

**INAA AND XRF DETERMINATION OF ACTIVE ELEMENTS
THAT PROMOTE SEXUAL AROUSAL IN SOME HERBS USED BY
NORTHERN NIGERIAN WOMEN AS APHRODISIACS**

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**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL,
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AHMADU BELLO UNIVERSITY, ZARIA.**

AUGUST, 2015

CERTIFICATION

This thesis titled “*INAA AND XRF DETERMINATION OF ACTIVE ELEMENTS THAT PROMOTE SEXUAL AROUSAL IN SOME HERBS USED BY NOTHERN NIGERIAN WOMEN AS APHRODISIACS* “ by *Rakiya HARUNA* meets the requirements governing the award of degree of masters of science (radiation biophysics) of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literrypresentation.

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DEDICATION

This work is dedicated to my mother Hajiya Mairo Ibrahim Makarfi

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My sincere thanks go to my supervisors Dr. Y.A Ahmed and Dr. Nasiru Rabi'u whom had taken time to offer useful suggestion and enlightenment on how to carry out the research. Their endurance has led to the completion of this work I'm indeed grateful for the valuable contributions offered.

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ABSTRACT

Several plants are used for the purpose of causing sexual arousal, inducing venereal desire or increasing sexual pleasure and performance. The effect produced by these herbs could be associated to their composition of certain mineral elements that were known to have aphrodisiac effect such as: Fe, I, Mg, Mn, Se and Zn. One of the major problems which may be associated with the use of herbal remedies is the presence of potentially toxic mineral elements in the herbs. The main purpose of this study is to determine the essential elements, which the elements of interest for this study belong to and non-essential elements. Instrumental neutron activation analysis and X-ray fluorescence spectroscopy methods of analysis were used in the determination of the active elements that promote sexual arousal in the herbs: (*Euphorbia hirta*, *Abrus precatorius* (seeds), *Abrus precatorius* (leaves), *Desmodium velutinum*, *Leptadenia hastatae*, *Evolvulus alsinoides*, *Schwenkia americana*, *Pentadon pentondrus*, *Crotalaria lachnesoma*, and *Crotalaria mucronata*). Potassium and calcium were found to have the highest concentration in all the studied herbs except *abrus precatorius* seed with magnesium having the highest concentration. The concentration of potassium ranges from $24220 \pm 388 \text{ mg/g}$ in *Euphorbia hirta* to $9281 \pm 501 \text{ mg/g}$ in *crotalaria mucronata*. and that of calcium ranges from $22220 \pm 756 \text{ mg/g}$ in *leptadenia hastatae* to $3878 \pm 283 \text{ mg/g}$ in *crotalaria lanchnesoma*. Some of the active elements in aphrodisiacs were also determined by this work they include (Fe, Mg, Mn and Zn,,) with the concentration of Fe ranging from $10660 \pm 181 \text{ mg/g}$ in *Schwenkia americana* to $289 \pm 11 \text{ mg/g}$ in *crotalaria lanchnesoma*, and that of Mg ranges from $41785 \pm 148 \text{ mg/g}$ in *Abrus precatorius* (seeds) to $1782 \pm 219 \text{ mg/g}$ in *crotalaria lanchnesoma*, the concentration of Mn ranges from $527 \pm 1 \text{ mg/g}$ in *Crotalaria mucronata* to $24.3 \pm 0.2 \text{ mg/g}$ in *Euphorbia hirta*. All the studied herbs were found to be very good source of essentially nutritional elements.

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Herbs have been used for centuries by millions of people around the world to treat various ailments. They provide a balance within our bodies that we some time fail to achieve naturally. There are herbal remedies available for just about any ailment including lack of sexual drive. The right combination of herbs can create a very powerful aphrodisiac. An aphrodisiac is define as any food or drug that arouse the sexual instinct, induces venereal desire and increases pleasure and performance. This word is derived from 'aprodite' the Greek goddess of love and these substances are derived from plants, animals or minerals Yakubu *et al.*, (2007). Aphrodisiacs have been used for thousands of years, by every culture, to enhance sexual activity. Almost every culture has used various 'substances' of herbal origin to intensify their love lives or attempt to cure impotent. These herbal preparations used as aphrodisiacs have been found to range from the useless to the extremely dangerous, even being seriously toxic.

It has been reported that whatever is taken as food could cause metabolic disturbance subject to the allowed upper and lower limits of trace metals Prasad (1976). Both the deficiency and excess of essential micronutrients and trace of toxic metals may cause serious effects on human health Underwood (1997) and Reilly (1980).

The use of medicinal plants in therapeutics or as dietary supplements goes back beyond recorded history, Woods (1999). How-ever, the safety of their use has been questioned due to the reports of illness and fatalities Stewart *et al* (1999). WHO recommends that medicinal plants which form the raw materials for the finished products may be checked for the presence of heavy metals, further it regulates maximum permissible limits of

toxic metals like arsenic, cadmium and lead, which amount to 1.0, 0.3 and 10 ppm, respectively WHO (1998). Medicinal herbs are easily contaminated during growth, development and processing. The heavy metals confined in plants finally enter the human body and may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, leading to hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancers.

The present study would examine the elemental composition of frequently used plants by northern Nigerian women for aphrodisiac purposes. It is hoped that this study will provide baseline data that will help define the dose rates of these plants for their safe use. Also, elemental characterization of these plants will serve as quality assurance for traditional health care.

1.2 Research Problem

A major hazard which may be associated with the use of herbal ingredients is the presence of potentially toxic mineral elements such as the accumulative elements copper, lead, cadmium, mercury, arsenic, fluorine, selenium, molybdenum and vanadium.,

Due to the excessive use of the herbs the individual taken it might be exposed to high intake of the essential metals which could produce toxic effects.

Some of the herbs while taken during pregnancy were said to have caused abortion which might probably be due to the presence of toxic element in it.

Large doses of zinc(one of the mineral elements responsible for sex drive)was reported to result in some health complications such as fatigue and dizziness which are common problems experienced by the users of the herbs for this study.

1.3 Justification

For many years foods were accepted as the source of all the nutrients required to accomplish the physiological functions needed for development, growth, health, and reproduction. But, little or no attention was directed on the effects of nutrients on the development of diseases different than those caused by the nutrient deficiency. Based on the increased knowledge of the biological mechanisms ruling life, as well as the increase in life expectancy and the resultant increased incidence of chronic and degenerative diseases, the concept that increasing the intake of certain nutrients may influence the onset and development of the disease becomes a public concern. Mokdad et al., (2004). Furthermore, the passive acceptance of the concept that “more is better.” has led to unjustified high supplementation with many trace elements Harper (1999). For trace elements, given the absence of metabolization of the metal or non-metal atoms, it is possible to establish clear separations among essentially, health benefits and toxicity.

It has been established fact that over dose or prolonged ingestion of medicinal plants leads to the chronic accumulation of different elements which causes various health problems WHO (1992); Sharma et al., (2009). several authors, reported many studies on the importance of elemental constituents of the herbal drug plants which enhanced the awareness about trace elements in these plants Wong et al., (1993) in China; Sharma et al., (2009) in India; Sheded et al., (2006) in Egypt; Koe and Sari, (2009), Basgel and Erdemoglu, (2006) in Turkey; Ajasa et al., (2004) in Nigeria; Kaniyas and Loukis, (1987) in Greece). Most of these studies concluded that essential metals can also produce toxic effects when the metal intake is in high concentrations, whereas non-essential metals are toxic even in very low concentrations for human health.

In this context, elemental contents of the medicinal plants are very important and need to be screened for their quality control

1.3 Aim and Objectives

The aim of this research work is to determine the concentration of essential and toxic mineral elements in some herbs used by northern Nigerian women as aphrodisiac using instrumental neutron activation analysis (INAA) and x-ray fluorescence spectroscopy (XRF) methods.

The objectives include

- i. Identification and documentation of herbs used by northern Nigerian women as aphrodisiac
- ii. Determination of mineral elements in the herbs
- iii. Determination of the elements responsible for aphrodisiac properties in the herbs.
- iv. Comparison, of the level of concentration of the minerals in the sample with the recommended dietary allowance (RDA) reference level.

1.4 Scope of the Study

- Application of INAA in human nutrition.
- Application of XRF in human nutrition.
- Identification of the herbs.
- Elemental analysis of the herbs
- Classification of the elements into essential and toxic elements.
- Comparison of the data obtain with the RDA reference level to ascertain their harm or usefulness

1.6 Previous Work

Nuclear Analytical techniques such as Instrumental Neutron Activation Analysis (INAA)) have been in use for decades in the identification and monitoring of the

nutrition and health Yeh et al., (1976). The techniques have been used to measure mineral content of foods and diets as well as human tissues such as blood and hair and body composition in relation to the nutritional body status Ferguson et al., (1989), Clement et al., (2004). Results from such measurements could provide scientific basis for food programmes suited to the local needs and conditions. The techniques have been successfully used to determine the influence of dietary trace elements to infectious and chronic diseases.

Fatima I et al., (2011) in their study on Essential and toxic elements in three Pakistan's medicinal plants (*Punica granatum*, *Ziziphus jujuba* and *Piper cubeba*) by INAA. Found that, the studied medicinal herbs are a good source of the essential elements while toxic elements are found in trace amounts

Jackson et al., (2011) in their study on heavy metals in some aphrodisiac herbs sold in Blantyre City by atomic absorption spectroscopy shows that some metals that could be dangerous to human health are present in herbal aphrodisiacs sold in markets around Blantyre city and that the presence of these metals is related to how the aphrodisiacs are stored.

Traditional Chinese medicine, were analysed by Instrumental Neutron Activation Analysis (INAA) at the 15 MW heavy water reactor in China Institute of Atomic Energy (CIAE). The induced activities were counted by a well calibrated low background γ -spectrometer equipped with a high efficiency coaxial high-purity germanium (HPGe) detector. The concentrations of eighteen trace elements (Ca, Fe, Na, Zn, Ba, Rb, Ce, Cr, La, Co, Th, Cs, Sb, Sc, Sm, Hf, Eu and Tb) in the herbs were determined. Fei et al., (2010)

Traditional Indian medicinal herbs, used for strengthening the body immune system, are rich source of many essential nutrient elements in bioavailable form. Instrumental neutron activation analysis (INAA) employing short (5 minutes) and long (14 hours and 3 days) reactor irradiation followed by high resolution gamma-ray spectrometry has been used for the determination of Al, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cu, Eu, Fe, K, La, Mg, Mn, Na, P, Rb, Sb, Sc, Sm, Th, V and Zn in 15 medicinal herbs commonly used in Indian household for treatment of various ailments). . Several herbs are enriched in Ca, Co, Cu, Mg, P, Fe, Mn and Zn, which play a vital role in biochemical and enzymatic processes. Jatamansi, often used as antibacterial, antipyretic and heart tonic is specially enriched in Co, Cr, Cu, Na, Mn, Fe, Rb and Zn. Also Guduchi and Laghu Haritaki are enriched in Ca and Mg, respectively of various herbs. Garg (2007)

Five different brands of Trikatu, (an Ayurvedic formulation of three dried powder spices, ginger, black pepper and pipali in equal proportion) and its three constituents were analysed for 31 elements by instrumental neutron activation analysis (INAA) using 5-minute and 6-hour thermal neutron irradiation followed by high-resolution γ -ray spectrometry. Heavy toxic metals Cd, Ni and Pb determined by atomic absorption spectrometry (AAS) were found below permissible limits. Most elements in different brands vary in a narrow range. Ginger is particularly enriched in Ca, Fe, Mg and Mn whereas black pepper is enriched in Cr, Se, P and Zn. Choudhury et al., (2006)

Several studies on determination of essential and toxic elements in various kind of medicinal herbs using different kind of analytical techniques have been reported however, studies on the active elements responsible for the curative effect of the herbs has not been found. It is the hope of this work to determine active elements in some herbs used by northern Nigerian women as aphrodisiacs.

1.7 limitations of the Study

The major limitation of this study is lack of agreement among the analytical results obtained which is beyond the researcher's control due to the fact that the irradiation of the sample and analysis of the results can only be done by the experts.

CHAPTER TWO

LITERATURE REVIEW

2.1 Theory and Principle of NAA

2.1.1 Neutron Activation Analysis

Instrumental Neutron Activation Analysis is based on the detection and measurements of γ -rays emitted from an element irradiated with neutrons. When a neutron is bombarded to a target the compound nucleus forms an excited state. Then it de-excites instantaneously to a ground state through the emission of prompt γ -rays.

