Chapter one

1-1 Introduction:

In fact, most of Sudanese people's have benificial from crops such as Sorghum, Degace, and Wheat. The benefits are for the whole country in food security across all states Mohamed et al, (2013). Therefore, measuringing contaminated crops due to the impact of agriculture managements under different cropping varieties is needed to target uncontaminated and/or save food in Sudan.Without doubt electrical emission overer agricultural practices can considering as a main contribution of pollution to these crops, which predicted in increases in concentrations of unneeded elements (toxic or radioated). Of course, the quality of these crops will be affected most strongly by contamination. A change in the the quality of these crops will lead to disturbance human and animal health in Sudan. Many studies have been carried out to estimate heavey and trace elements in response to environmental factors. However, there are no studies estimated radioated elements in the crops at different states of Sudan. Therefore, this encouraged us through the necessity need to evaluate the elements concentrations from these states. In this study, we hypothesized that elecric emission is the main variable that deteriorate the rate of elements in those three states [1].

1· 2 Research problem

Contamination of crops and plants with heavy elements causes biological hazards. There are no extensive work that shows contamination sources and contamination degree.

1· 3 Literature Reviw

Different atempts were made for detection of heavy elements in crops, plants or soil [2]. Some attempts were made to detect and determine their concentration in water [3]. Due to the physical properties of tungsten (high density and high melting point), it is frequently used as anti-tank ammunition. The Swiss standard procedure for the determination of the total contents of heavy metals in soil samples is based on a nitric acid extraction procedure. Unfortunately, this method is not qualified for the analysis of tungsten, as in nitric acid solutions passivation and precipitation of tungsten occurs. Similar reactions are known for antimony and molybdenum. For the determination of tungsten and additional heavy metals such as chromium (Cr), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), cadmium (Cd), .antimony (Sb), and lead (Pb) a borate fusion and an ICP-MS method, based on matrix matched measurements, was developed. To avoid small pieces of tungsten and to get a representative laboratory sample, the soil was heated at 550°C and homogenized by milling [4].

1-4 Research objective

- Our aim was to estimate the amounts of elements and its values with the following objectives:

- quantify of radioactive elements in three crops collected from three different states.

- evaluate the differences between these crops.

- To identify the elemental composition of these samples

1-5 Outline of the thesis

This thesis consists from four chapters. Chapter one is Introduction, chapter two is about x-ray general, while chapter three is talking about XRF. Chapter four explain preparation of sample beside results and discussion and conclusion.

Chapter Two

X-Ray production

(2-1) Introduction

An interesting phenomenon was discovered by crooks when a discharge tube exhausted such that Crookes dark space fills the whole tube, Rontgen called these invisible penetrating radiations x-rays. They are also called Rontgen rays.

The discovery of x-rays has opened a new field of study particularly in the fields of medicines; surgery, industry etc. and many forms of x-ray tubes have been designed to produce x-ray highs for different needs [5].

(2-2) Bohr's Atomic Model

Bohr's atomic model describes the structure of an atom as an atomic nucleus surrounded by electron shells (see Figure 2 - 1). The electrons are arranged in certain. This means that a clearly defined amount of energy is required to release an electron of innermost shell from the atom. To release an electron of the second innermost shell from the atom, a clearly defined minimum amount of energy is required that is lower that needed to release an innermost electron. An electron's bond to an atom is weaker the further away it is from the atom's nucleus. The minimum amount of energy required .to release an electron from an atom, and thus the energy with which it is bound to the atom, is also referred to as the binding energy of the electron to the atom.
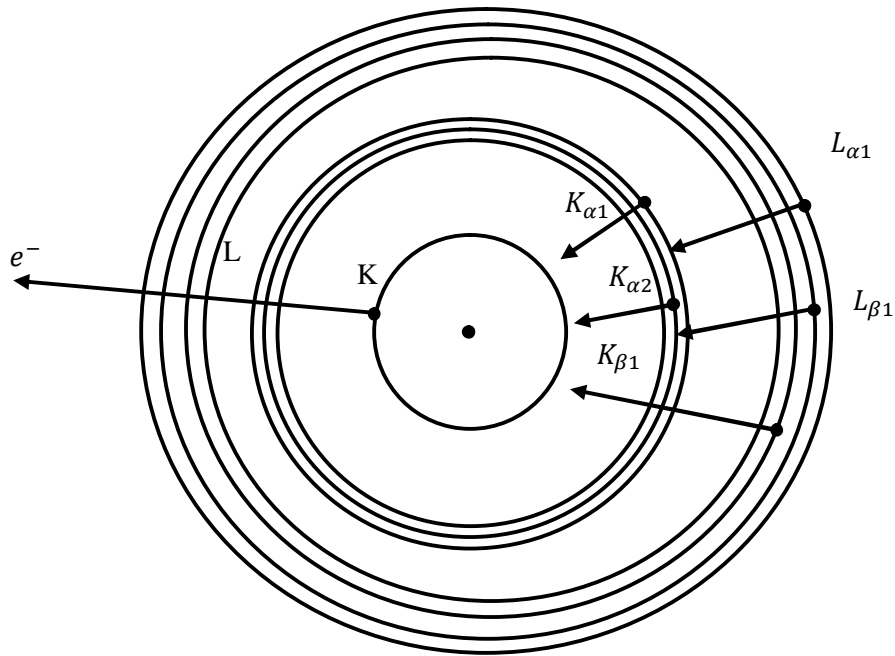
Figure (2 – 1): Bohr's atomic model, shell model.

The binding energy of an electron in an atom is established mainly by determining the incident. It is for this reason that the term absorption e edge is very often found in literature.

Energy level = binding energy = absorption edge

The individual shells are labelled with the letters K, L; M; N,…, the innermost shell being the K-shell, the second innermost the L-shell etc. the K-shell is occupied by 2 electrons; the L-shell has three sub-levels and can contain up to a total of 8 electrons. The M-shell has five sub-levels and can contain up to 18 electrons [6 ,7].

