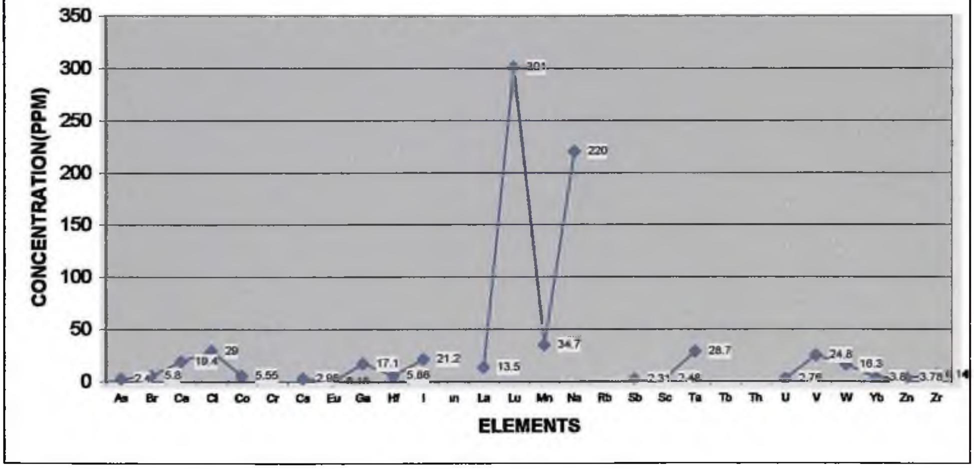
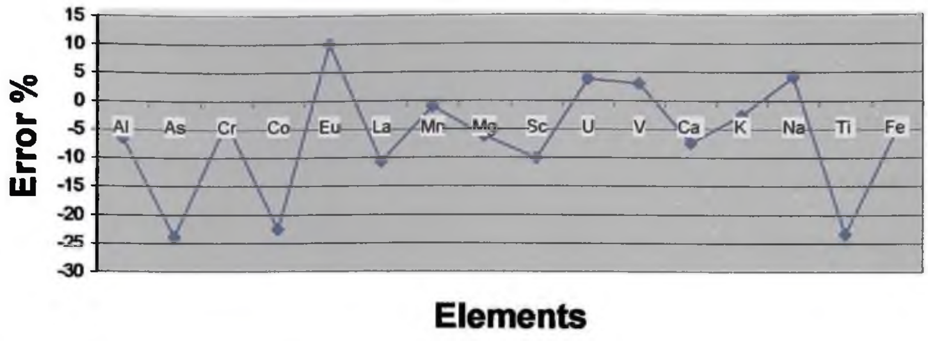


FIG 5.10 Graph of Deviation Of Measured Values From Certified Values Of IAEA SOIL-7



5.2 Discussion

5.2.1 INAA Technique

Comparison of results obtained using INAA at the GHARR-1 Centre and known concentration of elements of SOIL-7, a SRM supplied by the IAEA, indicates that INAA at the GHARR-1 centre is reliable and accurate (Table 5.1,Table 5.2 and Figures 5.1-5.10). Of the sixteen (16) elements whose concentrations were measured, eleven (11) showed deviation within 10%, whiles two (2) showed deviation between 10 and 11% as shown in figure 5.10. Manganese showed the lowest deviation of 1% and the highest being Arsenic with a deviation of 24%.

Intrumental Neutron Activation Analysis in the multi-element analysis of the five Ghanaian soils (Oda, Bekwai, Toje, Akuse and Ankasa series) failed to detect silicon in all the five soils. ^{30}Si has an unusually low isotopic abundance of 0.31%, very low thermal and epithermal cross-section of 0.108 and 0.106 barns respectively. The specific activity or gamma activity for the ^{30}Si nuclide with energy 1266KeV is 0.07 counts/µg (IAEA-TECDOC-564, 1990), which is extremely low. All these factors make it difficult for detecting ^{30}Si using INAA technique. Most of the elements detected had appreciably high specific activities (Tables 5.3 - 5.5).

