Analytical Study of Elements Concentrations in Samples of Medical Herbs Using X-Ray Fluorescence Technique

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Introduction:

Reports by the international health organization tell that more than two-third of the world population uses the herbs for medication, anyone who follows the history finds that the medicament of aspirin is extracted in origin from the willow bark [1]. An example of plants used in treatment: ginger is used as antioxidant and antimicrobial agent. It also prevents motion and morning sickness [2,3]. Indeed, many herbs like bee pollen, and red clover are used for treating dangerous diseases and strengthening the Immune System [4,5]. Rosmarinus officinal is known medicinal plant have recently demonstrated the importance of rosemary to lose weight, in addition to its usefulness in stimulating memory and brain weary and to help the stomach to digest [6]. Nigella sativa is taking of this soaked consume fat, helps in the process of representation of fatty substances, and then remove them from the body with the urine[7,8]. In the industrial countries the opinion of scientists, researchers, and doctors have changed about using materials, plants and herbs. For example, cardiologists recommend following a diet which contains garlic and plant oil [9].

The aim of this study is to investigate some herbs which are used for the medication of the weight loss using the Energy Dispersive X-ray Fluorescence (EDXRF) technique in order to spot light on their constituent of elements [10]. Therefore, their containing of elements has to be identified qualitatively and quantitatively. It is thought that one or more element could be common in these herbs that are used for some purposes. The knowledge of these common elements could reveal their role in the weight loss proves.

Medical Herbs

Medication using herbs has been known for a long time in the Arab World and people who were specialists in this filed were called herbalists. Since that, herbal medicine has pared the way to the development in science and medicine since analyzing and classifying the necessary ingredients in herbs in addition to mixing them with chemicals have become possible. Human beings knew about the advantages of these herbs by tasting and smelling them, as a result, they noticed their effects [11,12].

Despite the development of chemical-based medicine, medical herbs are still vital in modern medicines because they have a lot of qualities and advantages. As a result, about 60 % of materials used in medicines are taken from plants. The climate of Jordan plays an important role in this as there are many types of wild plants and others which can be cultivated in Jordan. There are about 2000 types of wild plant; more than 150 are medical herbs which we use for treatment with no side effects, unlike chemical medicines. There are two sources to get medical herbs from: wild herbs or plants and cultivated herbs.

There are great numbers of medical plants so that it is necessary to classify them into small and large groups to make it easier to study them. This classification differs because each one has a different way to study: Active constituents, Used Parts, Modern Plants Classification (For the rest of other Plants) [11,12].

Theoretical part

3.1 The Discovery of X-ray

Roentgen discovered x-ray in 1895, and this led to the development of the modern theory of atomic structure, while studying cathodes ray in a gas discharge tube. In his darkened room, Roentgen shielded the tube with heavy black paper, and noticed that a green colored fluorescent light could be seen coming from a screen setting a few feet away from the tube, he realized that he had produced a previously unknown "invisible light," or ray, that was being emitted from the tube, a ray that was capable of passing through the heavy paper covering the tube, through additional experiments. He also found out that the new ray would pass through most substances casting shadows of solid objects on pieces of film. Later, he named the new ray x-ray [13]. W. H. Bragg, who derived the famous Bragg's formula, was interested in Von Laue's experiment. This was starting of crystal structure analysis with x-ray.

The Bragg's formula

Equation 1

Where, n is the order of reflection (1, 2, 3 …), d is the spacing between the planes in the atomic lattice, θ is the angle between the incident ray and the scattering planes.

3.2 X-ray tube

It is obtained by x-ray tubes position at a private circle of air containing plates of metallic cathode and anode, difference between them and the constant high voltage (V) tried to accelerate the electrons emanating from anode and give it a high kinetic energy.

There priming near the cathode are heated as a result of the passage of electric current in box, setting free electrons from the cathode by the emission thermal based kinetic energy in the final difference applied voltage between the polar tubes x-ray.

And moving these electrons toward the elevator collide with atoms of the material of which the elevator irritating part of these atoms, and when you try these atoms get into the position stability, it launches photons of x-ray characteristic of atoms of target material (cathode). And is used in tube x-ray inside the spectrometer shine x-rays used for the purposes of this research a lift from a Rhodium (Rh).

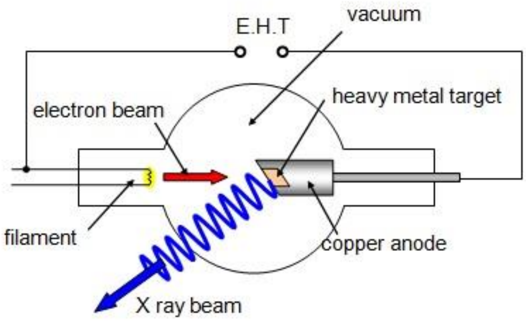


Figure 1 schematic diagrams of the X-ray tubes.

3.3 X-ray properties

X-rays are electromagnetic radiations that have exactly the same nature as light but of very much shorter wavelength, unit of measurement in x-ray region is A^{o} and nm. 1 A^{o}= (10-10) m, 1nm = 10 A^{o} = 10^{-9} = m, x-ray wavelengths are in the range (0.5-2.5) A^{o}. Wavelength of visible light ~6000 A^{o}. They are shorter in wavelength in comparison with UV rays the electromagnetic spectrum is shown in Figure (2.2).

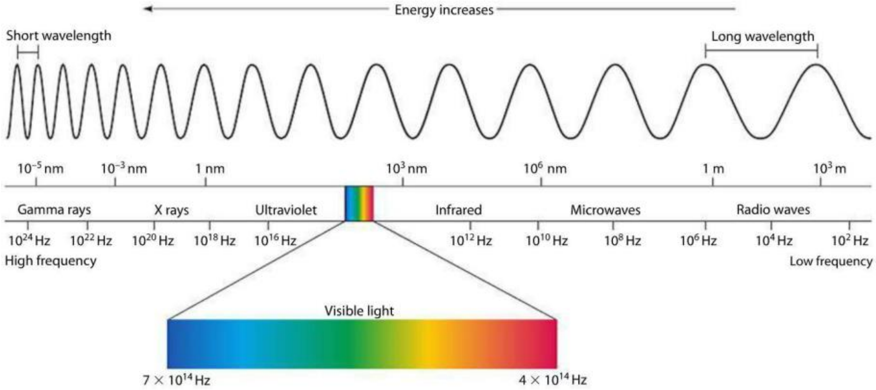


Figure 2 Electromagnetic spectrum

X-ray easily passes through material and becomes stronger as the material's atomic number decreases. X-ray can go through solid objects, and their major use is to take image of the inside objects in diagnostic radiograph and crystallography. As a result, the term x-ray is metonymically used to refer to a radiographic image produced using these methods, in addition to the method itself. X-ray is a form ionizing radiation, and exposure to them can be dangerous for health.

The continuous Spectrum

Continuous x-rays are produced when electrons or other high- energy charged particles, lose energy in passing through the coulomb field of a nucleus. In this interaction, the radiant energy (photons) lost by the electron through this process is called bremsstrahlung. The emission of continuous x-rays finds a simple explanation in terms of classic electromagnetic theory, because, according to this theory, the acceleration of charged particles should be accompanied by the emission of radiation. In the case of high- energy electrons striking a target, they must be rapidly decelerated as they penetrate the material of the target, and such a high negative acceleration should produce a pulse of radiation. The continuous x-ray spectrum generated by electrons in an x-ray tube is characterized by a short-wavelength limit λ_{min}, corresponding to the maximum energy of the exciting electrons:

Equation 2

Where Planck's constant (h) is = 6.626×10^{-34} J. sec., (c) is the velocity of light, (e) is the electron charge, and (V) is the potential difference applied to the tube. This relation of the short-wavelength limit to the applied potential is called the Duane-Hunt law [9].

