CHAPTER ONE

INTRODUCTION

1.1 ENVIRONMENTAL POLLUTION:

Environmental pollution whether in solid, liquid or gaseous form is causing adverse effects on the behavior and life of mankind and considerably damaging the animal and plant life.

The primary sources of these pollutants are garbage's, trash, raw sewage, chemical effluents of the industries and emission of irritant and harmful gases from various sources.

Chemicals contamination in human diet has been an international issue that needs more sophisticated strategies to face it.

Before industrial revolution, there has been a dramatic increasing in population numbers over the world, which counters parting with a decrease in food production.

This situation require more production techniques in order to face the existing demands, consequently it leads to use chemicals such as pesticides or may grow plants in a contaminated areas such as heavy metals to ensure a sustainable supply for their demands and therefore it causes food pollution [1].

Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, vitamins, minerals as well as trace elements.

The contamination of vegetables with heavy metals due to soil and atmospheric contamination poses a threat to its quality and safety.

High concentrations of heavy metals (Cu, Cd and Pb) in fruits and vegetables were related to high prevalence of upper gastrointestinal cancer [2].

Contamination of vegetables with heavy metal may be due to irrigation with contaminated water, the addition of fertilizers and metal-based pesticides,

industrial emissions, transportation, the harvesting process, storage or at the point of sale.

It is well known that plants take up metals by absorbing them from contaminated soil as well as from deposits on parts of the plants exposed to the air from polluted environments [3,4].

Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes, etc [5].

Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides [6].

Vegetables are vital to human diet as they contain essential nutrients such as carbohydrate, proteins, vitamins and trace elements which are vital to human existence as a result of their role in metabolism [7].

Vegetables are common diet taken by various populations throughout the world due to their richness in vitamins, minerals, fibers and anti oxidative effects. However, leafy vegetables such as Mallow and Cress are said to be good absorber of heavy metals from the soil [8,9].

Vegetables take up metals from contaminated soil through the crop roots and incorporate them into the edible part of plant tissues or as a deposit on the surface of vegetables [10,11].

Vegetables also act as buffering agents for acidic substances obtained during the digestion process.

However, these plants may contain both essential and toxic elements, such as heavy metals, at a wide range of concentrations [12].

Heavy metals are the most hazardous pollutants due to the spread of their dissemination in biosphere and their accumulative concentration.

They permeate the environment by various means, penetrate the circle of metabolism, become toxic and disturb physiological function of organisms [13].

The uptake of metals from the soil depends on different factors, such as their soluble content in it, soil pH, plant species, fertilizers, and soil type [14].

Roots and leaves of herbaceous plants retain higher concentration of heavy metal than stems and fruits [15].

Metals-accumulating plants are directly or indirectly responsible for much of the dietary uptake of toxic heavy metals by humans and other animals [16].

While some heavy metals are essential, excessive accumulation in living organisms is toxic.

All heavy metals at high concentrations have strong toxic effects and regarded as environmental pollutants [17,18].

Heavy metals such as Cr, Mn, Zn, Cu, and Fe are considered essential components of biological activities in the body, however, in excess are reported to cause problem to human [19].

On the other hand, Pb, Cd, and As have no important functions in human body rather play toxic role to living organism, hence are considered as toxic elements [19].

Heavy metal accumulation in agricultural soils cannot only lead to the disorder of soil function which in turn affects crop growth, but heavy metals can be transferred to crops thus posing a risk to human health [20,21].

Generally, the natural concentration of heavy metals in agricultural soils, derived from soil parent materials, is not sufficiently high to harm human health.

However, anthropogenic sources such as mining, smelting, waste disposal, urban effluent, vehicle exhausts, sewage sludge, and agrochemical can greatly increase heavy metal concentrations in agricultural soil [22,23].

1.2 Toxic effects:

Heavy metal they linked mind people they are toxic this conclusion based on scientific evidence.

Two facts should be kept in mind:

1. The effect of any substance on a living system is always dependent on the concentration of it available to cells.
2. This element several metal ions are crucial to the metabolism of cells at low concentrations but are toxic at high concentration this element called trace element.

1.2.1 Lead:

Lead is one of limited class of element that can be describe as purely a toxic Classification of some metals and metalloids according to covalent index it widespread use has caused extensive environmental contamination and health problems in many parts of the world.

Lead is a cumulative toxicant that affects multiple body systems .it's found in low level in earths curst and result of human activity [24].

And they has no known level beneficial effect in body, to studies on toxicity, lead grouped into three board categories:

1. Occupational and population to exposed the exposure level.
2. Epidemiological studies in the general population.
3. Animal studies investigation of mechanism of toxicity and they found that no evidence threshold to exposure Lead can get into your body when you breathe lead contaminated air [25].

Once in your lungs, the lead gets into your blood and travels to other parts of your body and is stored up in your bones.

They effect in body system by Encephalic apathies in the central nervous system (CNS), effect of IQ of children and behavior.

Abortion and preterm delivery in women and alterations in sperm and decreased fertility in men [26].

1.2.2 Zinc:

Zinc is an essential for the human nutrient, a cofactor for over more than 300 enzymes, and is found in all tissues, a list of key enzymes containing zinc or affected by zinc status are provided [27].

Zinc has three functions in these metal enzymes:

1. Participation in catalytic functions.
2. Maintenance of structural stability.
3. Regulatory functions Zinc is also involved in DNA and ribonucleic acid (RNA) synthesis and cell proliferation anhydrate.

The body contains (1.5 - 2.5grams) of Zinc Deficiency of this level affects reproduction adversely in both males and females since all the hormones and a wide range of enzymes involved in reproduction are sensitive to zinc stress, zinc fingers exercise significant controls on the biological effects of estrogens and androgens elements of the DNA that turn on the genes active in protein synthesis during early pregnancy, Anemia a Night blindness excess of this level is toxic and effect Acute gastrointestinal distress, Nausea and Cramping - Large amount of zinc intake reduces copper and iron utilization and vitamin A [28].

1.2.3 Copper:

Copper is critical for energy production in the cells. It is also involved in nerve conduction, connective tissue, the cardiovascular system and the immune system.

Copper is closely related to estrogen metabolism, and is required for women's fertility and to maintain pregnancy. Normal Values of Cu in Serum = 12 - 26 μ mol/L and Urine = 0.05 - 0.55 μ mol/da Deficiency of copper effect upon thyroid function caused Vascular lesions Central nervous system disorder and convulsion, Hair abnormalities [29] hyper-Copper caused Decreased hemoglobin and erythrocyte levels ,Death and Cancer [30].

1.2.4 Manganese:

Manganese is a component of the antioxidant enzyme superoxide dismutase (SOD) which is present in all aerobic cells, where it is required for the detoxification of oxygen metabolites.

Manganese is also a cofactor for the enzymes hexokinase, pyruvate carboxylase, PEP carboxylase, glutamine synthetase, and xanthine oxidase (among others).

It is required for the action of vitamin B1 (thiamine) and for normal brain function (due to its role as an activator of brain enzymes); manganese deficiency can be associated with epilepsy [31,32].

Mn is also required for bone and cartilage formation; low levels are often associate with joint surface diseases, e.g. arthritis [33,34].

1.3 HEAVY METALS IN PLANT:

Until 1920 it was believed that the total nutrient requirement of plants were fully satisfied by ten essential element : the seven inorganic elements (N, S, P, k, Ca, Na, and Fe) supplied by the cultural solution as salts plus carbon (C) from carbon dioxide and hydrogen (H) and oxygen (O) from water. Recent knowledge has revealed that plants require at least seven other elements in trace amounts (B, Cu, Cl, Mn, Mo, Na, and Zn).

The ultimate source of trace elements in the soil [35].

1.4 RESEARCH PROBLEM:

Some agricultural fields in Khartoum state use the fertilizer increase soil fertility and pesticides to improve the productivity of vegetables. Some of the near agricultural fields of highways to send the petition to cars from fuel combustion residues that due to contamination with heavy metals as a result of accumulation in the soil and vegetables.

In this study, we address through the analyze and compare whether there are side effects from the use of these reasons, using X-ray Fluorescence (XRF) technique and Flame Atomic Absorption Spectrometer (AAS) technique.

1.5 OBJECTIVES OF STUDY :

1. Estimation of the level of (Mn, Cu, Pb and Zn) in some vegetables and soils in the area of study by two techniques (XRF and AAS).
2. These mean concentrations should be compared to the recommended Values (IAEA-SOIL-7) and (IAEA-V-10).
3. Compare the ratio of the concentrations with various spectroscopic measurement techniques and interpretation of the differences.
4. Comparison between mean concentration of heavy metals in vegetables and soils measured by (XRF and AAS techniques)
5. Correlate the heavy metal levels in some vegetables with soils.

1.6 MATERIALS AND METHODS :

1. Prepare 8 samples of Onion, 8 samples of Mellow, 8 samples of Cress, 8 samples of marrow, 8 samples of cucumber and 40 samples of soils.
2. Use XRF to measure the concentration of heavy metals in Samples.
3. Use AAS to measure the concentration of heavy metals in Samples.
4. Use T-Test program to compare between results concentration of heavy metals measured by EDXRF and FAAS techniques.
5. Use correlation analysis to estimated heavy metals levels in some vegetables and soils.

1.7 THESIS OUT LINE :

The thesis consists of five chapters, chapter one is the introduction chapter two is devoted for theoretical background.

The chapter three is literature review, while materials and methods are in chapter four, Results and discussions are in chapter five.

CHAPTER TWO

THEORETICAL BACKGROUND

2.1 INTRODUCTION:

Many useful techniques can be used for environmental pollution.

The techniques are based on detection of toxic elements is presents in environmental. These techniques include spectral techniques like energy directive x-rays fluorescence or flame atomic absorption spectrophotometer techniques.

2.2 X-RAY SPRCTROMETRY:

X-ray spectrometry (i.e, x-ray fluorescence) is an emission spectroscopic technique that has found wide utility in many fields which require elemental identification and determination.

The technique depends upon the emission of characteristic x-ray radiation, usually in the 1-60 keV range following excitation of atomic electron energy levels by an external energy source such as charged particle, x-ray beam or δ-rays.

X- rays were discovered by Rontgen in 1895. It was H.G.J. Mosley who developed the relationship between atomic structure and x-ray emission and in 1913 published the first paper on x-ray spectrometry [36].

Fluorescence or the generation of secondary radiation is accomplished by a two – step process. In the first step, a high energy particle such as photon, a proton or an electron strikes an atom and knocks out an inner-shell electron (photoelectric effect).

The second step is readjustment in the atom almost immediately (10^{-12}_$10^{-14}s$) by filling the inner-shell vacancy with one of the outer shell electrons and simultaneous emission of an x-ray photon. The first step uses up the energy of the incident quantum, and in the second step energy is emitted as the characteristic x-ray photon. The incident quantum may have an energy greater than the binding

energy of the inner-shell electron, the excess energy is carried a way as kinetic energy of the electron being removed.

The energy released by the replacement of the inner electron by one of the outer-shell electrons corresponds exactly to the difference in energy between two levels [37].

Such as:

$$E_{x-ray} = Q_f + Q_i \qquad (2.1)$$

Where Q_f and Q_i are the energy of the electron in electronic states within the final shell that drops to the initial shell.

Fluorescence radiation is therefore of lower frequency than that of the absorbed radiation.

The probability for the photoelectric effect to occur is dependent on energy (approximately Z^{-3}) and for the atomic number Z ($\approx Z^4$) . This probability shows specific discontinuities called absorption edges.

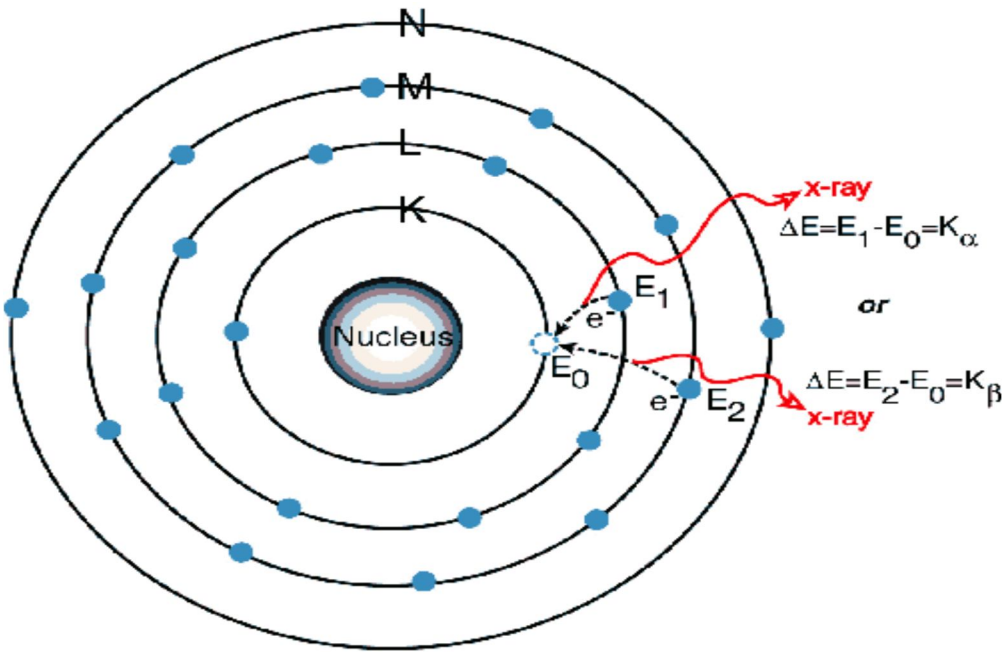


Fig (2.1): Shows the X-Ray Fluorescence Process Example: Titanium Atom

The maximum probability for the photoelectric effect occurs when the photon energy is just above this critical energy. This fact dictates one of the important

considerations in XRF, in order to obtain maximum analytical efficiency for a given element [37].

The development of routine instrumentation, leading to the x-ray spectrometer known today, took place over the following decades after Moseley experiments.

2.2.1 Moseley's law:

In 1914 Moseley measured the frequency ν of the characteristic x-ray from many metals, for a particular type of emitted x-ray such as k_α, the frequency varied in a regular way with the atomic number of the metal, see Fig (2.2). Moseley therefore gave an empirical relation, known as Moseley's law :

$$\nu = a(Z - b)^2 \qquad (2.2)$$

Where a, b are constants. Since the regularity of the graph was so marked, Moseley predicted the discovery of elements with atomic numbers 43, 61, 72, and 75, which were missing from the graph at that time, These were later discovered. He also found that though the atomic weights of iron, nickel and cobalt increased in this order, their positions from the graph were:

iron (Z = 26), cobalt (Z= 27), and nickel (Z =28).

The chemical properties of the three elements agree with the order by atomic number and not by atomic weight. Rutherford's experiments on the scattering of α-particles had shown that the atom contained a central nucleus of charge +Ze where Z is the atomic number, and Moseley's experiments confirmed the importance of Z in atomic theory [38].

2.2.2 Characteristic X-Rays:

The production of characteristic x-ray occurs in atoms that have electron vacancies in their inner shell electron structure In the process of filling these inner shells by electrons dropping in from outer orbits. There is a release of electromagnetic energy in the x-ray region. The characteristic x ray energy is determined by the energy shell difference; electrons filling in the k shell are more

energetic than those that fill an L shell because of the proximity to the nucleus and the higher binding energy [39].

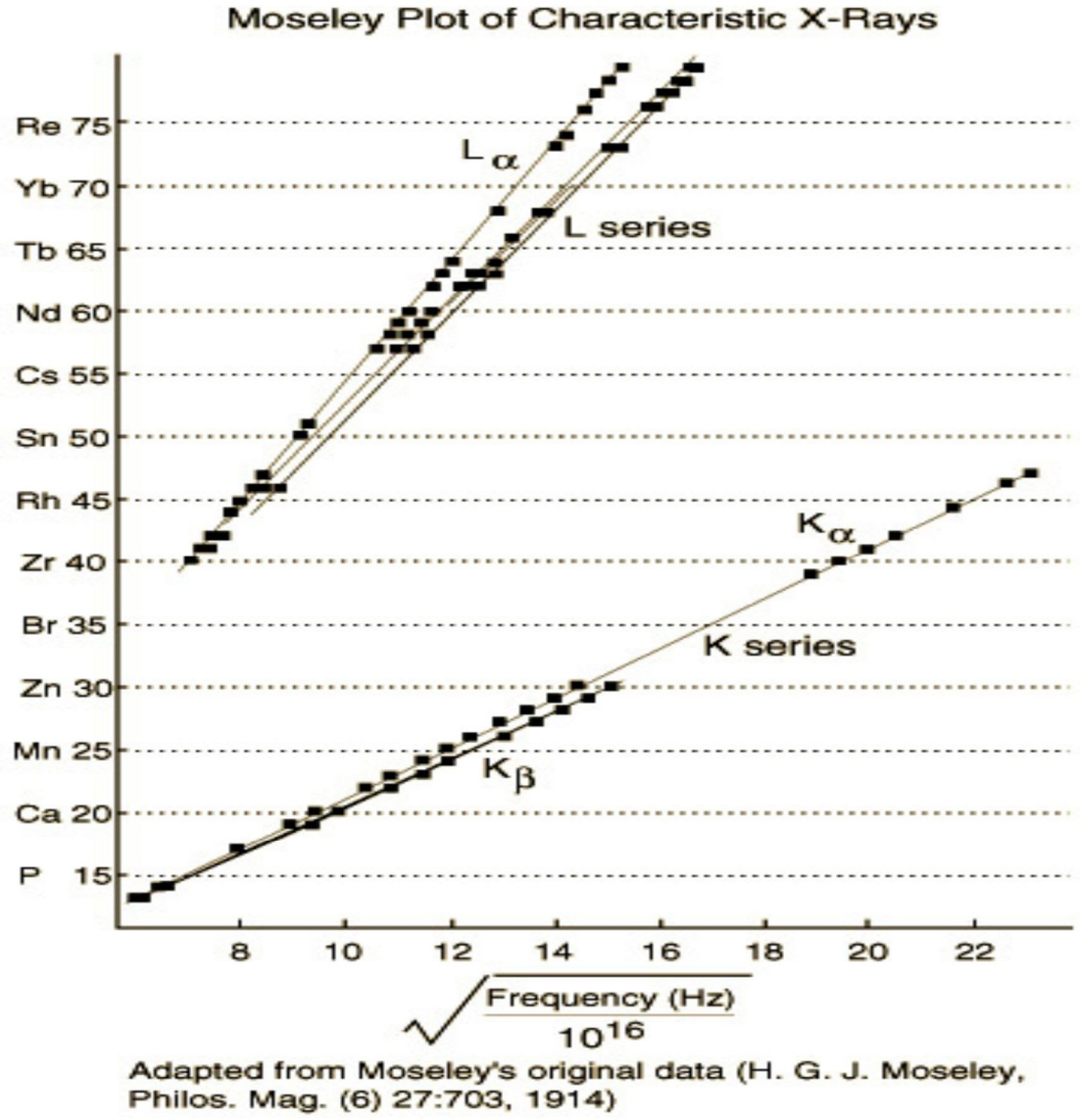


Fig (2.2): Relationship between atomic number & square root of frequency

2.2.3 Selection Rules:

As in all forms of spectroscopy, transitions are governed by quantum mechanical selection rules. Some transition are allowed by these rules while others are forbidden.

X-ray emissions lines from electron transition terminating in the K shell are called K lines .lines from transitions terminating in the L shell are called L lines.

There are three L levels differing by a small amount of energy and five M levels. These sublevels are different quantum states. An electron that drops from an L shell sublevel to the K shell emits a photon with the energy difference between this quantum state.

This transition results in a K_α line.

The K_β x-ray is produced from a transition of an electron from the M to a K shell, etc. Since within the shells there are multiple orbits of higher and lower binding energy electrons, a further designation is made as α_1, α_2 or β_1, β_2, etc. to denote transitions of electrons from these orbits into [40].

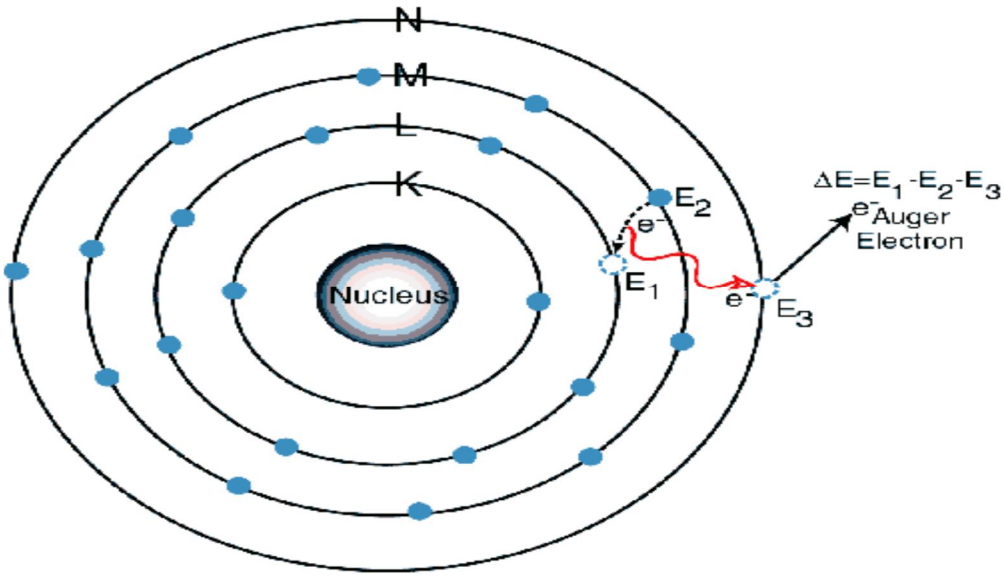


Fig (2.3): Shows the Auger electrons

2.2.4 Properties of X-Rays:

X-ray phenomena of particular significance in x-ray spectro-chemical analysis include :

2.2.4.1 X-ray Absorption:

X-rays impinging upon a target undergo interactions with the elements of the target which are of prime concern to the x-ray spectroscopic.

These processes are absorption and scatter.

Absorption of the radiation may occur by specific interactions which are of importance in sample excitation process in x-ray spectrometers, or it may occur by

more general interactions which have important influences on the emitted x-ray intensity from the sample.

Scatter of x-rays leads to background intensity in the absorbed spectra.

When an x-ray beam passes through a material.

The photons may interact with electrons in the orbits of the target elements in rather specific ways resulting in attenuation of the intensity of the x-ray beam.

The interaction may result in photoelectric ejection of electrons, or scatter of the x-ray beam, the overall result is frequently described in terms of an exponential decrease in intensity with the path length of the absorbing material.

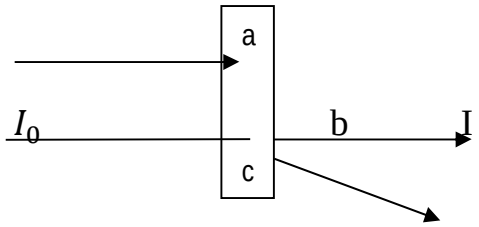
Figure (2.4) below illustrates a perfectly collimated, monochromatic radiation beam of intensity I_0which is incident on an absorber having length of *t* cm and density ρ (g/cm^3).

The incident beam may undergo absorption, transmission or scatter.

The emergent collinear beam consists of the transmitted rays and has intensity given by the Beer-Lambart's law [41].

Where:

$$I = I_0 \exp(-\mu t) \qquad (2.3)$$



a-photoelectric b-transmission c-scatter

Fig (2.4): Schematic representation of attenuation.

$\mu(cm^{-1})$is the linear absorption co-efficient of the absorber.

The negative sign indicates that the intensity always decreases, that is x-rays always undergo attenuation on passing through matter.

In terms of mass absorption coefficient the equation becomes :-

$$I = I_0 exp\left[-\left(\mu/\rho\right)\rho t\right] \qquad (2.4)$$

Where $[\mu/\rho]$ is the mass absorption coefficient $[cm^2/g]$ of the absorber and pt is the area density in $[g/cm^2]$.

The mass absorption coefficient is related to the probability that radiation will interact with matter.