5.2.2 Deciduous Forest Soils (Oda & Bekwai Series)

Concentration of Fe in Bekwai and Oda series is 4.59% and 0.6% respectively (Table 5.8). The presence of higher concentrations of Fe in Bekwai series is mainly due to the occurrence of substantial amounts of iron oxides (goethite and hematite) in Bekwai series (Owusu-Bennoah et al., 2000). The parent material of

Oda and Bekwai series are lower Birimian phyllites, shists and gneisses (Adu, 1992). Phyllites are rich in micaceous minerals such as biotite $[K_2(Mg,Fe^{+2})_{6-4}(Fe^{+3},Al,Ti)_{0-2}(Si_{6-5}Al_{2-3}O_{20})(OH,F)_4]$ and muscovite $[K_2AL_4(Si_6AL_2O_{20})(OH,F)_4]$. Chlorite, $(Mg,AL,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$,can also be found in phyllites. The presence of Al, Mg, K and Fe in all the minerals of the parent materials explains the high concentration of these elements in Oda and Bekwai series. Clay fraction in Bekwai and Oda series is 31.2% and 28.1% respectively (Adu, 2000), with kaolinite $[Al_4(Si_4O_{10})(OH)_8]$ being the major clay mineral (Edem, 2000). Aluminium concentration in Bekwai series is greater than that in Oda series primarily due to greater portions of kaolinite in Bekwai series, reflecting differences in mineral weathering.

Gneisses are made up of quartz and feldspars (Greenland et al., 1980). A typical feldspar mineral is plagioclase $[Na(AlSi_3O_8)\text{-}Ca(Al_2Si2O_8)]$ (Greenland and Hayes, 1980). The presence of Na in concentrations of 216 ppm and 472 ppm in Oda and Bekwai series, respectively, maybe due to plagioclase. Even though Si and Al are major components of the structure of clay, other elements such as Fe and Mg may occur as part of the crystal structure; and attracted to the clay crystal are various ions like Mn^{++}(Thompson, 1957). The presence of Mn in Oda and Bekwai series is attributed to the clay fraction of the soil where Mn is attached to the clay minerals. Layer silicates also called phyllosilicates commonly contain, besides oxygen and hydrogen, Si, Al, Fe, Ca, Na and K (Deer et al., 1982). Some amounts of Ti and Mn may also be present, and uncommon rare layer silicates are known that contain substantial concentrations of V, Ga and Cr (Deer et al., 1982). The observed concentrations of V and Ga in Oda and Bekwai series may be due to substitution of some macroelements with V and Ga.

Titanium occurs in nature as the dioxide TiO_2 in three polymorphic forms namely; rutile, brokite and anatase. In all the three forms titanium is octahedrally coordinated to six oxygen ions and each oxygen is surrounded by three titanium ions. Rutile the most common mineral is a high temperature form and is common as a detrital in the sand fraction of soils. Anatase is the low temperature form of TiO_2 and usually occurs as an alteration product of other titanium bearing minerals (Greenland et al., 1980). The observed Ti concentration of 0.96% for Oda series and 0.83% for Bekwai series maybe due to presence of rutile and anatase in the clay and sand fractions of both soils. Sand fractions are 42% and 16.4% in Bekwai and Oda series respectively, while clay fraction is 31.2% and 28.1% in Bekwai and Oda series, respectively (Adu, 1992). Since clay and sand fractions are greater in Bekwai than in Oda series Ti concentration in Bekwai series should be higher than that of Oda series. Some less common elements occur replacing Ti^{+4} in TiO_2. Tantalum, Ta^{+5} has ionic radii very similar to Ti^{+4} and quite large amounts of Ta_2O_5 can occur (Greenland et al, 1978). Tatanium concentrations of 152 ppm and 32.6 ppm for Bekwai and Oda series respectively, are due to Ta_2O_5 occurring in place of TiO_2 in the kaolinite minerals of both soils. Tatanium concentration is higher in Bekwai series because there has been greater replacement of Ti by Ta in Bekwai series. This may explain the unexpected lower concentration of Ti in Bekwai series compared to that of Oda series (Table 5.8). Microelements such as Co and Zn also occupy structural positions as minor replacements for the major constituents of silicate minerals including clays (Thompson, 1957). The lower clay content in Oda series may explain the higher Co concentration in Bekwai series. Minerals of the alumite and plumbogummite group with formula $MY(XO_4)_2(OH_6)$ where M is a large cation, often an alkali or alkaline earth metal, Y a trivalent cation usually Al^{3+} or Fe^{3+} and X is S, P or As are found in soils (Deer et al.,1982). These minerals can be regarded as basic sulphates, phosphates or arsenates of aluminium or iron. An example of a plumbogumite mineral found in soils is florencite with formula $CeAl_3(PO_4)(OH_6)$ (Greenland and Hayes, 1978). Cerium concentrations observed in Bekwai and Oda series are due to presence of florencite in the soils.