The continuum spectrum approximated by the Kramer's formula

$I \lambda \alpha iZ$ (Equation 3

Where, Iλ is the intensity of wavelength is λ, λmin is the short wavelength limit, I is the x-ray tube current, and Z is the atomic number of the x-ray tube target, Iconc is the total intensity of the x-ray tube target.

$I_{conc} \alpha iZV_2$ Equation 4

The minimum wavelength cutoff represents the complete conversion of the electrons kinetic energy to x radiation. When the equation is applied to an x-ray tube from full wave applied, where, V is peak potential and I int is integrated continues intensity.

$I_{int}= (1.4x\ 10^{-9})\ (ZiV_2)$ Equation 5

The last equation (2.4) is the effective of x-ray tube target atomic number Z, current I and potential V.

A charge in the X-ray tube current caused a proportional charge in continuum intensity because the number of electrons arriving at the target is directly proportional to the current. The atomic number of target has much the same effect because the number of orbital electrons in each target atom is proportional to Z.

Interaction of X-ray with Matter

X-rays possess intrinsic energy that may be imparted to the matter they interact with. That interaction takes place as either:

-Absorption (transfer of energy from the x-ray photon to the absorbing material) Scattering (in which the x-ray photon is "redirected" by interaction with the scattering material). The process of scattering is the primary process responsible for diffraction, but both processes (that are, in many ways, interdependent) result in the production of potentially damaging secondary radiation. When the x-ray beam passes through matter, some photons will be absorbed inside the material or scattered away from the origin path [10]. The intensity I° of an x-ray beam passing through a layer of thickness d and density p is reduced to intensity I according to the well know of Lambert- Beer Formula:

$$I = I^{\circ} \exp (\mu P d) \qquad \text{Equation 6}$$

The number of photons (the intensity) is reduced their energy is generally unchanged [8]

The intensity of the beam, as measured by the number I of photons it contains, decreases exponentially as the thickness of the slab increase.

The product $\mu 1 = \mu P$ is called the linear absorption co-efficient and is expressed in cm-1. μ (E) is sometimes called the total cross- section for x-ray absorption of energy E, the mass absorption coefficient μ (M) of a complex matrix M consisting of a mixture of several chemical elements, can be calculated from the mass attenuation coefficient of the n constituting element

$$\mu (M) = \qquad \text{Equation 7}$$

Where, μI is the mass attenuation coefficient of the i-th pure element and wi is mass fraction in the sample considered.

The mass absorption coefficient μ plays a very important role in quantitative X-ray Fluorescence (XRF) analysis. Both the exciting primary radiation and the fluorescence radiation are attenuated in the sample. To relate the absorbed fluorescence intensity to the concentration, this attenuation must be taken into account [11]

X-ray Spectrum

X-ray is produced by x-ray tube when accelerated electrons collide with the target (anode). The loss of energy of the electrons because of the impact is shown as x-ray. Most of the kinetic energy of the electrons striking the target is converted into heat, less than 1% is being transformed into x-rays.

The kinetic energy of the electron can be expressed through this equation

Equation 8

Where, e is the electric charge, V is the applied voltage, v is the electron velocity, and m is the mass of the electrons.

X-ray line Spectra

x-ray line spectra are of particular interest because they are significant features of x-ray, which have so many useful applications in technology and science. These spectra are theoretical interest because they give information about the energies of electrons in the inner sub- shells of atoms. The energy levels of an atom which are involved in the emission of its X-ray line spectrum are most conveniently shown in terms of an energy- level diagram that is rather different from the standard type with which we have become familiar.

The transitions that are allowed by the selection rules are shown in figure (2.3) which contains the main lines in the K and L spectra [12].

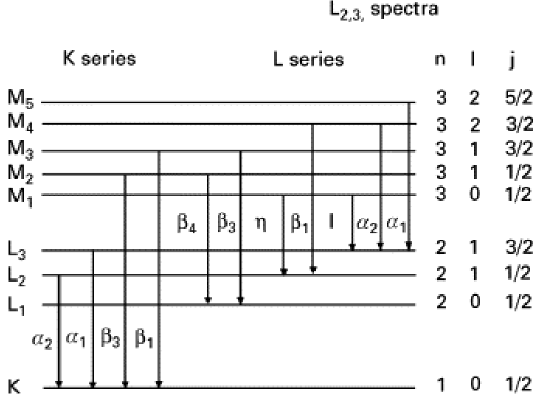


Figure 2.3 energy level diagram of the main line in the K and L spectra.

The energy levels in the above figure are also identified by a notation that is commonly used in discussing x-ray spectra.

If the energy of an atom with an electron of quantum numbers n, I, J is particularly negative, the energy of an atom with a hole of the same quantum number will be positive since more energy must be given to the atom remove the electron.
Here is a set of selection rules for the change in quantum numbers for the hole [13]:

Δ 1= ± Equation 9

Δ J = 0, ± Equation 10

±n= No restuctions Equation 11

X-ray Energy Spectra

X-ray photons produced by an x-ray machine are let erogenous in energy. The energy spectrum shows a continuous distribution of energies for the bremsstrahlung photons superimposed by characteristic radiation of discrete energies. Then we can calculate the energy spectrum by using the following Kramer's equation [14]
IE= KZ (Em- E) (2.12)

Where , IE the intensity of photon with energy E, Z the atomic number of the target, Em the maximum photon energy and K is a constant.

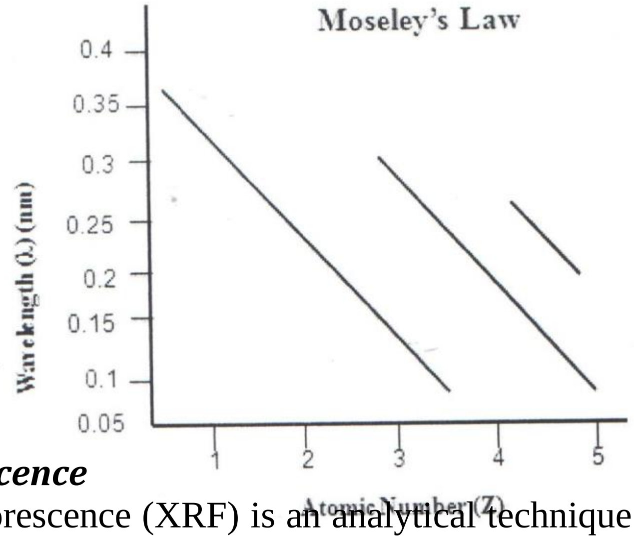
Moseley's Law

The wavelength of any particular line decreases as the atomic number of the emitter is increased, and it important in determining the places of elements in the periodic table.

There is a linear relation between the line of frequency v and the atomic number Z as in the equation below:

$$V= C^2 (Z- ð)^2 \qquad \text{Equation 12}$$

Where C and ð are constant



X-ray fluorescence

X-Ray Fluorescence (XRF) is an analytical technique that involves the interaction of x-rays with a material to determine its elemental composition. There are two main XRF methodologies:

1-Energy Dispersive X-Ray Fluorescence (EDXRF).
2-Wavelength Dispersive X-Ray fluorescence (WDXRF).

The range of detectable elements varies according to instrument configuration and set up, but typically EDXRF covers all elements from sodium (Na) to uranium (U), whilst WDXRF an extend this down to beryllium (Be). Concentrations can range from 100% down to ppm (part per million) and in some cases sub- ppm levels.