It's an atomic property of chemical elements and is a measure of their x-ray "stopping power".

It is a function only of wavelength, atomic number and is independent of the chemical combination or physical aggregation.

X-ray absorption can also be expressed by use of the concept of cross-section. This is a measure of the probability for those interactions to occur in a material. It exhibits a characteristic dependence on the energy, as well as on the atomic number of the atom in which the interaction takes place.

If equation (2.3) is written in terms of numbers of x-ray photons incident upon n_0 and transmitted by n, an absorber of thickness / cm and linear absorption coefficient μcm^{-1}, one gets.

$$n = n_0 \exp(-\mu t) \qquad (2.5)$$

If the volume of the absorber traversed by the x-ray beam contains n_{at} atoms/cm1, each of which presents an imaginary target area or cross-section σcm^2 to the photons,

$$\mu = n_{at}\sigma or \sigma = \mu/n_{at} \qquad (2.6)$$

then cross-section and mass absorption coefficient are related as follows [6]:

$$\mu/\rho = \sigma(N/A) \qquad (2.7)$$

Where: N is the Avogadro number, A is the Atomic Weight

The fundamental unit of atomic cross-section is the barn $(1\ barn = 10^{24} cm^2)$ and mass absorption coefficients are often tabulated as barns per atom.

The linear absorption coefficient and therefore the mass absorption coefficient gives a measure of the total absorption of the radiation which passes through the material, regardless of the mode of interaction, hence

$$\mu = \tau + \sigma + \pi \quad (2.8)$$

$$\mu/\rho = (\tau/\rho) + (\sigma/\rho) + (\pi/\rho) \quad (2.9)$$

Where τ, σ and π represent losses by photoelectric absorption , scatter and pair production [41].

2.2.4.2 Photoelectric Effect:

This is one of the processes leading to absorption of x-rays as they pass through matter.

lt involves the ejection of electrons from the orbital's of elements in the x-ray target.

This process is a major contributor to the absorption of the x-rays, and is the mode of excitation of the x-ray spectra emitted by elements in samples.

Primarily as a result of the photoelectric process, the mass absorption coefficient decreases steadily with increasing energy of the incident x-ray radiation, leading to sharp discontinuities in the absorption versus energy curve for a given element. These results from characteristic energies at which the photoelectric process is especially efficient. Energies at these discontinuities are called absorption edges [41,42] .

In an atom, the innermost electrons are bound most tightly while the outer electrons are only loosely bound. The more loosely bound an electron is, the lower the exciting radiation energy needed to eject it (i.e, absorption edge).

For example, in an atom the closer lo the nucleus an electron is, the higher the incident radiation energy needed to eject it.

Hence the wavelength of an x-ray beam needed to eject an L-shell electron is longer (less energy) than that which is needed to eject an electron from K-shell.

On photo ejection of an electron, unstable states in the electron orbital's of atoms are created. Once the vacancies in the inner orbital's are formed, the excited state relaxes by filling the vacancy with an electron from an outer orbital which results

in the emission of characteristic secondary radiation. Only certain transitions are allowed because of quantum mechanical rules called selection rules [42].

The quantum numbers of the initial and final energy levels must obey the following selection rules.

$$\Delta n \geq 1 \qquad (2.10)$$

$$\Delta l = \pm 1 \qquad (2.12)$$

$$\Delta j = \pm 1 \; or \; 0 \qquad (2.13)$$

Where n is the principle quantum number l is the angular quantum number $j = l + s$is the vector sum of l and s, where s is the spin quantum number.

The transitions predicted by the selection rules are shown in figure (2.5) which contains the lines that are of most interest to the analyst.

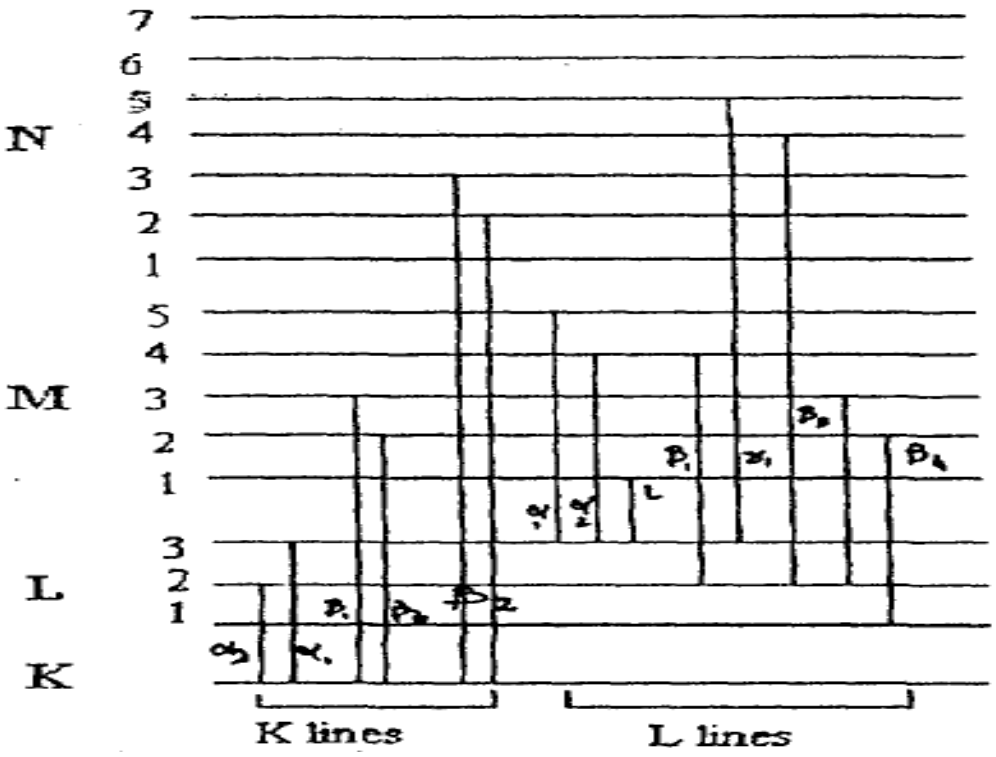


Fig (2.5): Partial energy level diagram showing the origin of the main lines in the K and L spectra [42] .

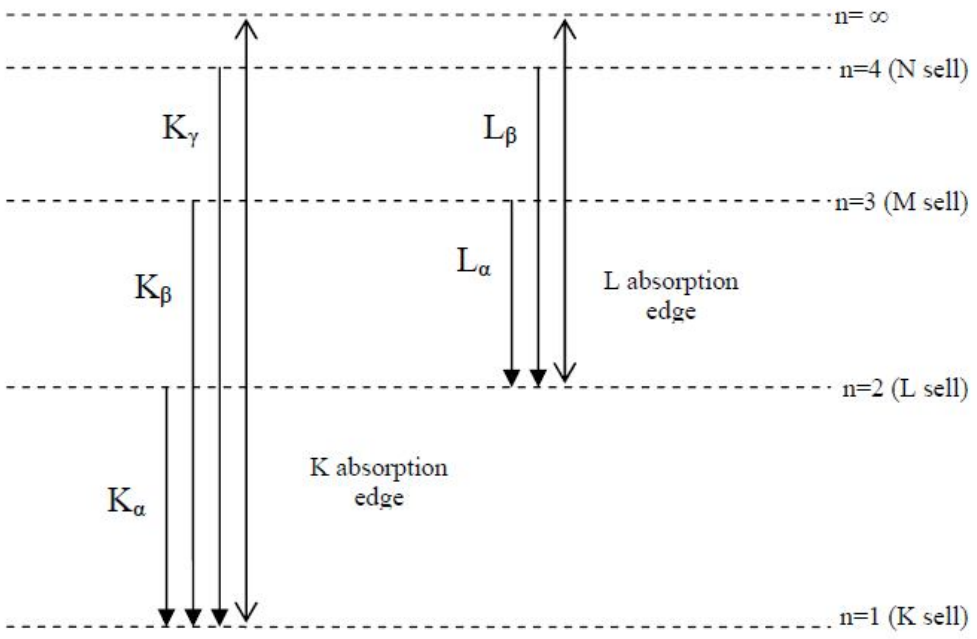


Fig (2-6): Hypothetical x-ray energy-level diagram

2.2.4.3 Auger Effect:

When an electron is ejected from an atomic orbital by the photoelectric process, there are two possible results, secondary radiation and auger or secondary electron ejection.

The secondary radiation may succeed in getting out of the sample in which case characteristic x- rays are observed.

On the other hand, it may be energetic enough to knock off an electron from one of the higher shells, e.g. L.

This process is considered to be radiation less since it does not lead to the observation of characteristic x-rays.

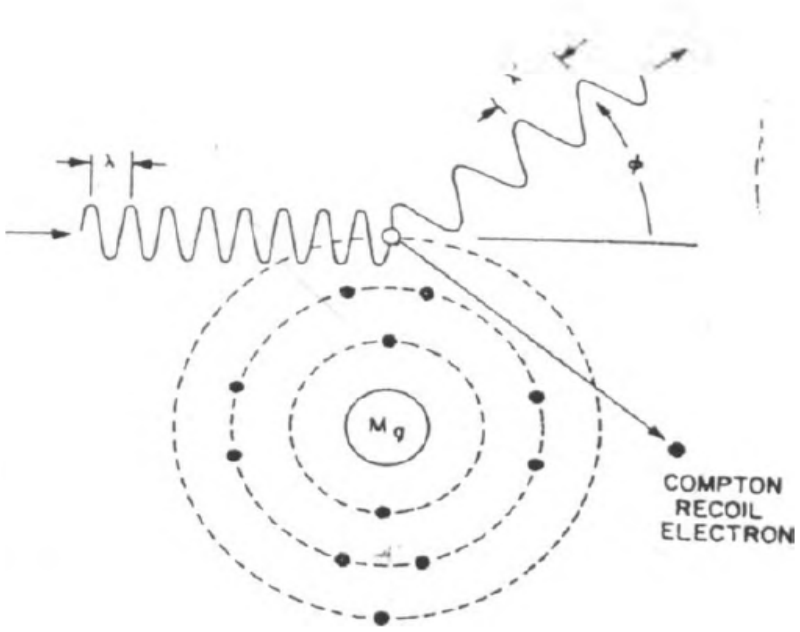
It's referred to as the auger effect and the ejected electron as the auger electron.

The effect may also be visualized as the re absorption of the characteristic x-ray internal to the atom.

Therefore, auger electron production is a process which is competitive with x-ray photon emission from excited atoms in a sample.

The fraction of the excited atoms which emit x-rays is called the fluorescence yield i.e, electron and the scatter is incoherent otherwise known as Compton scatter.

It should be recognized that, although the total amount of scattered radiation increases with increasing atomic number because of the greater number of electrons, a larger observed scatter is seen from samples with low atomic number matrices because there is less absorption by the sample [42].



where λ *and* λ' *are* wavelengths (cm) of the incident and modified scattered x-rays and (ϕ is the angle between unscattered and scattered x-rays.

Fig (2.7): Schematic representation of modified (Compton scatter) of an x-ray photon by an atom [41].

2.2.4.4 Pair Production:

In pair production, x-ray photons interact with the atom's nuclei, expending all their energy in creating and imparting kinetic energy to electron-positron pairs (e, -e). This phenomenon occurs only at photon energies$\geq$ 1.02 Mev and is of no importance in x-ray spectrometry.

2.2.4.5 EDXRF Technique:

Is a non destructive instrumental method of qualitative and quantitative analysis for electron and the scatter is incoherent otherwise known as Compton scatter , It should be recognized that, although the total amount of scattered radiation increases with increasing atomic number because of the greater number

of elections, a larger observed scatter is seen from samples with low atomic number matrices because there is less absorption by the sample.

2.2.5 EDXRF Set Up:

The x-ray fluorescence spectrometer used in this work consists of the following parts:

1. The excitation source which excites characteristic x-rays in the specimen, Radioisotope Cd -109 was used as excitation source.
2. Specimen presentation system, which holds the sample in a precisely defined geometry during analysis and provides for introduction and removal of the specimen from the excitation position.
3. Computer and memory unit which also incorporates x-y recorder and printout display units.
4. The x-ray spectrometer consisting of the Si(Li) detector (Canberra SI-30180).

   High voltage bias supply (EG and ORTEC Type 459), amplifier (EG and ORTEC Series 571), preamplifier (Canberra Model 2008), and the multichannel analyzer.

The detector is a crystal of lithium drifted silicon that is processed to form a diode. In operation, the x-rays are absorbed in the lithium-drifted layer.

The x-rays enter the cryostat trough a thin beryllium window.

Each absorbed x-ray photon transfers it's energy to a Photoelectron, which in turn expends its energy producing electron-hole pairs.

The more energetic the x-ray photon, the more electron-hole pairs it can produce providing the basis for proportionality of detector output pulse height and x-ray photon energy in Si(Li) detectors.

Lithium drifting serves to compensate for impurities in the silicon crystal hence minimizing other sources of charge carriers.

The detector is maintained at liquid-nitrogen temperature (77°K) in its vacuum cryostat at all times.

This reduces noise, ensures optimal resolution and minimizes diffusion of the highly mobile lithium atoms and enhances the life time of the detector.

Vacuum operation is required to prevent condensation of moisture on the detector.

The information of the absorbed radiation from the detector is presented as a burst of charge (pulse) collected at the detector terminal.

The purpose of the pre-amplifier is to convert the burst of electrons into a voltage signal which may be conveniently transmitted to the measurement system while retaining the proportionality of the energy deposit.

The preamplifier is also required to keep the electronic noise low, a field effect transistor (FET) is built into the system for the purpose.

The pre-amplifier is coupled to the amplifier which serves to shape and amplify the signal for eventual presentation to the multichannel analyzer for pulse height analysis.

The MCA also includes a micro-processor which is pre-programmed to perform simple data analysis operations like: energy calibration, integration and subtraction of background, etc[42].

2.2.6 Quantitative analysis in EDXRF and WDXRF:

Quantitative analysis is the same EDXRF and WDXRF.

The only difference is that in EDXRF the area of a peak gives the intensity, while in WDXRF the height of peak gives the intensity.

The exact same mathematical methods can used to calculate the composition of samples.

In quantitative analysis, the net intensities converted into concentrations.

The usual procedure is to calibrate spectrometer by measuring one more reference materials.

The calibration determines the relationship between the concentration of elements and the fluorescent lines of those elements.

Unknown concentrations can be determined once the relationship known the intensities of the elements with unknown concentration measured, with the corresponding concentration being determined from the calibration [41].

2.2.7 Matrix effects and matrix correction model:

Ideally, the intensity of an analytical line is linearly proportional to the concentration of the analytic and across a limited rang this is the case.

However the intensity of an analytical line does not only depends on the concentration of the originating element. It also depends on the presence and concentrations of other elements. These other elements can lead to attenuation or to enhancement. Matrix correction medals use terms to correct for the absorption and enhancement effects of the other elements.

This done in various ways, but they all, in one way or another, use the equation:

$$C_i = (D_i + E_i . R_i) M_i \qquad (2.14)$$

But the method is also applicable to the second equation.

M is matrix correction factor, and the difference between the models the lies in the way define and calculate M.

2.2.8 Fundamental Parameter (FP) Matrix Correction Models:

Fundamental parameter models are based on the physics of X-rays.

In the 1950 Sherman derived the mathematical equations that describe the relationship between the intensity of an element and composition of sample.

This equation contains many physical constants and parameters that are called fundamental parameters.

The Sherman equation is used to calculate the values of the matrix correction M fully by theory and the model becomes:

$$C_i = D_i + E_i . R_i . M_i \qquad (2.15)$$

At least two standards are required to calculate D and E, or just one if only E has to be calculated. M is calculated for each individual standard, and the factors D and E are determined for all elements.

The matrix factors M can only be calculate accurately if the full matrix is known because all absorption and enhancements have to be taken into account.

The calculations are quite complicated and require a powerful computer, which until recently, made these models unsuitable for routine operations.

Because FB accounts for all effects, it can be used over virtually the full concentration range and for all types of samples as long as the majors are known [43].

2.2.9 Compton Matrix Correction Models:

The Compton method is an empirical one .

The intensity of a Compton scattered line depends on the composition of the sample.

Light elements give high Compton scatter, and heavy elements low Compton scatter.

Which used to compensate for the influence of matrix.

The model is:

$$C_i = D_i + E_i . \frac{R_i}{R_c} \qquad (2.16)$$

The Compton line can be a scattered tube line, or a line originating from a secondary target if 3D optics are use[43].

2.2.10 Line Overlap Correction:

The fractions were determined by measuring dedicated standards.

Another model is to determined the overlap factors by regression.

The calibration model is extended with terms that describe the line overlap:

$$C_i = D_i + E_i . \left[R_i + \sum_{overlapinglines} F_{ij} R_j \right] \qquad (2.17)$$

The overlap factors F_{ij} are determined by regression.

The problem with this equation is that it can be non-linear, which makes difficult to calculate the factors.

If the calibration is limited to a small range, and when the variation in M is small, it can be approximated by:

$$C_i = D_i + \sum_{overlapinglines} F_{ij} R_j + E_i . R_i . M_i \qquad (2.18)$$

This is linear equation, and it is mathematically by easy to calculate the overlap factors $F_{ij}$and the other calibration parameters simultaneously.

These methods require that the overlapping intensities be measured.

In EDXRF this is not a problem because the whole spectrum is generally measured.

In WDXRF, often only the lines of the elements of interest are measured and not the overlapping lines.

The intensity of the overlapping lines is over a limited range, proportional to the concentration of the originating element [42].

The following equation can therefore be used:

$$C_i = D_i + \sum_{overlapinglines} F_{ij} R_j + E_i . R_i . M_i \qquad (2.19)$$

2.3 ATOMIC ABSOPTION SPECTROSCOPY (AAS):

An atomic absorption spectrophotometer is a comparatively simple instrument.

It has been an important tool for determination of various trace elements during toxicological investigations [44].

AAS may be defined as a method for determining the concentration of an element in a sample by measuring the absorption of radiation (in atomic vapor produced from the sample) of wavelength that is specific and characteristic of the element under consideration [45].

The characteristic radiation in visible and ultraviolet region of certain elements emitted by an appropriate source, the absorption of electromagnetic radiation occurs when radiation characteristic of a particular element is passed through an atomic vapor of the same element [45].

The atoms, which are in the ground state, absorb radiation predominantly of wavelength, which correspond to the transition from the ground state to upper excited states [45].

When these atoms absorb their characteristic radiation they are raised from the ground state to higher excited state.

The decrease in intensity is measured by using a detector after passing through a monochromatic [45].

The degree of the absorption is a quantitative measure of concentration of the ground state atom in the vapor.

The analytic concentration is determined from the amount of absorption concentration measurement are usually determined from a working curve after calibrating the instrument with standards of known concentration [45].

We use this technique in the present study due to its higher sensitivity, and it has a wider range of application [46].

However, it is easier to operate.

Also is a good quantitative tool, and being capable of detect a fairly wide range of elements [47].

It was recommended as being rapid and easy to apply, whilst at the same time being sufficiently accurate for the purpose and in most cases relatively free from interferences [45].

Two types of the atomic absorption apparatus have been employed in analysis [45,48,49].

1. (a) Single beam d.c. System. (b) Single beam a.c. system.
2. Double beam a.c. system.

The a.c. type has the advantage of being unaffected by extraneous light emitted from the flame.

2.3.1 General principles of Atomic Absorption Spectrometry :

Atomic absorption is a physical process involving absorption of radiation by ground state atoms (i.e, free atoms) at a wavelength specific to that element, e.g, nickel absorbs at

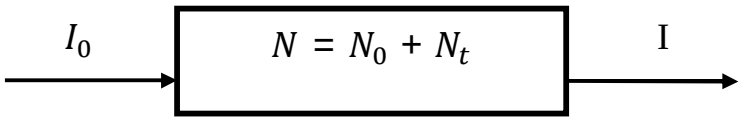


Fig (2.8): Schematic representation absorption of radiation by atomic population *N*.

In the flame the total number of atoms *N* is distributed into N_0atoms in the ground state andN_1, excited atoms, i.e, $N = N_0 + N_1$. It can be assumed that thermodynamic equilbrium exists in the flame because the atoms and the molecules all have the same mean velocity. The proportion of the excited to ground state atoms in the population at a given temperature is given by the statement of Maxwell -Boltzmann law [50] .

$$\frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\frac{E_i}{kT}} \qquad (2.20)$$

Where, g_i, and,g_0 are the statistical weights of the excited and ground atomic stales *(g=2j+i,* where *j* is the internal quantum number).

$E_i$is the excitation energy.

K is the Boltzmann constant *T* is the absolute temperature 0 and I represent ground and excited states respectively.

At most temperatures likely to be encountered in flames and electro thermal atomizers, all the atom's with electrons in higher states than the first excited states can be neglected. Unless *T* is very large, the exponential term is very small.

The specific wavelengths at which an atom’s valence electrons in the ground state can absorb 'radiation is called resonance wavelengths.

To determine how much radiation is absorbed by a cloud of atoms, consider the incident beam of monochromatic radiation I_0 on absorption cell of length *b* containing C atoms

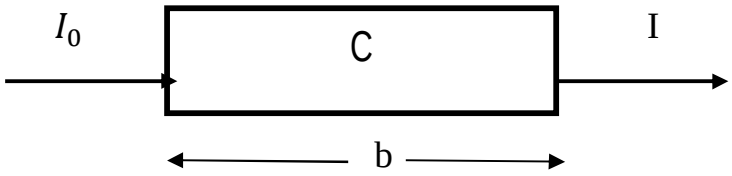


Fig (2.9): Atomic absorption cell of length *b*

The transmittance is given by:

$$T = \frac{I_t}{I_0} = e^{-kbc} \qquad (2.21)$$

Where *T* is the transmittance, *b* is the cell length, *c* the concentration of the analysis atoms in the flame and *K* the absorption coefficient (i.e, the fraction of energy absorbed per unit area per unit length).

2.3.2 Beer-Lambert's Law:

The beer-Lambert's law is the linear relationship between absorbance and concentration. It can be represented by the intensity of transmitted radiation.

$$Log\frac{I_0}{I_t} = \varepsilon CL \qquad (2.22)$$

Where: I_0 = incident radiation intensity.

ε = Molar absorbability or molar absorbance.

C = concentration of the analyzed.

L= path length of the absorbing medium or cell length (cm).

The quantity on the right of the equation (2.12) is called the Absorbance, this can be represented as follow:

$$A = Log\frac{I_0}{I_t} \qquad (2.23)$$

Where A= absorbance.

Experimental measurements are usually made in terms of transmittance (T), which is defined as:

$$T = \frac{I_0}{I_t} \qquad (2.24)$$

WhereI_t = beam intensity after absorption

The relationship between A(2.13)and T (2.14)is:

$$A = -LogT = -Log\frac{I_0}{I_t} \qquad (2.25)$$

The intensity of the transmitted radiation can be represented as:

$$I_t = I_0 e^{-kcl} \qquad (2.26)$$

Where:-

k ≡ absorption coefficient at wavelength a.

c ≡ concentration of the absorbing atoms.

l ≡ length of the absorption path.

Equation (2.16) can be represented as follows:

$$Log\frac{I_0}{I_t} = kcl = A \qquad (2.27)$$

Usually the basic requirements of the methods are: [17,18,19].

1. Narrow line radiation source suitable for the element being determined.
2. A flame (or other) device for producing the free atoms from the sample.
3. A monochromatic to select the appropriate resonate line to be measured;
4. A detection and measured system-usually a photomultiplier tubes, amplifier and meter for reading the output signal.

2.3.3 Source of Radiation:

The sources mostly used in AAS are: hallow cathode lamps and high-frequency electrode-less discharge tubes, Geissler, Xenon lamps and mercury vapor lamps [45].

2.3.3.1 Hollow Cathode Lamps:

Hollow cathode lamps are the most important line source required for AAS. It is low-pressure gaseous discharge tube [45] .

It consists of a tungsten anode and a cylindrical cathode made of specific element (or an alloy of that element), sealed in a glass tube containing an inert gas, such as argon, at low pressure [45,47].