In many cases, the isotope formed is radioactive, and hence decays generally by β -particle emission to another nuclide, which de-excites by emission of one or more delayed γ -rays. The emission of delayed γ -rays is a function of the half-life of the radionuclide, which could range from fractions of a second to several years. All of these γ -rays are characteristic of the radionuclide formed and therefore of the element.

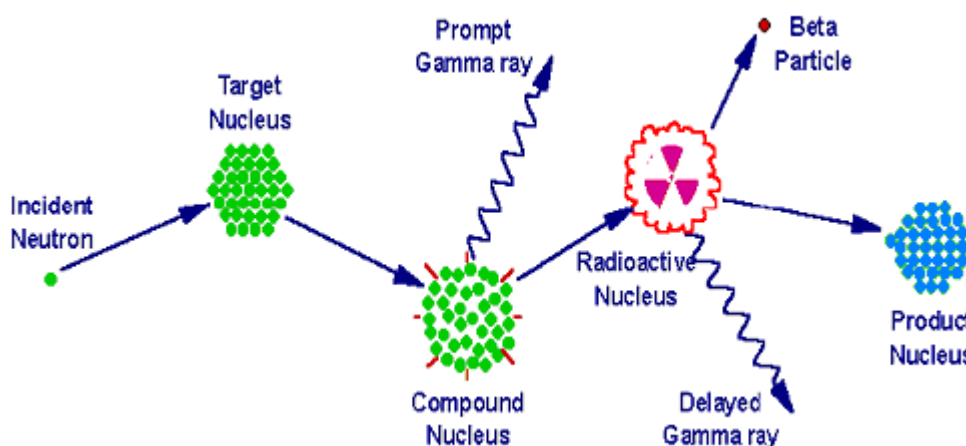


Fig 2.01: The diagram illustrating the process of neutron activation of a target followed by emission of γ -rays (redrawn from web.missouri.edu/~glascockm/naa_over.htm)

The sensitivity of INAA depends on neutron flux, the efficiency of the detector, irradiation time and the neutron cross-section of the elements in the sample.

The irradiation time on the other hand is dependent of the neutron flux and the half life of the isotope of interest. In NAA isotopes with short half live such as ^{66}Cu , ^{27}Mg , ^{56}Mn , ^{80}Br , $^{199\text{m}}\text{Hg}$ and ^{49}Ca are determined by short irradiation, while ^{59}Fe , ^{65}Zn , ^{75}Se are determined by long irradiation and $^{77\text{m}}\text{Se}$ (with the shortest half-life) is normally determined by cyclic NAA.

2.1.2 Neutron capture cross-section (σ (E))

Neutron capture cross-section is defined as the probability that a target will interact with neutron. It describes the apparent reacting area exhibited by individual interacting sites hence it is usually expressed in terms of area (barn), where 1 barn = 10^{-24} cm^2 . Neutron capture cross-sections are function of the energies of incident neutron, target nuclide and reaction channel. Generally, cross-sections of low energy neutron are higher than those for reactions involving high energy neutron, charged particles or photons.

2.1.3 Reaction rate

The neutron energy distribution in a nuclear reactor is a broad spectrum that consists of thermal, epithermal and fast neutrons. Thermal neutrons are low energy neutrons that are at thermal equilibrium with the moderator atoms. Their energy distribution follows the Maxwell-Boltzmann's distribution with a given energy:

$$E = kt \tag{2.1}$$

Where, k = Boltzmann's constant

T = temperature of the neutrons.

At room temperature the thermal neutrons have a velocity of a Maxwellian distribution of 2200 m/s corresponding to energy of about 0.025 eV. A Cd foil of 1 mm thickness

sets the maximum energy for the thermal neutron. The foil acts as a filter through which only neutrons with energies higher than 0.5 eV will pass.

The neutrons with energies above the threshold of 0.5 eV – 1 MeV are classified as the epithermal neutron whilst the fast neutrons have energies up to 14 MeV. The energy distribution for the epithermal neutrons follows $\frac{1}{E}$ slope beginning at the Cd threshold energy to about 1 MeV. In a research reactor the fluxes for epithermal and fast neutron are on the order of 2-3% and 7-10% respectively of the thermal ν neutron flux Glascock (2003).

The cross-section distribution functions for the epithermal neutrons are characterised by a number of resonance peaks (see fig. 2.02). Because of that, the neutron resonance integral (I_0) given by equation 2.2 is used to refer to the epithermal neutron cross-section.

$$I_0 = \int_{E_{cd}}^{1\text{Mev}} \sigma(E) dE/E \quad (2.2)$$

Where σ = neutron capture cross-section.

E = energy of the neutrons.

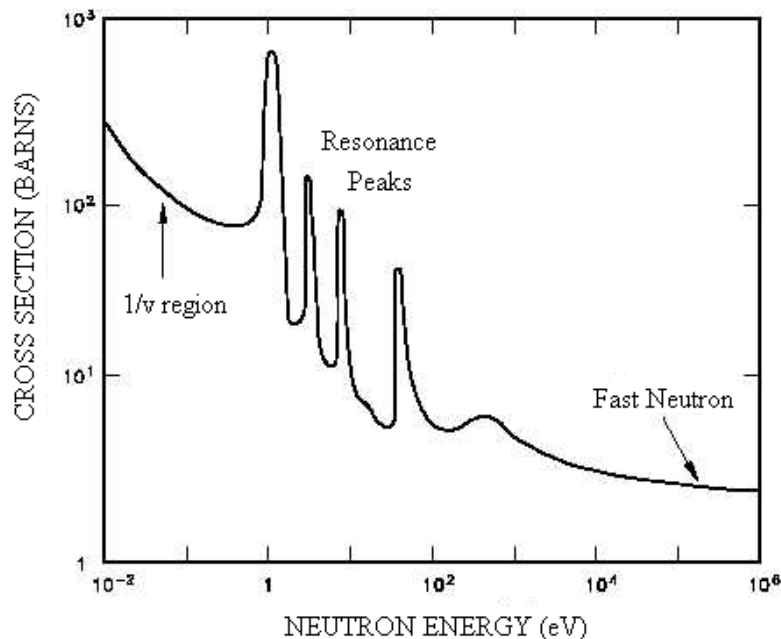


Fig 2.02: Neutron cross section as a function of neutron Energy
http://www.tpub.com/content/doee/h1019v1/css/h1019v1_113.htm

The neutron flux, Φ , (neutron cm⁻²s⁻¹) is defined as the products of the number of neutrons per unit volume and the neutron velocity. The neutron fluxes for each class of neutron (thermal, epithermal and fast) in a reactor may vary depending on the material used to moderate the primary fission neutrons.

Thus the total reaction rate, R , of a particular element in the sample can be calculated from:

$$R = N \int \sigma(E) \Phi(E) dE \quad (2.3)$$

Where R = rate of activation

$$N = \text{total number of target nucleus given by: } N = \frac{N_A \theta_{ms}}{A_w}$$

θ = fractional abundance of target nucleus

σ = cross-section of the activation reaction at energy E

Φ = the flux of neutrons for the energy interval of E and $E + dE$

Equation 2.3 can be separated into three terms according to the classes of neutrons in the reactor:

$$R = R_{th} + R_{Epi} + R_{fast} \quad (2.4)$$

Since both thermal and epithermal neutrons can cause (n, γ) reaction. Hence,

$$R = N \int_0^{E_{cd}} \sigma(E) \Phi(E) dE + N \int_{E_{cd}}^{1\text{mev}} \sigma(E) \Phi(E) dE \quad (2.5)$$

Therefore,

$$R = N(\sigma_{th} \Phi_{th} + I_0 \Phi_{Epi}) \quad (2.6)$$

The resonance integral I_0 contains contributions from the resonance (I_r) as well as $\frac{1}{v}$ part of the distribution

$$I_0 = \frac{1}{v} + I_r \quad (2.7)$$

The $1/v$ contribution depends on the Cd cut off value and was found to be $0.45\sigma_{th}$ for E_{Cd} of 0.5eV De Soete *et al* (1972). Therefore equation (2.4) becomes:

$$R = N(\sigma_{th} \Phi_{th} + \Phi_{Epi} (I_r + 0.45\sigma_{th})) \quad (2.8)$$

2.1.4 The neutron Activation Equation

As explained earlier, neutron activation produces radionuclide by absorption of incident neutrons. The rate of production and hence the growth in activity of the produced isotope is equal to the difference between the rate of formation and the rate of decay. Therefore,

$$\frac{dn}{dt} = R - \lambda n \quad (2.9)$$

Where n = number of isotope produced

R = the reaction rate given by equation (2.8)

λ = the decay constant for the product isotope

2.1.5 Spectral background

The background on which the full energy photopeaks are standing is mainly due to the interaction of γ -rays with the detector the main contribution to the background in INAA is from: Detector Compton scattering. The Compton scattering events in a detector is the main producer of the continuum background in INAA. When a γ -ray of energy between 150 keV – 9 MeV interacts with the Ge detector it may undergo Compton scattering to produce a continuing background at low energies of ≤ 250 keV.

Back scattering the γ -rays before entering a detector might be Compton scattered by the surrounding materials to produce a broad peak of backscattered radiation at low energies. However, Pb shielding of the detector normally reduces this contribution.

Natural radioactivity Contribution from the natural radioactivity decreases with detector shielding.

β - Particles Isotopes produced in the activation of samples usually decay by emission of β - particles which when interacting with surrounding materials emit bremsstrahlung radiation.

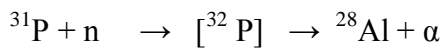
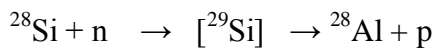
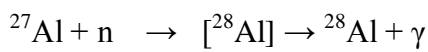
2.1.6 Interference

In INAA for biological samples, there are two main interferences which if not corrected might introduce error to the determined elemental concentrations.

a. Interference from primary reaction

Fast neutrons in a reactor may result into (n, p) and (n, α) reaction that might produce the same isotopes as those produced from (n, γ) reaction of thermal neutron. For example,

^{28}Al may be produced by the following three reactions:



The effect of this type of interference is a function of the relative concentrations of the isotopes in a sample as well as the ratio of fast/thermal flux within the reactor. The primary reaction interference normally occurs when the interfering element has much higher concentration than the measured element.

Since the contribution from the measured element to the produced isotope is negligible, then the contribution of the interfering element is calculated in terms of a ratio. This ratio is used to normalise the concentration of the interfering element in the samples with the two elements.

The difference between the concentration of the measured element and the normalised concentration of the interfering element is the correct value of the measured element.

b. Spectral interference

This takes place when two isotopes emit γ -rays of the same, or nearly the same energy. For instance, both ^{64}Cu and ^{24}Na produce 511 keV peak. Thus this peak produced when a

sample containing the two isotopes is counted will have contributions from both isotopes. Correction for this interference follows the same procedures as those explained for primary reaction interference.

Another example of spectral interference is from unresolved close peak lines. A peak from ^{56}Mn (846.7 keV) may interfere with a peak from ^{27}Mg (843.8 keV) because their energies are too close to be properly resolved by Ge detectors of normal resolution. Since both isotopes produce more than one peak line, to avoid error, other peak lines for each isotope are used even if they have lower intensity than the interfered peaks.

2.1.7 Minimum Detection Limit

In INAA several definitions of MDL have been proposed but the most Common one is that by Currie which can be written as Knoll (2000):

$$\text{MDL} = 4.65\sqrt{B} + 271 \quad (2. 10)$$

MDL in INAA is strongly affected by spectrum continuum background mainly from Compton scattering and β - bremsstrahlung continuum energy which has been explained earlier. In biological samples where elements such as Al, Na, K and Cl occur in percentage levels, high Compton continuum from these elements will raise the MDL of elements such as Br, Mn, Sc, Zn and Cu normally present in minor levels. The background from β - bremsstrahlung does also affect the analysis of minor elements in a sample. As an example, ^{38}Cl emits β - of energy up to 4.9 MeV, which depending on the concentration of Cl in the sample, might decrease the sensitivity for the determination of ^{37}S (3104 keV). Biological samples contain also P (β - emitters) in percentage levels, which result into more background effects on MDL particularly at higher energies.

2.1.8 Detection of γ -rays

The most common detectors used for INAA analysis are the Ge detectors (Ge(Li) or Hyper Pure Ge detector (HPGe)) due to their superior resolution to separate γ -ray lines

of close energies. Samples are placed on a sample holder and positioned at a certain distance from the detector. The optimum sample to detector distance will depend on the activity of the sample. That is, samples are placed at a distance above the detector that will produce low dead time and enough counting statistics within the scheduled collecting time.