The electron moving in a circular orbit of radius r is subjected to electric force F_e, beside centrifugal force F_c, which balance each other, ie

$$F_c = F_e$$

$$\frac{mv^2}{r} = \frac{q_1 q_2}{4\pi\varepsilon r^2} = \frac{ze^2}{4\pi\varepsilon r^2} \qquad (2\text{-}1)$$

Where

M is mass of electron

V is velocity of electron

$$q_1 = ze = \text{nucleus charge}$$

The kinetic energy is

$$T = \frac{1}{2}mv^2 = \frac{ze^2}{8\pi\varepsilon r} \qquad (2\text{-}2)$$

And the potential energy is

$$V = -\frac{ze^2}{4\pi\varepsilon r} \qquad (2\text{-}3)$$

Total energy

$$E = T + V \qquad (2\text{-}4)$$

$$E = -\frac{ze^2}{8\pi\varepsilon r} = -\frac{1}{2}mv^2 \qquad (2\text{-}5)$$

According to Bohr hypothesis

$$n\lambda = 2\pi r$$

Thus, the momentum is given by

$$P = \frac{h}{\lambda} = \frac{hn}{2\pi r} = \frac{\hbar n}{r} = mv \qquad (2\text{-}6)$$

$$m^2 v^2 = \frac{\hbar^2 n^2}{r^2}$$

$$E = -\frac{1}{2}mv^2 = -\frac{\hbar^2 n^2}{2mr^2} = -\frac{ze^2}{8\pi\varepsilon r} \qquad (2\text{-}7)$$

Thus

$$R = \frac{4n^2\hbar^2\pi\varepsilon}{mze^2} \qquad (2\text{-}8)$$

$$E_{n=} -\frac{mze^2}{8\varepsilon_0 n^2 h^2} \qquad (2\text{-}9)$$

The electromagnetic spectra results for transition from upper energy level E_2 to a lower energy E_1

The energy of emitted photon has given by

$$hf = E_2 - E_1 \qquad (1\text{-}10)$$

2-3 electromagnetic radiation quanta

x-rays are electromagnetic radiation .all x-rays represent energy portion of the electromagnetic spectrum (table 2-1) and have short wavelengths of about 0.1 to 100 angstroms (A^0) range .they are bounded by ultraviolet light at long wavelengths and gamma rays at short wavelengths x-rays in the from 50 to 100 A^0 are termed soft x-rays because they have lower energies and easily absorbed .

Table 2-1: energy and names of various wavelength range:

Energy range(ev)	Wavelength range	Name
$< 10^{-7}$	Cm to km	Radio waves(shirt, medium, long waves)
$< 10^{-3}$	mm to cm	Micro wave
$< 10^{-3}$	mm to mm	Infrared
$0.0017 - 0.0033$	380 to 750 nm	Visible light
0.033–0.1	10 to 380 nm	Ultra violet
0.11– 100	0.100 t0 12 nm	x-rays
10– 500	0.0002 to 0.12nm	Gamma radiation

The range of intensity for x-ray is approximately 0.1 to 100 A^0 although angstroms are used throughout these notes; they are not accepted as SI unit. Wavelengths should be expressed in nanometers (nm) which are 10^{-9} meters ($1A^0 = 10^{-10}m$), but most texts and articles on microprobe analysis retain the use of the angstroms. Another commonly used unit is the micron, which more correctly should be micrometer (μm); a micrometer is 10^4 A^0 [7].

The relationship between the wavelength of electromagnetic radiation and its corpuscular energy (E) is derived as follows. for all electromagnetic radiation

$$E = hv;$$

Where:

H is the plank constant $(6.62 \times 10^{-24}j.s)$;

V is the frequency expressed in Hertz.

For all wavelength

$$v = \frac{c}{\Lambda};$$
(1-11)

Where:

C is the speed of light $(2.99782 \times 10^8 m/s)$;

Λ is the wavelength (A^0)

Thus

$$E = \frac{hc}{\Lambda} = 1.986361 \times \frac{10^{-24}}{\Lambda};$$

Where E is in joule. and Λ in meters

The conversion to angstroms and electron volts (1ev = 1.6021×10^{-19} joule)

yields the Duane equation:

$$E \text{ (ev)} = \frac{12.396}{\Lambda} (A^0)$$
(1-12)

2-4 x-rays production

X-rays are production when the electrons are suddenly decelerated these rays are called bremsstrahlung radiation. or braking x-rays are also produced when electrons make transitions between lower atomic energy levels in heavy elements. X-rays produced in this way have definite energies just like other line spectra from atomic electrons. They are called characteristic x-rays since they have energies determined by the atomic energy levels [8].

2-4-1 Bremsstrahlung x-rays

Bremsstrahlung means "braking radiation" and is retained from the original German to describe the radiation, which is emitted when electrons are decelerated, or "braked" when they are fired at a metal target. Accelerated charges given off electromagnetic radiation, and when the energy of the bombarding electrons is

high enough, that radiation is in the x-ray region of the electromagnetic spectrum. x-ray continuum radiation (bremsstrahlung).

2-5 The interaction of X-Ray with matter

The interaction of electromagnetic radiation with matter is a complex subject encompassing many aspects of modern physics. If abeam of x-ray interacts with a substance, the X-Ray beam intensity is attenuation is examined carefully, it is found that several distinct types of interactions can occur, all of which result in the decrease in the incident beam of X-Ray the magnitudes of these sub interactions are strongly influenced by the following:

a-the energy of the incident X-Ray beam

b-the degree of monochromatization

c-the average atomic number and crystalline structure of the scattering substance

Two basic interaction processes dominated for low photon energies ($\leq \mathrm{M}\, \mathrm{e}v$)

The photoelectric effect and X-Ray scattering

The photoelectric interaction results as a photon strikes a bound electron and the energy of the photon is greater than the binding energy of the electron in its shell. The photo disappears in this processes it is energy is transferred to the electron which is ejected out from its shell the ejected electron is called the photoelectron. The photoelectron emitted with energy $(\mathrm{E} - \varphi)$ where E is the original photon energy and φ is the binding energy of the electron in it,s shell, if one of the K-shell electrons has been removed, the absence may cause an electron from a shell with a lower binding energy to be transferred to the K-shell of higher binding energy φ_κ to fill the vacancy. The difference in the binding energies

between the two shells can be given off in the form of a characteristic X-Ray photon

Electrons are thought to be responsible for the scattering of X-Ray by matter. All scattering events involving X-Rays and matter for convenience, can be referred or compared to the scattered intensity (I_0) from a single electron. (I_0) is the energy scattered per unit solid angle per second by a classical free electron struck by an polarized X-Ray beam having an energy flux (I_o) per square centimeter of area it necessary at this point to distinguish between two types of X-Ray scattering, when the scattered photon has the same energy as the incident photon, the scattering is called coherent, if the energy of the scattered has modified, the scattered X-Ray is said to be incoherently or Compton scattered. Compton was the first to show that the X-radiation scattered by a single free electron changed its energy [9].