The application of a high potential across the electrodes a discharge which creates positive ions of the noble gas, this a process known as sputtering [45].

It is a process in which atoms or ions are ejected from a surface by a beam of charged particles [51].

These atoms then accept energy of excitation and emit radiation. The emissions consist of discrete lines of the metal, plus those of the filled gas [52].

2.3.3.2 Burner Types:

The burner system is a most important part of an atomic absorption instrument.

It should be stable, responsive, sensitive, and free from background and memory of a previous sample.

There are two main types of burner system:

a. The pre-mix or laminar-flow burner.
b. The total consumption or turbulent or diffusion burner.

In the premix type of burner the sample, fuel, and carrier (oxidant) gas are mixed in the chamber before entering the flame, yield and essentially non-luminous flame of low turbulent [51].

The total consumption type burner consists of three concentric tubes.

The sample solution is carried by a fine capillary tube or directly into the flame.

The fuel gas and the oxidant gas are carried along separate tubes so that they only mix at the tip of the burner [51].

2.3.3.3 Monochromatic:

In atomic absorption spectroscopy the function of monochromatic is to isolate the resonance line from all non absorbed lines emitted by the radiation source [45,53].

This can be done with filters-better with interference filters but because their band pass is very broad, filter interference must be confined to the analysis of elements having simple spectrum [45].

2.3.3.4 Detector and Readout:

In atomic absorption spectroscopy, in view of the improved spectral, sensitivity required, photomultipliers are employed.

The output from the detector is fed to a suitable read-out system, and in this connection it must be borne in mined that the radiation received by the detector originates not only from the resonance line which has been selected, but may also arise from emission within the flame [47].

2.3.3.5 Limit of detection:

Sensitivity is defined as the concentration of an element in a water solution, which will produce absorption of 1%.

It is generally expressed as part per million per 1% absorption (ppm/1%).

It is suggested that the concentration of a specific element chosen to test the performance of an instrument should be ten to one hundred times the sensitivity [48].

A detection limit is the smallest concentration of a solution of an element that can be detected with 95 percent certainty [47].

Also is defined as that concentration in aqueous solution, which gives signal twice the size of the variability of the background [48].

Electronic stability, signal-to-noise ratio, matrix and sensitivity are all factors in determining the detection limit for an element [48].

The sensitivity of these methods depend on a complicated way on the optical properties of the atomic vapor, the temperature, the relative line widths of lamp and absorber, and the geometry of the optical system [49].

2.3.4 Instrumental principles of Atomic Absorption Spectrometry:

The most important component of AAS are:

2.3.4.1 Radiation Source:

Hollow cathode atomic spectral lamps are the most common radiation sources for atomic absorption spectroscopy.

These lambs can produce resonance radiation of narrow line width typically <0.01 angstroms for most elements that are determined by atomic absorption.

The cathode is constructed from the metal or an alloy of the element being determined.

A small current is passed between the cathode and anode resulting in ionization of inert gas atoms. Atoms of the cathode metal (analysis) are sputtered from the surface due to interaction with these ions.

Excitation results from collisions between analysis atoms and inert gas atoms in the discharge tube.

2.3.4.2 Atomization System:

To have atomic absorption its necessary to produce free ground-slate atoms of the elements of interest. This occurs in the atomizer.

A variety of commercial atomizers are available for use with atomic absorption equipment, the most common being flames and furnaces.

2.3.4.3 Signal Processors:

A Photomultiplier tube sensitive to radiation over the wavelength range 1900-8000 angstroms is commonly used.

Signals generated by this device are very small (in nano ampere range).

The photomultiplier is a current source.

The intensity of the current produced is Proportional to signals strength.

Micro-processors have recently been introduced into atomic absorption equipment mainly for setting of integration time, scale expansion, for instrument calibration and curve correction .

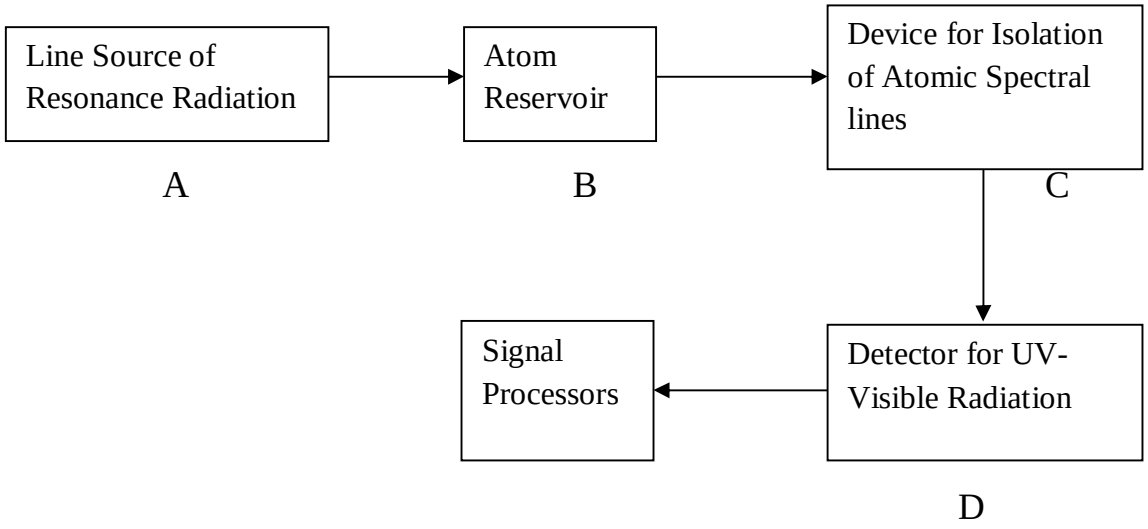


Fig (2.10): Schematic representation of atomic absorption spectrometer

A- hollow cathode lamp

B- a flame or electro thermal device

C- a grating monochromatic

D- a photomultiplier

The principle of operation of atomic absorption spectrometer is simple, the hollow cathode lamp emits radiation characteristic of the cathode material, usually a single element (analysis).

The beam consisting largely of resonance radiation, is electronically rechanical pulsed.

Analysis atoms are produced thermally in the reservoir.

Ground state atoms, which predominate under the experimental conditions absorb a resonance radiation from the lamp, reducing the intensity of the incident beam.

The monochromatic isolates the desired resonance line and allows this radiation to fall on the photomultipler, an electrical signal is generated.

The electronics of the unit are designed to respond selectively to the pulsed radiation emanating from the radiation source, signal processing occurs, which results in electronic output proportional to the absorption by the analysis atoms.

2.3.5 Interferences:

Various factors may affect the atomic absorption and lead to interference. These factors may be broadly classified as:

(a) Spectral interferences. (b) Chemical interferences [47,49].

2.3.5.1 Spectral Interferences:

In AAS arise mainly from overlap between the frequencies of a selected resonance line with lines emitted by some other elements; these arise because in practice a chosen line has in fact a fini [47,51].

te “band-width” Since in fact the line width of an absorption line is about 0.005 nm only a few cases of spectral overlap between the emitted lines of hallow cathode lamp.

Selection of an alternative resonance line will overcome spectral interferences from other atoms or molecules and from molecular fragments

2.3.5.2 Chemical Interferences:

Two main forms of chemical interference may inhibit the production of ground gases state:

(a) Stable compound formation:

Leads to incomplete dissociation of the substances to be analyzed when placed in the flame, or it may arise from the formation within the flame of refractory compounds, which fail to dissociate into the constituent atoms.

Alternation of flame composition or of flame temperature can be used to reduce the likelihood of stable compound formation within the flame.

(b) Ionization of ground state gaseous atoms:

Ionization of the element to be determined will reduce the extent of absorption in AAS.

This may be reduced by addition of an excess of an ionization upperessant, this is a solution containing action having a lower ionization potential than that of the analysis.

It is necessary to take account of so-called matrix effects.

These are predominately physical factors, which will influence the amount of sample reaching the flame, and are related in particular to factors such as the viscosity, the density, the surface tension and the volatility of the solvent used to prepare the test solution.

Ensure if possible those standards and sample solutions are of similar bulk composition to eliminate matrix effects.

In some circumstances interference may result from molecular absorptions[47,51].

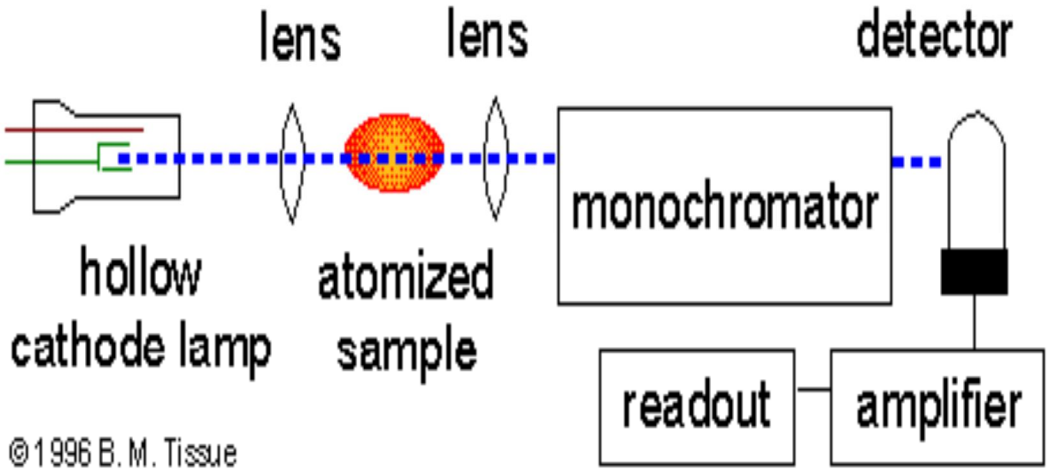


Fig (2.11): Schematic diagram of atomic absorption spectroscopy.

CHAPTER THREE

LITERATURE REVIEW

3.1 THE IMPORTANCE OF VEGATABLES AS FOODS:

Consumption and use of vegetable crops was once very limited in Sudan. People used to rely on subsistence staples such as sorghum and wild vegetables. Introduction of exotic species and varieties of vegetables started very early this century, mainly from Egypt [52].

Vegetables play an essential role in human's diet.

They provide and assist their bodies with a variety of important constituents such as minerals, vitamins, complex carbohydrates, high dietary fiber, low fats and water.

Encouraging vegetables consumption is a major emphasis of the Federal Government’s dietary guidance policy.

A healthy balanced diet composes of vegetables, fruits, animal product and grain products. So increasing consumptions of vegetables is a fundamental goal that aiming to supply humans diet.

Governmental adoption of awareness increasing of consumptions of vegetables among population is serving more to fulfill this goal [53].

Vegetables are important sources of numerous vitamins and essential minerals, as well as dietary fibers, while providing little fat and calories. In 1988, for example, vegetables accounted for only 8% of the calories and 1% of the fat in the American food supply, while providing 94% of the carotenes and 90% of the vitamin C [53].

3.2 HEAVY METALS:

Heavy metals is a general collective term applied to metals and metalloids with an atomic density greater than 6g/cm^3 although it is only a loosely defined term it is widely recognized and usually applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn which are commonly associated with pollution and toxicity

problems an alternative and theoretically more acceptable name for this group of elements is “trace metals” but it is not as widely used [54] .

Unlike most organic pollutants, such as organohalides, heavy metals occur naturally in rock-forming and ore minerals and so there is a range of normal background levels [55].

There are different sources of heavy metals pollutants plant.

Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans [56].

Metal contamination of garden soils may be widespread in urban areas due to past industrial activity and the use of fossil fuels [57-58-59-60-61].

Heavy metals may enter the human body through inhalation of dust, direct ingestion of soil, and consumption of food plants grown in metal contaminated Soil [62-63-64].

Potentially toxic metals are also present in commercially produced foodstuffs [65].

Exposure to potentially toxic metals from dust inhalation or soil ingestion is usually modeled simply as the concentration of a contaminant measured in the soil multiplied by the quantity of dust inhaled or soil ingested [66].

This is a conservative approach to estimating dose, because the bio accessibility of heavy metals adsorbed on ingested soil is not 100% [67].

However, predicting exposure to potentially toxic metals from consumption of food crops is more complicated because uptake of metals by plants depends on soil properties and plant physiologic factors.

This leads to much larger uncertainties associated with estimating potential doses through food chains compared to the uncertainties associated with other exposure pathways such as soil ingestion and dust inhalation [68].

Increasing industrialization has been accompanied throughout the world by the extraction and distribution of mineral substances from their natural deposits.

Following concentration, many of these have undergone chemical changes through technical processes and finally pass, dispersed and in solutions, by way of effluent, sewage, dumps and dust, into the water, the earth and the air and thus into the food chain.

These include metals and the heavy metals relevant for this research [69].

Together with essential nutrients, plant and animals also take up small amounts of contaminated heavy metal compounds and can concentrate them. As certain heavy metals such as lead, cadmium, and mercury have been recognized to be potentially toxic within specific limiting values, a considerable potential hazard exits for human nutrition [70].

Not all the traces of heavy metals in plants and animals are the results of human activity.

Some arise through the absorption processes of naturally occurring soil components.

Purely theoretically, every 1000 kg of “normal” soil contains 200g chromium, 80g nickel, 16g lead, 0.5 g mercury, and 0.2 g cadmium. Therefore, it is not always easy to assign a definite cause for increased heavy metal content.

Even foodstuffs produced in completely unpolluted areas are not entirely free of heavy metals.

The absorption of very small amounts is therefore unavoidable in principle and has always occurred [71,72].

Those metals are described as “heavy metals” which, in their standard state, have specific gravity (density) of more than 5 g/cm3 and are normally regarded as the ones having an atomic number of 22 to 92 in all groups from period 3 to 7 in the periodic table. But there is no really satisfactory grouping by which they can be identified in the periodic table [73].

Heavy metals almost have unique physical properties.

Among these are high electrical and thermal conductivity, attributed to free electrons, great opacity and high relativity for light, due to the same cause and responsible for luster; commonly associated with metals malleability- a sort of plasticity by virtue by which a metal may be called – worked and rolled into thin sheets: ductility- a combination of malleability and toughness which permits a metal to be drown into wire-metals in their normal pure state are crystalline [74].

Some heavy metals, such as copper, nickel, chromium, iron and others, are essential in very low concentrations for the survival of all forms of life.

These are described, as essential trace elements [71].

In higher concentrations, it can also be quite toxic, for example when they are present in an organic compounds, or in greater quantities.

Other heavy metals like lead, cadmium and mercury, are already toxic in very low concentrations [75,76].

There are 60 heavy metals. These also include the precious metals platinum, silver and gold.

For this study, however; only one element of toxic heavy metals (Pb) and essential trace elements (Cu, Zn, and Co) are considered [69].

3.3 THE CONTEXT OF HEAVY METALS PROBLEMS:

Essentially, the heavy metals have only become a focus of public interest since analytical techniques have made it possible to detect them even in very small traces.

The relatively reckless handling of heavy metals and their compounds in former times can partly be explained by the fact that their effects were unknown.

Today analytical detection is possible down to thousandth of a mg/kg for certain matrixes.

This has made it possible for toxicologists, in animal experiments, to follow up the effect of individual substances down to the smallest concentrations.

Their warnings, particularly with regard to the effects on health of chronic consumption and the accumulation to which this leads, have startled the public and, at times, mostly as a result of the activities of so -called pressure groups, have generated genuine hysteria.

All this has taken place against the background of a steady increase in the processing of all types of heavy metals in industry and the household.

Therefore; proper disposal, recycling and the regulation of the application of sewage to agricultural land, have assumed great importance [69,77,78].

3.4 BIOLOGICAL ROLE AND TOXIC EFFECT OF SPECIFIC HEAVY METALS:

3.4.1 Copper (Cu):

Copper deficiency in plants was first recognized as “reclamation disease” in crop grown on sandy and gravelly soils [79].

The presence of high concentrations of the divalent copper metal ion in the soil solution often give rise to toxicity symptoms in plants, thus, is highly susceptible to the disease stem. Copper photo toxicity associated with increased levels of some sludge [80, 81].

Copper concentration in plants generally varies between 5 and 20 ppm. Concentrations below which plants show deficiency symptoms vary among plant species [82].

The copper content of soils is reported to range between 2 to 100ppm with an average value of around 55ppm [82].

3.4.2 Zinc (Zn):

Zinc is an essential element, said to be absorbed through leaves more rapidly than other elements.

zinc and copper are classified as moderately mobile in the plants [79].

Plant zinc concentrations are a reflection of the available zinc levels in soils [80], which is a function of its partition among different forms [81].

The zinc present in water-soluble, exchangeable and absorbed fractions is rapidly available to plants; zinc associated with primary and secondary soil minerals is relatively unavailable to plants [81].

Certain soil conditions, however; may reduce availability as a plant nutrient, zinc becomes critical around pH 5.5 to 6.5; in clay, acid soils it tends to combine with organic matter [79].

Concentration of zinc commonly observed lies between 20 to 100 ppm [80].

Zinc in soil is present as a part of the mineral structure or as salts such as ZnS, ZnCO3, ZnSO4, c.

Total zinc in soils varies from 10 - 300 ppm with an average of around 80 ppm [80].

3.4.3 Lead (Pb):

An understanding of the uptake of lead by plants is necessary in order to develop agricultural practice which will minimize the movement of these elements through plant to animals and man [83].

This is because lead pollution is a threat to human and animal health, and has toxic effects on human health [84].

Lead is one of the heavy metals commonly encountered in the environment, and is highly toxic and is the largest quantitative element, therefore; the atmospheric pollution may be most significant for lead [85].

Lead is the trace element commonly occurring in plant species this metal is hazardous to human health [85].

Its concentration in plants commonly observed lies between 0.05 –3ug/g, its concentration in soils varies from (2 – 20 μg/g), [86] and 16g in every 1000kg of “normal” soil [78].

3.4.4 Manganese (Mn):

Essential human nutrient: recommended daily intake 0.14 mg/kg [87].

Organic and inorganic (seven species, valences from 1 to 7) forms Very hard and brittle metal widely used in industry: constituent of steel alloys, battery production, glass and ceramics production Manganese oxides (permanganates) are used as disinfectants and for bleaching, metal cleaning, flower preservation etc.

Organic manganese compounds are petrol and fuel oil additives

(methyl cyclo pentadienyl manganese tricarbonyl, MMT)

3.5 METALS SOURCES:

3.5.1 Air and Water Pollution:

Metals can impact soils and biota by deposition from polluted air.

Plants can become heavily contaminated by surface particulate [88].

Industrialization has resulted in increased mobilization and deposition of heavy metal pollutants in natural habitats.

Generally; most metals are deposited within a few kilometers of the stack; however; significant depositions have been found as far away as 100 km.

Automobile Pb emission are generally restricted to 30 meters [87].

Also automobiles using leaded gasoline as fuel are a major source of heavy metal in the atmosphere [72, 88].

because lead is used in order to increase the octane number in petrol [89].

Metal smelters, industrial production processes and their emissions foundries[90].

steel mills, coal power plants, incinerators and the smoke and dust emissions of coal and gas - fired power stations [90].

are demonstrated air emission sources for Cd, Pb, Zn, and Cu [91].

The laying of lead sheets by roofers as well as the use of paints and antirust agent are the main sources of lead pollution [72].

3.5.2 Sources of Heavy Metals in Vegetables:

The consumption of vegetables is varying from country to another and even between families in one country according to food habits and consumer awareness. In the last decades the consumption of vegetables was increased particularly in the urban areas where a systematic education, food culture and a cosmopolitan interference are available.

found that the intake of vegetables is low compared with current dietary recommendations, particularly in those of lower levels of educational attainment and social class [92].

In the Sudan, the main feature of these vegetables that has been chosen are their widely uses as a fresh or a table salad vegetables and its availability among all living level of population, giving attention to it's abundance and cheapness in certain season campaign with a mess in displaying near railways station and in the ground, therefore, introducing contaminations . Farmers aiming to catch the market demands, they grow vegetables in small scale farms around the cities and beside the rail ways in order to minimize the traveling cost, hence, treated vegetables with high doses of insecticides aiming to ensure a good prevention of insects. Several studies have indicated that vegetables, particularly leafy crops, grown in heavy metals contaminated soils have higher concentrations of heavy metals than those grown in uncontaminated soil [93].

A major pathway of soil contamination is through atmospheric deposition of heavy metals from point sources such as:

metaliferous mining, smelting and industrial activities. Other non point sources of contamination affecting predominantly agricultural soils include inputs such as, fertilizers, pesticides, sewage sludge, organic manures and composts [94].

Additionally, foliar uptake of atmospheric heavy metals emissions has also been identified as an important pathway of heavy metal contamination in vegetable crops [95,96].

Vegetable growing areas are often situated in, or near sources of atmospheric deposits, and thus have an elevated risk of potential contamination. sorted out that the main sources of heavy metals in vegetables are [97].

1. Metallurgical industries can contribute to plants pollution in several ways:

a) by emissions of fumes and dusts containing metals which are transported in the air and eventually deposited onto soil and vegetation;

b) by effluents which may pollute soil when watercourses flood and there for to the vegetation.

2. Agricultural fertilizers and pesticides: several of these including phosphoric fertilizers, slugs from iron manufacture, pesticides and herbicides contain various combinations of heavy metals, either as impurities or active constituents.
3. Atmosphere pollution from motor vehicles; the use of leaded petrol has been responsible for the global dispersion of Pb aerosols.
4. The combustion for fossil fuels: this results in the dispersion of many elements in the air over a large area.

The disposal of ash is further source of heavy metals Whatever their sources, toxic elements can reach the soil, where they become part of the life cycle (fig (3.1)). Unfortunately, once the elements become parts of this cycle they may accumulate in animal and human body tissue to toxic levels [98] .

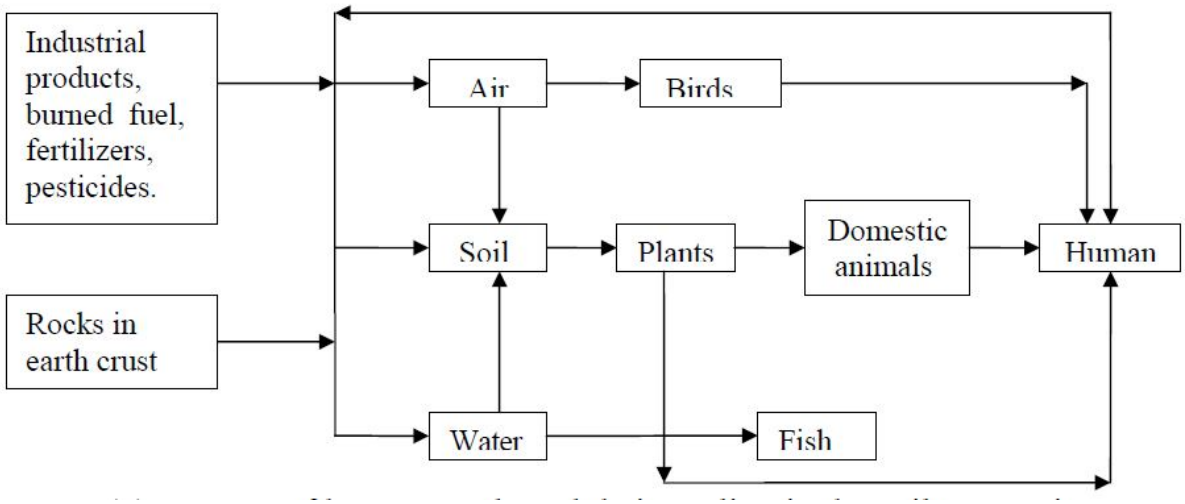


Fig (3.1): Diagram Sources of heavy metals and their cycling in the soil-water-air organism ecosystem.

It should be noted that the content of metals in tissue generally build up from left to right, indicating the vulnerability of humans to heavy metal toxicity.

3.6 STUDIES OF HEAVY METALS IN PLANTS:

The increasing interest in environmental pollution has led to investigation on heavy metal uptake and binding in plants [99 ,100] .