Of the most important applications: metallurgy, forensics, polymers, electronics, archaeology, environmental analysis, geology and mining. Recent advances in x-ray technology have led to the development of XRF instruments capable of high spatial resolution analysis, which are now a field of interest by researchers and analysts within these application areas.

X-ray fluorescence- The Basic Process

1. X-Ray fluorescence (XRF) can be considered in a simple three step process occurring at the atomic level:
2. An incoming X-ray knocks out an electron from one of the orbitals surrounding the nucleus within an atom of the material.
3. A hole is produced in the orbital, resulting in a high energy, unstable configuration for the atom.

To restore equilibrium, an electron from a higher energy, outer orbital falls into the hole. As this is a lower energy position, the excess energy is emitted in the form of a fluorescent X-ray. The energy difference between the expelled and replacement electrons is characteristic of the element atom in which the fluorescence process is occurring- thus, the energy of the emitted fluorescent x-ray is directly linked to a specific element being analyzed. It is this key feature which makes XRF such a fast-analytical tool for elemental composition.

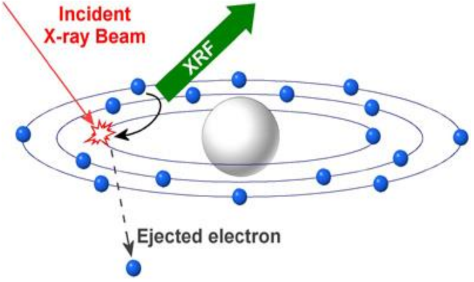


Figure 2.5 the Basic process of XRF.

Multiple transitions:

Atoms comprise a number of electron orbitals (eg, K shell, L shell, and M shell) a number of possible fluorescent transitions are possible. K transitions: interaction of x-rays with an atom with K, L and M shells could result in a hole forming in the K shell, which is then filled by an electron from the L shell or from the M shell. L transitions: interaction of x-ray with an atom could result in a hole forming in L shell, which is then filled by electron from M shell or from the N shell.

intensity

The absorption of x-rays differs from one material to another one because it depends on several factors. If the x-ray photons of energy is greater or equal to the binding energy of the electron is released from orbit. Atom becomes unstable. Is transmission electron orbit of the highest energy to which at least, which leads to the production XRF.

The diagram below illustrates the K and L fluorescence yield as a function of atomic number, Z [5].

Figure 2.6 the relation between x-ray fluorescence yield (%) and atomic number (z) [16]

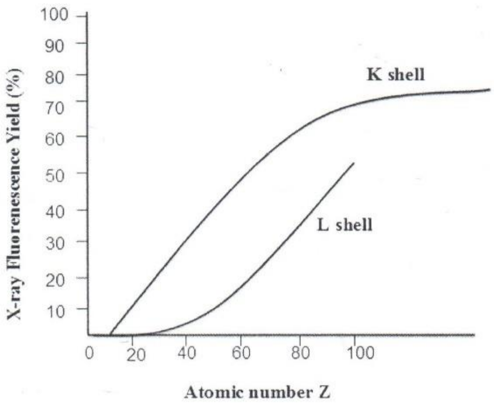


Figure 2.6 the relation between x-ray fluorescence yield (%) and atomic number

Auger- Electron

A hole in an inner shell (K shell) is generated by an incident high- energy electron that loses the corresponding energy E transferred to the ejected electron; the hole in the K shell is filled by an electron from an outer shell (L2). The superfluous energy is transferred to another electron which is subsequently ejected (from the L3 level).

The energy of an Auger Electron:

$$EA = E1 - E2 - E3 \qquad \text{Equation 13}$$

Where, E1= energy of atom with inner- shell vacancy, E2= energy of atom with outer- shell vacancy, and E3= binding energy of emitted (Auger) electron.

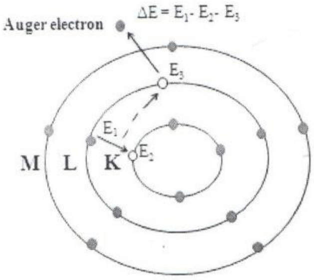


Figure 2.7 Auger Electron process

Standard Addition Methods

The standard addition method is based on the addition of small quantities of the analyst element to the specimens. The method is interesting when the anlayst's concentration is low; there are no standards similar to the unknown available, and the analyst is only interested in one or few constituent elements in specimen. The method is based on the following by adding a known quantity ΔC, of the analyst I element to the unknown specimen, the intensity I1 of the analyst's radiation will be increased by an amount ΔI,I

$$Ci = KiIi \qquad \text{Equation 14}$$

For the original specimen

$$C1 + \Delta Ci = Ki\ (Ii + \Delta\ Iii) \qquad \text{Equation 15}$$

Where Ki is the calibration constant, and Ci is the concentration of an analyst I in a sample. The unknown scaling factor can be determined empirically by one or more reference samples [17]

Standardized method

XRF is the best method to get results in a perfectly reproducible way. XRF analysis is considered as an important tool for quality and process control in industry. For these applications, consistency of results is often much more necessary than the true value. The results of various laboratories have much within a clearly defined experimental error [18]

Standardized procedures sometimes define each detail from instrument type to the reproducibility of the final result.

The following items are included:

1. Method, instrument and measurement process.
2. Standard samples and sample preparation.
3. Calculation methods.
4. Precisions of results.

All standardized methods defined minimum precision requirements and thus make sure that the results of laboratories using the same method are consistent within the permissible tolerance [19]

X-ray Detector

There are many X-ray detector and we will to talk about the principle of X-ray detectors.

Basic principle of X-ray Detectors

The interaction of x-rays in the detector material is mainly determined by photoelectric effect, Compton scattering and pair production.

An X-ray detector is used to convert the energy released by an x-ray photon in the detector material into an electric signal. The read out and processing of the electric signal by means of a suitable electronic chain is used to measure the energy released by the photon and arrived time at the event.

The energy released in the detector material during the radiation interaction is converted into an electrical signal by means of a direct or an indirect process and with a conversion factor, which depends on the specific type of detector considered. In semiconductor, the energy is directly converted into a certain amount of charge which is then suitably collected in the output electrode of the device. In most x-ray detectors, the charge collected at the output electrode of the device represents the basic electrical signal available for further processing [20].

The amount of charge $_\varrho$ is proportional to the photon energy E by

Equation 16

Where, ε the conversion factor differs considerably among different detectors.

Semiconductor detectors

On the basics of the wide application of semiconductors in a different scientific areas and commercial applications, there exists a multitude of excellent monographs on the type of detector to which readers are referred .

Build up semiconductor detectors work in a solid-state ionization chamber. They use properties of semiconductor materials with p-and n- conduction produced by doping pure conductor materials with donors or acceptors:

1.P-Conduction: means an acceptor i.e. mobile positive charge.

2.n-Conduction: means an excess on donor, i.e. negative charge.

If n and p conducting materials are brought into contact, electrons and holes diffuse in the adjacent area with the opposite type of charge.

In a signal crystal of semiconductor material such as silicon and germanium the sharply defined atomic electron states are broadened into bands of energy states. As shown in figure (2.8) blow

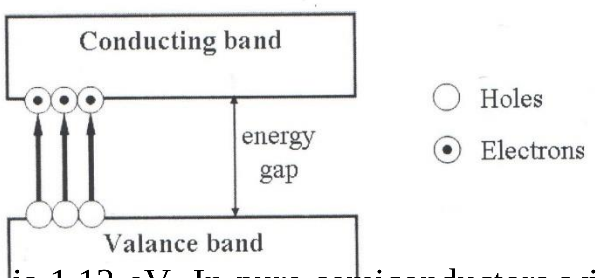


Figure 2.8 band structure of a semiconductor material.