A vertical Ge detector is very sensitive to a small change in the counting position. This is because a change in the sample position will alter the solid angle, which in turn will produce a different absolute efficiency of the detector. The same argument applies to the volume of the sample and standard. A small change in volume of the sample, particularly the height, will affect the accuracy of the detection. Because of that, it is crucial for the sample and the standard to be in the same geometry (volume and position). The solid angle and the position of the sample are related by inverse square law:

$$\Omega \propto \frac{1}{r^2} \quad (2.11)$$

2.1.9 NAA methodology

2.1.9.1 Absolute method

This method involves the use of the fundamental equation without using any standard for the determination of elemental concentrations

Hence

it relies on the accuracy of the nuclear data from the literature and the detector efficiency.

mass of the atom in the sample is given as:

$$m_a = \frac{N_c A_w}{N_A P_y \theta \varepsilon \sigma_{th} [\phi_{th} + \phi_{epi} (Q_0 + 0.45)] SDC} \quad (2.12)$$

2.1.9.2 The K_0 method

This is a development of a single-comparator method, in which analysis is performed by irradiating and counting a sample together with a single element (comparator) instead of using standards prepared from known weights of elements to be determined. The K_0 method combines the simplicity of the absolute method with nearly the same accuracy attained in the relative methods. In contrast to the comparative method, k_0 method does not require a large number of standards for the comparisons. The preparation, irradiation and measurement of a large number of standards as that required by comparative method are time consuming and may introduce errors.

According to Simonitis et al. (1980), the specific count rate A_{sp} is given as Simonitis *et al.*, (1980):

$$A_{sp} = \frac{N_c}{SDCma} \quad 2.13$$

Substituting the mass (ma) of the element in a sample given by equation 2.12 in equation 2.13:

$$A_{sp} = \frac{N_A P_Y \theta \varepsilon \sigma_{th} [\Phi_{th} + \Phi_{epi} (Q_0 + 0.45)]}{A_w} \quad 2.14$$

The ratio of the specific count rates of the sample to that of a comparator is

$$K_{sc} = \frac{(A_{sp})_x}{(A_{sp})_y} = \frac{(A_w)_y (P_Y \theta \sigma_0)_x \varepsilon_x}{(A_w)_x (P_Y \theta \sigma_0)_y \varepsilon_y} \left[\frac{\Phi_{th} + \Phi_e (Q_0 + 0.45)_x}{\Phi_{th} + \Phi_e (Q_0 + 0.45)_y} \right] \quad 2.15$$

Multiplying equation 2.15 by $\frac{\Phi_e \Phi_{epi} \Phi_e}{\Phi_e \Phi_{epi} \Phi_e}$ then

$$K_{sc} = \frac{(A_{sp})_x}{(A_{sp})_y} = \frac{(A_w)_y (P_Y \theta \sigma_0)_x \varepsilon_x}{(A_w)_x (P_Y \theta \sigma_0)_y \varepsilon_y} \left[\frac{\Phi_{th}/\Phi_e + (Q_0 + 0.45)_x}{\Phi_{th}/\Phi_e + (Q_0 + 0.45)_y} \right] \quad 2.16$$

$$\text{If we define } K_0 = \frac{(A_w)_y (P_Y \theta \sigma_0)_x}{(A_w)_x (P_Y \theta \sigma_0)_y} \quad 2.17$$

Substituting equation 2.13 and 2.17 in equation 2.16

$$\frac{(N_c)_x(\text{SDCma})_y}{(N_c)_y(\text{SDCma})_x} = K_0 \frac{\varepsilon_x}{\varepsilon_y} \left[\frac{\Phi_{\text{th}}/\Phi_e + (Q_0 + 0.45)_x}{\Phi_{\text{th}}/\Phi_e + (Q_0 + 0.45)_y} \right] \quad 2.18$$

Therefore the ratio of the mass of the element (x) to the mass of the of the comparator element (y) is given by:

$$\frac{(\text{ma})_x}{(\text{ma})_y} = \frac{(\text{SDC})_y [f + (Q_0(\alpha))]_y}{(\text{SDC})_x [f + (Q_0(\alpha))]_x} * \frac{(N_c)_x}{(N_c)_y} * \frac{\varepsilon_y}{\varepsilon_x} * \frac{1}{K_0} \quad 2.19$$

where $f = \frac{\Phi_{\text{th}}}{\Phi_{\text{epi}}} =$ thermal to epithermal neutron ratio.

Since in most cases the epithermal neutron spectra deviates from 1/E law and

Therefore Q_0 has to be corrected for the deviation as:

$$Q_0(\alpha) = \frac{Q_0 - 0.429}{E_r^\alpha} + \frac{0.429}{(2\alpha + 1)E_{\text{Cd}}^\alpha} \quad 2.20$$

Where $Q_0(\alpha) =$ corrected Q_0

$\alpha =$ epithermal shape parameter

$E_r =$ effective resonance energy (eV)

$E_{\text{Cd}} =$ Cd cut-off energy = 0.55 eV

The K_0 and Q_0 values are literature values, which can be taken from the compilation of De Corte and Simonits. These are experimentally determined values obtained from irradiation of known amounts of the elements together with Zr wire or Al alloy of gold foils and are reported with <1% relative error for many γ -ray lines. If the flux characteristics are known to remain constant in sample (sam) and standard (std)

This method has an advantage of eliminating the uncertainties from nuclear data and geometric factors used in the absolute method.

2.1.9.3 Comparative method (relative method)

This involves the irradiation of the unknown sample and a standard containing a known amount of the element of interest under the same conditions. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is:

$$C_{\text{sam}} = C_{\text{std}} \frac{m_{\text{std}} A_{\text{sam}}}{m_{\text{sam}} A_{\text{std}}} \quad 2.21$$

where A = activity of a sample (sam) and standard (std)

m = mass of the element in sample (sam) and standard (std)

C = concentration of the element

2.2 Theory and Principle of XRF

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons emitted from a sample, the elements present may be identified and quantify.

Henry Moseley was perhaps the father of this technique, since he, building on W.C. Roentgen's discovery of the high-energy radiation dubbed X-rays, built an X-ray tube which he used to bombard samples with high-energy electrons. Moseley in 1912 discovered a mathematical relationship between the element's emitted X-ray frequency and its atomic number. In 1925 Coster and Nishina were the first to use primary X-rays instead of electrons to excite a sample. After Glocker and Schreiber were the first to perform quantitative analysis of materials using XRF in 1928, detector technology had to catch up in order to make the technique practical, which didn't begin to happen until the 1940's. The 1950's saw the first commercially produced X-ray spectrometers. In 1970,

the lithium drifted silicon detector was developed, and this technology is still in use today Jenkins (1988)

X-ray fluorescence

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays.

Underlying physics

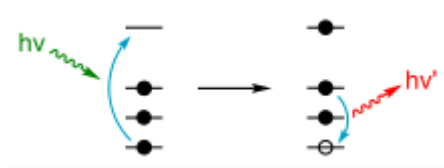


Figure 2.03: Physics of X-ray fluorescence in a schematic representation.

When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionization consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with energy greater than its ionization potential. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way renders the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. Thus, the material emits radiation, which has energy characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy (generally lower).

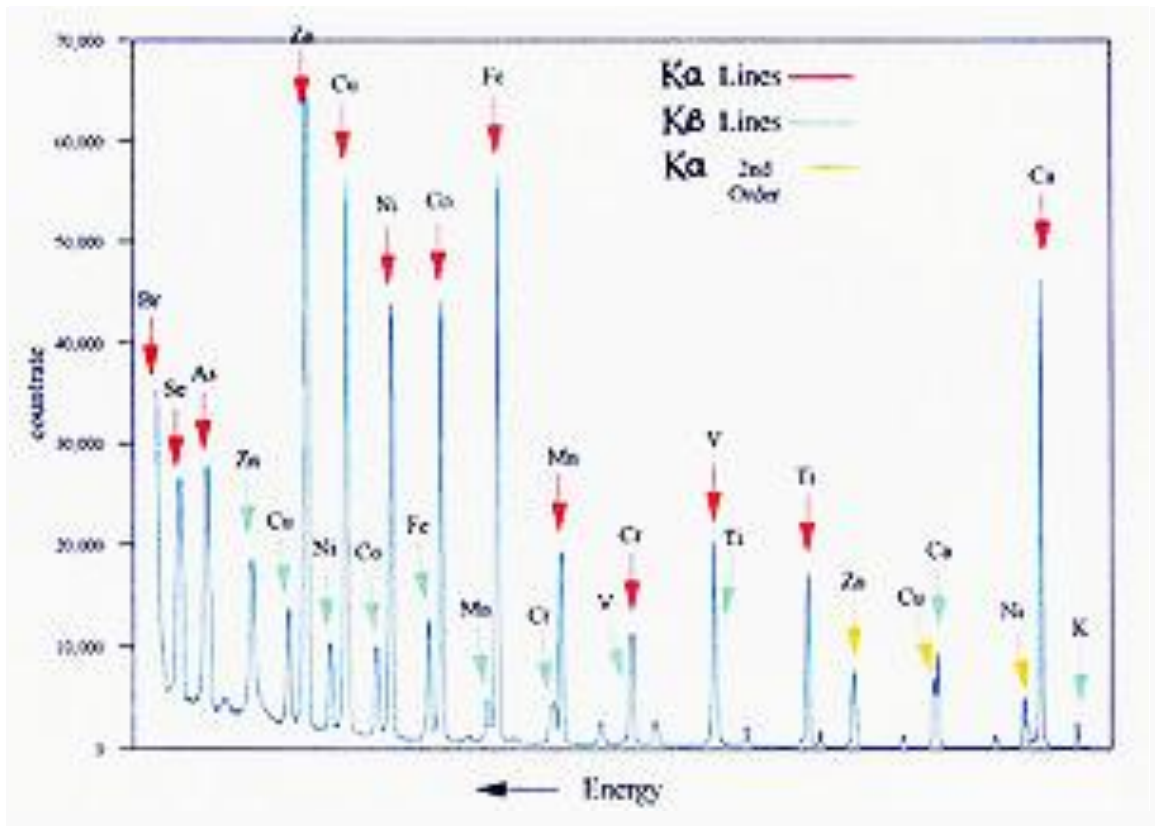


Figure 2.04: Typical energy dispersive XRF spectrum

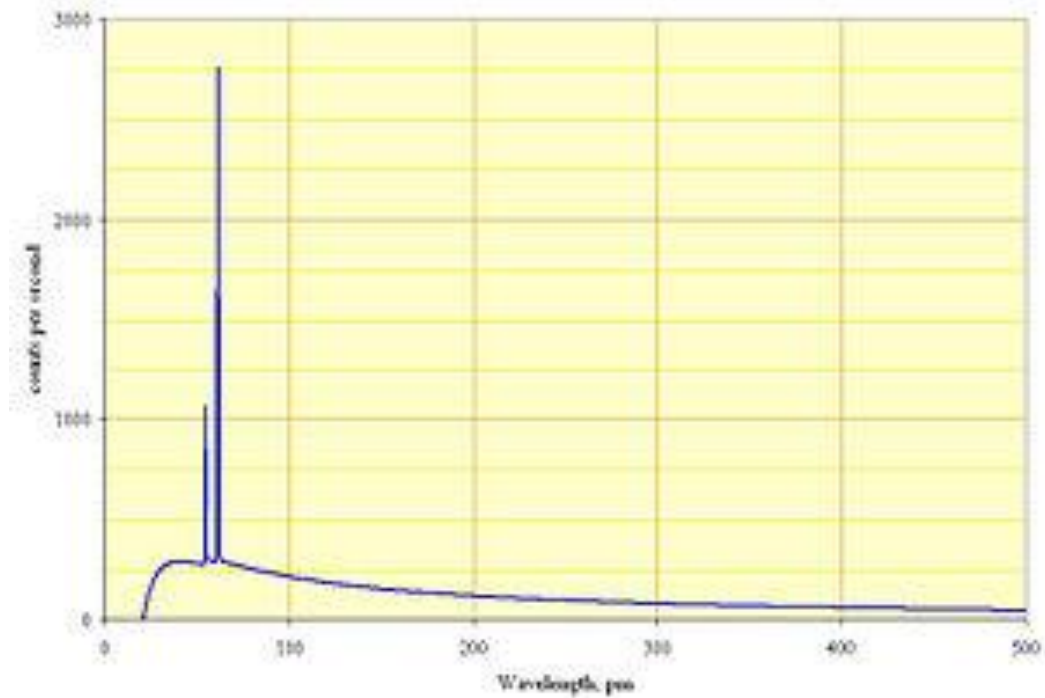


Figure 2.05 : Spectrum of a rhodium target tube operated at 60 kV, showing continuous spectrum and K lines

2.2.1 Characteristic radiation

Each element has electronic orbitals of characteristic energy. Following removal of an inner electron by an energetic photon provided by a primary radiation source, an electron from an outer shell drops into its place. There are a limited number of ways in which this can happen, as shown in Figure 1. The main transitions are given names: an L→K transition is traditionally called $K\alpha$, an M→K transition is called $K\beta$, and an M→L transition is called $L\alpha$, and so on. Each of these transitions yields a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital. The wavelength of this fluorescent radiation can be calculated from Planck's Law:

$$\lambda = h, c / E \quad (2.22)$$

The fluorescent radiation can be analysed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength-dispersive analysis). Once sorted, the intensity of each characteristic radiation is directly related to the amount of each element in the material. Figure 2 shows the typical form of the sharp fluorescent spectral lines obtained in the energy-dispersive method.