Also rapid industrialization and urbanization in the last century due to enormous technological innovations has led to the problem of environmental pollution and ecological concerns [101] .

Studied the heavy metals in the aquatic plants, the results illustrated that ability of these plants to absorb and accumulate high levels of heavy metals [102].

Compared the amount of zinc taken up by the *ryegrass* to the bare soil. They suggested that a selective extraction was not a good measuring of zinc uptake by grass [103].

Studied zinc uptake by corn as affected by vesicular-arbuscularmycorrhizae, they found that plants differ in their sensitivity of zinc deficiencies, which are usually associated with high pH or calcareous soils [104].

Governed that heavy metal absorbed by soil characteristics such as pH and organic matter content [105].

Found that heavy metal reach the soil by direct application, direct deposition of emissions and indirectly by contaminated litter [106].

Studied the effect of lead contamination of soils, air on its accumulation in pollen, they found that, lead contents of *pollen* is mainly via a translocation process from root to flower [107].

Studied the physiology of metal toxicity in plants.

They found that, common symptoms of heavy metal toxicity reduce root growth and chlorosis of herbaceous plants [87].

Found that, the uptake of element by plants depended on meteorological conditions such as temperature or air moisture [108].

Distributed zinc fraction and their transformation in submerged rice soil.

The results, therefore, very clearly show what the transformation of different forms of zinc in soil upon submergence is very much related to changes in the different form of iron particularly the reaction of Fe2O3 and the subsequent formation of insoluble hydroxides of iron [109].

found that, entry of toxic ions into plant tissue may also take place by competion with essential ions of similar ionic radii [110, 111].

found that, the presence of certain heavy metals in influents from industrial sources can lead to poor crop growth, and endanger the health of man or animal [112].

studied lead uptake from solution by *perennial ryegrass* and its transport from roots to shoots, they found that, root of actively growing *ryegrass* provide a barrier with restricts the movement of lead to the above-ground parts of plants, and so to animals and man [113] .

studied the concentration level of heavy metals in *taratacumofficinal web plant*, He found that, the heavy metal level in the root of the plant is of higher significance than in the leaves [114] .

investigated the kinetics of zinc desorption using DTPA (diethylenetriaminepenta-acetic acid) as an extractant and examined the effects of aging time and temperature [115].

They found that, the amount of zinc adsorbed by DTPA however; continued to decrease with increasing aging time and elevated temperature enhanced zinc aging and reduce extrability.

found that lead was absorbed and deposited mainly on the plant surface [116].

found that the uptake depends on the chemical features and quantity of element in atmosphere, its mobility in soil and on the type of lands [117].

They found the highest transfer rates through atmosphere are those found for lead and mercury concentration.

studied the effect of road-traffic pollutants and the amount of lead on tree fine-roots along a motor road, they found that, lead concentration in dead fine roots were higher close to the road than in the forest [118].

studied the effect of contamination of soil with copper, lead and arsenic, they found that, contaminated soil, which is ingested with plant material, may be a significant source of the toxic element by grazing animals [119].

Also they found temperature is an important factor controlling the uptake of these elements by plants.

characterized the elements uptake by means of the following common parameter: concentration of element in the soil, amount of bio-available element form and transport of element through interface soil-root system of plant [120].

found that the uptake of elements by plants does not depend only on the element concentration in soil, but also on the ratio between soil and air contamination, and on how long lasts the emission, on the bio-chemical condition of soils (content and type of humic acids, microbiological activity, pH, reduced potential), on which part of plant is taken for analysis (tissues type, and age) [121].

found that high levels of heavy metals in the soil do not always indicate similar high concentration in plant [122].

Also they found the extent of accumulation and toxic level will depend on the plant and heavy metal species under observation. Also they concluded that copper and lead plant concentration correlated with aerial deposition but not with soil concentration.

Studied lead pollution in the plants He found that when the source of lead pollution is the burning of leaded gasoline by cars along major highways with the heavy traffic usually lead concentration on vegetation and in the soil gradually decrease with the increasing distance of the sampling point from the highway [123].

studied the potential effects of heavy metals in municipal solid waste composts on plants and the environment they found that in the small amounts, many of these metals (boron, zinc, copper and nickel) are essential for plant growth [124].

However, in higher amounts they may decrease plant growth.

Other metals arsenic, cadmium, lead and mercury are of concern primarily because of their potential to harm soil organisms and animals and human who may eat contaminated plants or soil.

Concluded that Cu and Pb plant concentrations correlated with aerial deposition but not with soil concentrations [125].

said that, the entrance of solutes is not restricted to roots, but also occur through leaves and even though stems [126].

Absorption through stems occurs at limited extent.

Ordinarily the amounts which enter by these pathways (leaves, stem) are a small, being limited to the minerals.

More of the absorption of solute occurs through young than through old leaves.

Either because the latter is more heavily cutinized, or possibly they have a lower level of metabolism and less capacity to accumulate ions.

Much of mineral entrance is believed to occur through lenticels, leaf scars, pruning wounds, and other breaks in the bark.

studied the heavy metal contents in medicinal and spice plants [127].

They found that zinc, copper and manganese could be in correlation with the herbicide treatments, the lead and cadmium are the consequence of air pollution and fuel impurities, were higher in the plants grown near roads.

said that, there is a tremendous difference in the uptake and accumulation of polluting elements among the different plant parts like root, stalk, leaves and seeds [128].

found that the presence in the soil solution of high concentrations of the divalent metal ions zinc, cadmium, mercury, copper and lead often gives rise to toxicity symptoms in plants [129].

3.7 STUDIES MEASUREMENT METHODS OF HEAVY METALS IN PLANTS:

Was supplied one-way analysis of the variance (ANOVA) to examine the heavy metal [102].

He found that, high heavy metal concentration coincided with sites of heavy industrialization, dense populations, mining and sewage wastes discharge.

used atomic absorption spectroscopy (AAS) and X-ray fluoresce (XRF) to determine some elements in sugar cane [82].

He found that the agreement between the results obtained by these two techniques greatly improved the quality of the data.

used atomic absorption spectroscopy (AAS) to determine lead uptake from soils by perennial ryegrass and its relation to the supply of an essential element (sulphur), they found that, in soil-grown ryegrass that roots restrict the movement of lead into the tops of high-yielding plants, but when growth is limited by sulphur deficiency the concentration in the top increases markedly [113].

used atomic absorption spectrophotometer (AAS) to determine the heavy metals in falling dusts, soil and dandelion plant. He found that, the deposition of cadmium and lead metals did not exceed the values standardized in the Polish Legislation, and the content [114].

The mean metal concentration in dandelion leaves and root was within the values accepted as background in professional literature.

used atomic absorption spectroscopy (AAS) for heavy metal, they found that, the metal concentration decrease with maturity, where they attribute this to plant species and the element, not to the metal concentration in the soil [116].

They fount that, this method was successfully introduced to measure heavy metals and it was shown that the method is applicable to study evaporation and potentially incineration and justification process.

used atomic absorption spectroscopy (AAS) to determine heavy metal concentration in plant growth in soil treated with compost and other plants growth in untreated soil [130].

They found that, no significance different for heavy metal concentration between two samples.

used atomic absorption spectrophotometer (AAS) to determine the content of lead, nickel, chromium, cadmium and cobalt in peppermint *(MenthapiperitaL.)*medicinal plant cultivated on different soil types [131].

They found that, heavy metals were within their normal content range in plant material, except for plants grown on the contaminated soil and plant by ferronickel smelter occurred.

used atomic absorption spectroscopy (AAS) and X-ray fluoresce (XRF) to determine the concentration of some elements [132].

He found that, these methods were significantly similar.

used atomic absorption spectroscopy (AAS) for determine copper concentration in(*Spinacia Oleracea*L.)they found that, copper was accumulated mainly in roots and to a minor extent in leaves [133].

used Graphite Furnace Atomic Absorption (GFAA) and Inductively Coupled Plasma (ICP) techniques, to determined content of heavy metals (cadmium, lead ,copper, manganese and zinc) and other trace elements in essential soils and plant extracts from the genera (*Rosa, Lavassopus, Mentha, Salvia, Foeniculum, Anethum, Hyssopus*and *Rhus*), medicinal and aromatic plants [134].

3.8 EFFECTS OF HEAVY METALS IN PLANTS:

3.8.1 Nature of Heavy Metals:

Heavy metals are natural components cannot be degraded or destroyed biologically. Life cannot develop and survive without the metal ions as life is as much inorganic as organic. Trace element to designate the elements which occur in small concentrations in natural biological systems concern over the deteriorating quality of the environment led to a trace element. The elementary constituents of plant, animal and human life may be classified as major and trace

elements, the latter group comprising both essential and non-essential elements (including toxic elements).

3.8.2 Essential Heavy Metals:

Some of heavy metals (Fe, Cu and Zn) are essential for plants and animals [134], their availability in medium varies, and metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients [135], whose uptake in excess to the plant requirements result in toxic effects [136].

Range of a few important heavy metals in plants like As 0.02-7; Cd 0.1-2.4; Hg 0.005-0.02; Pb 1-13; Sb 0.02-0.06; Co 0,05-0.5; Cr 0.2-1; Cu 4.15; Fe 140; Mn 15-100; Mo 1-10; Ni 1; Sr 0.30 and Zn 8-100 in μg g-1 dry wt. on land plants [137].

3.8.3 Effect of Heavy Metals:

The heavy metals available for plant uptake are those present as soluble components in the soil solution or those solubilized by root exudates [138].

Plants require certain heavy metals for their growth and upkeep, excessive amounts of these metals can become toxic to plants and ability of plants to accumulate essential metals equally enables them to acquire other nonessential metals [139]. As metals cannot be broken down, when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly and some of the direct toxic effects caused by high metal concentration include inhibition of cytoplasmic enzymes and damage to cell structures due to oxidative stress [140, 141].

Indirect toxic effect is the replacement of essential nutrients at cation exchange sites of plants [142].

The negative influence of heavy metals on the growth and activities of soil microorganisms also indirectly affect the growth of plants. Reduction in the number of beneficial soil microorganisms due to high metal concentration may lead to decrease in organic matter decomposition leading to a less fertility of soil. Enzyme activities are very much useful for plant metabolism, hampered due to heavy metal interference with activities of soil microorganisms. These toxic effects (both direct and indirect) lead to a decrease in plant growth which finally results in the death of plant [143].

The effect of heavy metal toxicity on the growth and development of plants differs according to the particular heavy metal for that process. Metals such as Pb, Cd, Hg, and As which do not play any beneficial role in plant growth, adverse effects have been recorded at very low concentrations of these metals in the growth medium. Kibra [144] noticed significant reduction in height of rice plants growing on the soil contaminated with 1 mg Hg/kg with reduction in tiller and panicle formation.

For Cd toxicity which reduces the shoot and root growth in wheat plants when Cd as low as 5 mg/L in the soil [145].

Most of the reduction in growth parameters of plants growing on polluted soils can be attributed to reduced photosynthetic activities, plant mineral nutrition, and reduced activity of some enzymes [146].

Like every living organisms, plants are often sensitive both to the deficiency and to the excess availability of some heavy metal ions as essential micronutrient, while the same at higher concentrations and even more ions such as Cd, Hg, as are strongly poisonous to the metabolic activities. Research has been conducted throughout the world to determine the effects of toxic heavy metals on plants [147].

Contamination of agricultural soil by heavy metals has become a critical environmental concern due to their potential adverse ecological effects. Such toxic elements are considered as soil pollutants due to their widespread occurrence and their acute and chronic toxic effect on plants grown of such soils.

3.8.3.1 Effects of Copper on Plants:

Copper is an essential metal for normal plant growth and development, although it is also potentially toxic. Copper (Cu) is considered as a micronutrient for plants [148].

And plays important role in CO2 assimilation and ATP synthesis [149].

Study conducted at Malanzkhand Copper Project (MCP) of Hindustan Copper Limited (HCL) at Malanzkhand, district Balaghat, M.P in which it was found that copper dust had adverse effect on various photosynthesis pigmentation secretions in many trees species leaves [150,151].

Cu is also an essential component of various proteins like plastocyanin of photosynthetic system and cytochrome oxide of respiratory electron transport chain [152].

But enhanced industrial and mining activities have contributed to the increasing occurrence of Cu in ecosystems.

Cu is also added to soils from different human activities including mining and smelting of Cu containing ores. Mining activities generate a large amount of waste rocks and tailings, which get deposited at the surface. Excess of Cu in soil plays a cytotoxic role, induces stress and causes injury to plants. This leads to plant growth retardation and leaf chlorosis [153,154].

Exposure of plants to excess Cu generates oxidative stress and ROS [155].

In bean (*Phaseolus vulgaris*) accumulation of Cu in plant roots and root malformation and reduction seen [156,157].

3.8.3.2 Effect of Zinc on Plants:

The function of zinc is to help a plant to produce chlorophyll. Leaves get discolor when the soil is deficient in zinc and plant growth is stunted [158].

Zinc deficiency causes leaf discoloration called chlorosis tissue of the veins to turn yellow.

Chlorosis by zinc deficiency usually affects the base of the leaf near the stem. Chlorosis appears on the lower leaves first, and then gradually moves up to the plant. In severe cases, the upper leaves become chlorotic and the lower

leaves turn brown or purple and die. When plants show symptoms this severe, it's best to pull them up and treat the soil before replanting.

Zinc (Zn) is an essential micronutrient that affects several metabolic processes of plants [159] and hasa long biological half life.

The phytotoxicity of Zn and Cd is indicated by decrease in growth and development, metabolism and an induction of oxidative damage in various plant species such as Phaseolus vulgaris [160] and Brassica juncea [161].

Cd and Zn have reported to cause alternation in catalytic efficiency of enzymes in Phaseolus vulgaris [162] and pea plants [163].

Concentrations of Zn found in contaminated soils frequently exceed to those required as nutrients and may cause phytotoxicity. Zn concentrations in the range of 150–300 mg/kg have been measured in polluted soils [164].

High levels of Zn in soil inhibit many plant metabolic functions; result in retarded growth and cause senescence. Zinc toxicity in plants limited the growth of both root and shoot [165].

Zinc toxicity also causes chlorosis in the younger leaves, which can extend to older leaves after prolonged exposure tohigh soil Zn levels [166].

Excess Zn can also give rise to manganese (Mn) and copper (Cu) deficiencies in plant shoots. Such deficiencies have been ascribed to a hindered transfer of these micronutrients from root to shoot. This hindrance is based on the fact that the Fe and Mn concentrations in plants grown in Zn rich media are greater in the root than in the shoot [166].

Another typical effect of Zn toxicity is the appearance of a purplish red color in leaves, which is ascribed to phosphorus (P) deficiency [167].

Zinc in excess reduces the germination, chlorophyll, carotenoid, sugar, amino acid and growth of cluster beans (Cyamopsistetragonoloba) [168].

3.8.3.3 Effects of Lead on Plants:

Plants on land tend to absorb lead from the soil and retain most of this in their roots.

There is some evidence that plant foliage may also take up lead (and it is possible that this lead is moved to other parts of the plant).

The uptake of lead By the roots of the plant may be reduced with the application of calcium and phosphorus to the soil. Lead (Pb) is one of the ubiquitously distributed most abundant toxic elements in the soil. It exerts adverse effect on morphology, growth and photosynthetic processes of plants. Lead is known to inhibit seed germination of Spartianaalterniflora, Pinushelipensis [169].

Inhibition of germination may result from the interference of lead with important enzymes, Mukherji and Maitra observed 60 μM lead acetate inhibited protease and amylase by about 50% in rice endosperm [170].

Early seedling growth was also inhibited by lead in soya bean, rice [171], maize [172], barley, tomato and certain legumes [173].

Lead also inhibited root and stem elongation and leaf expansion in Allium species barley and Raphanussativas [174].

The degree to which root elongation is inhibited depends upon the concentration of lead and ionic composition and pH of the medium [175].

Concentration dependent inhibition of root growth has been observed in Sesamumindicum [176].

A high lead level in soil induces abnormal morphology in many plant species. For example, lead causes irregular radial thickening in pea roots, cell walls of the endodermis and lignification of cortical parenchyma [177].

Lead also induces proliferation effects on the repair process of vascular plants [178].

Lead administrated to potted sugar beet plants at rates of 100–200 ppm caused chlorosis and growth reduction [179].

High Pb concentration also induces oxidative stress by increasing the production of ROS in plants [180].

3.8.3.4 Effects of Manganese on Plants:

Manganese (Mn) is an essential plant mineral nutrient, playing a key role in several physiological processes, particularly photosynthesis.

Manganese deficiency is a widespread problem, most often occurring in sandy soils, organic soils with a pH above 6 and heavily weathered, tropical soils.

Mn is readily transported from root to shoot through the transpiration stream, but not readily remobilized through phloem to other organs after reaching the leaves [181].

Necrotic brown spotting on leaves, petioles and stems is a common symptom of Mn toxicity [181].

This spotting starts on the lower leaves and progresses with time toward the upper leaves [182].

With time, the speckles can increase in both number and size resulting in necrotic lesions, leaf browning and death [183].

Another common symptom is known as ‘‘crinkle leaf’’, and it occurs in the youngest leaf, stem and petiole tissue. It is also associated with chlorosis and browning of these tissues [181,183].

Manganese toxicity in some species starts with chlorosis of older leavesmoving toward the younger leaves with time.

This symptom starts at the leaf margins progressing to the interveinal areas and if the toxicity is acute, the symptom progresses to marginal and interveinal necrosis of leaves [183].

Excess Mn is reported to inhibit synthesis of chlorophyll by blocking a Fe concerning process [185].

Manganese toxicity is a relatively common problem compared to other micronutrient toxicity, In the broad bean (Viciafaba) Mn accumulation in shoot and root; reduction in shoot and root length, chlorosis [186].

Otherside in spearmint (Menthaspicata) Mn decrease thechlorophyll a and carotenoid content; increase accumulation of Mn in plant roots [187].

Moreover, Mn in pea (Pisumsativum) reduces chlorophylls a and b content; reduction in relative growth rate; reduced photosynthetic O2 evolution activity and photosystem II activity [188].

However, in tomato (Lycopersiconesculentum) Mn slower plant growth; decrease in chlorophyll concentration [189].

CHAPTER FOUR

MATERIALS AND METHODS

4.1 STUDY AREA:

The study area lies entirely in Khartoum State (Khartoum, Omdurman and Bahri), the area is located between latitudes 15.39 and 15.59 N, longitudes 32.33 and 32.50 E.

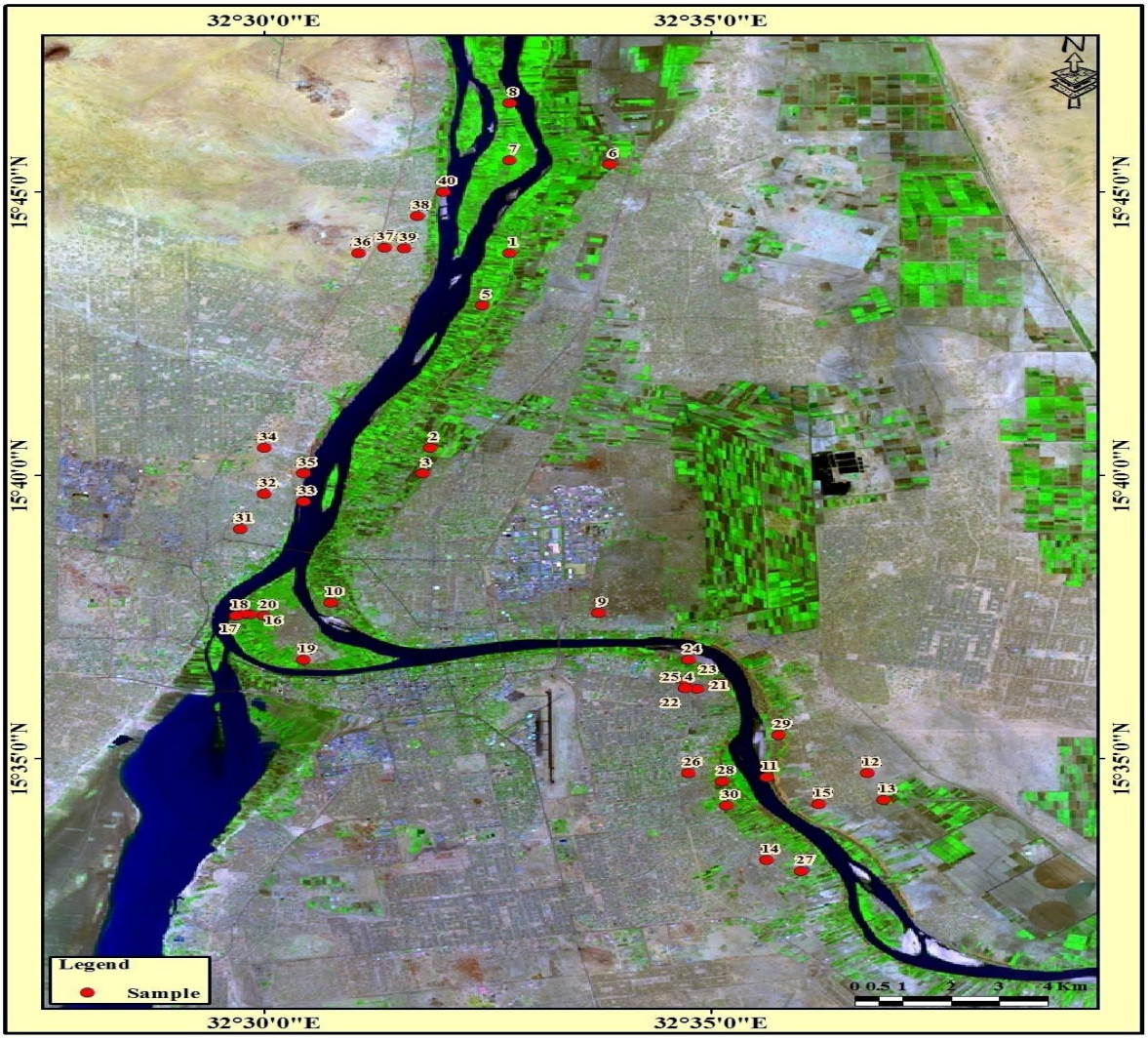


Fig (4.1):A map showing the area from which plants and soil samples have been collected

4.2 SAMPLES COLLECTION:

Forty samples soils and forty samples of five vegetables (Cucumber, Marrow, Mallow, Watercress and onion)were chosen as it's the most consumable fruits in Sudan.

Samples were collected from different three locations (Omdurman, Khartoum and Bahri) in Khartoum state on the period between October 2015 and March 2016.

All soil and vegetable samples were packed into polyethylene bags and taken to the laboratory for analysis.

4.3 SAMPLES PREPARATION:

The samples were cleaned using tab water, and then they were cut into slices after the covers were taken off figure After that the samples were dried in 100C oven figure (4.1) until the samples were completely dry, which was achieved by reaching constant weight.

Fig (4.2): show Oven

The particles size was obtained.

The samples were passed through 200 mechsieve, and homogenized.

Approximately 1.00 g of each dried sample was accurately weighed in sensitive scale (figure (4.3)) and pressed using SPECAC manual hydraulic press pressing machine (20 tons) as shown in (Figure (4.4)) .

The pellet diameter was 2.5cm standard reference materials SRMs of hay standard reference material (IAEA-V-10) was treated as above. Blank samples were also prepared for each set.

Fig (4.3): sensitive scale

Fig (4.4):SPECAC manual hydraulic press pressing machine

4.4 SAMPLES MEASUREMENTS:

4.4.1 X-Ray Fluorescence Technique:

4.4.1.1 Experimental set-up:

The sample was grinded firstly up to become soft, then pressed by the pressing machine and placed on the sample holder.

The XRF spectrometer system was used which composed of a radioisotope excitation source cd-109, together with (ORTEC) Si(Li) detector and associated electronics, Canberra multi channel analyzer and computer.

The amplifier settings were adjusted for optimum values. Then analyzed samples, respectively (Onion, Cucumber, Jew Mellow, Water cress and Marrow) each sample was separate over lapping, fitting the spectra by the (win QXAS), and appointed the elements within each sample by the (QXAS) software in addition to the peak area and concentration of each element. The bias supply was used 600V for Si (Li) detector.