2-6 the mass attenuation coefficient:

When a beam of X-Ray photons pass through a material, some of the photons will suffer interactions with the atoms composing the material. The interactions, which take place, are photoelectron effect. Incoherent scattering and diffraction, which is passing through the material without interacting is conveniently described using the concept of the mass attenuation coefficient

A competing process for consuming the difference in binding energies following interaction is emission of Auger electrons from the outer shells. When a vacancy in an inner shell is filled, the atom changes to a state of lower energy, and this energy may be released either directed by emission of an X-Ray [9, 5].

Photon or alternatively may be used to release an electron from the outer shell-known as the Auger electron. For low atom number elements Auger electron

emission is more probable for high atomic number elements, characteristic X-Ray emission becomes more probable. The mass attenuation coefficient accounts for photoelectric absorption based coherent and incoherent scatting.

2-7 Absorption of x-rays

When a homogenous beam of x-rays passes through a solid, liquid or gas, a portion of the incident beam is absorbed. Traversing a thickness dx. The intensity I and the thickness dx.

$$dI \propto Idx \qquad\qquad (2\text{-}13)$$

$$dI = -\mu Idx$$

Where μ is a constant of proportionality and the negative sign indicates that the intensity decreases.

$$\frac{dI}{I} = -\mu dx \qquad\qquad (2\text{-}14)$$

Integrating, $\qquad\qquad log_e I = -\mu X + K$

When, $\qquad\qquad x = 0, I = I_0$

$$\therefore \qquad\qquad log_e I_0 = K$$

Substituting the value of k in equation (i),

$$log_e I = -\mu X + log_e I_0 \qquad\qquad (2\text{-}15)$$

$$log_e \frac{I}{I_0} = -\mu X \ or \ \frac{I}{I_0} = e^{-\mu x} \qquad\qquad (2\text{-}16)$$

$\therefore \qquad I = I_0 e^{-\mu x}$

Therefore, the intensity of x-rays decreases exponentially, and this shown that the beam of x-rays can never be completely absorbed.

The proportionality constant μ is called the linear absorption coefficient since, μx is a mere number, μ has a dimension reciprocal to length i.e., per cm or per meter.

The mass absorbing coefficient $= \frac{\mu}{\rho}$

Where ρ is the density of the absorbing material? [9].

2-8 continuous x-rays

The study of x-ray spectra using Bragg's x-ray spectrometer has shown that the spectrum has two distinct types.

-A continuous x-ray spectrum

-A sharp line spectrum superimposed on the continuous x-ray spectrum.

With an operating voltage of the order of $35 \times 10^3 \ v$ and using Molybdenum and Tungsten as targets it is found that in case of tungsten a continuous x-ray spectrum is obtained . In (figure 2- 2) , the graph has been drawn between wavelength the X-axis and intensity along the Y-axis. In the case of Molybdenum, apart from the continuous spectrum, two sharp spectral lines $k_\alpha \ and \ k_\beta$ characteristic of Molybdenum are obtained. The $k_\alpha \ and \ k_\beta$ lines could also be observed for Tungsten when the operating voltage is of the order of $70 \times 10^3 \ V$.

Further, for a given operating voltage, the minimum wavelength is the same for Molybdenum and Tungsten.

The sharp X-ray spectrum is due to the energy changes that take place in the rearrangement of the electrons in different energy levels of the atom due to the transfer of energy to the atom by the incident accelerated electron. The continuous X-ray spectrum is due to radiations emitted by the which are accelerated in coulomb field due to the nuclei of the target atoms. These continuous X-ray radiations are called Bremsstrahlung, brake radiation [10].
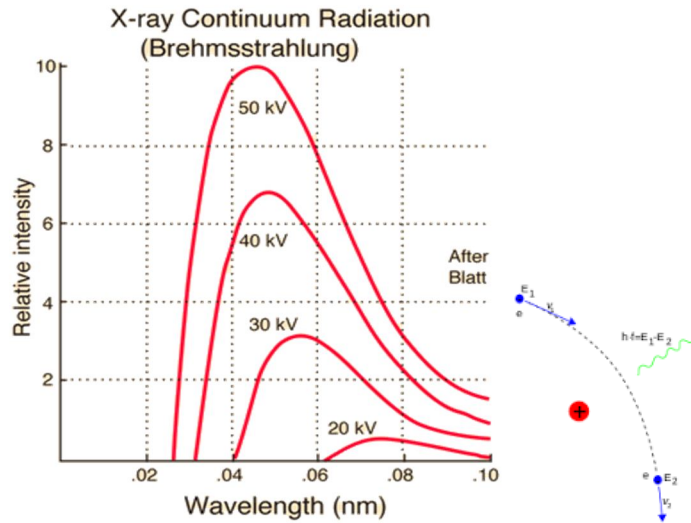
(Figure 2 - 2) continuous of x-ray radiation

However, for the same material of the target, the minimum wavelength limit depends upon the operating voltage of the X-ray tube. Here

$$ev = h\nu_{max} = \frac{hc}{\lambda_{min}}$$

With increase in the operating voltage, the maximum possible frequency of X-rays increases and the value of short wavelength limit decreases.

2-9 properties of X-rays

1. They are electro-magnetic radiations of very small wavelength of the order of 10^{-8} cm and are photons of high energy.

2. They travel with the velocity of light i.e. 3×10^8 m/s.

3. They affect a photographic plate.

4. They are not deflected by magnetic or electric fields and therefore they do not possess any charge.

5. Si milar to light, X-rays, due to their energy, liberate photoelectrons from some metals, when incident on them.

6. They ionize the gas through which they pass.

7. They produce fluorescence in barium-platinocyanid, zinculphide and cadmium tungstate

8. They are highly penetrating and can, pass through many solids which are opaque to visible light e.g., wood, flesh, paper, cardboard, thin sheets of metals, ebonite etc. the penetrating power depends upon the energy of the photons of the x-rays. But x-rays cannot penetrate through heavy metals and bones [10].