2.2.2 Primary radiation

In order to excite the atoms, a source of radiation is required, with sufficient energy to expel tightly held inner electrons. Conventional X-ray generators are most commonly used, because their output can readily be "tuned" for the application, and because higher power can be deployed relative to other techniques. However, gamma ray sources can be used without the need for an elaborate power supply, allowing an easier use in small portable instruments. When the energy source is a synchrotron or the X-rays are focused by an optic like a polycapillary, the X-ray beam can be very small and very intense. As a result, atomic information on the sub-micrometre scale can be obtained. X-ray generators

in the range 20–60 kV are used, which allow excitation of a broad range of atoms. The continuous spectrum consists of "bremsstrahlung" radiation: radiation produced when high-energy electrons passing through the tube are progressively decelerated by the material of the tube anode (the "target"). A typical tube output spectrum is shown in figure 2.05

2.2.3 Dispersion

In energy dispersive analysis, the fluorescent X-rays emitted by the material sample are directed into a solid-state detector which produces a "continuous" distribution of pulses, the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyser (MCA) which produces an accumulating digital spectrum that can be processed to obtain analytical data. In wavelength dispersive analysis, the fluorescent X-rays emitted by the material sample are directed into a diffraction grating monochromator. The diffraction grating used is usually a single crystal. By varying the angle of incidence and take-off on the crystal, a single X-ray wavelength can be selected. The wavelength obtained is given by the Bragg

Equation:

$$n \cdot \lambda = 2d \sin \theta \quad (2.23)$$

where, d is the spacing of atomic layers parallel to the crystal surface.

2.2.4 Detection

In energy dispersive analysis, dispersion and detection are a single operation, as already mentioned above. Proportional counters or various types of solid-state detectors (PIN diode, Si(Li), Ge(Li), Silicon Drift Detector SDD) are used. They all share the same detection principle: An incoming X-ray photon ionises a large number of detector atoms with the amount of charge produced being proportional to the energy of the incoming

photon. The charge is then collected and the process repeats itself for the next photon. Detector speed is obviously critical; as all charge carriers measured have to come from the same photon to measure the photon energy correctly (peak length discrimination is used to eliminate events that seem to have been produced by two X-ray photons arriving almost simultaneously). The spectrum is then built up by dividing the energy spectrum into discrete bins and counting the number of pulses registered within each energy bin. EDXRF detector types vary in resolution, speed and the means of cooling (a low number of free charge carriers is critical in the solid state detectors): proportional counters with resolutions of several hundred electron-volts cover the low end of the performance spectrum, followed by PIN diode detectors, while the Si(Li), Ge(Li) and Silicon Drift Detectors (SDD) occupy the high end of the performance scale.

In wavelength dispersive analysis, the single-wavelength radiation produced by the monochromator is passed into a photomultiplier, a detector similar to a Geiger counter, which counts individual photons as they pass through. The counter is a chamber containing a gas that is ionised by X-ray photons. A central electrode is charged at (typically) +1700 V with respect to the conducting chamber walls, and each photon triggers a pulse-like cascade of current across this field. The signal is amplified and transformed into an accumulating digital count. These counts are then processed to obtain analytical data.

2.2.5 X-ray intensity

The fluorescence process is inefficient, and the secondary radiation is much weaker than the primary beam. Furthermore, the secondary radiation from lighter elements is of relatively low energy (long wavelength) and has low penetrating power, and is severely attenuated if the beam passes through air for any distance. Because of this, for high-

performance analysis, the path from tube to sample to detector is maintained under high vacuum (around 10 Pa residual pressure). This means in practice that most of the working parts of the instrument have to be located in a large vacuum chamber.

2.2.6 XRF methodology

2.2.6.1 Energy dispersive spectrometry

In energy dispersive spectrometers (EDX or EDS), the detector allows the determination of the energy of the photon when it is detected. Detectors historically have been based on silicon semiconductors, in the form of lithium-drifted silicon crystals, or high-purity silicon wafers.

2.2.6.2 Processing

Considerable computer power is dedicated to correcting for pulse-pile up and for extraction of data from poorly resolved spectra. These elaborate correction processes tend to be based on empirical relationships that may change with time, so that continuous vigilance is required in order to obtain chemical data of adequate precision.

2.2.6.3 Wavelength dispersive spectrometry

In wavelength dispersive spectrometers (WDX or WDS), the photons are separated by diffraction on a single crystal before being detected. Although wavelength dispersive spectrometers are occasionally used to scan a wide range of wavelengths, producing a spectrum plot as in EDS, they are usually set up to make measurements only at the wavelength of the emission lines of the elements of interest. This is achieved in two different ways:

"Simultaneous" spectrometers have a number of "channels" dedicated to analysis of a single element, each consisting of a fixed-geometry crystal monochromator, a detector, and processing electronics. This allows a number of elements to be measured simultaneously, and in the case of high-powered instruments, complete high-precision

analyses can be obtained in under 30 s. Another advantage of this arrangement is that the fixed-geometry monochromators have no continuously moving parts, and so are very reliable. Reliability is important in production environments where instruments are expected to work without interruption for months at a time. Disadvantages of simultaneous spectrometers include relatively high cost for complex analyses, since each channel used is expensive. The number of elements that can be measured is limited to 15–20, because of space limitations on the number of monochromators that can be crowded around the fluorescing sample. The need to accommodate multiple monochromators means that a rather open arrangement around the sample is required, leading to relatively long tube-sample-crystal distances, which leads to lower detected intensities and more scattering. The instrument is inflexible, because if a new element is to be measured, a new measurement channel has to be installed.

"Sequential" spectrometers have a single variable-geometry monochromator (but usually with an arrangement for selecting from a choice of crystals), a single detector assembly (but usually with more than one detector arranged in tandem), and a single electronic pack. The instrument is programmed to move through a sequence of wavelengths, in each case selecting the appropriate X-ray tube power, the appropriate crystal, and the appropriate detector arrangement. The length of the measurement program is essentially unlimited, so this arrangement is very flexible. Because there is only one monochromator, the tube-sample-crystal distances can be kept very short, resulting in minimal loss of detected intensity. The obvious disadvantage is relatively long analysis time, particularly when many elements are being analysed, not only because the elements are measured in sequence, but also because a certain amount of time is taken in readjusting the monochromator geometry between measurements. Furthermore, the frenzied activity of the monochromator during an analysis program is a challenge for

mechanical reliability. However, modern sequential instruments can achieve reliability almost as good as that of simultaneous instruments, even in continuous-usage applications.

2.2.6.4 Extracting analytical results

At first sight, the translation of X-ray photon count-rates into elemental concentrations would appear to be straightforward: WDX separates the X-ray lines efficiently, and the rate of generation of secondary photons is proportional to the element concentration. However, the number of photons leaving the sample is also affected by the physical properties of the sample: so-called "matrix effects". These fall broadly into three categories:

- X-ray absorption
- X-ray enhancement
- sample macroscopic effects

All elements absorb X-rays to some extent. Each element has a characteristic absorption spectrum which consists of a "saw-tooth" succession of fringes, each step-change of which has wavelength close to an emission line of the element. Absorption attenuates the secondary X-rays leaving the sample. For example, the mass absorption coefficient of silicon at the wavelength of the aluminium $K\alpha$ line is $50 \text{ m}^2/\text{kg}$, whereas that of iron is $377 \text{ m}^2/\text{kg}$. This means that a given concentration of aluminium in a matrix of iron gives only one seventh of the count rate compared with the same concentration of aluminium in a silicon matrix. Fortunately, mass absorption coefficients are well known and can be calculated. However, to calculate the absorption for a multi-element sample, the composition must be known. For analysis of an unknown sample, an iterative procedure is therefore used. It will be noted that, to derive the mass absorption accurately, data for the concentration of elements not measured by XRF may be needed, and various

strategies are employed to estimate these. As an example, in cement analysis, the concentration of oxygen (which is not measured) is calculated by assuming that all other elements are present as standard oxides.

Enhancement occurs where the secondary X-rays emitted by a heavier element are sufficiently energetic to stimulate additional secondary emission from a lighter element. This phenomenon can also be modelled, and corrections can be made provided that the full matrix composition can be deduced.

Sample macroscopic effects consist of effects of inhomogeneities of the sample, and unrepresentative conditions at its surface. Samples are ideally homogeneous and isotropic, but they often deviate from this ideal. Mixtures of multiple crystalline components in mineral powders can result in absorption effects that deviate from those calculable from theory. When a powder is pressed into a tablet, the finer minerals concentrate at the surface. Spherical grains tend to migrate to the surface more than do angular grains. In machined metals, the softer components of an alloy tend to smear across the surface. Considerable care and ingenuity are required to minimize these effects. Because they are artifacts of the method of sample preparation, these effects cannot be compensated by theoretical corrections, and must be "calibrated in". This means that the calibration materials and the unknowns must be compositionally and mechanically similar, and a given calibration is applicable only to a limited range of materials. Glasses most closely approach the ideal of homogeneity and isotropy, and for accurate work, minerals are usually prepared by dissolving them in a borate glass, and casting them into a flat disc or "bead". Prepared in this form, a virtually universal calibration is applicable.

Further corrections that are often employed include background correction and line overlap correction. The background signal in an XRF spectrum derives primarily from scattering of primary beam photons by the sample surface. Scattering varies with the sample mass absorption, being greatest when mean atomic number is low. When measuring trace amounts of an element, or when measuring on a variable light matrix, background correction becomes necessary. This is really only feasible on a sequential spectrometer. Line overlap is a common problem, bearing in mind that the spectrum of a complex mineral can contain several hundred measurable lines. Sometimes it can be overcome by measuring a less-intense, but overlap-free line, but in certain instances a correction is inevitable. For instance, the $K\alpha$ is the only usable line for measuring sodium, and it overlaps the zinc $L\beta$ (L2-M4) line. Thus zinc, if present, must be analysed in order to properly correct the sodium value.

2.2.7 Sample Analysis for XRF

2.2.7.1 Qualitative analysis in EDXRF

The first step in the analysis is to determine the top positions and area of the line profiles. The positions of the top represent the presence of elements and the area represents intensities of the lines. The qualitative analysis requires net intensities, meaning that the background has to be subtracted from the spectrum.

2.2.7.2 Peak search and peak match.

Peak search and peak match were used to find which elements are present in the sample. Peak search uses a mathematical technique to find the peaks in a spectrum. Peak match determines the element to which the peak profile belongs. This is done by comparing the positions of the peaks to a database holding the positions of all possible lines.

2.3 Some Herbs Used by Northern Nigerian Women as Aphrodisiac

2.3.1 Table of Herbs for the Study

The table 2.4.1 list the samples under study, botanical name, common name, family name, and the part used.

Botanical name	Family name	hausa name	Part use
<i>Euphorbia hirta</i>	Euphorbiaceae	Nonon kurciya	Stem and leave
<i>Abrus precatorious</i>	Legminosae	Idon zakara	Seed
<i>Abrus precatorious</i>	Legminosae	Kagarana	Leave
<i>Desmodium vellutinum</i>	Legminosae	Dankadafi	Leave
<i>Leptadenia hastate</i>	Asclepiadaceae	Yadiya	Leave
<i>Schwenkia Americana</i>	Solanaceae	Minannas	Leave and flowers
<i>Pentadon pentandrus</i>	Rubiaceae	Geron mata	Seed
<i>Evolvulus alsiniodes</i>	Convolvulaceae	Kafi malam	Leave
	Legminosae	Bitu zaizai	Leave
<i>Crotalaria mucronata</i>			
<i>Crotalaria lachnosema</i>	Legminosae	Farar biya rana	Leave

2.3.2 *Euphorbia Hirta*

E. hirta belongs to the plant family Euphorbiaceae and genus Euphorbia. It is a slender-stemmed, annual hairy plant with many branches from the base to top, spreading upto 40 cm in height, reddish or purplish in colours. Leaves are opposite, elliptic - oblong to oblong-lanceolate, acute or sub-acute, dark green above; pale beneath, 1- 2.5 cm long, blotched with purple in the middle, and toothed at the edge. The fruits are yellow, three-celled, hairy, keeled capsules, 1-2 mm in diameter, containing three brown, four-sided, angular, wrinkled seeds. Williams (2002), Prajapati *et al.*,(2003), Kirtikar (2003),The wealth of India (2005).