The machine was cleaned before you start pressing to avoid inaccuracies in the experiment and the surface area of the sample holder was matched with a surface area of samples in the development of the sample holder specimens.

MCA and the QXAS software were calibrated before the start of analysis

X-Ray Fluorescence spectrometers use high energy X-rays or gamma rays to excite fluorescent radiation (or photons) from a sample for chemical or elemental analysis. In an energy dispersive X-ray fluorescence spectrometer (EDXRF Spectrometer), the fluorescent photons from the irradiated sample are detected without being separated first (as they are in wavelength dispersive XRF spectrometers) .

Limits of detection for EDXRF spectrometers is typically in the parts per million (ppm) range.

4.4.1.2 Samples Analysis:

The pellets were present to the XRF spectrometer system, where each of them was measured for 1000 sec.

The spectra obtained as a result of X-ray excitation usingCd-109 (30 mci), x-ray source (figure 3.6) were transferred to a computer.

The spectra were the analyzed and concentration of the elements present in the samples were obtained using Axil, XRF software available in the compute a plant standard was used to ensure reliability of the results (Hay standard reference material obtained from the International Atomic Energy Agency(IAEA)).

The concentration of the elements was calculated using relative method as in equation (3.1):

$$C_{st} = KI_{st} \qquad (4.1)$$

WhereC_{St}Concentration of the standard is,K is Proportional constant, $I_{St}$is Intensity of the standard. And

$$C_{un} = KI_{un} \qquad (4.2)$$

Where C_{un}concentration of the unknown sample is proportional constant, $I_{un}$is Intensity of the unknown sample .

From equation (3.1).

$$K = C_{st}/I_{st} \qquad (4.3)$$

When we substitute the value of K from equation (3.3) in equation (3.2) we get:

$$C_{un} = \frac{C_{st}}{I_{st}} I_{un} \qquad (4.4)$$

Fig (4.5): X-Ray Fluorescence machine

4.4.2 AAS Technique:

4.4.2.1 Samples Treatment:

Collected vegetable and soil samples were immediately transported without soft powder in sterile bottles to the laboratory Microbiology, Faculty of Agriculture Khartoum University.

Approximately one 1g of finally powdered sample was weighed accurately and placed into 250 ml beaker. 5ml of conc. Nitric acid was added and the mixture evaporated slowly on hot plate to near dryness, other 5ml of conc. nitric acid was added and evaporated until the production of brown NO2 fume ceased.

10ml aqual regia (1 HNO3: 3HCl) prepared recently were added and evaporated to near dryness or semi-dryness. Finally, 5 ml of per choleric acid HClO4 was added and evaporated until complete digestion was achieved, which was indicated by a non-turbid and/or a white solution. The residue was diluted with de ionized water into 100ml volumetric flask. The 36 prepared solutions was placed into 100ml of glass bottle and stored at room temperature.

4.4.2.2 Experimental Set Up:

Shimadzu, AA model 6800 was used for the measurement of the concentration of the heavy metals Mn, Cu, Zn, and Pb under the following settings of wavelength and hollow cathode lamp current.

Table(4.1): Instrumental settings for the determination of Cu, Zn, Pb, and Mn by AAS.

Element	Wavelength (nm)	Lamp Current low (mA)	Lamp Mode	Slit Width (nm)	Fuel Gas Flow Rate (L/min)	Flame type
Mn	279.5	10	NON-BGC	0.2	2.0	Air-C2H2
Cu	324.8	6	BGC-D2	0.5	1.8	Air.C2H2
Zn	213.9	8	NON-BGC	0.5	2.0	Air-C2H2
Pb	217.0	10	BGC-D2	0.5	2.0	Air-C2H2

Apparatus and equipments:

- Plastic container.
- Stainless steel knives.
- Glass vials 25 ml.- Crucible dishes.
- Muffle furnace 550°C.
- Crucible vessels.
- Heating block.
- Glass ware: funnels, volumetric flasks, pipettes, glass rod.

- Atomic Absorption Spectroscopy (AAS), model: A6800, Shimadzu, Japan.
- Standard solutions for lead, manganese, copper and zinc prepared according to AAOC, (1990) method with some modifications.

4.4.2.3 Samples analysis:

Total elements concentration was determined for all samples by the dry a shing method described by Pearson's, (1981). The amounts of lead, manganese,

copper and zinc were determined by Atomic Absorption Spectrometer (AAS), model: A6800, Shimadzu, Japan.

Firstly standard solutions of each element were prepared as fallow:

250 µl was taken from the stock standard solution (1000µg/ml) in a plastic volumetric flask (25ml) and made up to the mark with 0.5 normality of hydrochloric acid solution, thus made the intermediate standard solution (10µg/ml) secondly, working standard solutions were prepared to be suitable to the concentration of each elements in the sample solution by the following:

Zn: a series of 10,20,400 and 1000µLwere taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.02,0.1,0.4,0.7 and 1ppmof zinc respectively.

Mn: a series of 5,500,1000 and 2000µLwere taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.005,0.5,1, and 2ppmof manganese respectively.

Cu: a series of 30,100,300,700 and 1000µLwere taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.03,0.1,0.3,0.7 and 1ppmof manganese respectively.

Pb: a series of 20,60,80 and 100µLwere taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.02,0.06,0.08 and 0.1ppmof manganese respectively.

Fig (4.6):Atomic Absorption Spectrometer

4.5 STATISTICAL ANALYSIS:

4.5.1 T-Test Analysis:

In the study, statistical analysis of data was performed using Microsoft Office Excel and the computing package called Statistical Package for Social Science (SPSS 16.0 for Windows, SPSS Inc., IL, U.S.A.).

Parametric independent T-test has been employed to identify the comparison of mean concentration of heavy metal between two techniques (XRF and AAS).

Statistical test shows that there has significant difference between two villages either in Mn, Cu, Pb and Zn with significant value ($p\text{-value}<0.05$).

4.5.2 Correlation Analysis:

In the study, statistical analysis of data was performed using correlation analysis to correlated concentrations of heavy metals in vegetables and soils measured by XRF and AAS techniques.

CHAPTER FIVE

RESULTS AND DISCUSSIONS

5.1 QUALITY CONTROL OF THE OBTAINED DATA:

Hay powder (IAEA-V-10) certified reference material was used and the recovery percentage and the error percentage were calculated as shown:

Table (5.1): Concentration of heavy metal of analytical Hay powder (vegetables) ppm compare with certificate value.

Techniques	Elements	Elements Analytical value (mg/Kg)	Certificate value (mg/Kg)	Recovery%	Error%
XRF	Mn	44.53	47	94.7	5.25
	Zn	11.64	24	48.5	51.5
	Cu	7.14	9.4	75.96	24.04
	Pb	0.99	1.6	61.88	38.13
AAS	Mn	47.58	47	101.2	1.2
	Zn	24.72	24	103	3
	Cu	11.71	9.4	124.57	24.57
	Pb	ND	1.6	ND	ND

ND refer to Non Detection

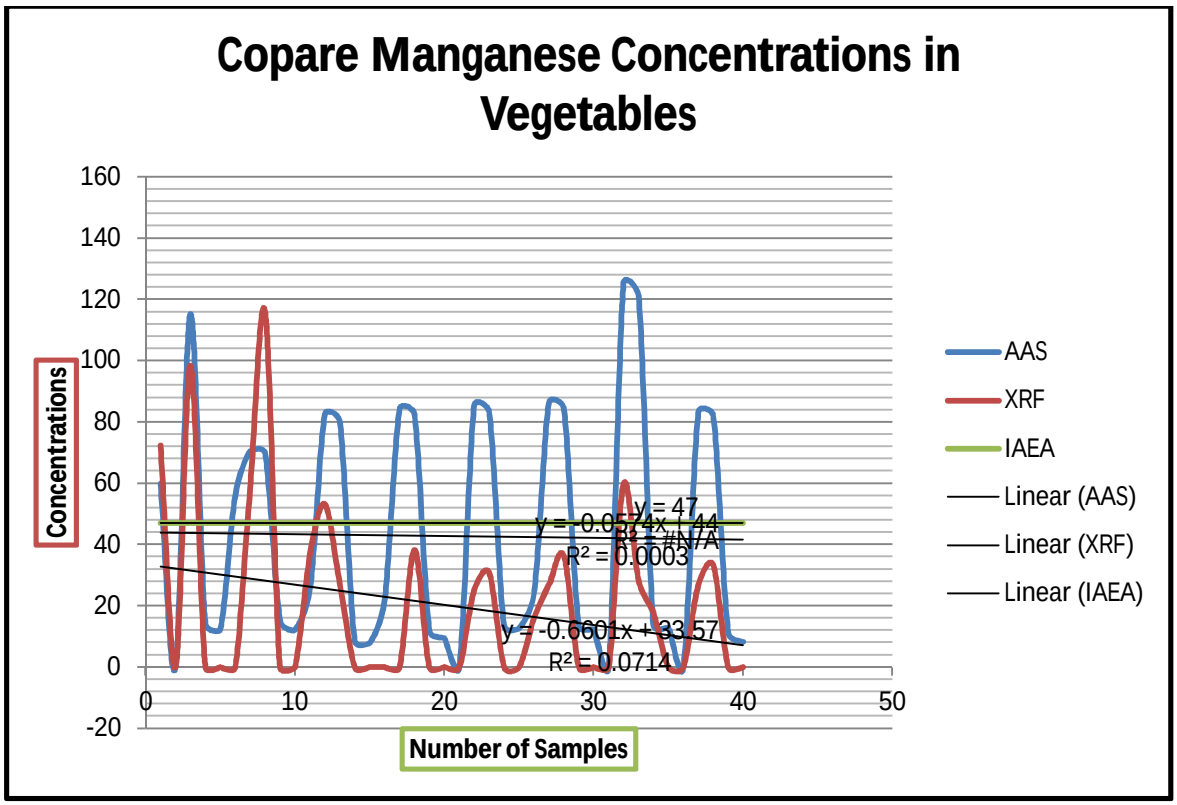


Fig (5.1): plot show Compare Manganese concentrations in Vegetables

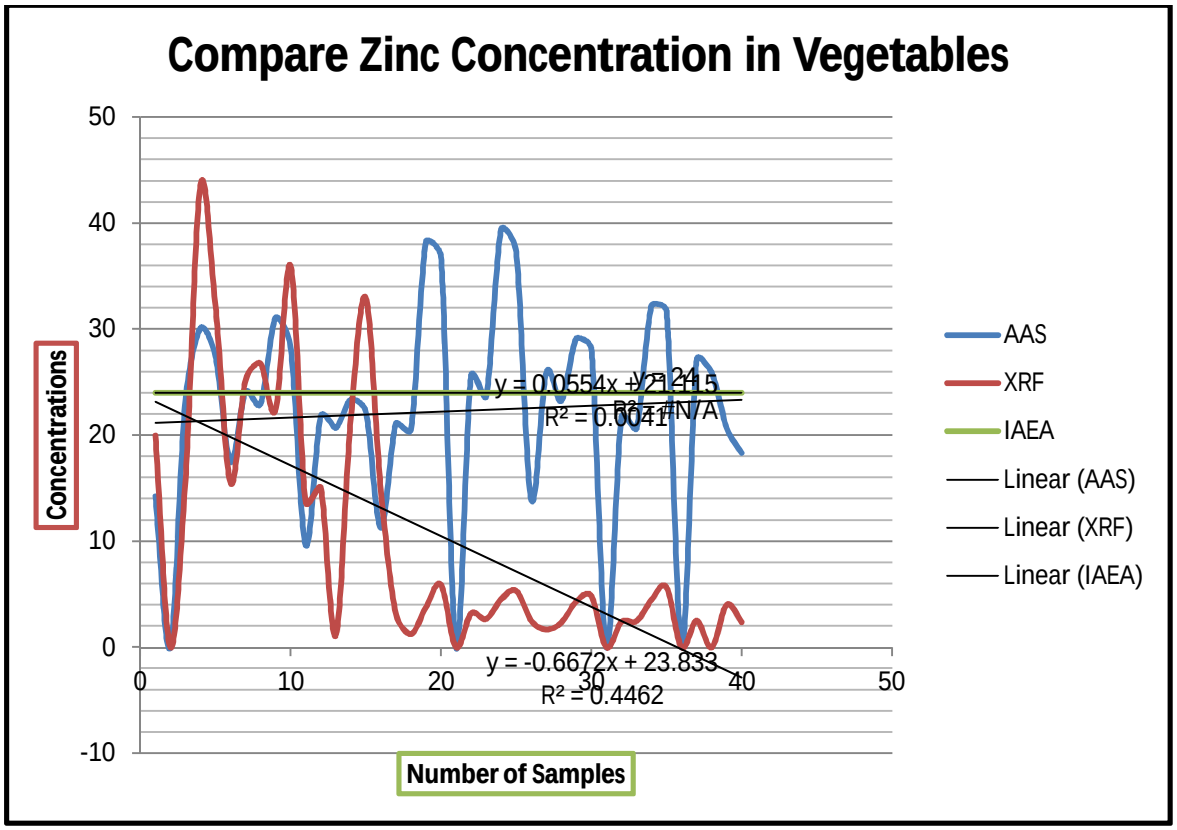


Fig (5.2): plot show Compare Zinc concentrations in Vegetables

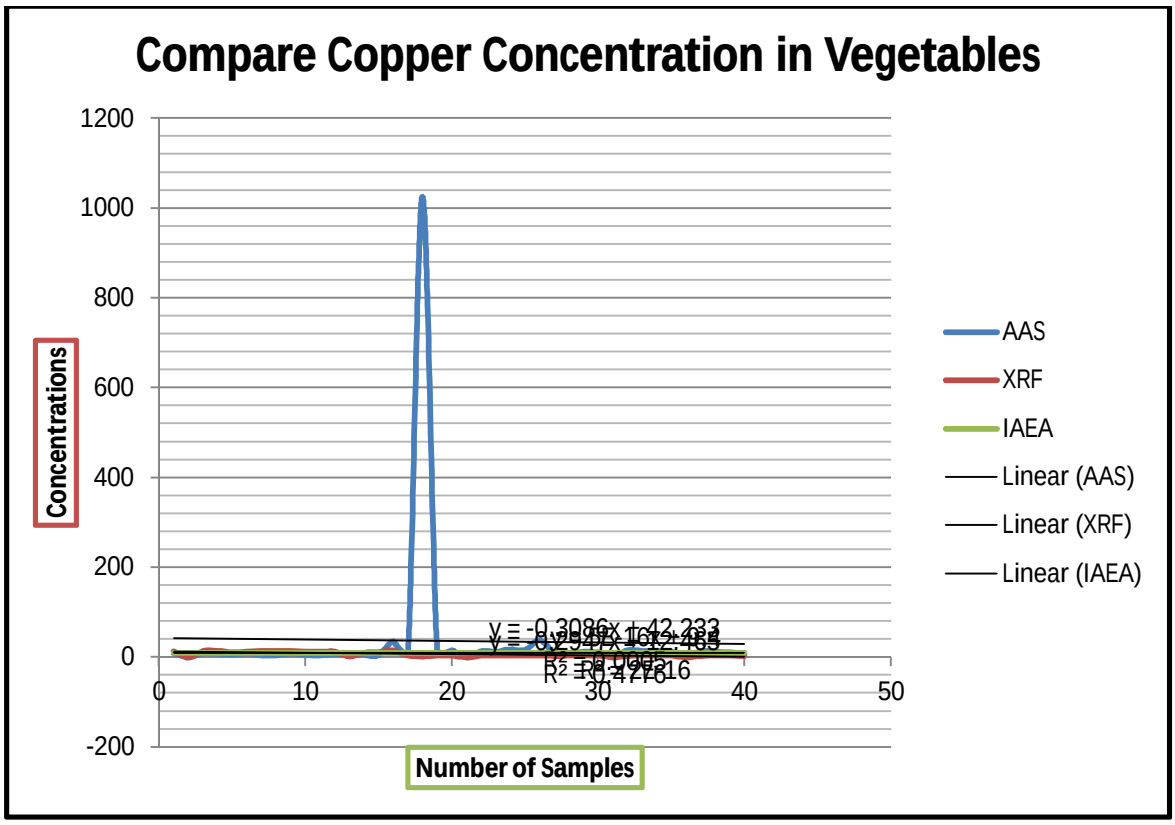


Fig (5.3): plot show Compare Copper concentrations in Vegetables

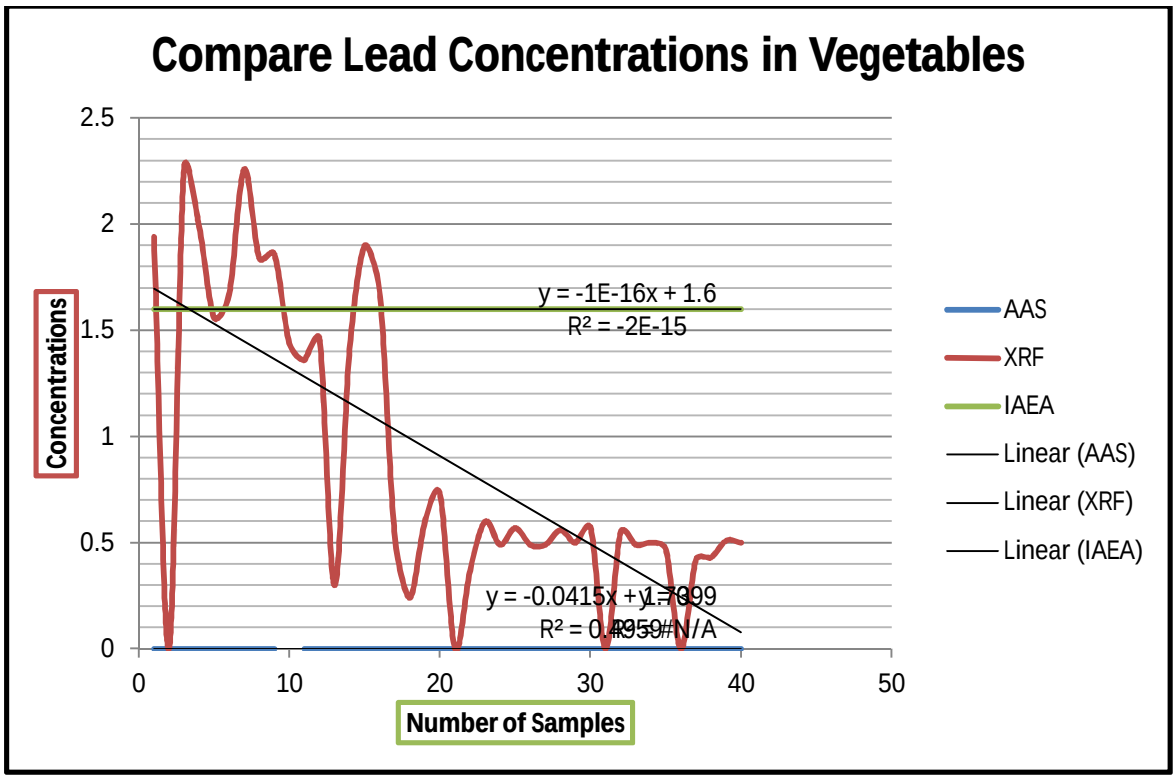


Fig (5.4): plot show Compare Lead concentrations in Vegetables

Trace Elements in Soil. (IAEA-Soil-7) certified reference material was used and the recovery percentage and the error percentage were calculated as shown:

Table (5.2): concentration of heavy metal of analytical Hay powder (soils) ppm compare with certificate value.

Techniques	Elements	Elements Analytical value (mg/Kg)	Certificate value (mg/Kg)	Recovery%	Error%
XRF	Mn	410.34	631	65.03	34.97
	Zn	23.89	104	22.98	77.02
	Cu	19.93	11	81.18	18.82
	Pb	14.41	60	24.01	75.99
AAS	Mn	897.7	631	142.26	42.26
	Zn	64.3	104	61.83	38.17
	Cu	46.1	11	119.09	19.09
	Pb	ND	60	ND	ND