2-10 the origin of X-rays

An electron cane be ejected from it is atomic orbital by the absorption of alight wave (photon) of sufficient energy. The energy of the photon ($h\nu$) must be greater than the energy with which the electron is bound to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will transfer into the vacant lower energy orbital (figure 2 - 3   ). During this transition, a photon may be emitted from shell the atom. To understand the processes in the atomic shell, we must look at the Bohr's atomic model

The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by electron making the transition. Due to the fact that the energy difference between two specific orbital shells, in a given elements, is always the some (i.e., characteristic of a particular elements), The photon emitted when an electron moves between two levels will always have the same energy, therefore, by determining the energy (wavelength) of the x-ray light (photons) emitted by a particular element, it is possible to determine the identity of that element [11].
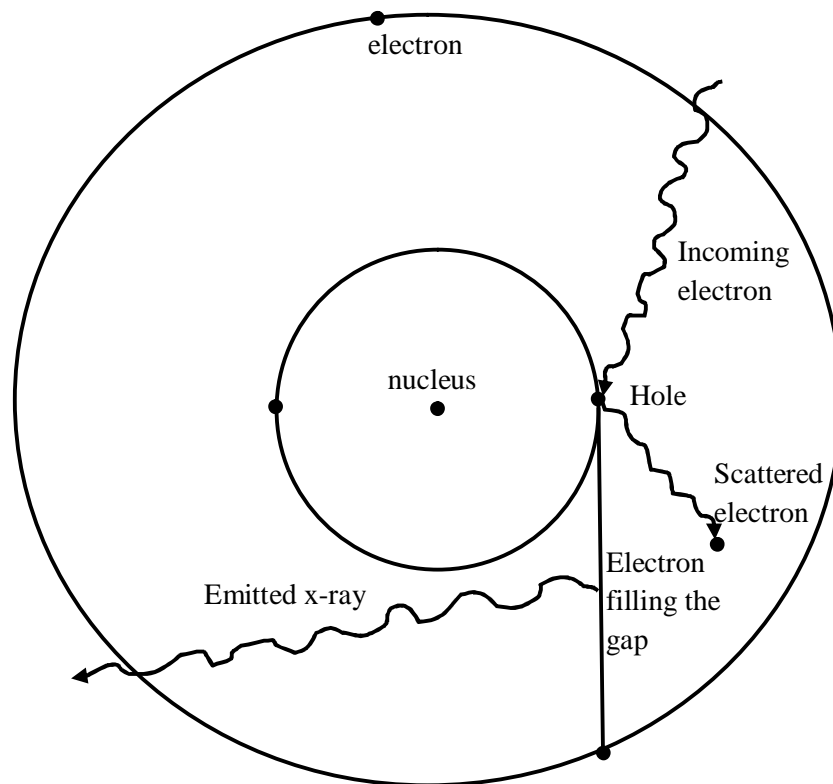
Figure 2-3 A pictorial representation of X-ray fluorescence using a generic atom and generic energy levels this picture uses the Bohr's model of atomic structure and is not to scale.

Chapter Three

X-ray fluorescence (XRF)

3-1 introduction

XRF analysis is a powerful analytical tool for the spectrochemical Determination of almost all the elements present in a sample. XRF radiation is induced when photons of sufficiently high energy, emitted from an X-ray source, impinge on a material.

x-ray florescence (XRF) is phenomenon where a material is exposed to X-ray of high energy , and as the X-ray (or photon) strikes an atom (or a molecule) in the sample , energy is absorbed by the atom. The atom release this energy again in the form of characteristic x-ray. This chapter is concerned with x-ray spectrometer techniques [12].

3-2 principle Florescence of X-ray

When an atom is excited such that electrons in inner most shell is ejected an electron from an outer shell then drops into the unoccupied orbital, to fill the hole left behind. This transition gives off an X-ray of fixed, characteristic energy that can be detected by a fluorescence detector. The energy needed to eject a core electron is characteristic of each element, and so is the energy emitted by the transition. The transition of an L .shell electron dropping into the K-shell is termed a k_α transition, while an M shell electron dropping in to the K shell is a Kk_β transition.
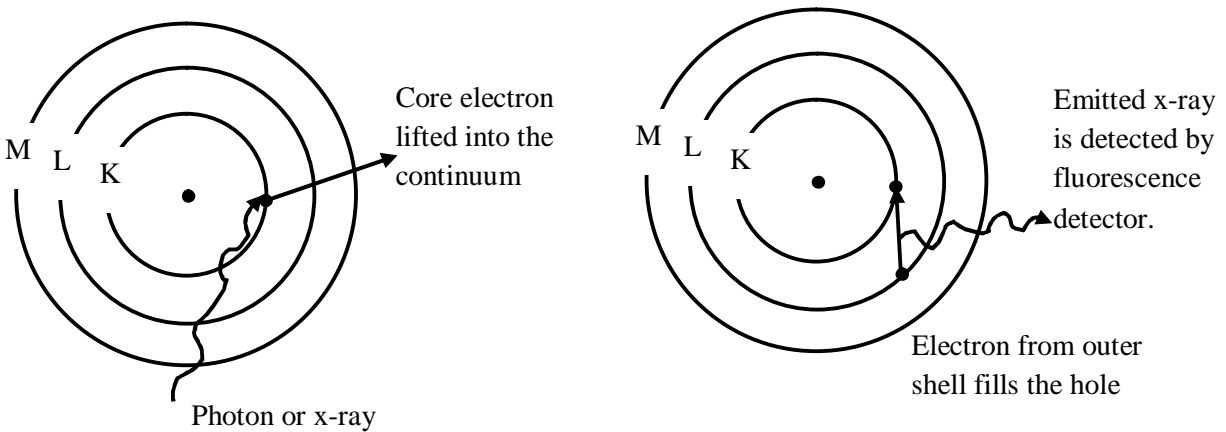
Figure 3-1

Typically the lightest element that can be analyzed is beryllium (2= 4) , but due to instrumental limitations and low X-ray yield for the light elements , it is often difficult to quantify elements lighter them sodium (Z=11).