E. hirta is used in the treatment of gastrointestinal disorders (diarrhea, dysentery, intestinal parasitosis, etc.), bronchial and respiratory diseases (asthma, bronchitis, hay fever, etc.), and in conjunctivitis. Hypotensive and tonic properties are also reported in *E.*

hirta. The aqueous extract exhibits anxiolytic, analgesic, antipyretic, and anti-inflammatory activities. The stem sap is used in the treatment of eyelid styes and a leaf poultice is used on swelling and boils. The wealth of india (2005)

Extracts of *E. hirta* have been found to show anticancer activity. The aqueous extract of the herb strongly reduced the release of prostaglandins I₂, E₂, and, D₂ (the wealth of India 2005). Decoction of dry herbs is used for skin diseases. Decoction of fresh herbs is used as gargle for the treatment of thrush. Root decoction is also beneficial for nursing mothers deficient in milk. Roots are also used for snake bites Williamson (2002).

The powdered *E. hirta* showed a galactogenic activity in guinea pigs before puberty by increasing the development of the mammary glands and induction of secretion. **Blanc *et al.*, (1963)**

E. hirta at a dose of 50 mg/kg reduced the sperm motility and density of cauda epididymal and testis sperm suspension significantly, leading to 100% infertility Mathur *et al.*, (1995).

2.3.3 Abrus precatorius,

A beautiful, much-branched, slender, perennial, deciduous, woody, prickly twining herb with cylindrical, wrinkled stem having smooth textured brown colored bark. Leaves stipulate and pinnately compound, leaflets 7-24 pairs, 0.6-2.5 x 0.4-1.2 cm, turgid, oblong, obtuse, truncate at both ends, appressed hairy. Known commonly as Jequirity, Crab's Eye, Rosary Pea, John Crow Bead, Precatory bean, Indian Licorice, Akar Saga, Giddee Giddee or Jumbie Bead in Trinidad & Tobago, is a slender, perennial climber that twines around trees, shrubs, and hedges. It is a legume with long, pinnate-leafleted leaves. The plant is best known for its seeds, which are used as beads and in percussion instruments, and which are toxic due to the presence of abrin. The plant is native to Indonesia and grows in tropical and subtropical areas of the world

where it has been introduced. It has a tendency to become weedy and invasive where it has been introduced Wikipedia, .(2012)

The seeds are highly toxic due to presence of Abrin, a protein. It may be fatal if eaten. The primary symptoms include nausea, vomiting, severe abdominal pain and diarrhea, burning in throat; later ulcerative lesions of mouth and esophagus Verma et al., (1989); USDA, NRCS, (2001); CES, (2004).

Ingested seeds can affect the gastrointestinal tract, the liver, spleen, kidney, and the lymphatic system. Infusion of seed extracts can cause eye damage, conjunctivitis and even blindness after contact. The major symptoms of poisoning are acute gastroenteritis with nausea, vomiting and diarrhoea leading to dehydration, convulsions, and shock. Dehydration, as well as direct toxicity on the kidneys, could result in oliguria that might progress to death in uraemia William (1999); Inchem, (2004).

Abrin, which consists of abrus agglutinin, and toxic lectins abrin a, b, c and d are the five toxic glycoproteins found in the seeds Budavari, (1989). Abrin is a ribosome - inactivating protein which blocks protein synthesis and is one of the most deadly plant toxins known. The toxin is released only after braking of seeds Tropilab, (2004).

The seeds are considered abortifacient Nath and Sethi, (1992), anodyne, aphrodisiac, antimicrobial, diuretic, emetic, expectorant, emollient, febrifuge, hemostat, laxative, purgative, refrigerant, sedative, vermifuge, antidote and used in various ailments to cure headache, snakebite, blennorrhagia, boil, cancer, cold, colic, conjunctivitis, convulsion, cough, diarrhea, fever, gastritis, gonorrhoea, jaundice, malaria, night-blindness, ophthalmia and rheumatism. The seeds are also used to treat diabetes and chronic nephritis Rain-tree (2004).

Leaves, roots and seeds are used for medicinal purposes. The plant is used in some traditional medicine to treat scratches and sores and wounds caused by dogs, cats and mice. It is also used with other ingredients to treat leucoderma. The leaves are ground with lime and applied on acne sores, boils and abscesses. The plant is also traditionally used to treat tetanus, and to prevent rabies. Various African tribes use powdered seeds as oral contraceptives Anonymous (1976); Nadkarni (1954); Chopra *et al.*, (1956); Chopra (1958) It is an ingredient of product "Tranquil" used in the treatment of stress and anxiety Members.rediff (2004).

2.3.4 Leptadenia hastate

Leptadenia hastata (Pers.) belongs to the family *Asclepiadaceae*, used as food by many African populations (Hutchinson and Dalziel, 1937). It is commonly used as a vegetable and is considered as a famine food due to its high content of valuable nutrients in Niger Freiburger *et al.*, (1998); Sena *et al.*, (1998). It is also used in herbal medicine against milk drying, sex-impotence, trypanosomosis, acute rhinopharyngitis and wounds Neuwinger, (1996); Tamboura *et al.*, (2005). The leaves are often chewed by shepherds against polydipsia and mouth dryness Olivier-Bover (1986). In some part of northern Nigeria, leaves extract is used for the treatment of stomach upset in children Aliero *et al.*, (2001).

Fresh leaves of *Leptadenia hastata* contain per 100 g: water 81 g, energy 226 kJ (54 kcal), protein 4.9 g, fat 0.2 g, carbohydrate 11.3 g, fibre 4.7 g, Ca 417 mg, P 94 mg, Fe 5.4 mg, vitamin A 4915 mg, thiamin 0.25 mg, riboflavin 0.35 mg, niacin 1.9 mg, ascorbic acid 78 mg Leung *et al.*, (1968). The latex contains the triterpene lupeol and derivatives of it, which possess anti-inflammatory activity.

2.3.5 *Schwenkia americana*

Schwenkia americana Linn. (Solanaceae) In Northern it is a common remedy for rheumatic pains and swelling, a decoction is taken internally and also applied locally. The plant is powdered up with natron and butter, shea butter or oil and rubbed on the forehead, limbs etc. If a nursing mother thinks her milk is purging the infant, she takes a decoction with natron and also gives it to the child. In Yoruba communities the plant is a common ingredient in agbo for children in the first and second year, or it is boiled and added to their food Dalziel (1956). In Ghana it is used as a cough medicine for children. A similar use for chest complaints is recorded from Angola. In Southern Nigeria it is used as a fish poison Dalziel (1956).

2.3.6 *Evulvulos Alsiniodes*

E.alsinoides L. (dwarf morning glory) belonging to the family Convolvulaceae is a perennial herb with a small woody and branched rootstock. Its branches are annual, numerous, more than 30 cm long, often prostrate, slender and wiry with long hairs. Leaves are small, entire, elliptic to oblong, obtuse, apiculate, base acute and densely hairy. Petiole is minute or nearly absent. Bracts are linear and persistent. Flowers mostly solitary in upper axils. Corolla blue rotate and broad funnel shaped. Austin (2008)

E. alsinoides L. is used mainly in traditional medicine of East Asia. The plant is used in Ayurveda as a brain tonic in the treatment of neurodegenerative diseases, asthma and amnesia. In Ayurveda, the plant is known as Shankpushpi. As regard to origin, the plant is of controversial in origin. Several plants including *Convolvulus pluricaulis* Linn., *Clitoria ternetae* L. and *Canscora decussata* L. are also used as Shankpushpi. Goyal *et al* (2005); Asolkar *et al* (1992); Shah *et al* (1961). Some traditional uses in Traditional Indian Medicine (TIM) are listed below Goyal *et al* (2005):

1. The whole herb is used medicinally in the form of decoction with cumin and milk in fever, nervous debility, loss of memory and syphilis.
2. Decoction of the drug, with *Ocimum sanctum* is administered in fevers accompanied by indigestion or diarrhoea. Decoction was given in cases of malarial fever.
3. The root is used by the santals, for intermittent childhood fever.
4. The leaves are made into cigarettes and smoked in chronic bronchitis and asthma.
5. The oil promotes the growth of hair.

In Sri Lanka, roots and stem extract of the plant are used to treat dysentery and depression. Leaves are recommended for asthma and mental disturbances Rajaqkaruna, *et al* (2002). Decoction of roots, thrice a day, is consumed in Eastern Ghats of Andhra Pradesh, India for three days for curing cough and cold. Rajaqkaruna *et al.*, (2002) ethnic groups in Southern Western Ghats of India, whole plant of *E. alsinoides* is used for the treatment of venereal diseases. Ayyanar *et al.*, (2005) In Uttara Kannada district of Karnataka, *E. alsinoides* is used as spermopiotic. Hedge *et al.*, (2006) The Valaiyan community of Piranmalai hills, Tamilnadu consumes leaf juice of *E. alsinoides* internally for three days for fever. Sandhya *et al* (2006)

Mohammedan physicians use the plant to strengthen the brain and memory. It is used in the Philippines for certain bowel irregularities. Infusions of roots, stalks and leaves are all used in Nigeria as stomachic. In Kenya (Kwale Province) sores are treated by application of the powdered leaves, and in Tanganyika (Lake Province) the pounded leaves are put onto enlarged glands in the neck. The plant is used to treat depression in Sekenani Valley, Maasai Mara, Kenya.

2.3.7 *Crotalaria Lachnosema* and its Efficacy

Crotalaria Lachnosema. Belong to the family Fabaceae (Leguminosae), subfamily Papilionoideae. It is a woody plant with a height of about 2m high. It is found along forest margin in damp sites Burkill (1995). In a study carried out on the traditional medicinal uses of *Crotalaria* species, *Crotalaria lachnosema* was found to be important in the treatment of scabies. It was also found to be highly sorted after in love matters and acceptance Nuhu *et al.*, (2009). Pyrrolizidine alkaloids, a poisonous compound has been found to be present in *Crotalaria* spp and according to WHO report, many species of the genus have been reported to be toxic with epidemic outbreaks in some part of the world WHO (1988); Arzt and Mount, (1999).

2.3.8 *Desmodium Velutinum* and its Efficacy

Desmodium velutinum is a perennial, erect or semi-erect shrub or sub-shrub, up to 3 m high. Branches often dark red, yellow-brown when young, velutinous and short hooked-hairy. Leaves 1-foliolate, rarely 3-foliolate, ovate, ovate-lanceolate, triangular-ovate, or broadly ovate, 4-20 cm long and 2.5-13 cm wide, chartaceous to coriaceous, upper surface continuously oppressed-pubescent, lower surface densely velutinous. Inflorescence often dense, terminal or auxiliary, racemose or paniculate, 4-20 cm long, with 2-5 flowers at each node; flowers purple to pink. Pods narrowly oblong, 1-2.5 cm long, 2-3 mm wide, with dense yellow straight hairs intermixed with short hooked hairs, 5-7-jointed. Seeds ovate, flat, 1.3-1.6mm x 1.8-2.5mm, yellow when ripe. Depending on the genotype, there are 320,000-830,000 seeds per kg. *Desmodium velutinum* belongs to the botanical family *Fabaceae*. It is a perennial, erect or semi-erect shrub, up to 3m high. The leaves are used for the control of non-specific diarrhoea. About 30 grams of whole leaves may be boiled in about 150-200ml of water and 20-50ml of the extract taken depending on the severity of the diarrhoea. The dose may be taken once but not more

than two doses may be taken in a day. Children may take lower doses. It is also claimed that the water extract of the leaves is used as an aphrodisiac. Akinola, et al., (1991), Schultz-Kraft (1996)

2.4 Reported Minerals that Increases Sex Drive

The body require doses of mineral, to operate at peak health,(likely more than 70 of the 80 naturally occurring stable elements on earth) the following mineral have been observed to have some direct or indirect effect on sexual function; potency; ability and enjoyment; these are Zn,I,Cu,Fe,Se,Mg and Mn. Nutricular (2013).