The band gap for the silicon is 1.12 eV. In pure semiconductors without impurities, the gap contains forbidden states. If an electron receives energy at least equal to that of the band gap, this electron can be promoted from the valance band to the conduction band.

As a result a number of electrons are transferred from the valance band to the conductor band and an equal number of electrons are transferred from the valance band to the conductor band and an equal number of holes are created in the valance band as shown in figure (2.8) [21].

X-rays Fluorescence Spectral Measurement

The electron hole pairs in turn are swept away by an applied bias to form a charge pulse. The charge pulse is converted to a voltage pulse by a preamplifier. The signal is further amplified and shaped by a linear amplifier (pulse processor) and then passed on to a multi- channel analyzer where the data is displayed as a histogram of intensity VS voltage as shown in the figure (2.9) below [22]

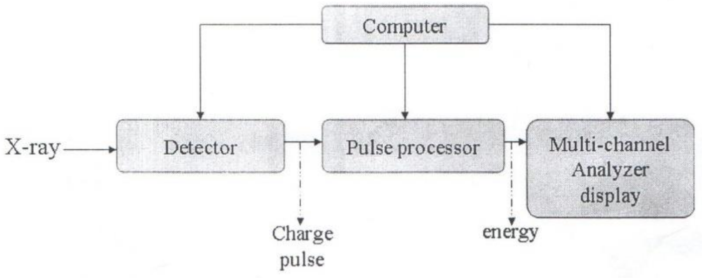


Figure 2.9 process of detection XRF in semiconductors.

The voltage pulse produced is proportional to the energy of the incoming x-ray photon. The EDXRDFs (Energy Dispersive X-ray Fluorescence's) system is comprised of three basic components [23]:

1-An x-ray detector which detects and converts x-ray into electronic signals.
2-A pulse processor which measures the electronic signals to determine the energy of each x-ray detected.
3-multi channel analyzer.

Experimental technique

Introduction

Minipal 2 is a compact energy dispersive x-ray spectrometer designed for the elemental analysis of wide range of samples. The system is controlled by a PC running the dedicated Minipal analytical software. The version of the minipal spectrometer: Minipal 2: PW4025 with Rh tube.

PW4025 x-ray spectrometer

The PW4025 spectrometer is simultaneous energy dispersive microprocessor controlled analytical instrument, designed for the detection and measurement of the elements in a sample from sodium (Na) to uranium (U).

Spectrometer Cabinet

The overall dimensions of spectrometer are: Height: 215 mm, width: 530 mm, and depth: 495. The operation of the spectrometer is controlled from a PC running the Minipal software .

Measuring Medium:

A helium system is fitted as standard in the spectrometer, measurements are normally carried out in air, helium is required for the analysis of elements with low atomic numbers, such as Na and Mg.

Detectors and HT power Supply

The High tension (HT) is stabilized by control electronics located across the front of the spectrometer. Anode current of the X-ray tube is controlled by the temperature of filament wire cathode. This is regulated by the current applied to the filament wire. The detectors are a Si-PIN detector. High voltage converter of maximum 30 KV and maximum current 1 MA

Counting Electronics:

The 2048 channel analyses board is used to count the detected X-ray photons. This data is passed to the Minipal analytical software as the row count rate.

Measuring sample by system:

Describe how to perform measurements of routine (unknown) samples. The measurement of normal samples is normally carried out within a defined application.

Measurement Overview:

The steps for carrying out measurements described in the following:

1-Loading the sample.
2-Opening the measure window for the required application in the device.
3-Giving the sample code.
4-Starting the measurement.

Sample definition information:

In this part of the window we provide all the information about the sample [24].

3.2: Analysis of Samples:

The spectrometer Minipal 2 changes the acceleration potential automatically from 0 to 30 KV, to measure the concentrations of the medium of the sample.

3.3 calibration Energy:

The spectrometer Minipal 2 changes the acceleration potential automatically from 0 to 30 KV, to measure the concentration of the medium of the sample.

calibration Energy:

The process is the measurement of standard samples (a mixture of elements with characteristic X-ray clues), and obtaining a relationship between the channel and measuring the energy represented by that channel. Through calibration, a relationship between the channel and energy is obtained by collecting the spectrum resulting from the standard sample. The relationship between the channel and energy to this energy line and fonts is then determined and stored in a computer data base.

Types of Analysis:

Types of analysis used in the analysis of samples:

Qualitative Analysis:

This method of analysis is used to identify the basic components of the samples used and to ensure compliance with the periodic table of elements from sodium (Na) to uranium (U) through the energies of these elements.

Quantitative Analysis:

After finding the elements of the sample through qualitative analysis quantitative analysis begins:

1-Collecting the spectrum crossing the sample.
2-Conversion tops the intensity of the spectrum to concentrations using the method of the basic parameters.

(Dead time) and lethal time: is needed by the detector and preamplifier and pulse processor for recording and measuring x-ray photon, and is expressed as a percentage in the total time scale [25].

In spite of these possibilities in the program Minipal 2, there a number of peaks that may be present in the spectrum but they are not represented by any of the elements. But the program recognizes some of the peaks as the peaks characteristic of the elements must be worry of such peaks when analyzing the spectrum and must be neglected and most important of these peaks:

1-Escape Peaks: Peaks resulting from the interaction of x-rays with silicon in Si (Li) the installation of the detector.

It should be noticed that the ionization energy of the electron orbit K is 1.742 Ke V in the silicon atom.

2-Pileup and sum peaks: When the processor operates in pulse discharge between each pulse and pulse during this short time does not exceed microseconds.

Accumulation pulse of two photons during the same time together on the detector, can be located in the spectrum at a location that is the sum of the energy two photons fallen together.

Such peaks occur several times if there is a high concentration for one of the elements in the sample.

3-Diffraction peaks: Occurs when the diffraction peaks correspond to the angle x-ray beam with primary distances has driven between the atoms in the sample, leading to repercussions of x-rays at a specific value of energy.

We can overcome these peaks during the analysis by moving the sample in the sample chamber.

An example of an x-ray fluorescence analysis spectrum, recorded using a Minipal 2 detector system is presented in figure (3.1) below:

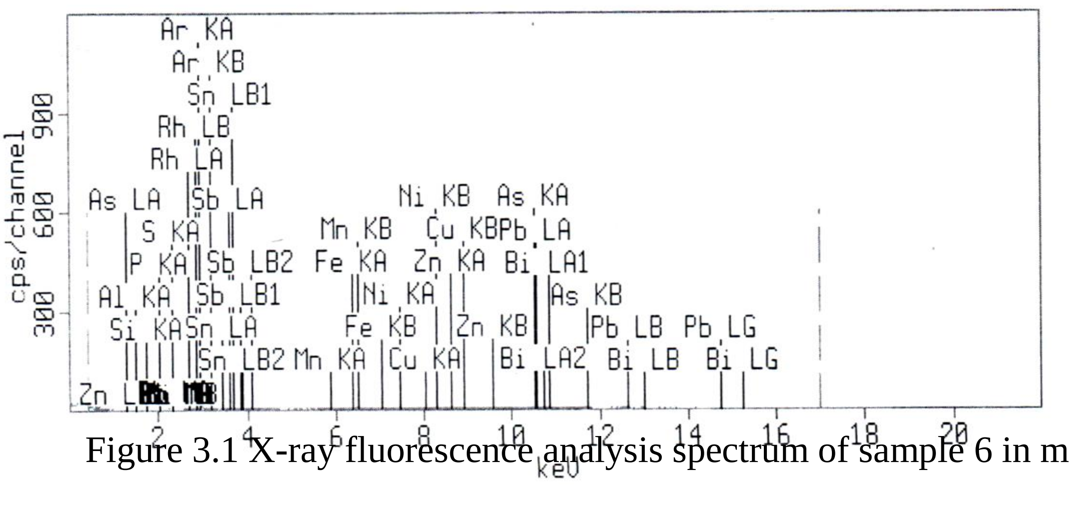


Figure 3.1 X-ray fluorescence analysis spectrum of sample 6 in maniple

(Results and Discussion)

Sample Preparation

Mixtures of medical herbs. Which are mainly used for body- weight losing, were bought, and then prepared as:

1-Each sample weighs (5g).