There are types of spectrometer:

- Wavelength dispersive spectrometer (WDX or WDS): the photons are separated by diffraction on a single crystal before being detected;
- Energy dispersive spectrometers (EDX or EDS): the detector allows the determination of the energy of the photon when it is detected; the EDX spectrometers are smaller (even portable), cheaper, the measurement is faster, but the resolution and the detection limit is far worse them the WDX spectrometers

EDXRF spectrometers is the one that we will focus later on [12, 13].

3-2-1 X- ray excitation:

X-ray excitation takes place when a primary X-ray photon has sufficient energy to eject electrons from inner shells and therefore vacancies are created. Vacancies

present an causes condition, electrons from the atom in the outer shell to fill this vacancy. The cause's emission of characteristic photon. Thus, x-ray fluorescence process takes place.
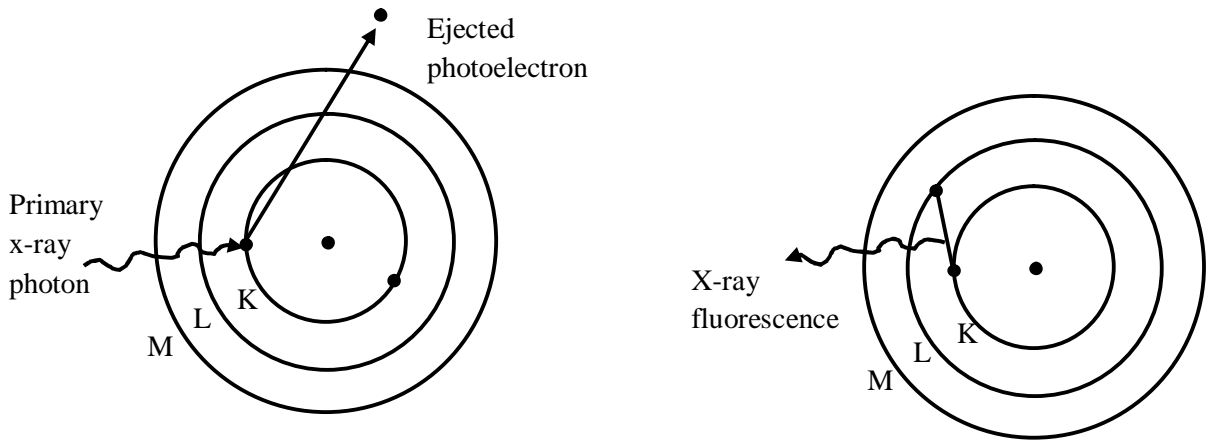

Figure 3-2 Sodium Atom

3-2-2 electron excitation:

Electron excitation is the movement of an electron to a higher energy state. When a high – energy electron is deflected from it is original trajectory it becomes a scattered electron. Thus, a secondary electron is generated as ionization product. It is called secondary; because is generated by other radiation (the primary radiation). This radiation can be in the form of ions, or photons, or photons with sufficiently high energy [12].

3-2-3 fluorescence yield

All ionization do not result in X-ray emission. The auger effect is a competing mechanism of atomic relaxation. In this process, the atom regains energy stability by emitting an outer shell electron. The ratio of the number of emitted   X-rays to the total number of ionizations is called the fluorescence

yield W_i , where i designates the shell involved. Fluorescence yield increases with atomic number and is greater than 95% for k X-rays of elements with Z > 78 (see figure 3-2) for a given element. The fluorescence yield decreases from the k series to the L and M series. The fluorescence yield be approximated

$$W_i = \frac{Z^4}{A_i + Z^4}$$

Where A_i is a approximately 10^6 for the K shell and 10^8 for the L shell [13].
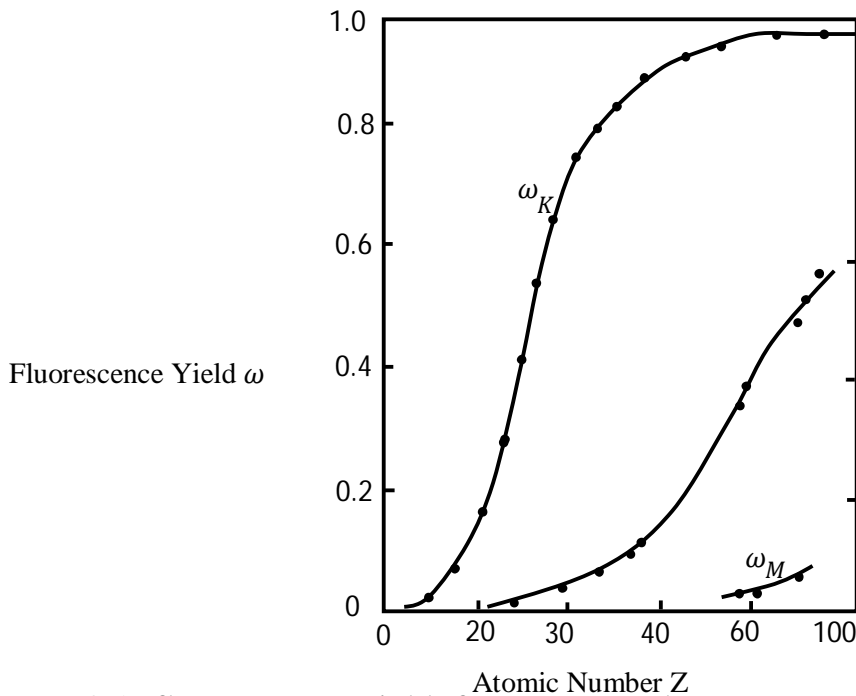

Figure 3-2 fluorescence yield for K, L, and M x-ray as a function of atomic number.

3-4 Wavelength Dispersive and Energy Dispersive XRF Compared

In X-ray fluorescence, we distinguish between two types of instruments:

20

The wavelength dispersive (WDX) and the energy dispersive spectrometer (EDX). Both WDX and EDX employ an X-ray source for exciting the sample.

Essentially, energy, disperse X-ray spectrometry differs from wavelength-dispersive only in the means used to disperse (separate) the several spectral lines emitted by the specimen. So basically they differ in the way the X-ray spectra emitted by the sample is detected

In wavelength-dispersive spectrometers (WDX), the fluorescence spectrum is dispersed into discrete wavelengths using a dispersion device (e.g. a crystal).