2.4.1 Boron

Boron can improve the production of oestrogen in menopausal women, and can bring back their sex drive within a few days of treatment. Boron increases the level of natural sex hormones in the body, thereby reducing the need for hormone replacement therapy or other pharmaceutical solutions. Organic facts (2014)

2.4.2 Iodine

Iodine plays an indirect role in healthy sexual performance. Iodine interacts with the protein L-tyrosine to produce thyroxine, the thyroid hormone that regulates body heat and cellular energy production. Nutricular(2013)

2.4.3 Iron

Iron has a role in synthesizing the neurotransmitters which regulate sex drive. Besides joint pain, fatigue, abdominal pain, irregular heartbeat and hair loss, a deficiency in this trace mineral may reduce sex drive.Nutricula (2013)

2.4.4 Magnesium

This is a trace mineral that is important for the production of sex hormones, such as androgen and oestrogen and neurotransmitters that modulate the sex drive.

2.4.5 Manganese

Manganese helps to produce sex hormones and boost sexual energy. It also helps to maintain the overall reproductive health. In women, manganese is particularly important in the production of breast milk and in both males and females, aids in the production of certain sex hormones. a deficiency of of manganese may lead to low sex drive, low sperm count, and even infertility.

2.4.6 Selenium

Selenium is important in the reproduction of humans and has been associated with male and female fertility. In males, Se is found in the two selenoproteins established in mammalian testes and epididymal spermatozoa Bertelsmann *et al.* (2007). The two selenoproteins are phospholipid hydroperoxide glutathione peroxidase (PHGPx) and sperm nuclei glutathione peroxidase (snGPx) are crucial in sperm physiology.

Significant lower concentrations of PHGPx, associated with lower sperm counts and mobility, were observed in infertile males compared to the control. Foresta *et al.*, (2002). The function of snGPx enzyme in male fertility has been associated with its role in chromatin condensation and protection of sperm DNA against oxidative damage Pfeifer *et al.*, (2001). Several animal and human studies have related female miscarriages with the deficiency of Se Barrington *et al.*, (1996) and Rayma *et al.*, (2000).

Barrington *et al.*, (1996) found significantly lower serum Se in women who had either first-trimester or recurrent miscarriage which they suggested to be due to reduced antioxidant protection of cell membranes and DNA caused by low concentrations of Se dependent enzyme GPx.

2.4.7 Zinc

Zinc is required for the production of testosterone. Testosterone has a dramatic effect on sexual desire both in men and women

A deficiency of zinc is associated with numerous sexual problems, including sperm abnormalities and prostate disease. Zinc not only assists testosterone production it also helps to maintain semen volume and adequate levels of testosterone which all add up to a higher sex drive and healthier sperm. Some reports indicate that, impaired sexual function which is common problems of uremic patient may be improved by zinc supplements Shils and Young (1988).

CHAPTER THREE

MATERIAL AND METHODS

3.1 Materials

- Nigerian research reactor 1(NIRR-1)
- high purity germanium detector (HPGe)
- Agate mortar and pestle
- Acetone
- Analytical
- weigh balance
- Standard reference material
- Vial
- Polythene bag
- Spatula and forceps

3.2 Collection of Herbs for the Study

3.2.1 Selection Methodology

Literature search and consultation of the traditional health providers were carried out to find out which plants are used as aphrodisiacs by the northern Nigerian women. Based on this, 10 different samples belonging to 6 families were selected for this study.

3.2.2 Samples Collection

The herbs of interest in this research were collected and identify by the herbarium of the Department of biological science Ahmadu Bello University, Zaria. All the herbs were obtained from and around Zaria local government area, Kaduna state, Nigeria

3.3 Samples Handling and Storage

The samples were sundried and stored in an air tight container until its needed for irradiation

3.4 Sample preparation for INAA

The samples were sundried and then crushed into powder using agate mortar and pestle. The weights of the samples were taken using analytical balance. After weighing, the samples were sealed in a polythene bag for long and short irradiation. The samples for long irradiation were identified with even numbers and those for short irradiation with odd numbers.

3.5 Sample Analysis

3.5.1 Irradiation and counting procedures

In INAA a sample is placed in a reactor that bathes the sample in a flux of Neutrons and the elements within the sample absorb neutrons to form gamma-ray emitting radionuclides. The sample is removed from the reactor and gamma spectrometry is employed to identify the elements present in the sample and to determine their concentrations.

The optimisation of scheme of analysis involving irradiation time, decaying time and counting time depends on the neutron flux, mass of the sample, half-life of the isotope of interest and the efficiency of the detector. To determine as many elements as possible, one has to compromise among the optimal schemes for different elements of similar half-lives.

a. Short irradiation

The samples were irradiated for 5min. the first count was carried out immediately after irradiation and the second count after 1hour.

b. Long Irradiation

For long irradiation, an irradiation time of 1 hour to several hours is suggested for good statistics (Grime 1994). In this work the samples were irradiated for 6 hours. The first count was carried out after 3 days and second count after 7 days.

The concentration level of the elements were calculated by the comparative method of INAA, Quality control was carried out using certified pitch leave (SRM 1547)

3.6 Sample preparation for XRF analysis

The powdered sample is pressed under a very high pressure into tablets. A binding material was added to improve the quality of the tablet. The tablet is then measured and analysed. The binding material has been taken into account during analysis because it does not belong to the original sample. And care were taken that the sample is homogeneous

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

Instrumental neutron activation analysis was used in the determination of active elements in some aphrodisiac herbs found in and around zaria local government area of Kaduna state Nigeria and twenty eight elements(Mg, Al, Cl, Ca, V, Cu, Se, Mn, Sr, Na, K, As, La, Sm, U, Sc, Cr, Fe, Co, Zn, Br, Rb, Sb, Ba, Eu, Yb, Lu, Th) where determined. Table 4.1 shows results for sample A,B,C and D , Table 4.2 shows results for sample E,F,G , and Table 4.3 shows results for sample I and J.

Two set of X-ray flourecence spectroscopy where carried out. The first XRF (XFR 1) was done at Centre for Energy Research & Development, Obafemi Awolowo University,Ile-Ife. X-Ray Fluorescence (XRF) Laboratory. And the second XRF (XRF 2) was done at Lead poisoning centre of excellence,Gusau Zamfara state Nigeria.

XRF has been used as a complementary technique with INAA for this work and a total of ten elements where determined BY XRF 1 (Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn).table 4.5 shows the XFR1 result for samples A,B,C,D and E.,table 4.6 shows the XRF1 result for samples F,G,H,I,and J.and twenty one Elements by XFR 2.(Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Ba Hg, Pb) .table 4.9 show results for samples A,C,D,E,G,I, and J.

TABLE 4.1 : INAA Results For Sample A,B,C and D

ELEMENTS	SAMPLE A (mg/g)	SAMPLE B (mg/g)	SAMPLE C (mg/g)	SAMPLE D (mg/g)
Mg	2490± 192	41785 ± 145	3863 ± 332	2909 ± 248
Al	1507± 17	82 ± 3	877 ± 21	924 ± 18
Cl	3464± 42	229 ± 12	1976 ± 36	334 ± 16
Ca	15090 ± 483	2082 ± 154	8734 ± 402	14620 ± 482
V	3.900± 0.5	BDL	6± 1	BDL
Cu	BDL	BDL	BDL	BDL
Se	BDL	NA	BDL	BDL
Mn	24.3 00 ± 0.200	109 ± 0.3	526± 1	460.7 ± 0.9
Sr	79 ± 7	BDL	BDL	BDL
Na	130 ± 2	47.48 ± 1.14	66 ± 2	78 ± 17
K	24220 ± 388	12270 ± 270	16520 ± 330	18760 ± 356
As	BDL	NA	BDL	BDL
La	4.250 ± 0.060	26 ± 2	7.89 ± 7.11	8.2 ± 0.7
Sm	1.015 ± 0.014	568 ± 58	2.41 ± 0.02	1.890 ± 0.019
U	0.004 ± 0.001	BDL	0.0032 ± 0.001	BDL
Sc	0.244 ± 0.013	BDL	0.14 ± 0.01	17 ± 1
Cr	1.284 ± 0.140	BDL	8.42 ± 0.23	15± 0.27
Fe	1186 ± 81	BDL	1180 ± 84	1515 ± 85
Co	0.04 0± 0.010	BDL	0.32 ± 0.03	31.1 ± 2.3
Zn	32 ± 4	18 ± 3	49.9 ± 3.7	45.4 ± 3
Br	3.15 0± 0.360	43 ± 4	1.76 ± 0.35	4.3 ± 0.4
Rb	39 ± 3	33 ± 3	49.9 ± 3.5	100 ± 4
Sb	BDL	BDL	BDL	BDL
Ba	16.9 00± 3.3	11.2 ± 3.2	36.9 ± 4.1	50± 5
Eu	0.230 ± 0.05	BDL	0.19 ± 0.5	0.24 ± 0.05
Yb	BDL	BDL	0.14 ± 0.03	BDL
Lu	0.24 0± 0.007	BDL	0.024 ± 0.007	0.027± 0.001
Th	0.500 ± 0.030	BDL	0.67 ± 0.03	0.16 7± 0.025

TABLE 4.2: INAA Results For Sample E,F,G and H

ELEMENTS	SAMPLE (mg/g)	E SAMPLE (mg/g)	F SAMPLE (mg/g)	G SAMPLE (mg/g)	H
Mg	4658 ± 536	2750 ± 272	2769 ± 327	2707 ± 322	
Al	879 ± 67	2629 ± 42	3383 ± 34	3694 ± 52	
Cl	23630 ± 118	2012 ± 32	1235 ± 26	2098 ± 34	
Ca	22220 ± 756	7223 ± 383	9430 ± 405	8069 ± 404	
V	BDL	10 ± 1	52 ± 1	11 ± 1	
Cu	BDL	BDL	BDL	BDL	
Se	BDL	BDL	BDL	BDL	
Mn	465 ± 0.9	102.3 ± 0.3	263 ± 0.5	140.1 ± 0.4	
Sr	BDL	BDL	BDL	46 ± 11	
Na	94 ± 2	239 ± 4	52 ± 2	170 ± 4	
K	22490 ± 405	14080 ± 479	12340 ± 481	19190 ± 653	
As	BDL	0.009 ± 0.001	181 ± 1	BDL	
La	9.38 ± 0.08	1.88 ± 0.05	1.74 ± 0.04	12.17 ± 0.11	
Sm	2.726 ± 0.025	0.63 ± 0.01	0.59 ± 0.01	2.84 ± 0.02	
U	BDL	0.005 ± 0.001	0.009 ± 0.001	0.018 ± 0.002	
Sc	14.7 ± 1.4	0.64 ± 0.02	0.82 ± 0.02	0.54 ± 0.02	
Cr	2.35 ± 0.18	0.69 ± 0.14	4.3 ± 0.2	0.51 ± 0.14	
Fe	1146 ± 87	2531 ± 116	10660 ± 181	1904 ± 103	
Co	0.12 ± 0.02	0.36 ± 0.03	0.28 ± 0.03	0.29 ± 0.04	
Zn	45.4 ± 3.7	40 ± 4	BDL	33 ± 3	
Br	21.97 ± 0.79	BDL	6.89 ± 0.76	6.4 ± 1.1	
Rb	167 ± 6	31 ± 3	67 ± 5	76 ± 5	
Sb	BDL	0.016 ± 0.004	BDL	BDL	
Ba	129 ± 6	BDL	BDL	70 ± 6	
Eu	0.35 ± 0.05	0.17 ± 0.04	0.17 ± 0.04	0.19 ± 0.04	
Yb	0.18 ± 0.04	BDL	BDL	0.32 ± 0.06	
Lu	0.0301 ± 0.007	BDL	0.04 ± 0.01	0.064 ± 0.009	
Th	0.105 ± 0.022	0.26 ± 0.02	0.59 ± 0.03	1.37 ± 0.03	