The presence of arsenic (As) in both soils, even though in low concentrations may be due to the presence of arsenates of aluminium or iron. Anatase is a constituent of clays particularly those rich in kaolin minerals and is an alteration product of sphene. Sphene [$CaTi(SiO_4)(O,OH,F)$] occurs chiefly in gneisses and schists rich in ferromagnesian minerals (Greenland et al., 1980). Chlorine is known as a principal substitute of oxygen in sphene (Deer et al., 1966). The detection of chlorine with concentration of 115 ppm in Bekwai series is due to the presence of sphene in the soil since Bekwai parent materials are made up of gneisses and schists. Chromium is normally present in Muscovites only in trace amounts (Deer et al., 1966). Muscovites are the parent materials of Oda and Bekwai series. Since Cr occurs only in trace amounts it is not surprising that 23.3 ppm was detected in Oda series. Biotite, a parent material of Oda and Bekwai often exhibits pleochroic haloes, which are attributed to the inclusion of zircon or other minerals containing elements belonging to the radioactive series U-Ra and Th-Ac. Thus, the detection of U, Th and Hf in the soils is due to the presence of zircon in the parent materials. Europium, La, Lu and Rb find their way into soils as minor elements by replacing major elements in soil minerals. This accounts for low concentration levels of Eu, La, Rb and Lu in the two deciduous forest soils.

5.2.3 Coastal Savanna Soils (Akuse & Toje Series)

The parent material of Toje series is Togo Quartzite Schist (Agbembiese, 2000) while that of Akuse series are Garnetiferrous Hornblende Gneisses (Stephen, 1984). Clay fraction of Akuse series is 38.32% while that of Toje is 9.2% (Stephen, 1984). The clay mineral in Akuse series is predominantly montmorillonite. Montmorillonite, hornblende and garnetiferrous minerals have the formula $(1/2Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al_8,O_{20})(OH)_4.nH_{2O}$, $(Na,K)_{0-1}Ca_2(Mg,Fe^{2+},Fe^{3+},Al)_5(Si_{6-7}Al_{2-1}O_{22})(OH,F)_2$ and $Fe_3Al_2Si_3O_{12}$ respectively (Greenland et al., 1980). Schists are rich in micaceous minerals (biotite and muscovite), quartz and feldspars (orthoclase and plagioclase). Aluminium, Fe and Na are in greater concentration in Akuse series than in Toje series. This is mainly due to the presence of montmorillonite in the clay minerals of Akuse series, which is rich in Al, Fe, Mg and Na. The presence of hornblende mineral in Akuse series (Stephen, 1984) further explains the relatively high Na concentration of 0.52% in Akuse series. Toje series, which does not have the hornblende minerals in its soil, has Na concentration of 208 ppm. Ti has concentration of 6.55% in Toje series and 0.85% in Akuse series (Table 5.8). It is known that biotite contains some Ti (Deer et al, 1966). The role of Ti in the biotite structure is uncertain since it may be replacing Si in the tetrahedral or (Fe, Mg) in octahedral sites; the latter appears more likely in view of the size of the ion (Deer et al, 1966). This replacement of Fe by Ti may explain the rather low concentration of 1.77% of Fe in Toje compared with the 5.66% in Akuse series. It may also explain the unusually high concentration of Ti in Toje series compared with Akuse series.