The several wavelengths are dispersed specially on the basis of their wavelength prior to detection; thus, in principle at least, the detector receives only one wavelength at a time which is detected using a gas proportional or scintillation counter.

In energy-dispersive spectrometers, one measures the entire fluorescence spectrum directly using a solid-state detector, which is then, processed using a multichannel analyzer to obtain the information on an energy scale.

The detector receives all excited lines of all the specimen elements at once. For each incident X-ray photon, the detector output is amplified and subjected to electronic pulse-height analysis to separate the pulses arising from several detected wavelengths on the basis of their heights and thereby on the basis photon energies of the incident X-ray lines. By appropriate setting of the operating parameters, the pulse of each line of interest can be measured individually [14, 15].

3-5 Advantages and Disadvantages of XRF Technique

3-5-1 Advantages

The appeal of X-ray analysis of archaeological specimens lies its remarkable combination of practical and economic advantages:

- Non-destructive

In the vast majoring of cases, analyzed samples are not destroyed or changed by exposure to X-rays. They can thus be saved for future reference or used for other types of testing that may be destructive. Such as obsidian hydration analysis.

- Minimal preparation

Many samples can be examine with little or no pre-treatment including almost all obsidian procedures that are both time. Consuming and costly in terms of the acids or other reagents required. While its best to wash any sediments off archaeological specimens, it has been shown that if the dirt is minimal, and the artifact has not been subjected to heat so high as to melt some sediment matrix on to the sample, vigorous cleaning is not necessary this is mainly due to the penetration of X-rays in the mid-z X-ray region beyond the surface and while it does incorporate any contamination on the surface it is generally not an issue if some soil remains in the flake scans. The analyzed volume is very large compared to any surface contamination. This is not the case with most metals, where pagination and chemical weathering can radically change the composition at the surface and yield erroneous results [15].

- Fast

X-ray spectrometry enables chemical composition to be determined in seconds.

Fast, so that large numbers of similar objects may be analyzed or a single object investigated at various positions on it is surfaces this property is very valuable since this is the only way of being able to discern between general trends in the data and outlying objects or data points; [16].

- Easy to use

Modern instruments run under computer control with effective software to handle measurement set-up and results calculation. Tasks that once required the constant attention of a trained analyst can now be handled by skilled students and are fully automated [17].

- Cost-effective

Without the more involved sample preparation necessary in most XRF and all destructive analyses, the cast is significantly lowered per sample. While this suggests that XRF will solve all our problems, it is not the all-knowing black box we would like it to be [18].

3-5-2 Disadvantages

- Restricted elemental acquisition: non-destructive XRF is restricted generally to a subset of the mid-z x-ray region, the best portion including Ti - Nb, contains excellent incompatible elements for volcanic rocks while some rare Earth elements and those with low atomic numbers or with very low concentrations can be useful in discriminating sources, in most cases XRF can't solve that problem.

- XRF can't characterize small components- XRF is a mass analysis every component in the irradiated substances is included in the analysis. It is possible to collimate the incoming X-rays from the tube and/or into the detector to focus on small components such as various minerals, but environmental scanning electron microscopy (ESEM), electron microprobe, or laser ablated inductively coupled plasma mass spectrometry (LA-ICP-MS) is much better suited for this kinds of analysis [19, 20].

3-6 Quantitative analysis in EDXRF and WDXRF

Quantitative analysis is the same for EDXRF and WDXRF. The only difference is that in EDXRF the area of a peak gives the intensity, while in WDXRF the height of a 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 the spectrometer by measuring one more reference materials. The calibration determines the relationship between the concentration of elements and the intensity of 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.

3-7 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 depend 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 models 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:

$$C_i = D_i + E_i . R_i . M_i$$

Or

$$C_i = (D_i + E_i . R_i). M_i$$

but the method is also applicable to the second equation. M is the matrix correction factor, and the difference between the models the lies in the way they define and calculate M.

3-7-1 Fundamental parameter (FP) matrix correction models

Fundamental parameter models are based on the physics of X-rays. In the 1950s, Sherman derived the mathematical equations that describe the relationship between the intensity of an element and the composition of a 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:

$$C_i = D_i + E_i . R_i . M_i$$

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 calculated 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 FP 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.

3-7-2 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 the matrix. The model is

$$C_i = D_i + E_i \cdot \frac{R_i}{R_c}$$

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

3-7-3 Line overlap correction

The fractions were determined by measuring dedicated standards. Another model is to determine the overlap factors by regression. The calibration model is extended with terms that describe the line overlap:

$$C_i = D_i + E_i \cdot \left[R_i - \sum_{\substack{overlap \\ lines\ j}} F_{ij} \cdot R_i \right]$$

The overlap factors F_{ij} are determined by regression. The problem with this equation is that it can be non-linear, which makes it 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:

$$C_i = D_i - \sum_{\substack{overlaping \\ lines}} F_{ij} \cdot R_j + E_i \cdot R_i \cdot M_i$$

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. The following equation can therefore be used:

$$C_i = D_i - \sum_{\substack{overrapping \\ lines}} F_i \cdot R_i + E_i \cdot R_i \cdot M_i$$

Chapter Four

Results and discussion

(4-1) Introduction

In this work samples of Wheat, Degace and Fiterita corps were collected from three states in Sudan during the period of 12/3/-5/8/2016 to measure their elemental concentrations. This element concentrations exrmined by using XRF technique.

(4-2) Materials and Methods

The materials consists of sample beside the devices used in determining their concentration .

(4-2-1) Crop samples collection

Samples of wheat, Degace and Fiterita corpin were collected from White Nile, River Nile and Gezira state . The number of sample from   each crop spieces and from each state are three samples but River Nile it has two samples .

(4-2-2) XRF Devices and Instruments

(B)

(A)

Photo represents the process for analyzing sorgum sample using XRF : (A), and (B) analysis the sample resultsin the computer screen . other experimental condition :

Excited by 40 kev X-rays and measurement time 60 sec.

Instrumentation used in XRF analysis is similar to that of other gamma-ray assay system: detector, associated electronics, multichannel analyzer, and excitation source. For the analysis of sorglum standard sample is determin the concentration using X-ray fluorescence spectrometer. The sample is cleaned and put under the

tube of XRF to locate the position of detection and this iead to show the sample in the computer screen. After 60 sec the XRF instrument gave the concentratin of the elements.