ND refer to Non Detection

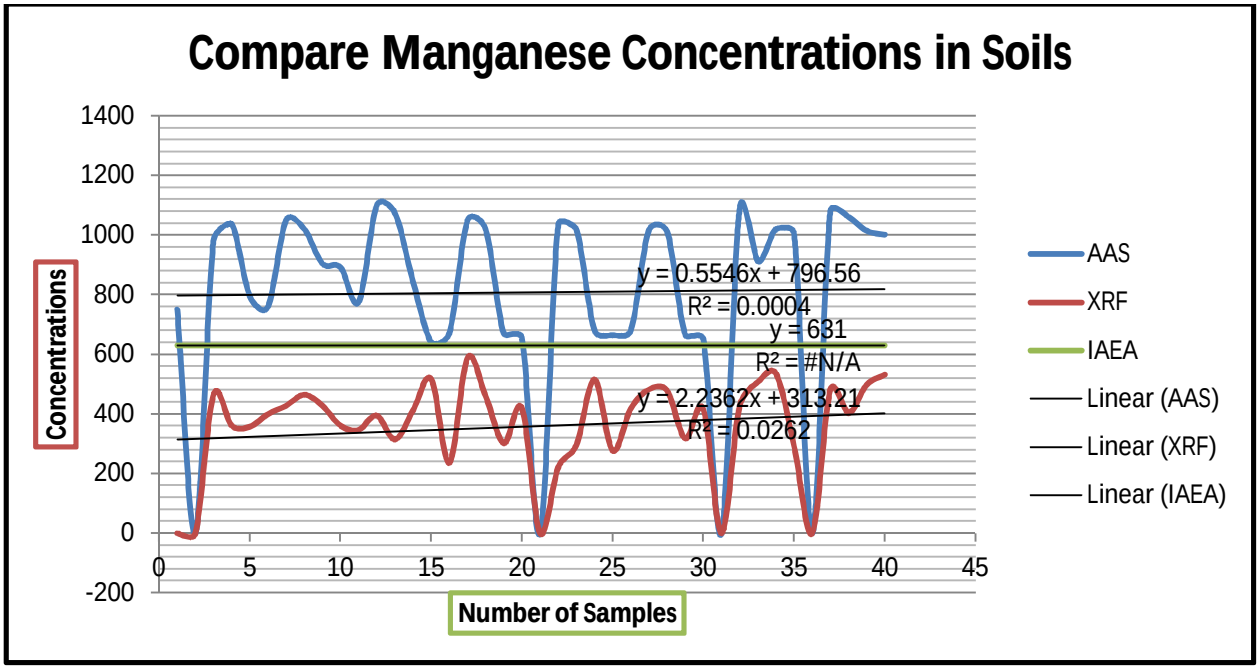


Fig (5.5): plot show compare Manganese concentrations in Soils

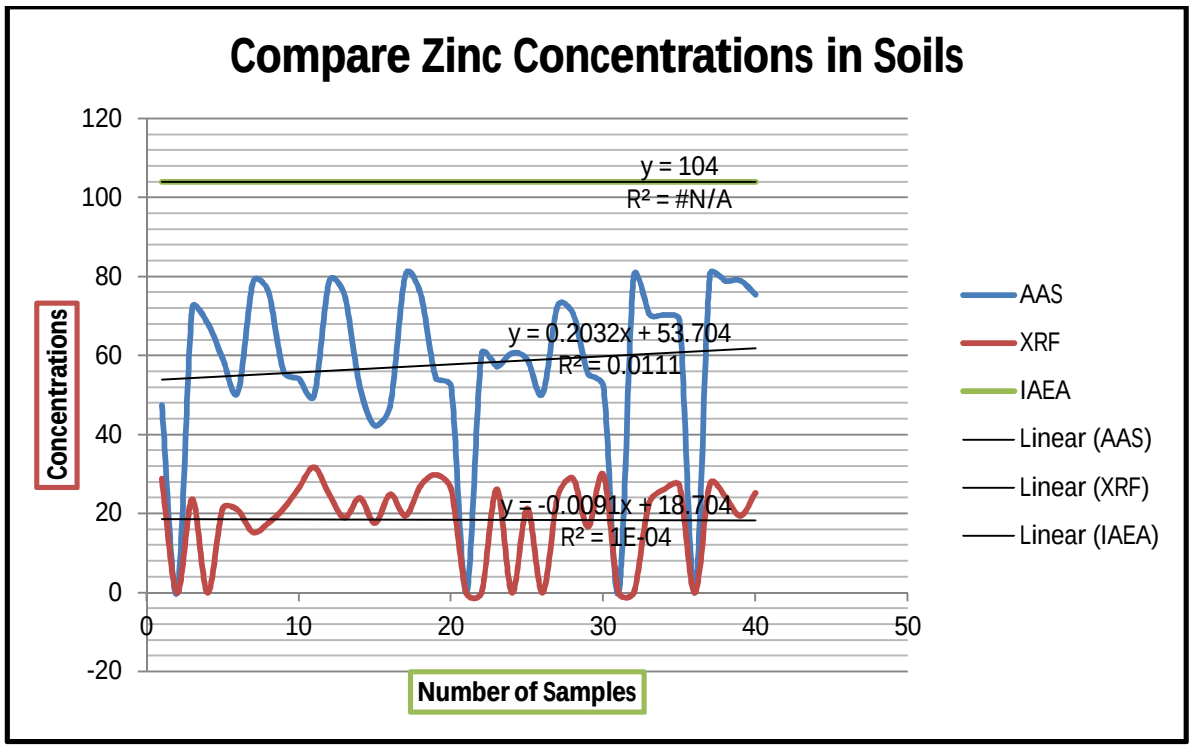


Fig (5.6): plot show compare Zinc concentrations in Soils

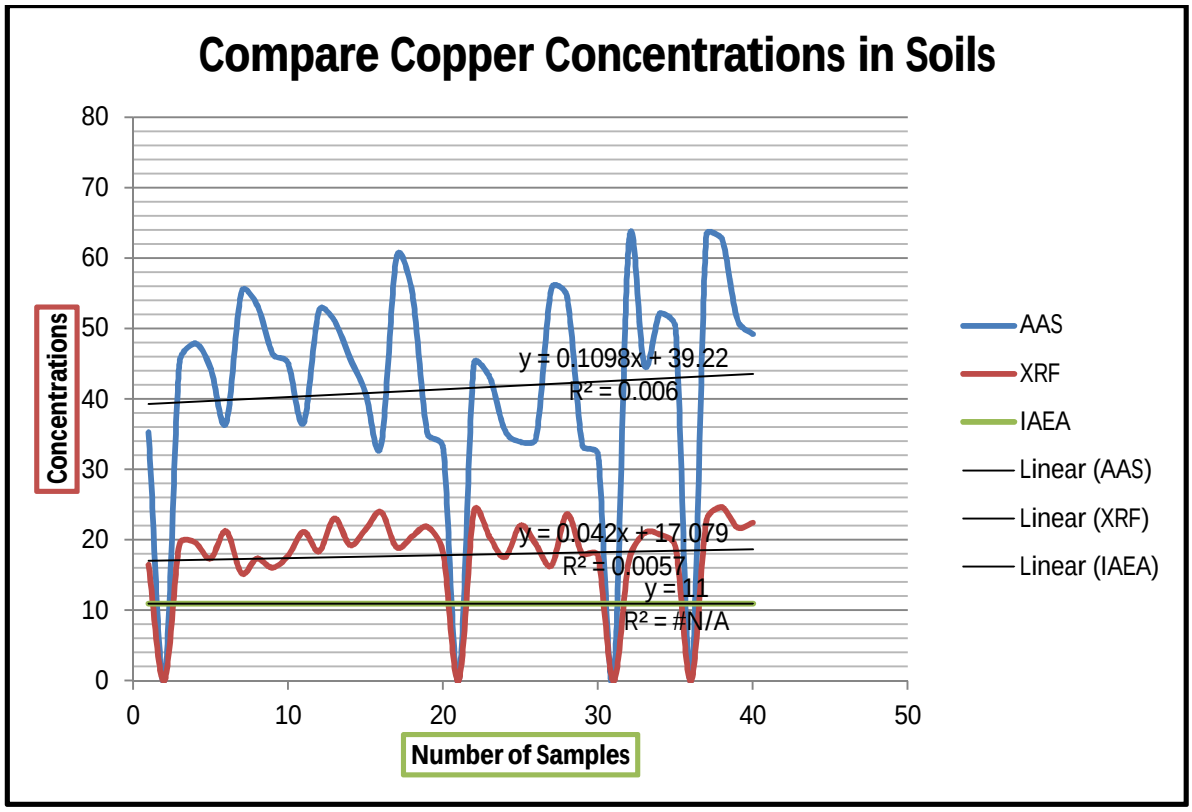


Fig (5.7): plot show compare Copper concentrations in Soils

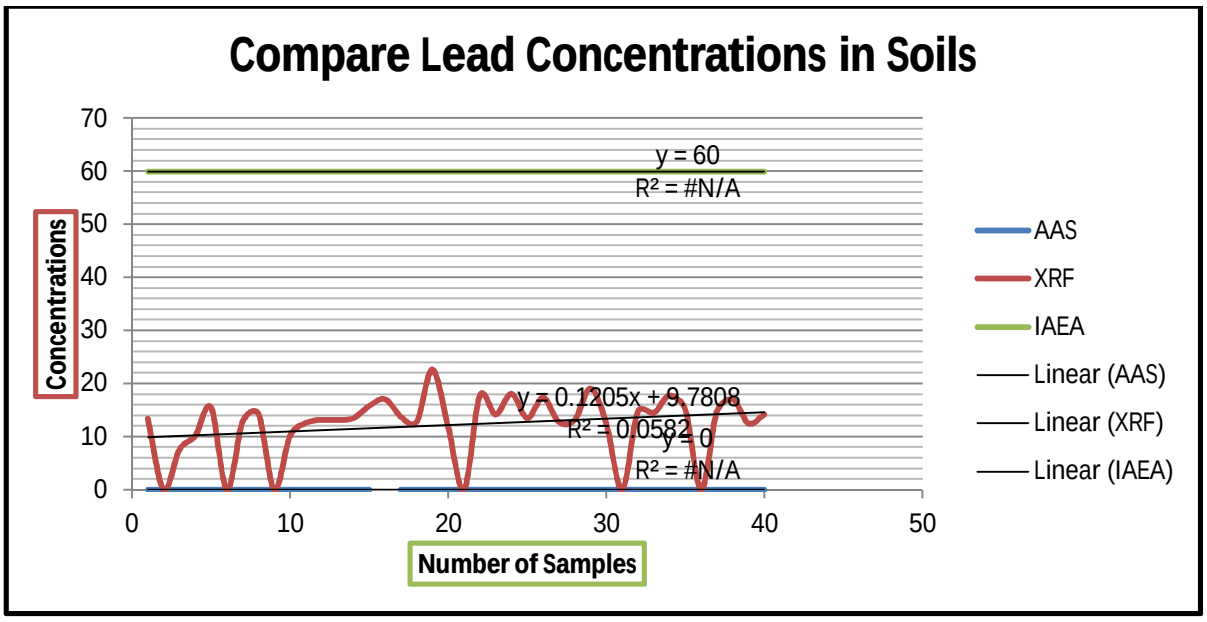


Fig (5.8): plot show compare Lead concentrations in Soils

From tables (5.1) to (5.2) and figures (5.1) to (5.8) the following remarks can be obtained:

From this table can conclude that there is agreement for comparisons between certified and analytical values, which indicates good accuracy and good recovery. Range of error percentage between (-10% to 10% percent) this give a good efficient of devise, and true value of metals under study without range is contaminated degree or non-contaminate degree.

5.2 SUMMARY OF STATISTICS:

X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS) were used to analyze the vegetables sample and soils sample:

Table (5.3): Summary of the statistics for the Metals concentration (ppm) except Mn, Zn, Cu and pb in Onion and soil samples using XRF technique

Samples	No	Elements	Mean	STD	Min	Max
Onion	8	Mn	41.67	28.54	16	72.4
		Zn	13.33	6.49	2.53	20
		Cu	11.32	4.30	3.92	15
		Pb	1.43	0.56	0.49	1.94

Soil	8	Mn	350.5	82.18	236	419
		Zn	26.63	4.75	20.9	31.8
		Cu	20.48	2.77	16.5	24
		Pb	15.13	2.48	12.6	17.4

Table (5.4): Summary of the statistics for the Metals concentration (µg/g) except Mn, Zn, Cu and pb in Onion and soil samples using AAS technique

Samples	No	Elements	Mean	STD	Min	Max
Onion	8	Mn	37.36	18.86	21.77	59.92
		Zn	13.33	3.01	9.66	17.5
		Cu	19.04	16.19	4.44	38.12
		Pb	ND	ND	ND	ND
Soil	8	Mn	728.01	48.07	671.92	776.22
		Zn	49.18	1.64	47.34	50.82
		Cu	35.28	1.4	33.4	36.62
		Pb	ND	ND	ND	ND

Table (5.5): Summary of the statistics for the Metals concentration (ppm) except Mn, Zn, Cu and pb in Mallow and soil samples using XRF technique

Samples	No	Elements	Mean	STD	Min	Max
Mallow	8	Mn	41.72	17.12	25.2	59.9
		Zn	7.61	9.06	1.7	25.2
		Cu	6.18	4.81	3.08	13.4
		Pb	0.87	0.72	0.37	2.26
Soil	8	Mn	432.14	112.23	221	589
		Zn	22.34	4.9	15.3	27.6
		Cu	19.01	3.29	15.3	24.1
		Pb	14.3	1.75	12.8	17.8

Table (5.6): Summary of the statistics for the Metals concentration (µg/g) except Mn, Zn, Cu and pb in Mallow and soil samples using AAS technique

Samples	No	Elements	Mean	STD	Min	Max
Mallow	8	Mn	88.25	17.21	70.47	125.35
		Zn	39.92	2.39	21.14	27.13
		Cu	4.58	15.52	10.89	3.87
		Pb	ND	ND	ND	ND
Soil	8	Mn	1060.9	30.65	1018.06	1100.15
		Zn	76.01	7.36	60.5	80.72
		Cu	51.15	10.35	32.69	63.38
		Pb	ND	ND	ND	ND

Table (5.7): Summary of the statistics for the Metals concentration (ppm) except Mn, Zn, Cu and pb in Watercress and soil samples using XRF technique

Samples	No	Elements	Mean	STD	Min	Max
Watercress	8	Mn	51.06	35.16	27.2	116
		Zn	7.48	9.96	1.11	26.8
		Cu	5.9	5.18	1.7	14.6
		Pb	0.84	0.77	0.24	2.26
Soil	8	Mn	423.75	78.63	296	507
		Zn	23.71	3.89	17.7	29
		Cu	21.3	2.4	17.4	24.7
		Pb	13.36	2.68	7.6	17.1

Table (5.8): Summary of the statistics for the Metals concentration (µg/g) except Mn, Zn, Cu and pb in Watercress and soil samples using AAS technique

Samples	No	Elements	Mean	STD	Min	Max
Watercress	8	Mn	89.84	18.18	69.8	121.28
		Zn	22.63	1.9	20.53	25.95

		Cu	9.95	3.35	4.11	14.33
		Pb	ND	ND	ND	ND
Soil	8	Mn	1012.9	50.14	912.5	1075.2
		Zn	72.12	6.66	57.26	78.95
		Cu	51.32	6.63	43.23	62.83
		Pb	ND	ND	ND	ND

Table (5.9): Summary of the statistics for the Metals concentration (ppm) except Mn, Zn, Cu and pb in Marrow and soil samples using XRF technique

Samples	No	Elements	Mean	STD	Min	Max
Marrow	8	Mn	17.7	0	0	17.7
		Zn	13.58	14.53	3.77	43.6
		Cu	7.05	4.79	3.41	14.5
		Pb	0.98	0.66	0.49	1.99
Soil	8	Mn	421.5	89.97	302	536
		Zn	22.93	4.77	16.7	29.9
		Cu	19.4	2.08	16.1	21.9
		Pb	16.27	4.36	10.2	22.7

Table (5.10): Summary of the statistics for the Metals concentration (µg/g) except Mn, Zn, Cu and pb in Marrow and soil samples using AAS technique

Samples	No	Elements	Mean	STD	Min	Max
Marrow	8	Mn	12.74	2.09	8.58	15.2
		Zn	30.56	6.46	20.72	39.42
		Cu	11.44	4.43	5.11	17.67
		Pb	ND	ND	ND	ND
Soil	8	Mn	854.94	164.69	665.48	1038.14
		Zn	62.03	9.51	52.32	79.02
		Cu	43.49	7.63	33.4	52.24

		Pb	Pb	ND	ND	ND

Table (5.11): Summary of the statistics for the Metals concentration (ppm) except Mn, Zn, Cu and pb in Cucumber and soil samples using XRF technique

Samples	No	Elements	Mean	STD	Min	Max
Cucumber	8	Mn	ND	ND	ND	ND
		Zn	15.67	15.04	2.38	36
		Cu	7.53	4.14	3.31	12.8
		Pb	0.97	0.57	0.47	1.9
Soil	8	Mn	396.92	93.73	277	532
		Zn	24.4	3.99	17.6	29.9
		Cu	19.56	2.12	17.4	22.5
		Pb	13.58	1.97	10.2	15.8

Table (5.12): Summary of the statistics for the Metals concentration (µg/g) except Mn, Zn, Cu and pb in Cucumber and soil samples using AAS technique

Samples	No	Elements	Mean	STD	Min	Max
Cucumber	8	Mn	10.98	2.09	7.9	12.88
		Zn	28.8	6.56	18.34	37.32
		Cu	9.89	4.74	4.5	16.32
		Pb	ND	ND	ND	ND
Soil	8	Mn	788.49	159.3	640.8	1005.82
		Zn	57.96	10.4	42.25	75.43
		Cu	41.15	7.27	32.2	50.22
		Pb	ND	ND	ND	ND

The following remarks can be obtained:

For samples result from table (5.5), (5.7) and (5.9) all elements except Zn (in which stander Deviation is slightly higher than Mean) the mean is higher than stander deviation which indicate the normal of the data and may be taken as

evidence for natural source for this elements the same conclusion can be getting when mean is compared with median.

For samples results from Table (5.3), (5.4), (5.6) ,(5.8). (5.10), (5.11) and (5.12) all elements show normal distributions (the stander Deviation is less than mean and median are approximately equal).

That indicates the scattering of the data for these elements, which can give indication for an anthropogenic source for these elements.