TABLE 4.3 : INAA Results For Sample I and J

ELEMENTS	SAMPLE I (mg/g)	SAMPLE J (mg/g)
Mg	2911 ± 486	1782 ± 219
Al	707 ± 26	3522 ± 35
Cl	707 ± 23	865 ± 23
Ca	3878 ± 283	8914 ± 401
V	BDL	10.2 ± 0.9
Cu	BDL	BDL
Se	BDL	BDL
Mn	527 ± 1	128.5 ± 0.39
Sr	BDL	BDL
Na	83 ± 3	567 ± 6
K	9281 ± 501	10750 ± 548
As	BDL	BDL
La	7.23 ± 0.09	3.62 ± 0.07
Sm	2.58 ± 0.02	1.44 ± 0.02
U	BDL	BDL
Sc	0.100 ± 0.12	0.76 ± 0.02
Cr	13.10 ± 0.26	9.79 ± 0.24
Fe	1406 ± 91	289 ± 11
Co	0.062 ± 0.009	0.32 ± 0.02
Zn	48 ± 4	33 ± 3
Br	3.45 ± 0.04	24 ± 1
Rb	97 ± 4	22 ± 3
Sb	BDL	BDL
Ba	68 ± 5	46 ± 6
Eu	0.28 ± 0.05	0.20 ± 0.05
Yb	0.22 ± 0.06	0.1762 ± 0.041
Lu	0.034 ± 0.007	0.023 ± 0.006
Th	0.45 ± 0.02	0.41 ± 0.02

TABLE 4.4: XRF1 result for sample A,B,C,D and E

Elements	Sample A (mg/g)	Sample B (mg/g)	Sample C (mg/g)	Sample D (mg/g)	Sample E (mg/g)
Cl	NA	NA	NA	NA	579±0
K	21395±1107	21587±1116	22377±1665	20206±591	19294±1188
Ca	6531±343	6589±346	3780±380	8665±226	8433±439
Ti	179±48	206±55	240±87	131±25	171±55
Cr	145±35	150±37	411±89	147±19	249±52
Mn	87±15	88±16	397±49	378±18	223±28
Fe	681±39	687±39	935±67	703±21	685±44
Ni	1593±99	1302±81	2294±159	503±24	1553±104
Cu	67±5	67±5	140±10	22±1	81±6
Zn	147±12	148±12	251±23	70±4	138±13

TABLE 4.6 :XRF1 result for samples F,G,H,I and J

Elements	Sample F (mg/g)	Sample G (mg/g)	Sample H (mg/g)	Sample I (mg/g)	Sample J (mg/g)
Cl	NA	NA	NA	NA	NA
K	19294±1188	16116±01195	22074±1422	19185±634	19213±1340
Ca	8433±439	5743±396	4622±362	8455±242	6488±433
Ti	171±55	570±109	564±95	143±27	798±129
Cr	249±52	454±76	79±25	240±26	342±64
Mn	223±28	338±38	173±28	898±30	219±31
Fe	685±44	5679±100	1917±82	1271±32	1659±77
Ni	1553±104	1576±108	1055±70	489±26	1792±116
Cu	81±6	104±7	94±7	32±2	98±7
Zn	138±13	244±19	247±19	112±6	217±18

NA = Not Analysed

TABLE 4.7: Common elements Analyzed by XRF1 and INAA for samples A,B,C,D and E

Elements	XRF1 Sample (mg/g)	A	INAA Sample (mg/g)	A	XRF1 Sample B(mg/g)	INAA Sample B(mg/g)	XRF1 Sample (mg/g)	C	INAA Sample C(mg/g)	XRF1 Sample (mg/g)	D	INAA Sample D(mg/g)	XRF1 Sample (mg/g)	E	INAA Sample E(mg/g)
Cl	NA		3464±	42	NA	229 ± 12	NA		1976 ± 36	NA		334 ± 16	579±0		23630 ± 118
K	21395±1107		24220 ±388		21587±1116	12270± 270	22377±1665		16520 ±330	20206±591		18760± 356	19294±1188		22490 ± 405
Ca	6531±343		15090 ± 483		6589±346	2082 ± 154	3780±380		8734 ± 402	8665±226		14620 ± 482	8433±439		22220 ± 756
Ti	179±48		ND		206±55	ND	240±87		ND	131±25		ND	171±55		ND
Cr	145±35		1.284 ±		150±37	BDL	411±89		8.42 ± 0.23	147±19		15± 0.27	249±52		2.35 ± 0.18
Mn	87±15		24.3 ±		88±16	109 ± 0.3	397±49		526± 1	378±18		460.7 ± 0.9	223±28		465 ± 0.9
Fe	681±39		1186 ± 81		687±39	BDL	935±67		1180 ±84	703±21		1515 ± 85	685±44		1146 ± 87
Ni	1593±99		ND		1302±81	ND	2294±159		ND	503±24		ND	1553±104		ND
Cu	67±5		BDL		67±5	BDL	140±10		BDL	22±1		BDL	81±6		BDL
Zn	147±12		32 ± 4		148±12	18 ± 3	251±23		49.9 ± 3.7	70±4		45.4 ± 3	138±13		45.4 ± 3.7

NA = Not Analysed

ND = Not Detected

BDL = Below Detection Limit

TABLE 4.8: Common elements Analyzed by XRF1 and INAA for samples F,G,H,I and J

Elements	XRF1 Sample (mg/g)	INAA sample F (mg/g)	XRF1 Sample G (mg/g)	INAA Sample G (mg/g)	XRF1 Sample H (mg/g)	INAA Sample H (mg/g)	XRF1 Sample I (mg/g)	INAA Sample I (mg/g)	XRF Sample J (mg/g)	INAA Sample J (mg/g)
Cl	NA	2012 ± 32	NA	1235 ± 26	NA	2098 ± 34	NA	707 ± 23	NA	865 ± 23
K	19294±1188	14080 ± 479	16116±1195	12340±481	22074±1422	19190 ± 653	19185±634	9281 ± 501	19213±1340	10750 ± 548
Ca	8433±439	7223 ± 383	5743±396	9430 ± 405	4622±362	8069 ± 404	8455±242	3878 ± 283	6488±433	8914 ± 401
Ti	171±55	ND	570±109	ND	564±95	ND	143±27	ND	798±129	ND
Cr	249±52	0.69 ± 0.14	454±76	4.3 ± 0.2	79±25	0.51 ± 0.14	240±26	13.10±0.26	342±64	9.79 ± 0.24
Mn	223±28	102.3 ± 0.3	338±38	263 ± 0.5	17333 ± 3±28	140.1 ± 0.4	898±30	527 ± 1	219±31	128.5 ± 0.39
Fe	685±44	2531 ± 116	5679±100	10660± 181	1917±82	1904 ± 103	1271±32	1406 ± 91	1659±77	289 ± 11
Ni	1553±104	ND	1576±108	ND	1055±70	ND	489±26	ND	1792±116	ND
Cu	81±6	BDL	104±7	BDL	94±7	BDL	32±2	BDL	98±7	BDL
Zn	138±13	40 ± 4	244±19	BDL	247±19		112±6	48 ± 4	217±18	33 ± 3

NA = Not Analysed

ND = Not Detected

BDL = Below Detection Limit

Table 4.9 : XRF2 results for samples A,C,D,E,G, I and J

ELEMENTS	SAMPLE A (mg/g)	SAMPLE C (mg/g)	SAMPLE D (mg/g)	SAMPLE E (mg/g)	SAMPLE G (mg/g)	SAMPLE I (mg/g)	SAMPLE J (mg/g)
Ti	934 ± 114	<LOD ±195	<LOD ± 313	<LOD ± 303	851 ± 95	<LOD ± 240	1083 ± 131
Cr	<LOD ± 47	<LOD ±32	<LOD ± 48	<LOD ± 47	<LOD ± 44	<LOD ± 38	<LOD ± 51
Mn	89 ± 15	1169 ±24	1059 ± 32	1398 ± 35	356 ± 18	548 ± 21	222 ± 20
Fe	9353 ± 99	1717 ±26	3159 ± 50	2067 ± 38	18406 ± 139	1598 ± 30	4616 ± 70
Co	<LOD ± 78	82 ±10	64 ± 18	46 ± 14	<LOD ± 92	43 ± 12	<LOD ± 65
Ni	<LOD ±19	<LOD ±13	26 ± 7	<LOD ± 21	<LOD ± 15	<LOD ± 18	<LOD ± 20
Cu	19 ±5	18 ± 3	15 ± 5	52 ± 5	14 ± 3	<LOD ± 11	<LOD ± 13
Zn	127 ±5	152 ± 4	187 ± 6	128 ± 5	47 ± 3	115 ± 4	55 ± 4
As	<LOD ±5.6	<LOD ± 3.9	<LOD ± 5.9	<LOD ± 5.3	<LOD ± 3.9	<LOD ± 4.9	<LOD ± 5.4
Se	<LOD ±2.6	<LOD ± 1.9	<LOD ± 2.7	<LOD ± 2.6	<LOD ± 2.2	<LOD ± 2.2	<LOD ± 3
Rb	55.4 ±1.7	40.2 ± 1.1	65.8 ± 1.9	125 ± 2	56.9 ± 1.4	71.8 ± 1.7	27 ± 1.5
Sr	327 ±4	320 ± 3	394 ± 5	443 ± 5	146 ± 2	279 ± 3	165 ± 3
Zr	223 ±5	163 ± 3	217 ± 5	130 ± 4	148 ± 3	148 ± 4	173 ± 5
Mo	28 ±3	38 ± 2	32 ± 3	46 ± 3	33 ± 2	34 ± 3	34 ± 4
Ag	<LOD ±26	<LOD ± 19	<LOD ± 26	<LOD ± 25	<LOD ± 21	<LOD ± 23	<LOD ± 29
Cd	<LOD ±31	<LOD ± 22	<LOD ± 31	<LOD ± 30	<LOD ± 25	<LOD ± 27	<LOD ± 34
Sn	<LOD ±49	<LOD ± 35	<LOD ± 50	<LOD ± 48	<LOD ± 40	<LOD ± 43	<LOD ± 53
Sb	<LOD ±55	<LOD ± 39	<LOD ± 56	<LOD ± 53	<LOD ± 44	<LOD ± 48	<LOD ± 58
Ba	<LOD ±338	<LOD ± 226	<LOD ± 356	<LOD ± 339	<LOD ± 286	<LOD ± 269	<LOD ± 377
Hg	<LOD ±5.8	<LOD ± 4.1	<LOD ± 5.5	<LOD ± 5.6	<LOD ± 4.7	<LOD ± 4.4	<LOD ± 6
Pb	32 ± 3	32 ± 2	37 ± 3	30 ± 3	14.8 ± 2	34 ± 3	22 ± 3

• LOD = Lowest Detection

Table 4.10: common elements analysed by XRF1 and XRF2 for samples A,C,D, and E

Elements	SAMPLE A XRF 1(mg/g)	SAMPLE A XRF2(mg/g)	SAMPLE C XRF1(mg/g)	SAMPLE C XRF2(mg/g)	SAMPLE D XRF1(mg/g)	SAMPLE D XRF2(mg/g)	SAMPLE E XRF1(mg/g)	SAMPLE E XRF2(mg/g)
Ti	179 ± 48	934 ± 114	240 ± 87	<LOD ± 195	131 ± 25	<LOD ± 313	798 ± 129	<LOD ± 303
Cr	145 ± 35	<LOD ± 47	411 ± 89	<LOD ± 32	147 ± 19	<LOD ± 48	342 ± 64	<LOD ± 47
Mn	87 ± 15	89 ± 15	397 ± 49	1169 ± 24	378 ± 18	1059 ± 32	219 ± 31	1398 ± 35
Fe	681 ± 39	9353 ± 99	935 ± 67	1717 ± 26	703 ± 21	3159 ± 50	1659 ± 77	2067 ± 38
Ni	1593 ± 99	<LOD ± 19	2294 ± 159	<LOD ± 13	503 ± 24	26 ± 7	1792 ± 116	<LOD ± 21
Cu	67 ± 5	19 ± 5	140 ± 10	18 ± 3	22 ± 1	15 ± 5	98 ± 7	52 ± 5
Zn	147 ± 12	127 ± 5	251 ± 23	152 ± 4	70 ± 4	187 ± 6	217 ± 18	128 ± 5

Table 4.11:common elements analysed by INAA and XRF2 for samples A,C,D and E

Elements	Sample A INAA(mg/g)	Sample A XRF2(mg/ g)	Sample C INAA(m g/g)	Sample C XRF2(mg/g)	Sample D INAA(mg/g)	Sample D XRF2(mg/ g)	Sample E INAA(mg /g)	Sample E XRF2(mg/ g)
Co	0.04±0.01	<LOD±78	0.32±0.03	82±10	31.1±2.3	64±18	0.12±0.02	46±14
Cr	1.2804±0.140	<LOD ±47	8.42±0.23	<LOD ±32	15±0.27	<LOD ±48	2.35±0.18	<LOD ±47
Fe	1186±86	9353±99	1180±84	1717±26	1515±85	3159±50	1146±87	2067±38
Mn	24.3±0.200	89±15	526±1	1167±24	461±0.9	1059±32	465±0.9	1398±35
Rb	39±3	55±1.7	49.9±3.5	40.2±1.1	100±4	65.8±1.9	167±6	125±2
Zn	32±4	127±5	49.9±3.7	152±4	45.4±3	187±6	45.4±3.7	128±5