(4-3) Results and Tables

(Table 4-4-1): Mean concentration of some elements for Wheat cropin three states.

Element	White Nile		RN State		Gezira State	
	%	STD	%	STD	%	STD
W^+	42.66	4.05	43.03	2.018	42.53	3.076
Ni^+	13.88	0.216	13.73	0.111	13.63	0.212
Fe^{+3}	3.69	2.488	4.16	1.412	6.27	2.817
Ti^+	5.36	6.665	2.76	1.884	1.76	1.619
Mn^{+2}	1.12	0.146	0.70	0.749	1.40	0.593
Cu^{+2}	0.21	0.184	0.44	0.166	0.36	0.288
Co^{+1}	0.61	0.453	0.20	0.21	0.42	8.13
Ta	0.08	0.134	0.89	1.017	0.04	0.073
Mo	16.9	0.745	16.99	0.862	17.03	0.636
Nb	13.74	0.221	13.89	1.123	13.63	0.966
Cr	1.69	0.156	0.44	0.672	1.35	0.336

RN: River Nile, STD: Standard deviation

(Table 4-4-2): Mean concentration of some elements for Degace cropin three states

Element	White Nile %	STD	RN State %	STD	Gezira State %	STD
W^+	36.09	1.674	24.11	4.613	32.01	0.913
Ni^+	13.90	0.265	13.69	0.212	13.97	0.098
Fe^{+3}	4.60	0.991	10.94	1.737	4.57	1.965
Ti^+	3.26	1.790	2.26	0.751	1.64	0.86
Mn^{+2}	0.81	0.449	0.32	0.375	0.01	0.013
Cu^{+2}	0.52	0.224	0.35	0.305	0.34	0.223
Co^{+1}	0.22	0.207	0.21	0.208	0.19	0.069
Ta	0.36	0.484	1.62	1.847	1.17	0.860
Mo	17.16	0.445	12.99	0.481	17.97	0.891
Nb	13.73	0.734	11.22	0.497	14.23	1.065
Cr	1.57	1.158	0.08	0.140	1.50	1.328

RN: River Nile, STD: Standard deviation

(Table 4-4-3): Mean concentration of some elements for Fiterita cropin two states

Element	White Nile %	STD	RN State %	STD	Gezira State %	STD
W^{+}	44.05	2.962	-	-	45.71	3.091
Ni^{+}	13.77	0.177	-	-	13.71	0.467
Fe^{+3}	5.89	2.187	-	-	3.51	1.96
Ti^{+}	3.07	0.436	-	-	1.84	1.48
Mn^{+2}	0.74	0.407	-	-	0.76	0.464
Cu^{+2}	0.29	0.255	-	-	0.26	0.144
Co^{+1}	0.40	0.562	-	-	0.02	0.042
Ta	1.61	2.796			1.78	1.338
Mo	17.30	0.512			21.13	5.752
Nb	12.82	0.830			14.78	3.178
Cr	3.22	1.135			1.33	0.155

RN: River Nile, STD: Standard deviation, not detected

(4-4) Analysis and discussion

for all concentrations of analyzed elements for crops showed highly variations in the three different states as shown by Table (4-1), (4-2) and (4-3) except Ni values. However, Ni ranged from 13.63-13.88, 13.69-13.97, and 13.71-13,77 for Wheate, Degace, and Fiterita respectively, with slight remarkable difference between selected crops.On average the value of Fe^{+3} in wheate at Gezira state tended to be higher than in the other two states (River Nile and White Nile). However, at Gezira state one have an average value of (6.27±2.8)% while for the other two States River Nile and White Nile one have lower average values, and

their values were (4.16±1.4), and (3.69±2.5)% respectively. In contrast average values of Fe^{+3} in the other two crops at Gezira state recorded the lowest values which are (4.57±1.9), and (3.5±1.9)% at Degace and Fiterita crops respectively as shown by Tables (4-2). While the highest value observed (10.94±1.7)% recorded at Degace crop from RNS,followed by (5.89±2.1)% recorded in Fiterita from WNS.The concentration of Ti for Wheate from in WNS, RNS, and GS are (5.36±6.6), (2.76±1.8), and (1.76±1.619)%, respectively, higher value recorded for WNS wheattype. Mean Ti for Degace from WNS, RNS, and GS were (3.26±1.7), (2.26±0.75), and (1.64±0.86)%, respectively. On the other hand, for Fiterita from WNS and GS the concentration are (3.07±0.4), and (1.86±1.48)%, respectively. With a significantly 56% higher concentration obtained for the Fiterita type from WNS compared to Fiterita type from GSTable(4-3).For Cr concentrations figure 1, there was a highly significant changed in the mean values of Cr between these crops. However, mean Cr concentrations in wheat collected from GS was 1.35%while it increased to almost 25% in wheat from WNS. In the same time, mean Cr concentrations for Degace from WNS, RNS, and GS were 1.57, 0.08, and 1.5% respectively. Lastly, for Fiterita which collected from WNS and GS were 3.22 and 1.33% consecutively.
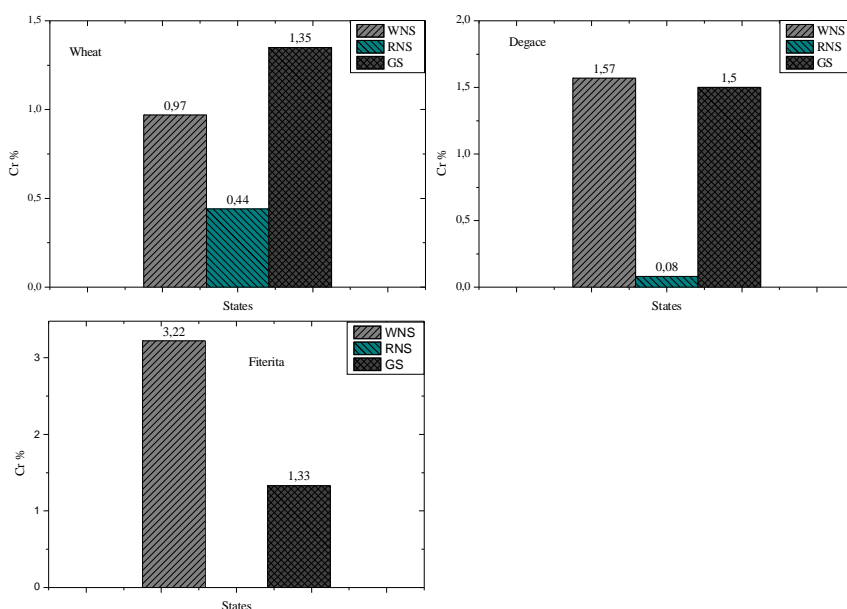
Figure (1): Mean Cr concentrations in three different crops collected from different States