5.3 COMPARISON BETWEEN CONCENTRATIONS MEASURED BY TWO TECHNIQUES:

5.3.1 Compare the Means of Concentration Heavy Metals Measured by two Techniques and Control Samples:

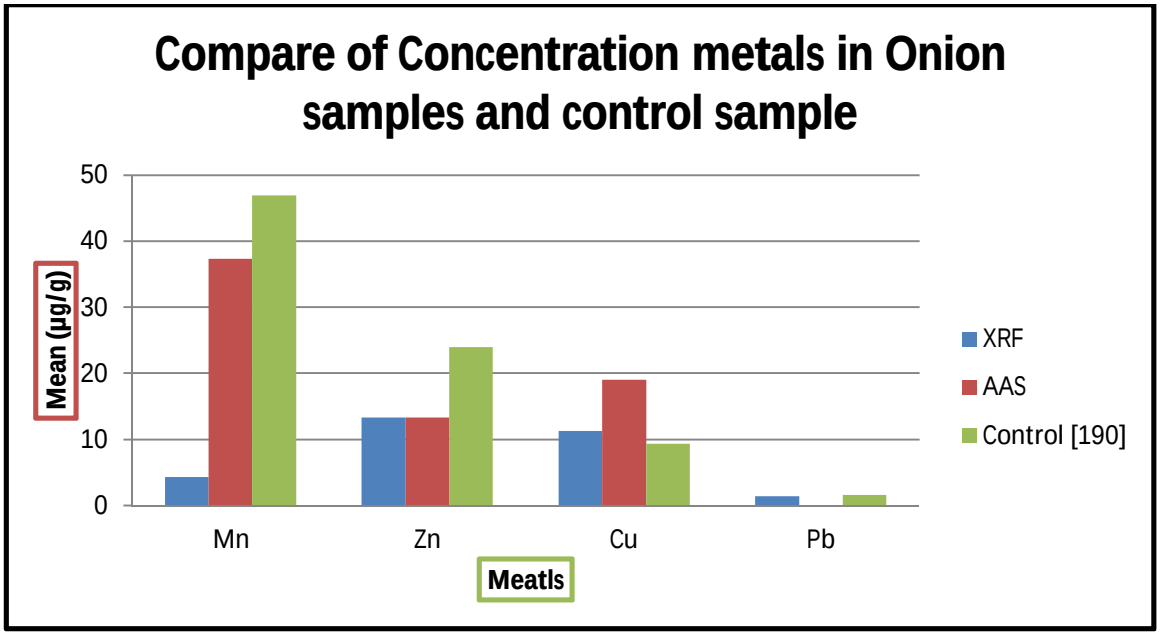


Fig (5.9): plot show concentration metals in Onion

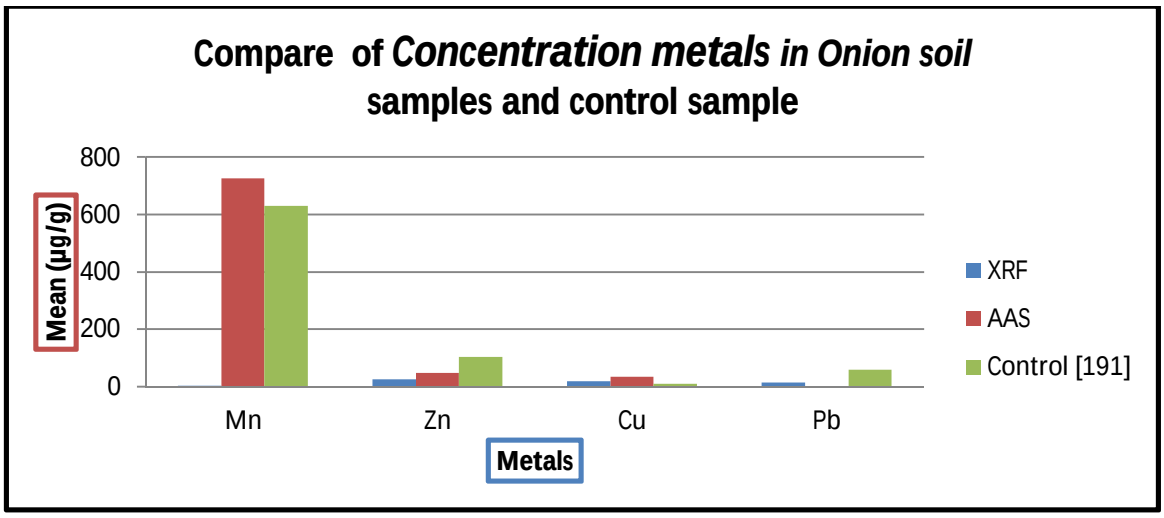


Fig (5.10): plot show concentration metals in Onion soil

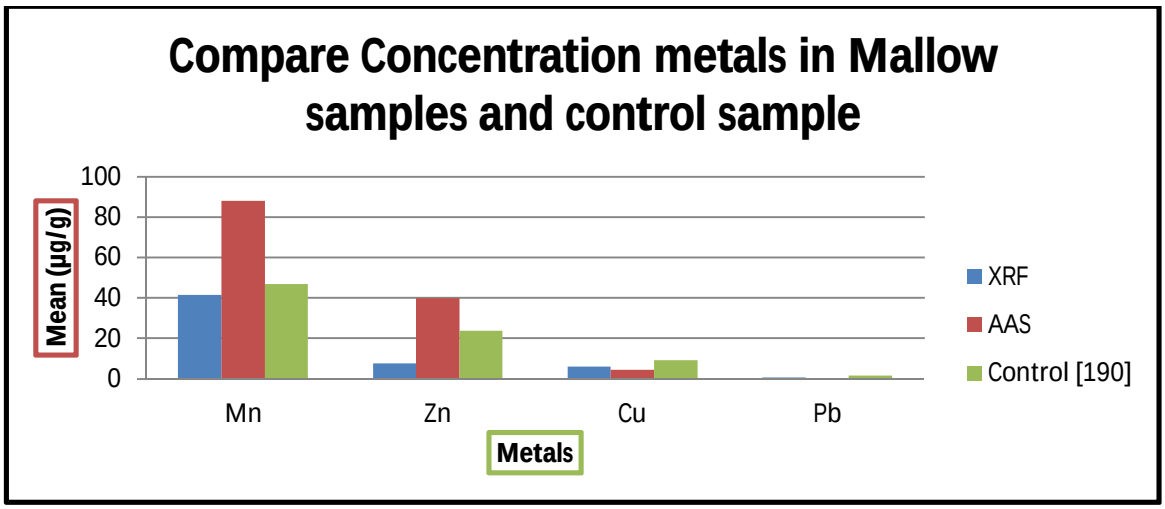


Fig (5.11): plot show concentration metals in Jew Mallow

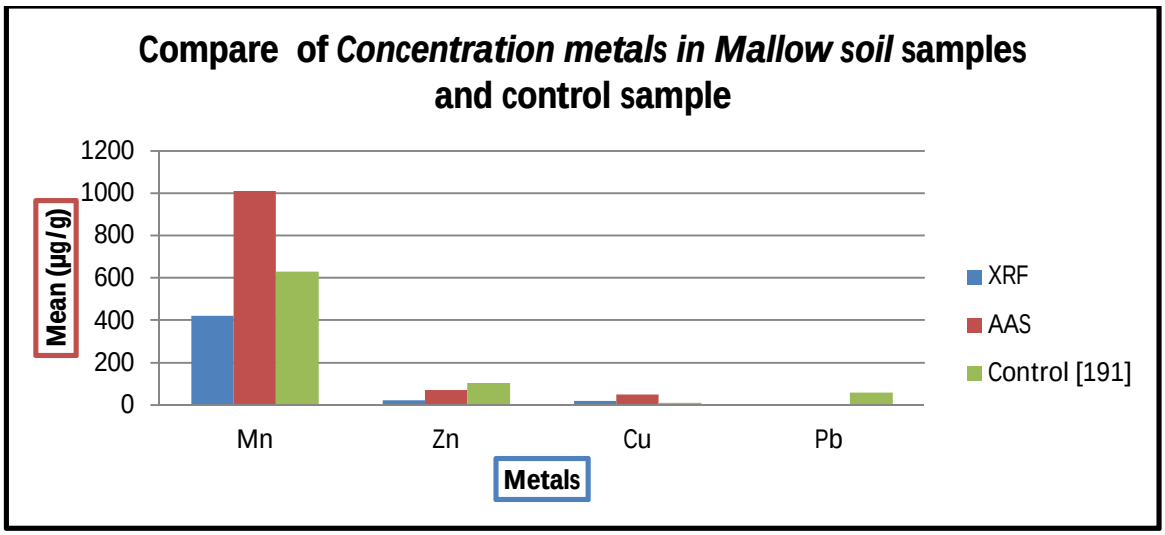


Fig (5.12): plot show concentration metals in Jew Mallow soil

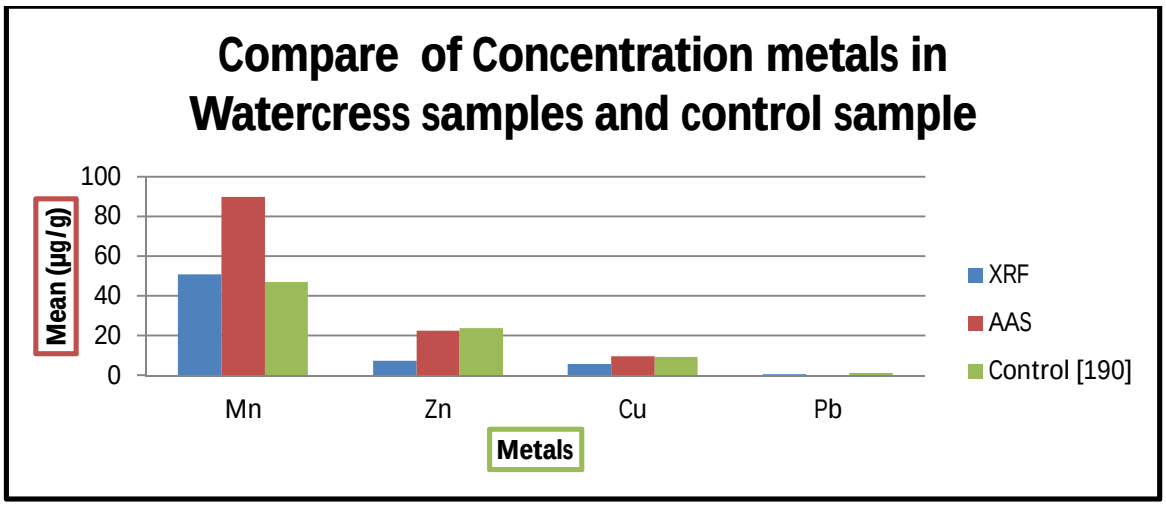


Fig (5.13): plot show concentration metals in Watercress

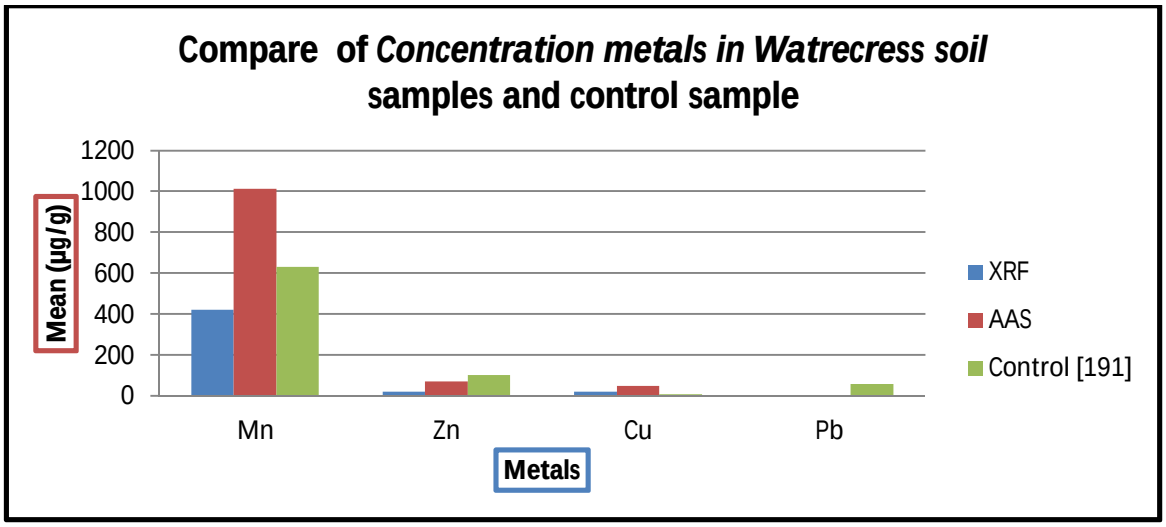


Fig (5.14): plot show concentration metals in Watercress soil

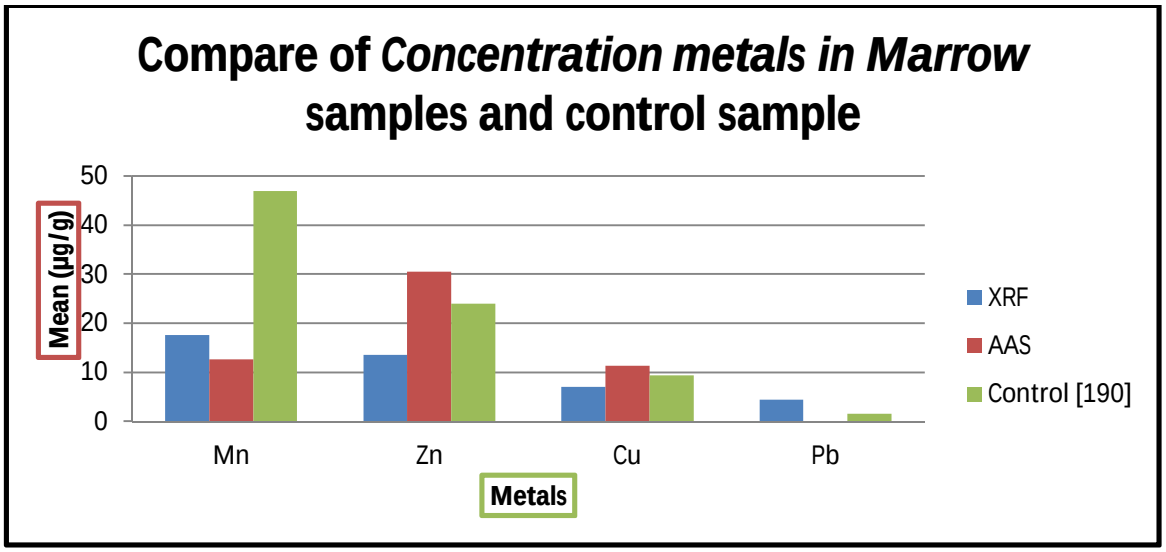


Fig (5.15): plot show concentration metals in Marrow

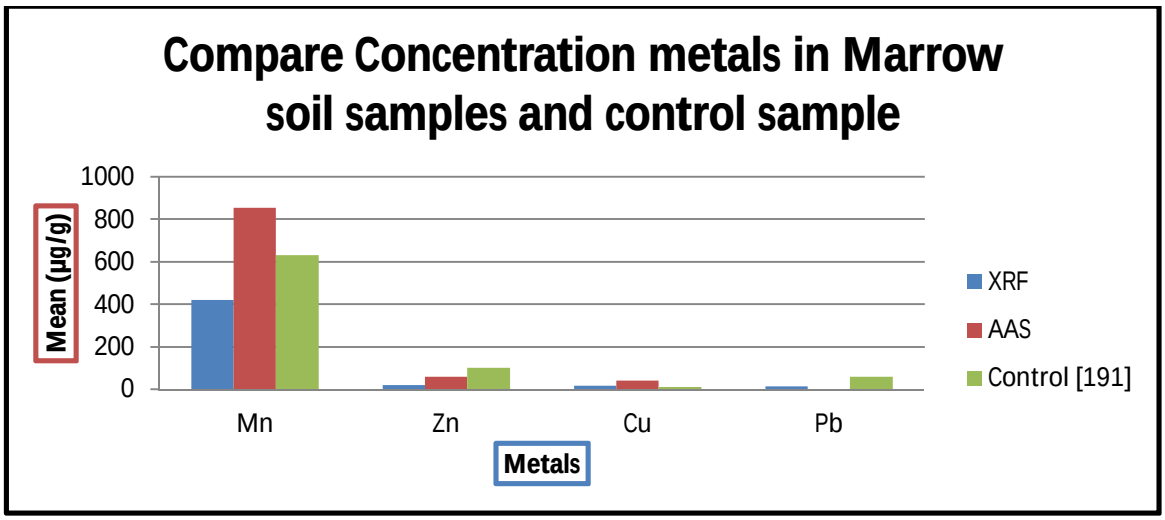


Fig (5.16): plot show concentration metals in Marrow soil

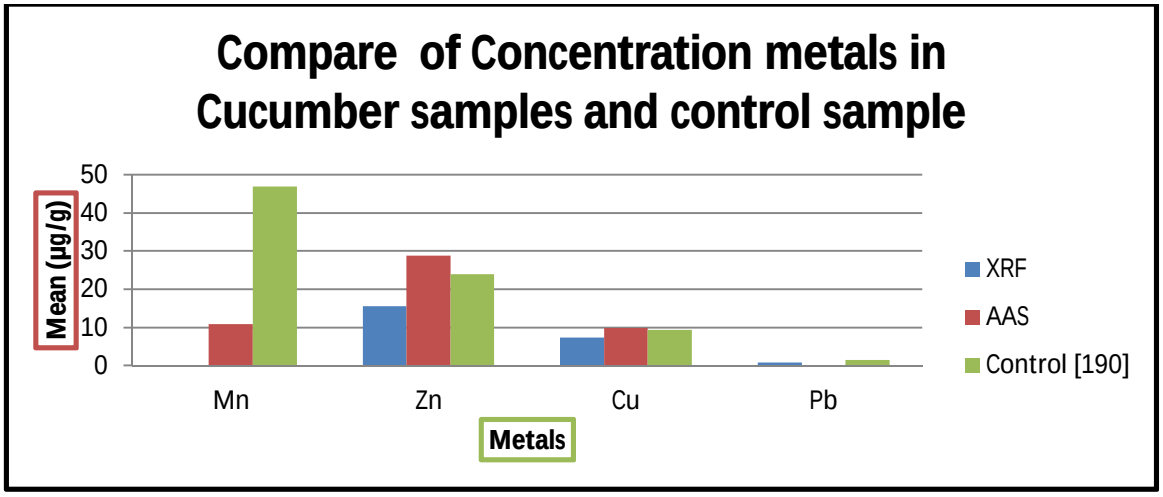


Fig (5.17): plot show concentration metals in Cucumber

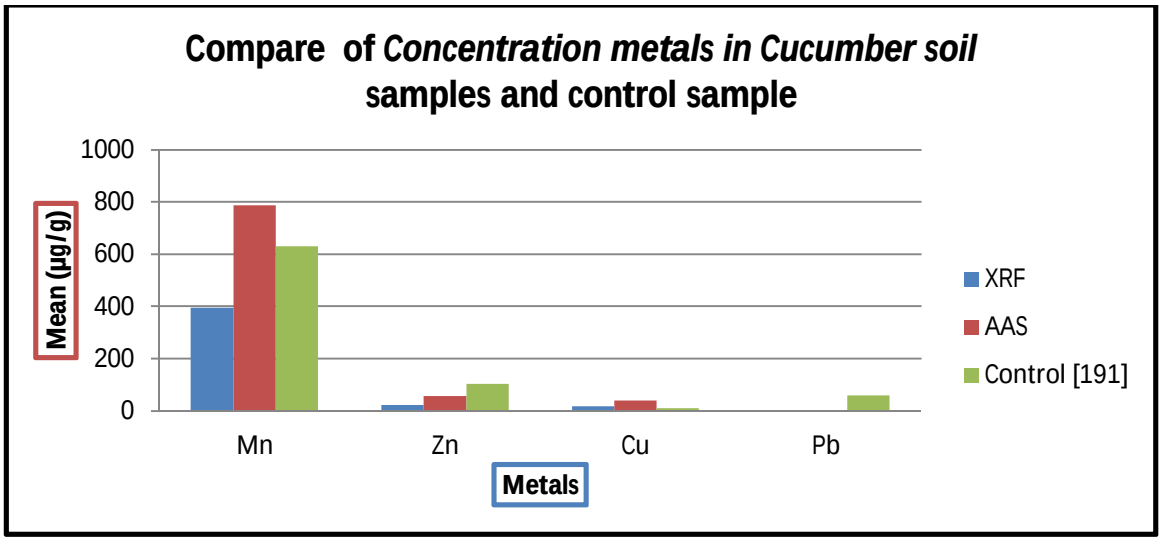


Fig (5.18): plot show concentration metals in Cucumber soil

5.3.2 Independent T-Test:

The statistical data for heavy metal that are Mn, Cu, Pb and Zn are shown in Tables (5.13) and (5.14).

Table (5.13): the statistical data for parametric independent t-test in concentrations of heavy metal in vegetables measured by two techniques

Heavy metals	AAS technique Mean (SD)	XRF technique Mean (SD)	Mean diff (95%CI)	T-Test (df)	P-value
Mn	47.58	44.53	3.06	11.76	P<0.05
	(38.69)	(27.53)	(17.47,23.58)	(52)	
Zn	24.72	11.61	13.12	11.787	P<0.05
	(7.14)	(11.79)	(8.52,17.72)	(69)	
Cu	39.90	7.14	32.76	3.571	P<0.05
	(169.03)	(4.74)	(23.45,88.97)	(70)	
Pb	ND	0.99	ND	ND	P<0.05
	(ND)	(0.66)	(ND)	(ND)	

Table (5.14): the statistical data for parametric independent t-test in concentration of heavy metal in vegetables measured by two techniques

Heavy metals	AAS technique Mean (SD)	XRF technique Mean (SD)	Mean diff (95%CI)	T-Test (df)	P-value
Mn	894.71	410.34	31.94	28.91	P<0.05
	(165.87)	(90.57)	(420.62,548.11)	(68)	
Zn	64.30	23.89	40.41	66.08	P<0.05
	(11.94)	(4.26)	(35.89,44.92)	(65)	
Cu	46.08	19.93	26.15	41.75	P<0.05
	(9.46)	(2.53)	(22.89,29.40)	(70)	
Pb	ND	14.41	ND	ND	P<0.05
	(ND)	(2.85)	(ND)	(ND)	

A study of comparison of concentration of heavy metal in soil was showed in Table (5.14).

5.4 CORRELATION ANALYSIS OF HEAVY METALS CONCENTRATIONS:

Table (5.15):Correlations Analysis of Heavy-Metal Concentrations in vegetables measured by AAS and XRF techniques

	Mn	Zn	Cu	Pb
Mn	1	0.029	0.146	0.795**
Zn	0.029	1	0.049	0.854**
Cu	0.146	0.049	1	0.965**
Pb	0.795**	0.854**	0.965**	1

** Correlation is significant at the 0.01 level (2-tailed).

The vegetable's heavy metal correlation analysis shows a similar trend displayed in Table (5.15) as the combined data except that Zn is not correlated with Cu and Mn. However, among the heavy metals in vegetable, the only significant correlation exists between Cu and Zn.

Table (5.16):Correlations Analysis of Heavy-Metal Concentrations in soils measured by AAS and XRF techniques

	Mn	Zn	Cu	Pb
Mn	1	.939**	.942**	-.206
Zn	.939**	1	.961**	-.020
Cu	.942**	.961**	1	.253
Pb	-.206	-.020	.253	1

** Correlation is significant at the 0.01 level (2-tailed).

The soil's heavy metal correlation analysis shows a similar trend displayed in Table (5.16) as the combined data except that Pb is not correlated with Zn and Mn.

However, among the heavy metals in vegetable, the only significant correlation exists between Cu and Zn.

5.5 DISCUSSIONS:

From table (5.3) to(5.12) and figures(5.1) to (5.10) noted that:

Manganese (Mn) in some samples concentration measured by AAS technique higher than control sample the higher contaminated found in Watercress (89.84µg/g)and Jew Mallow(88.25µg/g) lower level in Onion (37.36 µg/g), Marrow (12.74 µg/g) and Cucumber (10.98 µg/g).

But in the same soils of this vegetables the samples concentration higher than control sample the contaminated found in Onion soil (780µg/g), Watercress soil (1012µg/g), Marrow soil (855µg/g) and Cucumber soil (788µg/g) Lower level in Jew Mallow soil (106µg/g).

Mn in some samples concentration measured by XRF technique higher than control sample the higher contaminated found in Watercress about (51ppm), lower level in Onion (41.67ppm), Jew Mallow (41.72ppm),Marrow (17.7ppm) and Cucumber (ND).

But in the same soils of this vegetables the all samples concentration lower than control sample.

Copper (cu) in all samples concentration measured by AAS technique higher than control sample the higher contaminated found in Onion (19µg/g),Watercress (10.89µg/g), Jew Mallow (9.95µg/g), Marrow (11.44µg/g) and Cucumber (9.89µg/g)

But in the same soils of this vegetables the all samples concentration higher than control sample the contaminated found in Onion soil (35µg/g), Jew Mallow (52.15µg/g), Watercress soil (51µg/g), Marrow soil (43.49µg/g) and Cucumber soil (41.15µg/g).

Cu in some samples concentration measured by XRF technique higher than control sample the higher contaminated found in Onion about (51ppm), lower level in Jew

Mallow (6.18ppm), Marrow (7.05ppm),Watercress (5.9ppm) and Cucumber (7.53ppm).

But in the same soils of this vegetables the all samples concentration higher than control sample founded in Onion soil (20.48ppm), Jew Mallow soil (19ppm), Watercress soil (21.30ppm), Marrow soil (19.40ppm) and Cucumber soil (19.56ppm).

Zinc (Zn) also in some samples concentration measured by AAS technique higher than control sample the higher contaminated found in Marrow (30.56µg/g) and Cucumber (28.8µg/g) lower level in Onion (13.33µg/g), Watercress (23.92µg/g), Jew Mallow (22.63µg/g).

But in the same soils of this vegetables the all samples concentration lower than control sample found in Onion soil (49.18µg/g), Jew Mallow (76µg/g), Watercress soil (72.12µg/g), Marrow soil (62.03µg/g) and Cucumber soil (57.96µg/g).

Zn in all samples concentration measured by XRF technique lower than control sample the higher contaminated found in Onion (13.33ppm), Jew Mallow (7.61ppm), Marrow (7.48ppm), Watercress (13.58ppm) and Cucumber (15.67ppm).

But in the same soils of this vegetables the all samples concentration lower than control sample founded in Onion soil (26.63ppm), Jew Mallow soil (22.34ppm), Watercress soil (23.71ppm), Marrow soil (22.93ppm) and Cucumber soil (24.4ppm).

Lead (pb) in all samples concentration measured by AAS technique is Non-detectable in vegetables and soils.

Pb in some samples concentration measured by XRF technique lower than control sample found in Onion(1.43ppm), Jew Mallow (0.87ppm), Watercress (0.84ppm), Marrow (0.98ppm) and Cucumber (0.97ppm).

But in the same soils of this vegetables the all samples concentration lower than control sample founded in Onion soil (15.13ppm), Jew Mallow soil (14.13ppm),

Watercress soil (13.36ppm), Marrow soil (16.27ppm) and Cucumber soil (13.58ppm).

The problem of environmental pollution by heavy metals has attracted much attention in recent years.

Industrialization has resulted in increased mobilization and deposition of heavy metal pollutants in natural habitats. Automobiles using leaded gasoline as fuel are a major source of heavy metals in the atmosphere. Heavy metals being non-degradable become an integral part of the habitats after release into the environment.

The comparison of concentration of heavy metals by XRF and AAS techniques show interesting results.

In view of tables (5.3) to (5.12) and figures (5.1) to (5.10) noted that for Onion, Watercress, Marrow, Cucumber and corresponding soils shows that for light elements like Mn, Cu and Zn the concentration obtained by AAS spectrometer is larger than that obtained by XRF spectrometer.

This may be attributed to the fact that these elements have more electrons in the outer most shell than the inner ones according to the relation:

$$number\ of electrons = 2n^2 \qquad (5.1)$$

$n \equiv$ principal quantum number

thus these elements emits more visible photons from the outer most shells compared to less x-ray photons emitted from the inner most shells.

Since AAS account for visible photon, and XRF take care of X-ray photons, thus for AAS, which receipt more photons, the concentrations appears higher.

However for XRF it receipt less photons, thus the concentrations appears lower.

Also from tables (5.3) to (5.12) and figures (5.1) to (5.10) noted that Onion, Mallow, Watercress, Marrow, Cucumber and corresponding soils shows that for light elements like Mn, Cu and Zn the concentration obtained by XRF technique gives higher readings compared to AAS technique.

Thus the concentration of all elements appears lower than that of XRF which cannot detect those elements.

This may be attributed to the fact that the photon energy, which is related to the difference between energy levels is proportional to the atomic number Z .

$$hf = \Delta E \sim Z^2 \qquad (5.2)$$

thus heavy metals emits high frequency photons like x-ray ones, more that low frequency photons like visible photons.

Thus one expect XRF to receipt more photons than AAS.

Thus the Pb concentration for of XRF appears higher.

The situation for plants is also similar to that of soil, with some differences

Where light elements emit more visible photons thus AAS concentration appears higher.

However for heavy elements like Pb which emits more high frequency photons like XRF device read higher concentration.

5.6 CONCLUSION:

The Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry and the Atomic Absorption (AA) spectrometry are two analytical methods which can be successfully used in complementary mode to determine the heavy metal concentration in vegetables and soils. The combination of two different techniques, XRF and AAS, was well suited to this analysis.

XRF technique enable simultaneous determination of all the elements present in the sample (Z > 13), don't require a chemical sample preparation but, is limited by the detection limit. For this reason the elements which are a concentration less then 10 mg/kg had to be studied by the AAS technique.

The studied vegetables and soils contain minerals required in the human diet, such as Zn, Mn and Cu, and also toxic elements, such as Pb.

The level of toxic elements was lower than that of minerals.

The concentrations obtained for heavy metals in vegetables and soils to be acceptable for human consumption and nourishment value.

As expected, metal uptake seems to be species dependent accumulate more Cu and Pb and accumulate more Mn and Zn.

This work shows that the concentration of Mn and Zn obtained by AAS is larger than obtained by XRF, also that shows that the concentration of Pb and Cu obtained by AAS is lower than that obtained by XRF.

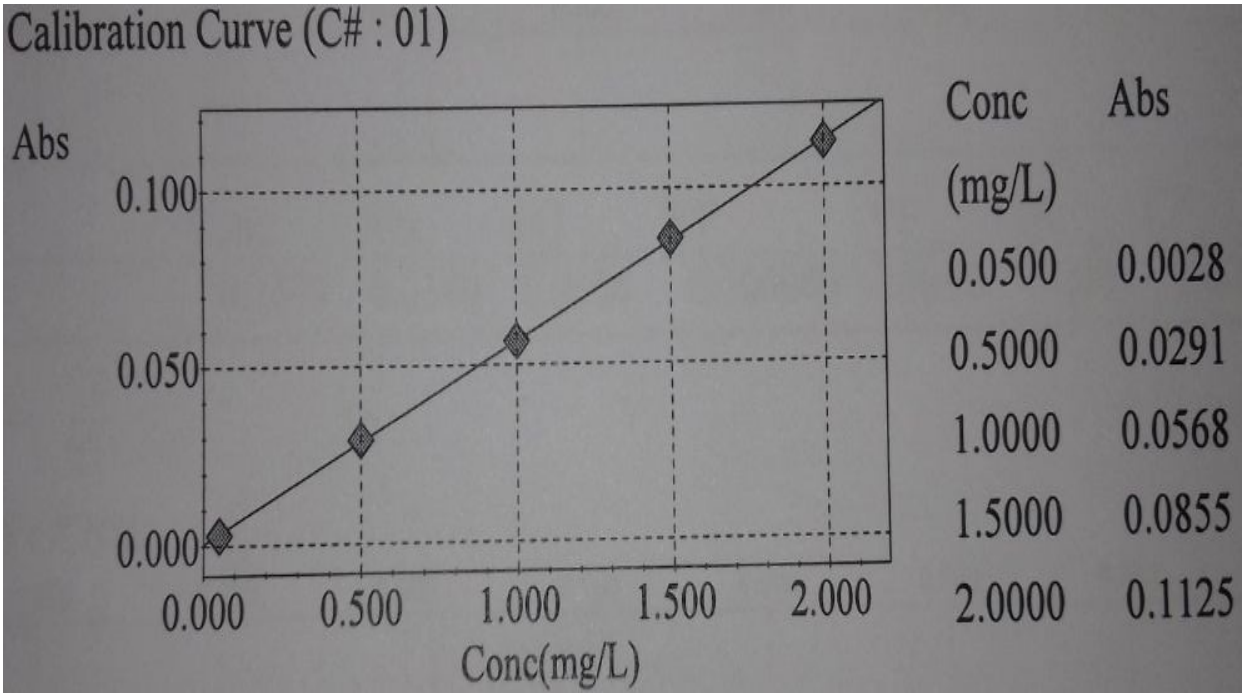
5.7 FUTURE WORK AND RECOMMEDATIONS:

This study emphasizes the need to follow the concentration of toxic heavy metals not only in vegetables and soils, but also in the most consumed vegetables, by conducting national survey, Specially wheat and maize and their products in Khartoum state.