2-Each sample was smashed and turned into powder with no filtration to keep the unknown elements in it.

3-The sample was pressed with a powder of 15 tons using piston (Pelletizer) to become a tablet radius of the disk almost 31 mm put in (Spectrometer cambint) in Minipal 2 device.

Table (4.1) list of specimens under study

Samples	Number
Ginger + Anise)	1
(Tamarindus indice + Ashrq + Artemisia Absiuthium + schumer)	2
(Ginger + Anise + Cassia August folia+ tilia + Rosmarinus officinal is + Hyssop	3
(Saliva officials+ Licorice+ Tamarindu indice+ Hyssop+ Cassia August folia)	4
(The seeds of lust + Nigeria Sativa+ Cassia August folia + Other herbs)	5
(Cassia August folia + Licorice+ Fennel+ Saliva Official's+ Hyssop+ The seeds of lust + Anise+ Nigeria Sativa)	6

Table (4.2)below shows the average concentrations of the elements of the medicinal herbs samples found using EDXRF.

Table (4.2) for studied medicinal samples, the average concentration of elements in percentage (%)

Average concentration of Samples %								
Sample	Ti	Zn	Si	As	Sn	Se	P	CU
1	0.0021	0.4425	0.019	0.021	0	0.119	0.04	0.212
2	0.0013	0.5021	0.013	0.032	0.013	0.134	0.072	0.361
3	0.034	0.5015	0	0.019	0.02	0.122	0.034	0.251
4	0.026	0.4772	0.012	0.015	0	0.149	10.052	0.231
5	0.048	0.4364	0.015	0.023	0.01	0.126	0.06	0.201
6	0.041	0.4162	0	0.142	0.009	0.133	0.013	0.241
Mean value	0.0254	0.4626	0.009833	0.42	0.0086	0.1305	0.0451	0.2495
Std. div	0.0015	0.0771	0.001527	0.016	0.00016	0.003	0.00115	0.018

Table (4.3) for studied medicinal samples, the average concentration of elements in part per million (PPm)

Average concentration of sample (PPm)						
Sample	Al	Ni	Mn	Pb	S	Fe
1	2.83671	99.352	0.2701	51.529	22.4910	23.0313

2	4.44339	105.566	0.2866	48.877	21.2163	36.4788
3	3.36759	103.623	0.2806	24.625	24.6255	20.4862
4	3.02685	114.709	0.3104	27.396	17.3849	19.9461
5	3.79294	94.887	0	36.792	23.9148	20.5719
6	2.46982	93.093	0	2.976	20.2018	27.7380
Mean	3.323	101.872	0.1913	32.033	21.639	24.7087
Std. dev	0.5538	18.12	0.4561	5.338	3.607	41.1812

Thus, we notice that (Zn= 0.64 %) has the highest rate of focus as Zn is existed in the world with a rate of (65 g) per ton and ranking (24) according to its spread in the crust of the earth.

Human body needs few amounts of Zn (15 mg) everyday and should not exceed (40 mg). In addition; Zn makes the body immunity stronger.

(Mn = 0.19 ppm) has the lowest rate of focus. Human bodies contain (12- 13 mg) mainly in the Skelton, liver, kidney and the heart.

(Pb= 32.033 PPm) is considered as one of most dangerous elements for human beings. Its increase affects the brain, kidney and blood and our bodies can afford a does of (50 mg/ kg).

The element (Cu = 0.2495 %) is a good conductor to electricity and heat or temperature. Our daily food contains (2- 5 mg) of copper. Its increase leads of illnesses and causes Wilson disease which is an increase of Cu in body surfaces or layers like the head and liver.

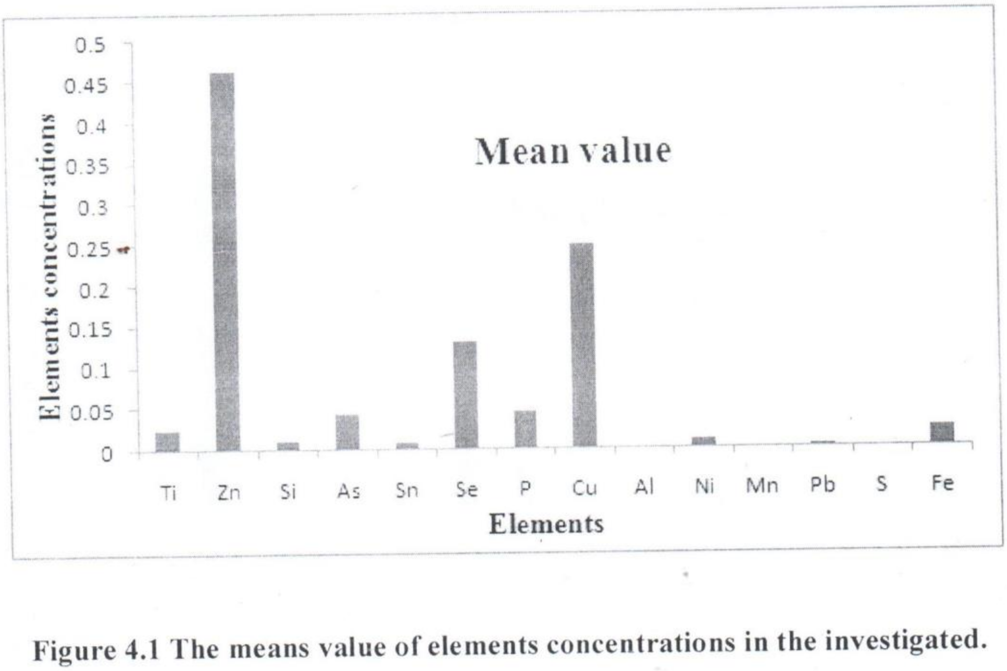


Figure 4.1 The means value of elements concentrations in the investigated.

4.2 Comparison the concentrations of elements of medicinal herbs:

The following Figures (4.3-4.8) demonstrate concentrations of elements in eacl sample.

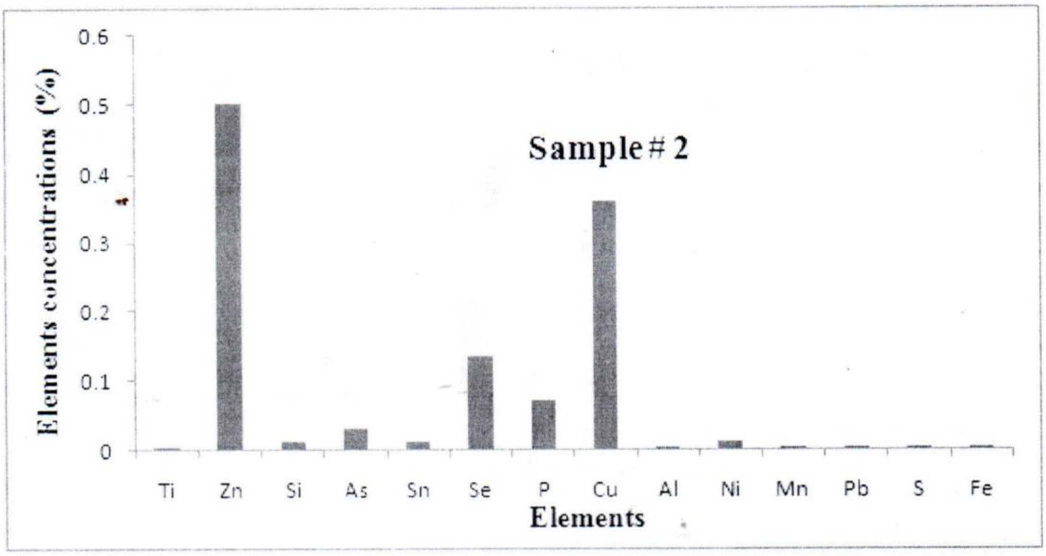


Figure 4.3 Average elements concentrations in sample#2.