Table 4.12:common elements analysed by INAA and XRF2 for samples G,I and J

Elements	Sample G INAA(mg/g)	sampleG XRF2(mg/g)	Sample I INAA(mg/g)	Sample I XRF2(mg/g)	Sample J INAA(mg/g)	Sample J XRF(mg/g)
Co	0.28±0.03	<LOD ±92	0.062±0.009	43±12	0.32±0.02	<LOD ±65
Cr	4.3±0.2	<LOD ±44	13.10±0.26	<LOD ±38	9.79±0.24	<LOD ±51
Fe	10660±181	18406±139	1406±91	1598±30	289±11	4616±70
Mn	263±0.5	356±18	527±1	548±21	128±0.39	222±20
Rb	67±5	56.9±1.4	97±4	71.8±1.7	22±3	27±1.5
Zn	BDL	47±3	48±4	115±4	33±3	55±4

Table 4.13: common elements analysed by XRF1 and XRF2 for samples G,I, and J

Elements	SAMPLE G XRF19(mg/g)	SAMPLE G XRF2(mg/g)	SAMPLE I XRF1(mg/g)	SAMPLE I XRF2 (mg/g)	SAMPLE J XRF1(mg/g)	SAMPLE J XRF2(mg/g)
Ti	570 ± 109	851 ± 95	143 ± 27	<LOD ± 240	798 ± 129	1083 ± 131
Cr	454 ± 76	<LOD ± 44	240 ± 26	<LOD ± 38	342 ± 64	<LOD ± 51
Mn	338 ± 38	356 ± 18	898 ± 30	548 ± 21	219 ± 31	222 ± 20
Fe	5679 ± 100	18406 ± 139	1271 ± 32	1598 ± 30	1659 ± 77	4616 ± 70
Ni	1576 ± 108	<LOD ± 15	489 ± 26	<LOD ± 18	1792 ± 116	<LOD ± 20
Cu	104 ± 7	14 ± 3	32 ± 2	<LOD ± 11	98 ± 7	<LOD ± 13
Zn	244 ± 19	47 ± 3	112 ± 6	115 ± 4	217 ± 18	55 ± 4

4.2 Discussion

Mineral element plays a vital role in human life. The most important pathway of minerals to transport into human is from soil to plants and from plants to human. Some elements such as Ca, Mg, Na, K, P, Cl, S, Fe, Zn, Mn, Cu, I, Co, Ni, F, Cr, Mo, Se, Sn, and Si have been reported to be essential for human health Wikipedia (2013). Whereas others such as Al, antimony, As, Ba, Be, Cd, Cr⁶⁺, Pb, Hg, Os, Ti, V, Po, Th, Ra, and U wikipedia (2012). Have been identified as toxic. The rest of the elements are not toxic to human health unless they are present in very high concentration. The present study provide the baseline data for the concentration of (Mg, Al, Cl, Ca, V, Cu, Se, Mn, Sr, Na, K, As, La, Sm, U, Sc, Cr, Fe, Co, Zn, Br, Rb, Sb, Ba, Eu, Yb, Lu, Th). in some aphrodisiac herbs used by northern Nigerian women.

4.2.1 Inaa Result

Among the essential elements detected five (Fe, Mg, Mn, Se, Zn) belongs to the active elements in aphrodisiacs.

The concentration of all the elements were found to be in trace amount in all the samples except Mg, Al, Cl, Ca, Mn, Na, K and Fe. With Ca and K having the highest concentration in all the samples.

Potassium and calcium where not reported to be among the active elements in aphrodisiacs however, they play an indirect role in sexual arousal by causing muscle contraction and relaxation. A study by giuliano et al documented that genital arousal is a neurovascular event that is characterised by increase in genital blood flow and smooth muscle relaxation Munarriz *et al.*, (2003) based on this we can classify calcium and potassium among the aphrodisiacs. The concentration of potassium range from 24220 ± 388 mg/g, to 9281 ± 501 mg/g in *Euphobia hirta* and *Crotalaria mucronata* and that of calcium ranges from 22220 ± 756 mg/g in *leptadania hastatae* to 3878 ± 283 mg/g ppm

in *crotalaria mucronata*. The recommended dietary intake of calcium and potassium were 1000mg/day and 3500mg/day Lentech (2014)

Magnesium is considered a multi-functioning mineral that makes large contribution to health and nutrition. Balanced levels of magnesium also contribute to muscle relaxation which is very vital for sexual arousal. It is also important in the production of sex hormones, such as androgen and oestrogen and neurotransmitters that modulate the sex drive. Raymond (2010). The concentration of magnesium ranges from 4658 ± 536 mg/g in *leptadania hastate* to 1782 ± 219 mg/g in *crotalaria lachnosema*. The recommended daily intake of magnesium was reported to be 350mg/day (Lentech 2014)

Manganese has been reported to help the body use Vitamin C effectively and Vitamin C acts as an antioxidant, It is required for the synthesis of collagen (structured component of blood vessels, tendons and bones) and norepinephrine (a neurotransmitter) and is also known to increase positive response to stress. It participates in the synthesis of the critical hormones that are involved in sex and fertility namely - androgen, estrogen and progesterone. Vitamin C might improve the production of nitric oxide which aids in the increase of blood flow and makes blood vessels stronger. Raymond (2010). In women, manganese is particularly important in the production of breast milk and in both males and females, aides in the production of certain sex hormones Foodpyramid (2013). The concentration of manganese ranges from 572 ± 1 mg/g in *cotalaria mucronata* to 24.3 ± 0.2 mg/g in *euphobia hirta*. The recommended daily intake of manganese was reported to be 350mg/day. Lentech (2014)

The concentration of iron ranges from 10660 ± 181 mg/g in *pentadon pentandrus* to 289 ± 11 mg/g in *cotalaria lachnosema*. As a trace mineral in the body, iron provides the necessary transport means for moving oxygen throughout bodily systems fluidly.

Additionally Iron has a role in synthesizing the neurotransmitters which regulate sex drive Van-stone (2013). Besides joint pain, fatigue, abdominal pain, irregular heartbeat and hair loss, a deficiency in this trace mineral may reduce sex drive. The recommended daily intake of iron was reported to be 15mg/day Lentech (2014)

Zinc is required for the production of testosterone. Testosterone has a dramatic effect on sexual desire both in men and women (Chandra 2012). A deficiency of zinc is associated with numerous sexual problems, including sperm abnormalities and prostate disease. Zinc not only assists testosterone production it also helps to maintain semen volume and adequate levels of testosterone which all add up to a higher sex drive Price (2008). Some reports indicate that, impaired sexual function which is common problems of uremic patient may be improved by zinc supplements Shils and Young (1988). The concentration of zinc in the studied herbs ranges from 49.9 ± 3.7 mg/g in *abrus precatarius* leave to 18 ± 3 mg/g in *abrus precatarius* seed. the recommended daily intake of zinc was reported to be 15mg/day Lentech (2014)

4.2.2 XRF Result

Both XRF 1 and XRF 2 results indicate high concentration of titanium in sample J (*crotalaria lachnosema*). Titanium exposure may be harmful to human brain. Titanium nano particles can enter directly into the hippocampus region of the brain through the nose and olfactory bulb. Research conducted by Escuela Superior de Medicina at Instituto Politécnico Nacional found that titanium dioxide had a toxic effect on glial cells in the brain, suggesting that exposure to titanium dioxide may cause brain injury and be a health hazardmarquez-ramirez *et al.*, (2012). Even though titanium dioxide is permitted as an additive in food and pharmaceutical products, it's also classified as "possible carcinogene to humans" by the International Agency for Research on Cancer and the National Institute for Occupational Safety and Health. Studies show that titanium dioxide

causes adverse effects by producing oxidative stress, resulting in cell damage, redness, and immune response. skocaj *et al.*, (2011)

Nickel plays a major role in helping the body absorb the iron it needs. food-pyramid(2013). Nickel Toxicity is usually not a problem unless several grams are ingested from non-dietary sources, or unless there is a natural tendency to retain too much nickel, which could lead to asthma, angina and/or other Cardiac symptoms as a result of nickel interfering with Vitamin E activity. However, nickel is quite toxic in its gaseous form of nickel carbonyl, and it has the potential to cause cancer of the sinuses, throat and lungs when insoluble nickel compounds are inhaled for long periods of time. This does not apply to soluble nickel compounds such as chloride, nitrate, or sulfate. The concentration of nickel in all the samples is presented in table 4.8 and table 4.9. there is, no recommended dietary allowance for nickel. however the daily intake of nickel should not exceed 1.0mg since beyond this level is toxic Mcgrath and Smith (1990).

Lead was reported to be toxic element for nervous system and kidneys Lozak et al (2002). The concentration of lead ranges from 37mg/g in sampled D (*Desmodium velulinum*) to 15 mg/g in sample G (*Pentadon pentandrus*). WHO (1989) prescribed limits for lead content in herbal medicine to be 10 mg/g while the dietary intake of lead is 3mg/week.

Despite the high concentration of lead in the studied herbs, most of the consumers does not show any adverse effect, this could be associated to the high content of other essential mineral elements (zinc, iron and calcium) in the herbs that were reported to prevent the human system from the effect of lead.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Ten herbs (*Euphobia hirta*, *Abrus precatorius* seeds, *Abrus precatorius* leave, *Desmodium velutinum*, *Shwenkia americana*, *Leptadania hastate*, *Pentadon pentandrus*, *Evolvulus alsinoides*, *Crotalaria mucronata* and *Crotalaria lanchnesoma*). Commonly used by northern Nigerian women as aphrodisiacs, were identified by the herbarium of biological science department, Ahmadu Bello University, Zaria. X-ray fluorescence spectroscopy and Instrumental Neutron Activation Analysis were used in the determination of the active elements that promote sexual arousals in the studied herbs, Twenty-eight elements (Mg, Al, Cl, Ca, V, Cu, Se, Mn, Sr, Na, K, As, La, Sm, U, Sc, Cr, Fe, Co, Zn, Br, Rb, Sb, Ba, Eu, Yb, Lu, Th) were detected by INAA technique. Twelve (12) elements were detected by XRF₂ (Ti, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Mo, Pb) and ten elements by XRF₁ (Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn). Results of this study revealed that Potassium and calcium were found to have the highest concentration in all the studied herbs except *abrus precatorius* seed with magnesium having the highest concentration. The concentration of potassium ranges from $24220 \pm 388 \text{mg/g}$ in *Euphobia hirta* to $9281 \pm 501 \text{mg/g}$ in *crotalaria mucronata*. and that of calcium ranges from $22220 \pm 756 \text{mg/g}$ in *leptadenia hastatae* to $3878 \pm 283 \text{mg/g}$ in *crotalaria lanchnesoma*.

Among the essential elements detected were some of the active elements that promote sexual arousal namely; Fe, Mg, Mn, Se, Zn with the concentration of Fe ranging from $10660 \pm 181 \text{mg/g}$ in *Schwenkia americana* to $289 \pm 11 \text{mg/g}$ in *crotalaria lanchnesoma*, and that of Mg ranges from $41785 \pm 148 \text{mg/g}$ in *Abrus precatorius* (seeds) to $1782 \pm 219 \text{mg/g}$

in *Crotalaria lanchnesoma*, the concentration of Mn ranges from 527 ± 1 mg/g in *Crotalaria mucronata* to 24.3 ± 0.2 mg/g in *Euphobia hirta*.

The concentration of the entire toxic element detected by this work was found to be below the acceptable level of intake except the unusual concentration of arsenic in sample G (*Pentadon pentandrus*) which could be associated to the geochemical of the herb or possible contamination during harvesting and processing. And the concentrations of lead detected by XRF2 which were found to be very high in the seven samples (*Euphobia hirta*, *Abrus precatorius* leaves, *Desmodium vellutinum*, *Leptadenia hastatae*, *Crotalaria mucronata*, and *Crotalaria lanchnesoma*) analysed by XRF2. All the studied herbs were found to be very good source of essentially nutritional Elements.

5.2 Recommendations

Further Studies on the herbs from different geographical location is recommended due to the high concentration of lead indicated by this work.

There is need for pharmacological studies of the herbs in order to provide a dose rate for the herbs.

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