In muscovite Mn, Cr and V have the potential of replacing octahedral Al (Greenland et al., 1980). Chromium is normally present in trace amounts while most muscovites contain less than 1% MnO (Deer et al., 1982). This explains the detection of 205 ppm for Mn, 57.3 ppm for V and 26.5 ppm for Cr in Toje series. Spessartine [$Mn_3Al_2Si_3O_{12}$], which is Mn-rich, is often present in Almadine a mineral of the garnetiferous gneisses that is also a parent material of Akuse series (Deer et al, 1966). The presence of Mn-rich spessartine mineral in garnetiferous gneisses accounts for the high concentration of 0.28% detected for Mn in Akuse series. The presence of Cr and V in Akuse series is likely due to substitution of these elements with macroelements like Al in certain micaceous minerals. Lepidolite [$K_2(Li,Al)_{5\text{-}6}(Si_{6\text{-}7}Al_{2\text{-}1}O_{20})(OH,F)_4$] a mica mineral has Ga present in low concentrations. Gallium concentration of 11.2 ppm detected for Akuse series and 14.5 ppm detected for Toje series is characteristic of low quantities of Ga in the parent materials of the two soils. Zircon with formula $Zr(SiO_4)$ always contains some hafnium, Hf (Deer et al.,1982). The HfO_2/ZrO_2 ratio is normally about 0.01(Deer et al., 1982). Radioactive Th and U are also present in Zircon (Greenland et al., 1980). Since mica minerals like biotite contain some zircon, it is expected that low concentrations of Hf, Th and U will be detected in Akuse and Toje series. The close similarity in ionic radii between Ti^{+4} and Ta^{+5} enables the Ta ions to be attracted to titanium minerals in the soil. This explains the detection of 2.07 ppm of Ta in Toje series. Ta was not detected in Akuse series because its concentration may be below detection limit. Low Co concentration of 11.4 ppm for Toje series and 34.7 ppm for Akuse series suggests that Co occupies structural positions as minor replacements for the major constituents of silicate minerals. Arsenic concentration of 56.6 ppm and 31.4 ppm in Toje and Akuse series respectively are due to the presence of plumbogummite minerals (Deerland et al., 1982) in Toje and Akuse series. Chlorine was not detected in Akuse series because its concentration was below detection limit. Detection of concentration of Eu, La, Sc, Tb and Yb in trace quantities implies that these elements exist in the interstitial spaces of the elemental assembly of the soil minerals.

5.2.4 Forest Soils (Ankasa, Oda & Bekwai Series)

The parent material of the Ankasa series is biotite granite schist (Haruna, 1994). These consist of biotite, muscovite, quartz and feldspar. Among the micaceous minerals biotite dominates. The detection of Al, Fe, K, Ti, Mn, Na, U and Zr in Ankasa series is due to parent materials rich in minerals consisting of these elements. Al concentration is greater in Bekwai and Ankasa series than in Oda series. This is likely the result of differences in the stage of mineral weathering in these soils. Ti concentration is 0.96% in Oda series, 0.83% in Bekwai series and 0.32% in Ankasa series (Table 5.8). The relatively high concentration of Ti in Oda series could be due to Ti replacing Fe and Mg in the biotite structure of parent material of Oda series.

Na concentration is 216 ppm in Oda, 220 ppm in Ankasa series and 472 ppm in Bekwai series. Plagioclase is the main contributor to the Na in the parent materials of the three soils. Bekwai series has a higher Na concentration than Oda and Ankasa series. This suggests that its clay minerals might contain montmorillonite. Montmorillonite is rich not only in Na but also in Fe (Deer et al., 1982). Fe has concentration of 4.59% in Bekwai series, 0.98% in Ankasa series and 0.6% in Oda series (Table 5.8). This suggests that montmorillonite is present in Bekwai. Zircon was detected in concentration of 6.14 ppm for Ankasa but was not detected in Bekwai or Oda series. Zirconium can be traced to Zircon, which is found in biotite, a parent material of Ankasa, Oda and Bekwai series. Zircon may be responsible for the presence of Hf, Th and U in the three forest soils. Generally the presence of Mn in the three forest soils is due to clay minerals. However, the detected higher Mn concentration of 472 ppm for Bekwai would seem to suggest that Mn has replaced octahedral Al in the muscovite mineral of the Bekwai series parent material. A similar story can be told for V, which has concentration of 37.5 ppm, 24.8 ppm and 124 ppm in Oda, Ankasa and Bekwai series respectively. The detection of trace elements La and Eu in Oda Bekwai and Ankasa series is due to their presence in the interstitial spaces in the elemental assembly of the three forest soils. Gallium was detected in all the three forest soils. Gallium is present in micaceous minerals such as lepidolite in small quantities. Since micas are parent materials of the three forest soils the detection of fairly low concentrations of Ga is expected.