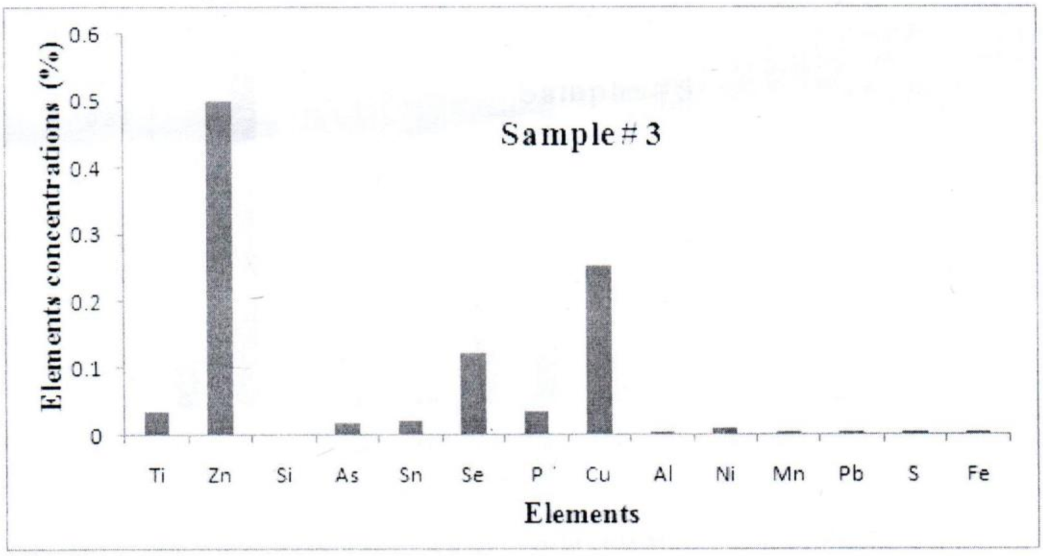


Figure 4.4 Average elements concentrations in sample#3.

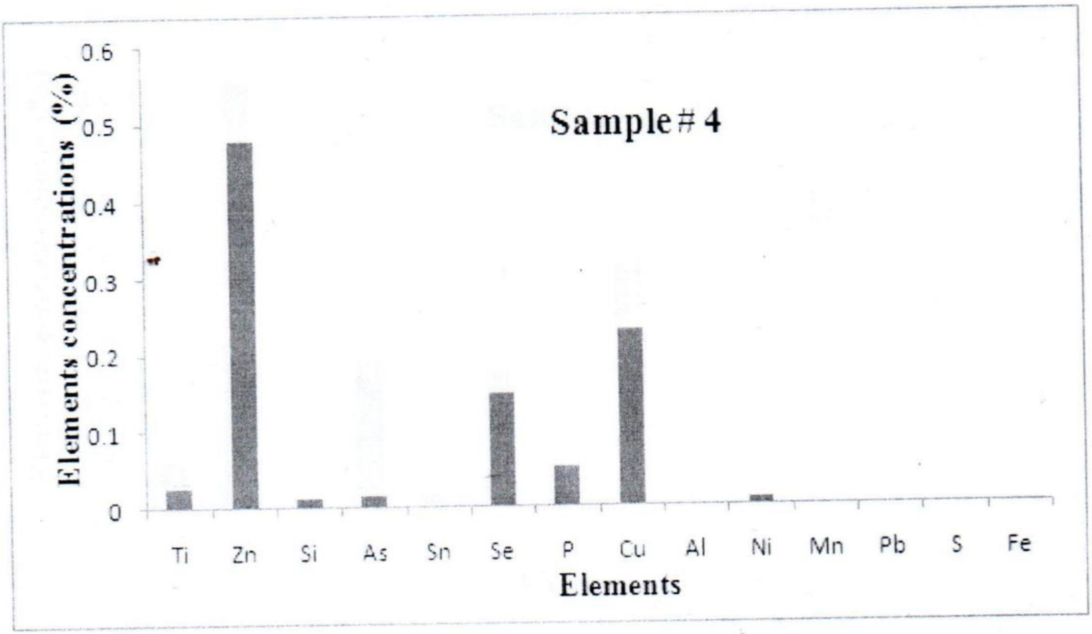


Figure 4.5 Average elements concentrations in sample#4.

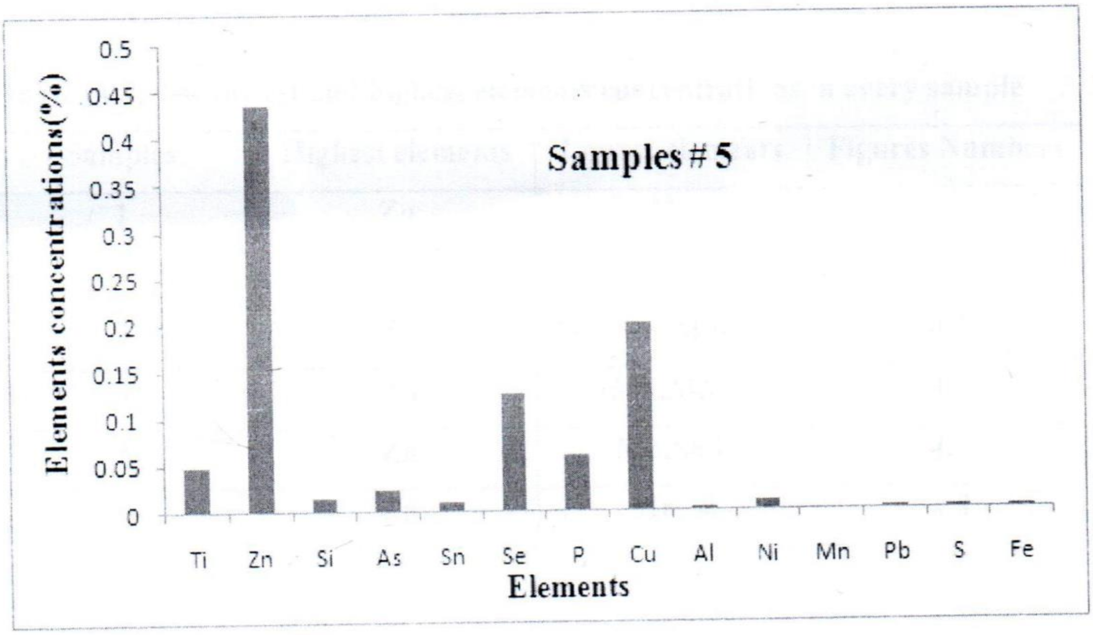


Figure 4.6 Average elements concentrations in sample#5.