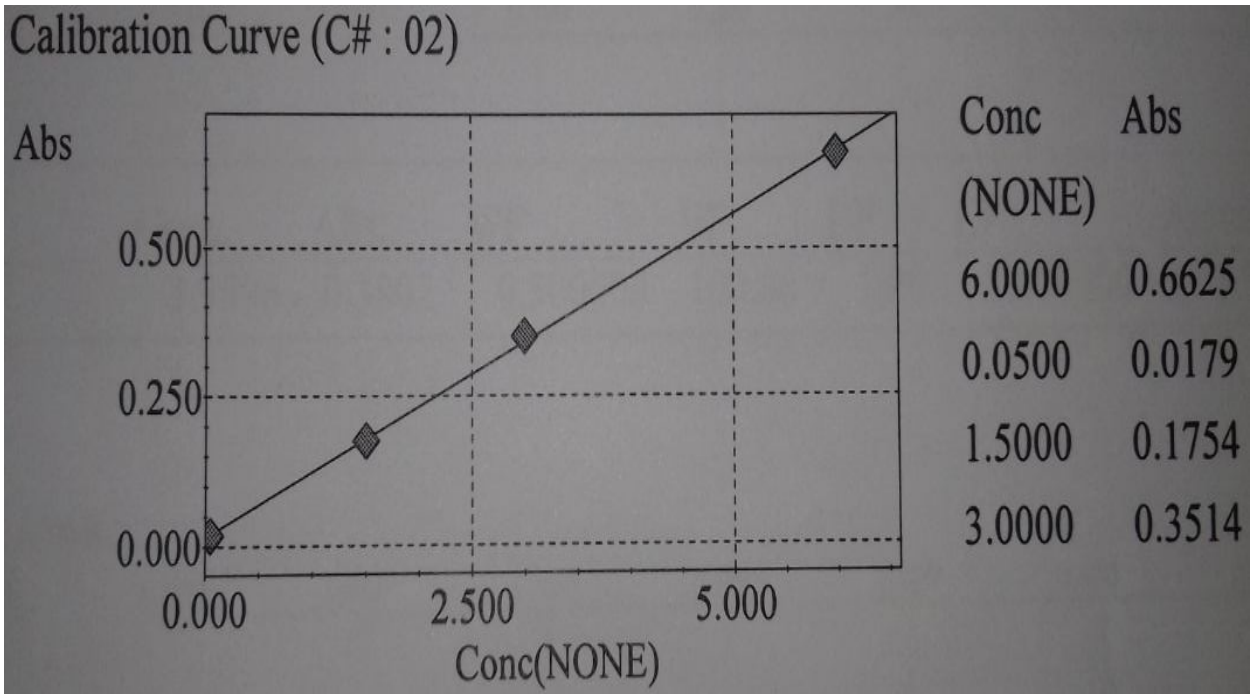
5.8 APPENDIXES:

Appendix (1)

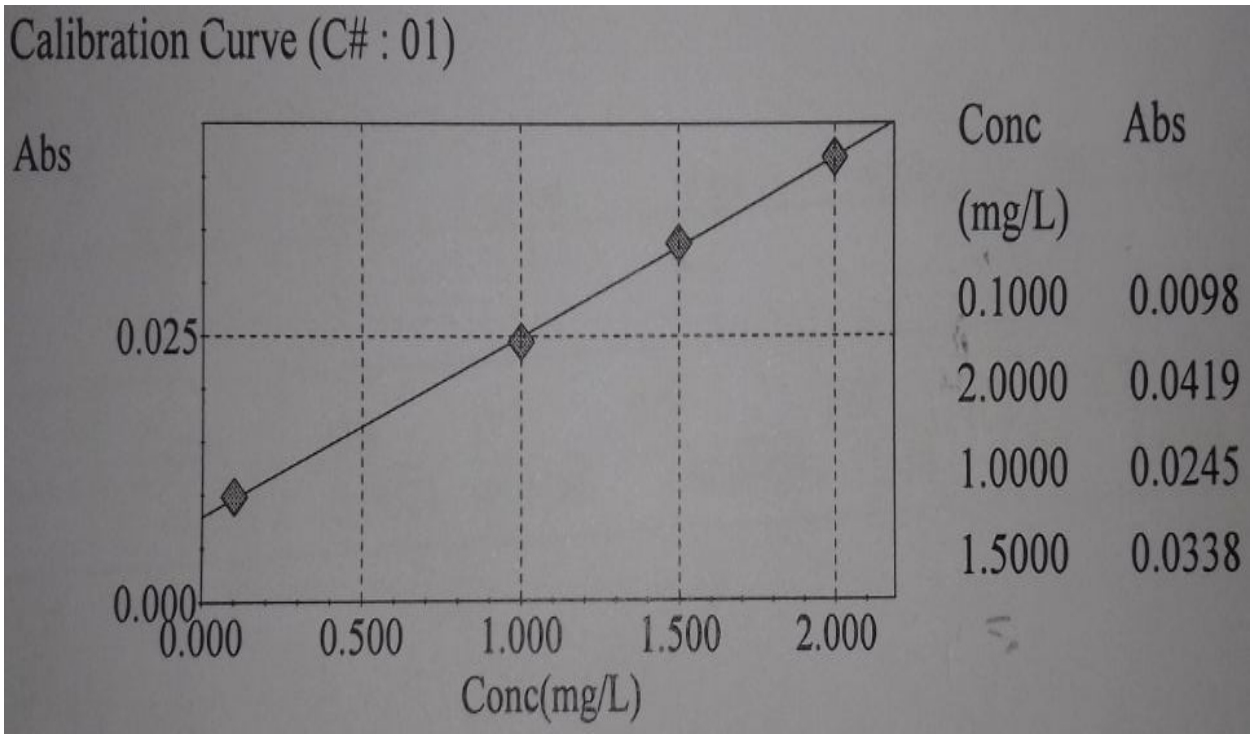
Copper calibration



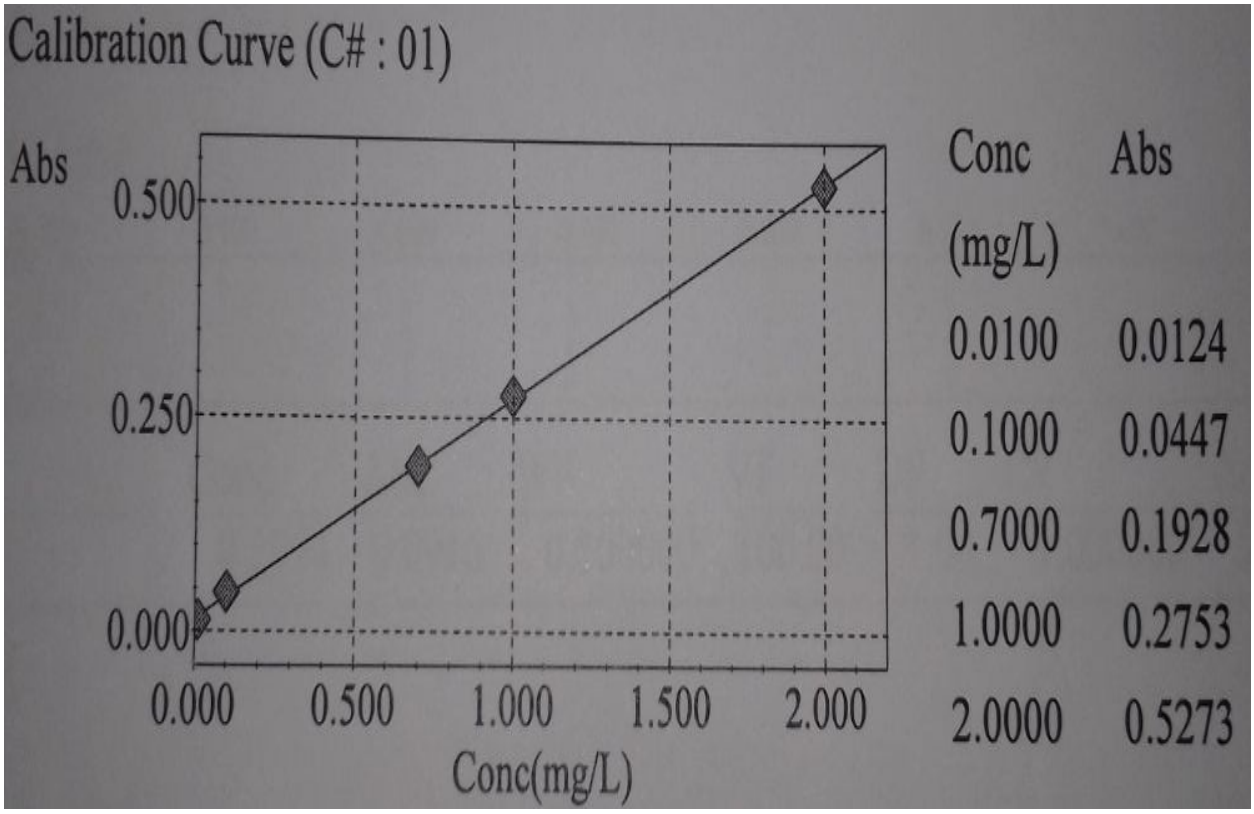
Manganese calibration



Lead calibration



Zinc calibration



Appendix (2)

Table (4.1): Concentration (µg/g) of Mn, Zn, Cu and Pb in vegetables of measured by (XRF technique).

Code	Name of Area	Vegetables	Parts Used	Metals			
				Mn	Zn	Cu	Pb
P1	Al-Halfaya	Onion	Tuber	72.40	20.00	13.20	1.94
P2	//////////////////////	Jew Mallow	Leaf	NA	NA	NA	NA
P3	//////////////////////	Watercress	Leaf	98.40	15.70	13.70	2.26
P4	//////////////////////	Marrow	Fruit	ND	43.60	14.50	1.99
P5	//////////////////////	Cucumber	Fruit	ND	32.20	10.70	1.56
P6	Al-kadro	Onion	Tuber	ND	15.50	12.60	1.67
P7	//////////////////////	Jew Mallow	Leaf	58.50	25.20	13.40	2.26
P8	//////////////////////	Watercress	Leaf	116.00	26.80	14.60	1.84
P9	//////////////////////	Marrow	Fruit	ND	22.40	13.50	1.86
P10	//////////////////////	Cucumber	Fruit	ND	36.00	12.80	1.44
P11	Al-Jerif East	Onion	Tuber	36.60	13.70	11.90	1.36
P12	//////////////////////	Jew Mallow	Leaf	53.20	15.10	13.00	1.46
P13	//////////////////////	Watercress	Leaf	27.20	1.11	1.84	0.30
P14	//////////////////////	Marrow	Fruit	ND	21.50	9.80	1.41
P15	//////////////////////	Cucumber	Fruit	ND	33.00	11.20	1.90
P16	Totti Island	Onion	Tuber	ND	14.90	15.00	1.68
P17	//////////////////////	Jew Mallow	Leaf	ND	3.13	3.83	0.53
P18	//////////////////////	Watercress	Leaf	38.20	1.24	1.70	0.24
P19	//////////////////////	Marrow	Fruit	ND	3.77	3.82	0.60
P20	//////////////////////	Cucumber	Fruit	ND	5.91	4.01	0.73
P21	Al-Jerif West	Onion	Tuber	NA	NA	NA	NA
P22	//////////////////////	Jew Mallow	Leaf	25.20	3.21	3.69	0.37
P23	//////////////////////	Watercress	Leaf	30.80	2.69	4.22	0.60

P24	//////////////////////	Marrow	Fruit	ND	4.53	3.41	0.49
P25	//////////////////////	Cucumber	Fruit	ND	5.34	3.77	0.57
P26	Buri	Onion	Tuber	16.00	2.53	3.92	0.49
P27	//////////////////////	Jew Mallow	Leaf	26.80	1.70	3.13	0.49
P28	//////////////////////	Watercress	Leaf	36.20	2.34	3.49	0.56
P29	//////////////////////	Marrow	Fruit	ND	4.34	3.91	0.50
P30	//////////////////////	Cucumber	Fruit	ND	4.85	4.03	0.57
P31	Abu Roff	Onion	Tuber	NA	NA	NA	NA
P32	//////////////////////	Jew Mallow	Leaf	59.90	2.41	3.13	0.55
P33	//////////////////////	Watercress	Leaf	28.40	2.47	3.92	0.49
P34	//////////////////////	Marrow	Fruit	17.70	4.48	3.63	0.50
P35	//////////////////////	Cucumber	Fruit	ND	5.66	3.74	0.47
P36	Kareri al-Ajeejh	Onion	Tuber	NA	NA	NA	NA
P37	//////////////////////	Jew Mallow	Leaf	26.70	2.52	3.08	0.42
P38	//////////////////////	Watercress	Leaf	33.30	ND	3.69	0.43
P39	//////////////////////	Marrow	Fruit	ND	4.03	3.79	0.51
P40	//////////////////////	Cucumber	Fruit	ND	2.38	3.31	0.50

ND refer to Non-Detection ,

NA refer to Non-Analyzed

Appendix (3)

Table (4.2) Concentration (µg/g) of Cu ,Pb,Mn and Zn in soil of vegetables of measured by (XRF technique).

Code	Name of Area	Vegetables	Parts Used	Metals			
				Mn	Zn	Cu	Pb
S1	Al-Halfaya	Onion	Soil	ND	28.90	16.50	13.40
S2	//////////////////////	Jew Mallow	Soil	NA	NA	NA	NA
S3	//////////////////////	Watercress	Soil	465.00	23.70	19.50	7.60
S4	//////////////////////	Marrow	Soil	361.00	ND	19.70	10.20
S5	//////////////////////	Cucumber	Soil	358.00	21.30	17.40	15.50
S6	Al-kadro	Onion	Soil	400.00	20.90	21.30	ND
S7	//////////////////////	Jew Mallow	Soil	428.00	15.30	15.30	12.90
S8	//////////////////////	Watercress	Soil	465.00	17.70	17.40	14.30
S9	//////////////////////	Marrow	Soil	428.00	21.30	16.10	ND
S10	//////////////////////	Cucumber	Soil	361.00	26.50	17.80	10.20
S11	Al-Jerif East	Onion	Soil	347.00	31.80	21.20	12.60
S12	//////////////////////	Jew Mallow	Soil	395.00	24.90	18.40	13.20
S13	//////////////////////	Watercress	Soil	315.00	19.00	23.10	13.20
S14	//////////////////////	Marrow	Soil	413.00	24.00	19.30	13.50
S15	//////////////////////	Cucumber	Soil	517.00	17.60	21.50	15.80
S16	Totti Island	Onion	Soil	236.00	24.90	24.00	17.10
S17	//////////////////////	Jew Mallow	Soil	589.00	19.50	19.00	13.80
S18	//////////////////////	Watercress	Soil	460.00	27.10	20.50	12.80
S19	//////////////////////	Marrow	Soil	302.00	29.90	21.90	22.70
S20	//////////////////////	Cucumber	Soil	419.00	26.20	18.30	11.80
S21	Al-Jerif West	Onion	Soil	NA	NA	NA	NA
S22	//////////////////////	Jew Mallow	Soil	221.00	ND	24.10	17.80
S23	//////////////////////	Watercress	Soil	296.00	26.20	20.50	14.20

S24	//////////////////////	Marrow	Soil	516.00	ND	17.60	18.10
S25	//////////////////////	Cucumber	Soil	277.00	21.30	22.10	13.50
S26	Buri	Onion	Soil	419.00	ND	19.40	17.40
S27	//////////////////////	Jew Mallow	Soil	482.00	24.40	16.40	12.80
S28	//////////////////////	Watercress	Soil	479.00	29.00	23.70	13.20
S29	//////////////////////	Marrow	Soil	318.00	16.70	18.00	19.10
S30	//////////////////////	Cucumber	Soil	416.00	29.90	17.80	12.50
S31	Abu Roff	Onion	Soil	NA	NA	NA	NA
S32	//////////////////////	Jew Mallow	Soil	428.00	ND	17.10	14.80
S33	//////////////////////	Watercress	Soil	507.00	22.60	21.00	14.50
S34	//////////////////////	Marrow	Soil	536.00	26.20	20.80	17.80
S35	//////////////////////	Cucumber	Soil	293.00	27.10	19.10	15.10
S36	Kareri al-Ajeejh	Onion	Soil	NA	NA	NA	NA
S37	//////////////////////	Jew Mallow	Soil	482.00	27.60	22.80	14.80
S38	//////////////////////	Watercress	Soil	403.00	24.40	24.70	17.10
S39	//////////////////////	Marrow	Soil	498.00	19.50	21.80	12.50
S40	//////////////////////	Cucumber	Soil	532.00	25.30	22.50	14.20

ND refer to Non-Detection ,

NA refer to Non-Analyzed

Appendix (4)

Table (4.3) Concentration (µg/g) of Cu, Pb, Mn and Zn in vegetables measured by (AAS technique).

Code	Name of Area	Vegetables	Parts Used	Metals			
				Mn	Zn	Cu	Pb
P1	Al-Halfaya	Onion	Tuber	59.92	14.27	8.79	ND
P2	//////////////////////	Jew Mallow	Leaf	NA	NA	NA	NA
P3	//////////////////////	Watercress	Leaf	115.20	23.30	8.9	ND
P4	//////////////////////	Marrow	Fruit	14.29	30.13	7.78	ND
P5	//////////////////////	Cucumber	Fruit	12.24	27.43	5.69	ND
P6	Al-kadro	Onion	Tuber	55.90	17.50	8.70	ND
P7	//////////////////////	Jew Mallow	Leaf	70.47	24.11	4.58	ND
P8	//////////////////////	Watercress	Leaf	69.80	23.00	4.11	ND
P9	//////////////////////	Marrow	Fruit	15.20	31.10	7.99	ND
P10	//////////////////////	Cucumber	Fruit	12.15	28.35	4.80	ND
P11	Al-Jerif East	Onion	Tuber	25.32	9.66	4.44	ND
P12	//////////////////////	Jew Mallow	Leaf	82.65	21.80	7.15	ND
P13	//////////////////////	Watercress	Leaf	80.15	20.70	6.90	ND
P14	//////////////////////	Marrow	Fruit	8.58	23.38	5.11	ND
P15	//////////////////////	Cucumber	Fruit	7.90	22.25	4.50	ND
P16	Totti Island	Onion	Tuber	21.77	11.29	35.16	ND
P17	//////////////////////	Jew Mallow	Leaf	84.32	21.14	11.57	ND
P18	//////////////////////	Watercress	Leaf	82.43	20.53	1025	ND
P19	//////////////////////	Marrow	Fruit	11.90	38.29	16.52	ND
P20	//////////////////////	Cucumber	Fruit	9.44	36.86	15.47	ND
P21	Al-Jerif West	Onion	Tuber	NA	NA	NA	NA
P22	//////////////////////	Jew Mallow	Leaf	85.42	25.62	13.45	ND
P23	//////////////////////	Watercress	Leaf	83.32	23.65	12.32	ND

P24	//////////////////////	Marrow	Fruit	13.45	39.42	17.67	ND
P25	//////////////////////	Cucumber	Fruit	12.65	37.32	16.32	ND
P26	Buri	Onion	Tuber	23.87	13.95	38.12	ND
P27	//////////////////////	Jew Mallow	Leaf	86.39	25.92	10.32	ND
P28	//////////////////////	Watercress	Leaf	84.40	23.25	9.80	ND
P29	//////////////////////	Marrow	Fruit	13.51	29.16	11.98	ND
P30	//////////////////////	Cucumber	Fruit	12.32	28.15	10.82	ND
P31	Abu Roff	Onion	Tuber	NA	NA	NA	NA
P32	//////////////////////	Jew Mallow	Leaf	125.35	21.72	15.52	ND
P33	//////////////////////	Watercress	Leaf	121.28	20.62	14.33	ND
P34	//////////////////////	Marrow	Fruit	13.66	32.27	13.92	ND
P35	//////////////////////	Cucumber	Fruit	12.88	31.72	12.95	ND
P36	Kareri al-Ajeejh	Onion	Tuber	NA	NA	NA	NA
P37	//////////////////////	Jew Mallow	Leaf	83.18	27.13	13.61	ND
P38	//////////////////////	Watercress	Leaf	82.11	25.95	12.95	ND
P39	//////////////////////	Marrow	Fruit	11.32	20.72	10.52	ND
P40	//////////////////////	Cucumber	Fruit	8.23	18.34	8.56	ND

ND refer to Non-Detection ,

NA refer to Non-Analyzed

Appendix (5)

Table (4.4) Concentration (µg/g) of Cu , Pb, Mn and Zn in soil of vegetables of measured by (AAS technique).

Code	Name of Area	Vegetables	Parts Used	Metals			
				Mn	Zn	Cu	Pb
S1	Al-Halfaya	Onion	Soil	750.80	47.50	35.30	ND
S2	//////////////////////	Jew Mallow	Soil	NA	NA	NA	NA
S3	//////////////////////	Watercress	Soil	980.10	72.20	45.30	ND
S4	//////////////////////	Marrow	Soil	1038.14	68.28	47.98	ND
S5	//////////////////////	Cucumber	Soil	796.08	59.28	44.42	ND
S6	Al-kadro	Onion	Soil	760.19	50.82	36.62	ND
S7	//////////////////////	Jew Mallow	Soil	1050.10	78.72	55.27	ND
S8	//////////////////////	Watercress	Soil	1021.20	76.22	53.42	ND
S9	//////////////////////	Marrow	Soil	905.20	56.00	46.50	ND
S10	//////////////////////	Cucumber	Soil	892.22	54.22	45.11	ND
S11	Al-Jerif East	Onion	Soil	776.22	49.90	36.62	ND
S12	//////////////////////	Jew Mallow	Soil	1100.15	78.92	52.63	ND
S13	//////////////////////	Watercress	Soil	1075.20	75.32	51.12	ND
S14	//////////////////////	Marrow	Soil	843.98	52.32	45.84	ND
S15	//////////////////////	Cucumber	Soil	640.80	42.25	40.85	ND
S16	Totti Island	Onion	Soil	671.92	47.34	33.40	ND
S17	//////////////////////	Jew Mallow	Soil	1050.20	80.50	60.20	ND
S18	//////////////////////	Watercress	Soil	1020.10	75.60	55.30	ND
S19	//////////////////////	Marrow	Soil	670.35	54.30	35.10	ND
S20	//////////////////////	Cucumber	Soil	655.25	52.20	33.20	ND
S21	Al-Jerif West	Onion	Soil	NA	NA	NA	NA
S22	//////////////////////	Jew Mallow	Soil	1035.03	60.50	45.10	ND
S23	//////////////////////	Watercress	Soil	1020.13	57.26	43.23	ND

S24	//////////////////////	Marrow	Soil	680.33	60.67	35.55	ND
S25	//////////////////////	Cucumber	Soil	665.27	59.01	33.95	ND
S26	Buri	Onion	Soil	680.91	50.34	34.45	ND
S27	//////////////////////	Jew Mallow	Soil	1018.06	72.72	55.78	ND
S28	//////////////////////	Watercress	Soil	1012.04	70.75	54.60	ND
S29	//////////////////////	Marrow	Soil	665.48	55.36	33.40	ND
S30	//////////////////////	Cucumber	Soil	650.15	52.25	32.20	ND
S31	Abu Roff	Onion	Soil	NA	NA	NA	NA
S32	//////////////////////	Jew Mallow	Soil	1091.18	79.99	62.39	ND
S33	//////////////////////	Watercress	Soil	912.50	70.62	44.78	ND
S34	//////////////////////	Marrow	Soil	1020.82	70.30	52.24	ND
S35	//////////////////////	Cucumber	Soil	1005.82	69.00	50.22	ND
S36	Kareri al-Ajeejh	Onion	Soil	NA	NA	NA	NA
S37	//////////////////////	Jew Mallow	Soil	1081.92	80.72	63.38	ND
S38	//////////////////////	Watercress	Soil	1061.72	78.95	62.83	ND
S39	//////////////////////	Marrow	Soil	1015.20	79.02	51.28	ND
S40	//////////////////////	Cucumber	Soil	1002.30	75.43	49.27	ND

ND refer to Non-Detection

NA refer to Non-Analyzed

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