5.2.5 COASTAL SAVANNA & FOREST SOILS

The parent materials of the three forest soils are mainly micas, chlorites, quartz and feldspar minerals. The parent materials of the two soils of the coastal savanna zone are micas, quartz, feldspars, hornblende and garnetiferrous minerals. These minerals are primarily responsible for the elemental composition of the soils from which they are formed. The presence of montmorillonite, a clay mineral, in the coastal savanna soils accounts for the high concentration of Fe, Na, Al, Ca and Mg in Akuse and Toje series compared to that of the forest soils (Ankasa, Oda and Bekwai series). The high concentration of Al, Fe and detected suggests that montmorillonite might be a component of Bekwai series. Less than 1% concentration of K was detected in each of the five soils. The forest soils had higher concentration of K than the coastal savanna soils. This suggests that the forest soils have more mica minerals present. Titanium concentration in both forest and coastal savanna soils is due to presence of rutile and Anatase in the soils. The high Ti concentration detected inToje series a coastal savanna soil, is due to substitution of Fe by Ti in some of the soil minerals. Zircon is responsible for detection of traces of U, Th and Hf in all the soils. Relatively equal concentration levels of Ga were detected in the soils of the coastal savanna and forest regions. Gallium thus exists in relatively equal concentrations in the mica minerals of all the five soils. Chlorine was detected in two soils of the forest region and one soil of the coastal savanna region (Table 5.8). Concentration of Cl detected in Toje series was the highest. This is not surprising since sphene to which Cl is a principal substitute of oxygen occurs chiefly in schist rich in ferromagnesian minerals. Vanadium concentration detected in both forest and coastal savanna zones were relatively equal in concentration. Inability to detect Ca, a constituent of the parent materials of the five soils in Oda, Ankasa and Toje series was because concentration of Ca was below detection limit of the set up. Ytterbium was detected in four out of five soils examined. Their concentrations ranged from 1.58 ppm to 3.80 ppm. It can be concluded therefore that Yb exists in the interstitial spaces of the elemental assembly of various minerals. Relatively equal concentrations of Co was detected in all five soil examined, the highest being 34.7 ppm in Akuse series. Cobalt presence in the soil is mainly due to substitution with macroelements of some minerals in the soils. Similarly the presence of As, Cr and Ce is due to substitution with major elements in the soil minerals.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

Multi-element analysis of five Ghanaian soils namely: Oda, Bekwai, Ankasa, Toje and Akuse series taken from three agro-ecological zones in Ghana and using INAA technique at the GHARR-1 Centre identified elemental composition and their levels in the soils. The analysis was done using the GHARR-1 reactor and a PC-based gamma spectroscopy system. A Standard Reference Material, SOIL-7 supplied by the International Atomic Energy Commission (IAEA) was used to validate the methodology used.

Comparison of the results obtained using INAA at the GHARR-1 Centre and the certified known concentration of SOIL-7 showed that the technique is reliable and accurate. 70% of the elements identified showed deviations within 10% while 13% of the elements showed deviations between 10% and 13%. Manganese showed the lowest deviation, and the highest being Arsenic. The detection of Si by INAA was not possible because the activities were below the detection limit of the set up.

The Single Relative Standardization Method used made the INAA technique quick and easy to operate. With the specific activities of the nuclides known constants, the number of counts under the photopeak areas were the measurable quantities and these were obtained by the Multi-Channel Analyzer (MCA) Emulation Software Card. Using equation (18) the amount of the element in the sample was calculated. Instrumental Neutron Activation Analysis technique applied on the five soils detected 24 elements in Oda series, 25 elements in Toje series, 22 elements in Akuse series, 26 elements in Bekwai series and 28 elements in Ankasa series. The concentrations of the elements were also determined. The inability to detect the presence of Ca, a constituent of the parent materials of the five soils in Oda, Ankasa and Toje series was because concentration of Ca was below detection limit of the set up. The detection of Al, Fe, K, Mg, Ti, La, Na, Mn, V and other elements with their concentrations is consistent with information from literature on the parent materials of the five soils. The difference in concentrations of the elements in the deciduous forest soils is accounted for by the difference in percentage composition of sand, clay and silt reflecting differences in weathering. Elements identified with their concentrations in coastal savanna soils, Akuse and Toje series, give credence to the fact that Togo Quartzite Schist and Garnetiferrous Hornblende Gneisses, respectively, are parent materials of the two coastal savanna soils. Identified elements in the Ankasa series reflect the composition of the parent material, biotite granite schist.

In view of the reliability, accuracy, quickness and ease of the INAA technique available at the GHARR-1 Centre the technique is recommended for mapping elemental composition of soils.

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