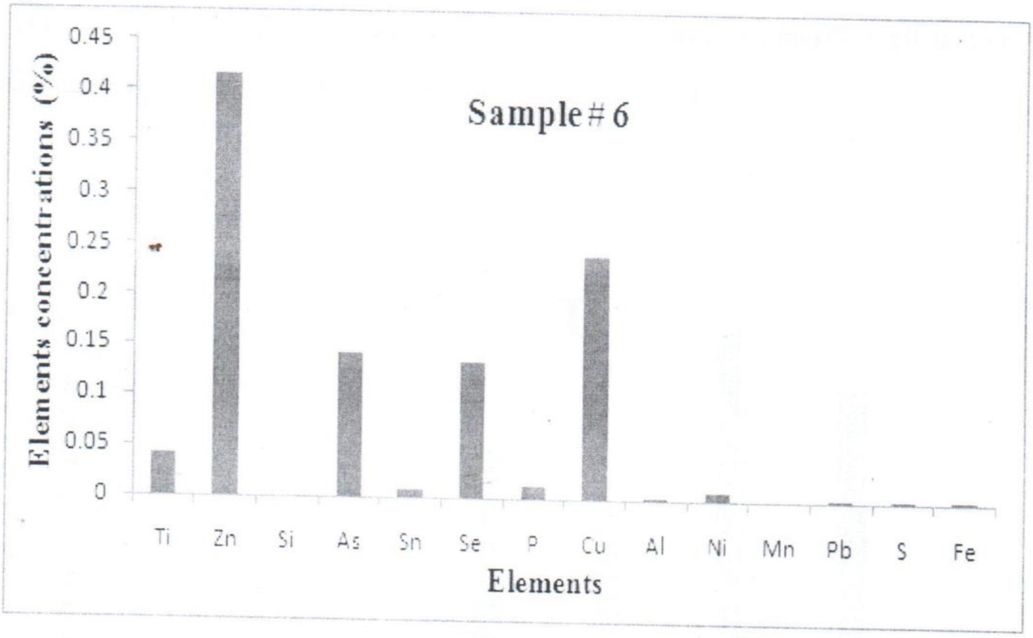


Figure 4.7 Average elements concentrations in sample#6.

Table (4.4) shows the highest and lowest concentrations of elements in each sample

Table (4.4) the lowest and highest elements concentrations in every sample

Sample	Highest elements	Lowest elements	Figures numbers
1	Zn	Mn	4.3
2	Zn	Mn, Al	4.4
3	Zn	Mn, Al ,Si	4.5
4	Zn	Mn, Al, Fe	4.6
5	Zn	Mn, Sn, P	4.7
6	Zn	Mn, Sn	4.8

The relationship between the averages of concentrations of elements in all samples of medicinal herbs is shown in the following figures of (4.9 - 4.22):

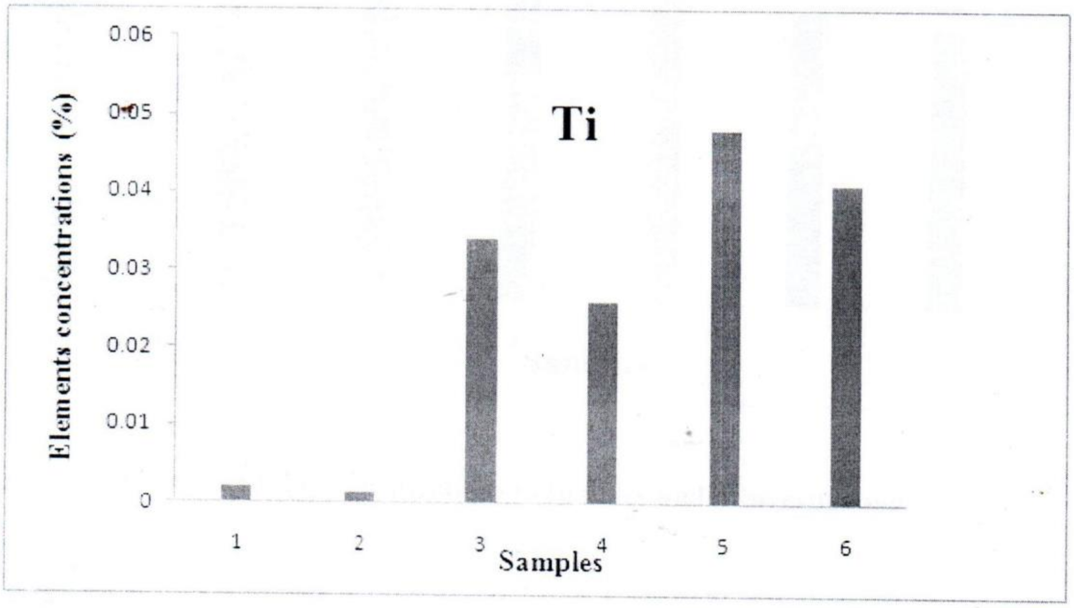


Figure 4.8 Ti concentrations in samples under investigation.

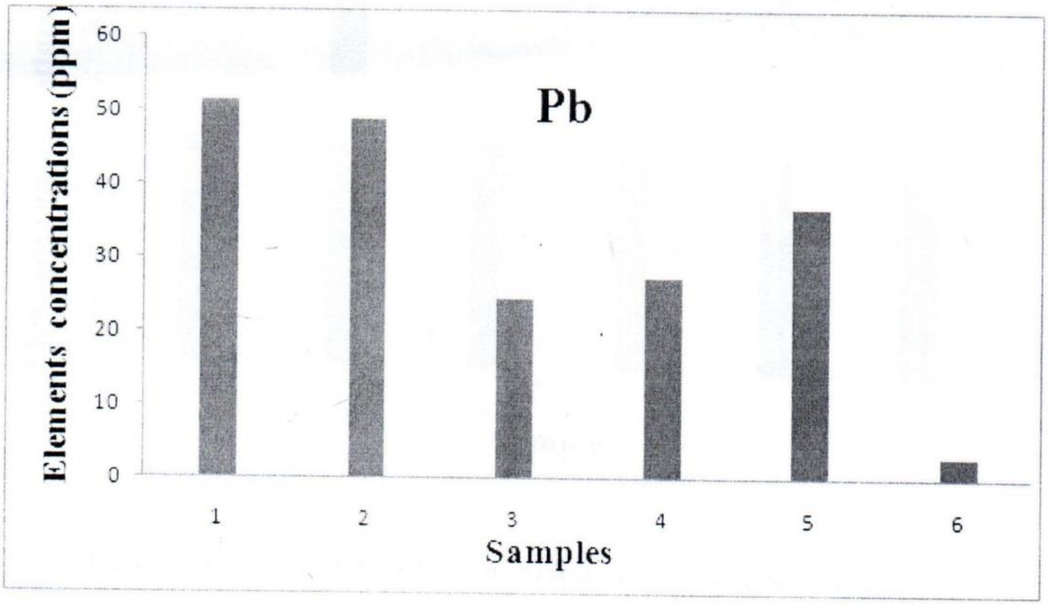


Figure 4.9 Pb concentrations in samples under investigation.