In terms of Mo concentrations in the selected crop varieties, the values of Mo for wheat degace crops were similar at all sites with average value 17% Figure (2). Mo value in Fiterita collected from GS was higher by nearly 23% than that from WNS.
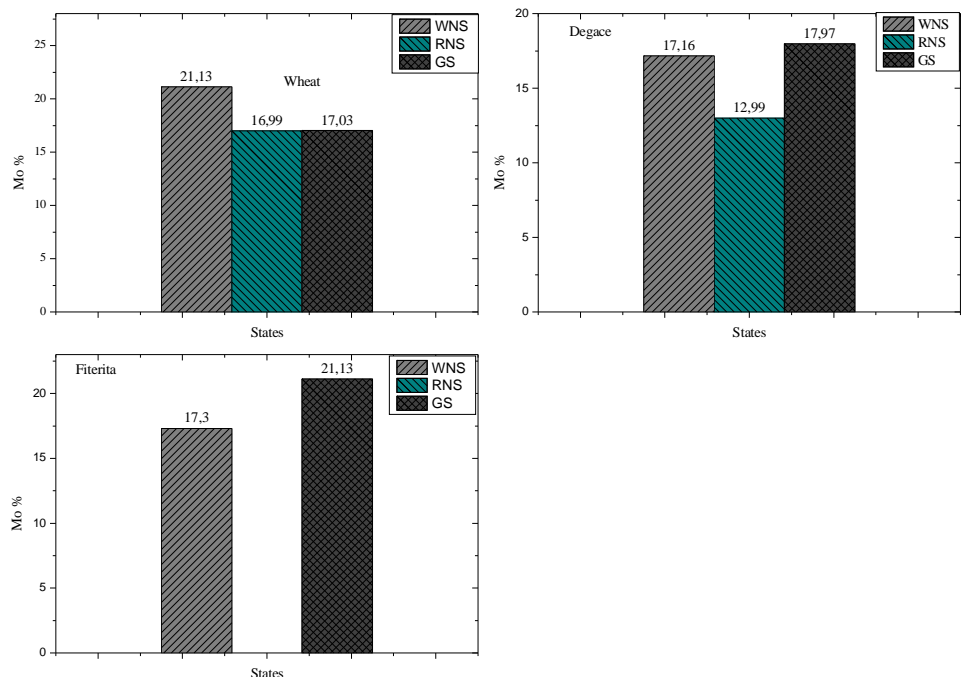
Figure (2): Mean Mo concentrations in three different crops collected from different states

The values of Nb for all crops were similar at all sites with average value 13% with slight increased by almost 13.6% in Fiterita crop at GS. Concerning Ta the lowest values recorded in wheat, ranged from 0.04 to 0.89 while the highest values recorded in Fiterita ranged from 1.61 to 1.78 at all states.

Tungsten (w) element, in all crops types (w) showed higher value for Fiterita crop collected from GS has higher concentration by 3.8% higher than Fiterita from WNS Table (4-4-3). In comparison to wheat crop from these states the values of w were lower by approximately 3.4%. While in Degace crop the analyses results illustrated lower values compare to the values of w from Fiterita and wheat Figur 3
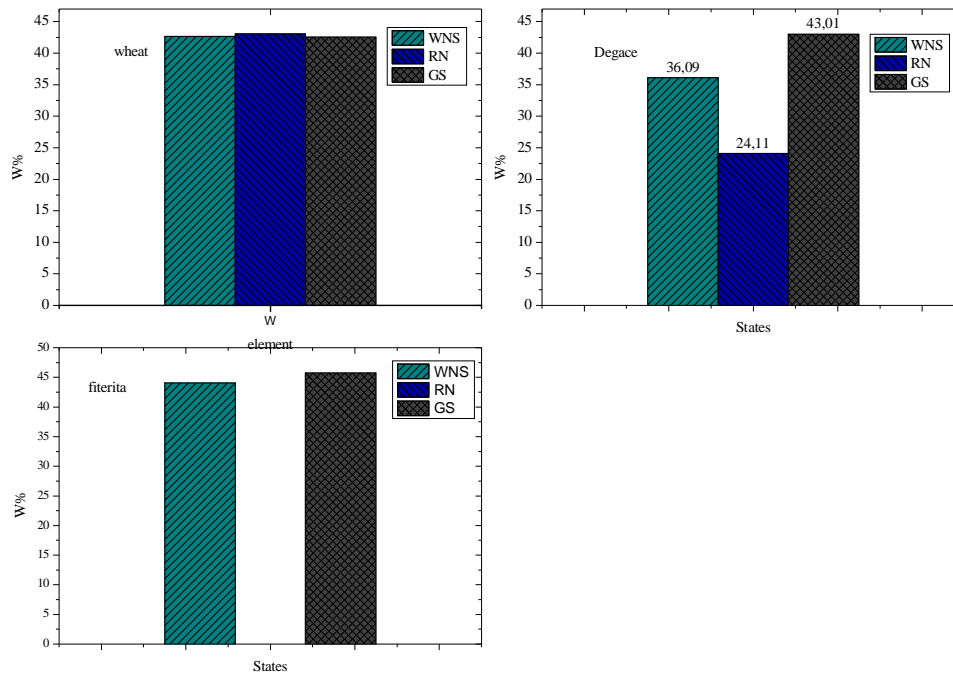
figure 3: Mean Tingustan (w) concentration in the three different crops collected from different states

It is very important to note that the existence of W with high concentration in all samples indicates high contaminator, which may result from damaged lambs, which are used widely for lighting in Sudan

4-5 conclusion

The spec tropic analysis of the selected crops shows that they are highly contaminated by tungsten. This need further studies to see the biological effects of this element.

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