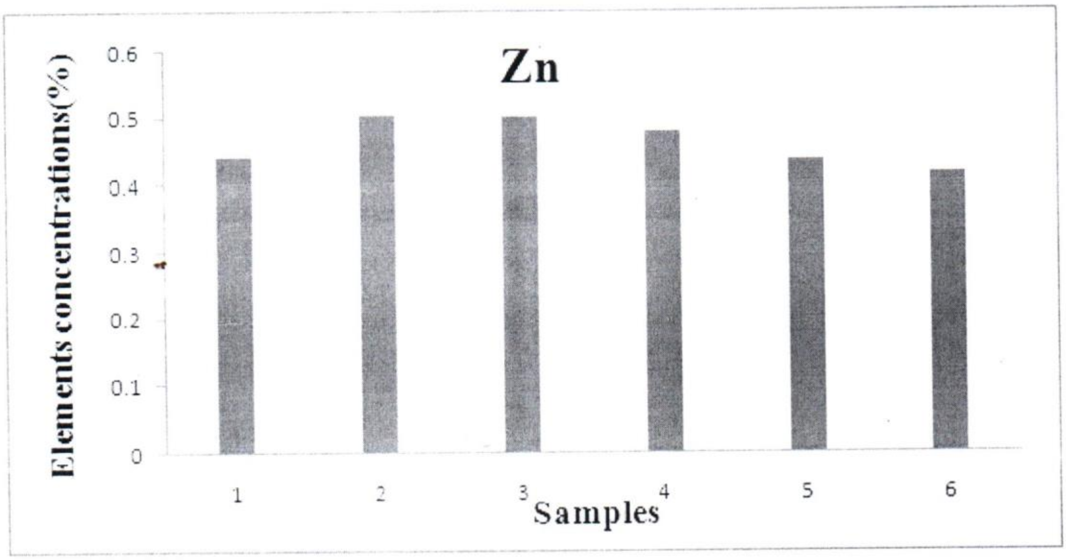


Figure 4.10 Zn concentrations in samples under investigation.

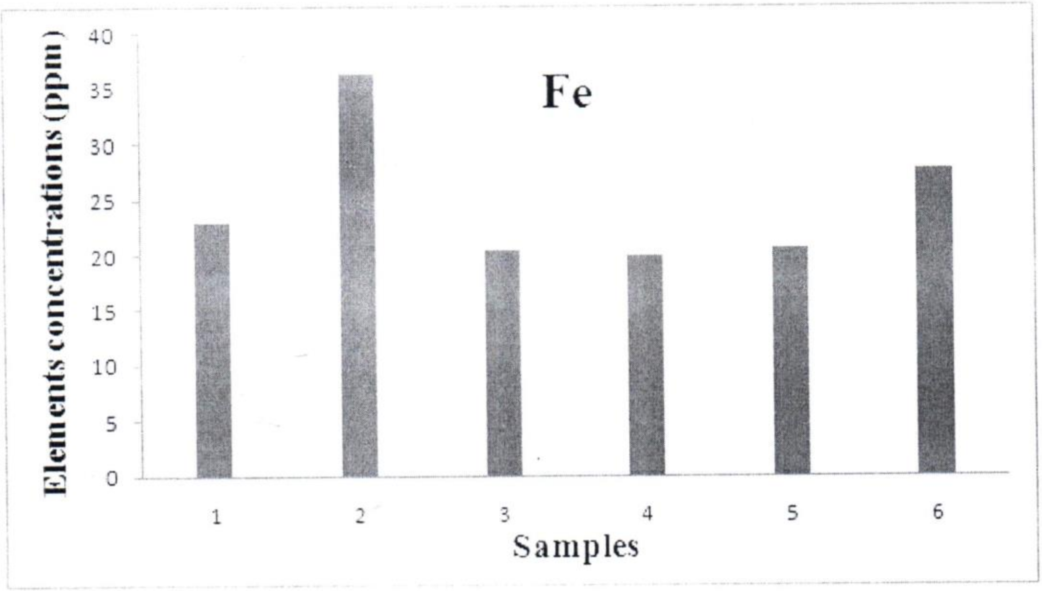


Figure 4.11 Fe concentrations in samples under investigation.

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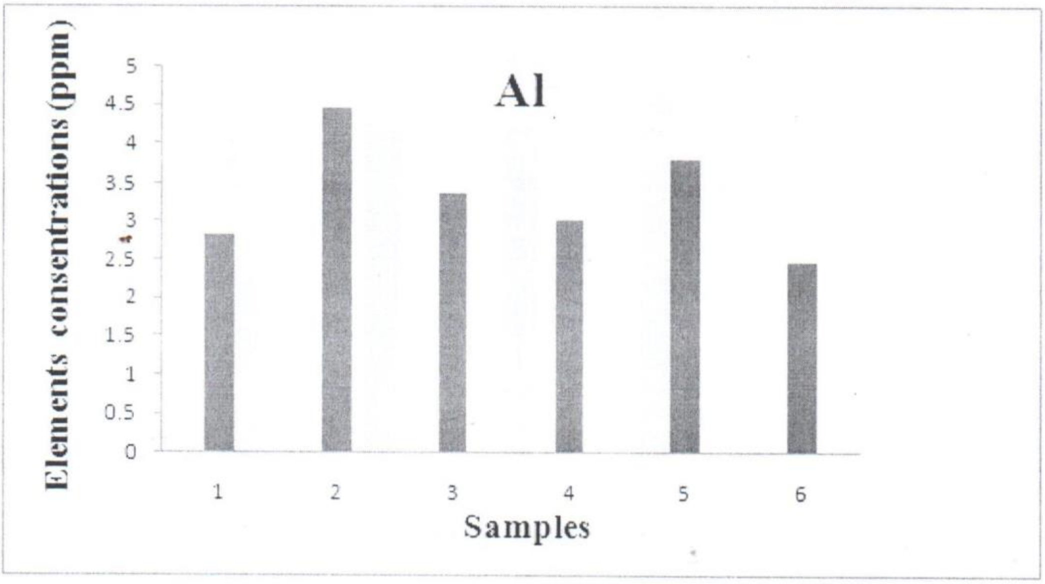

Figure 4.12 Al concentrations in samples under investigation.

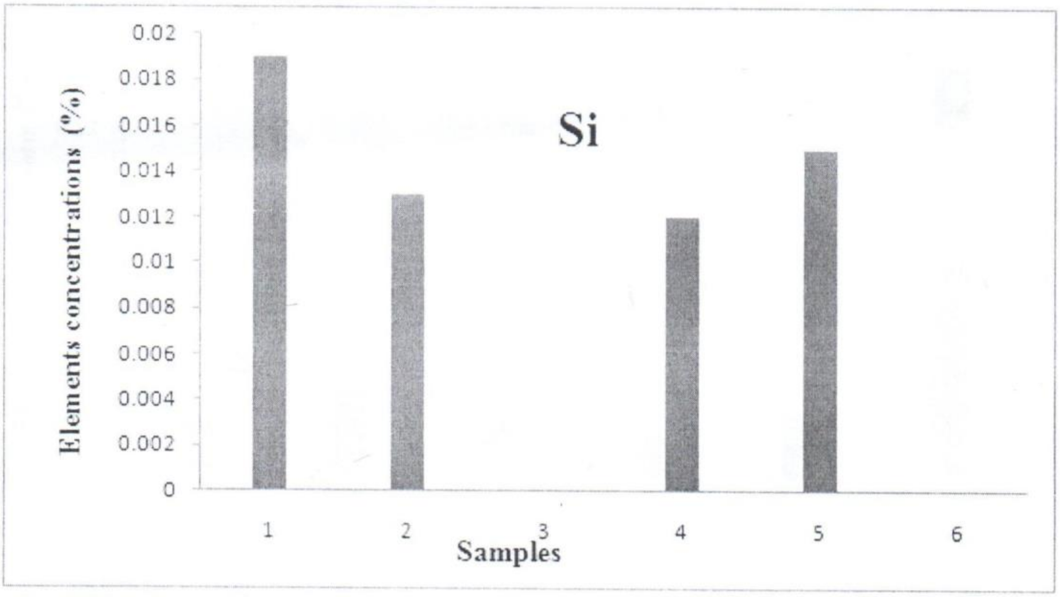

Figure 4.13 Si concentrations in samples under investigation.

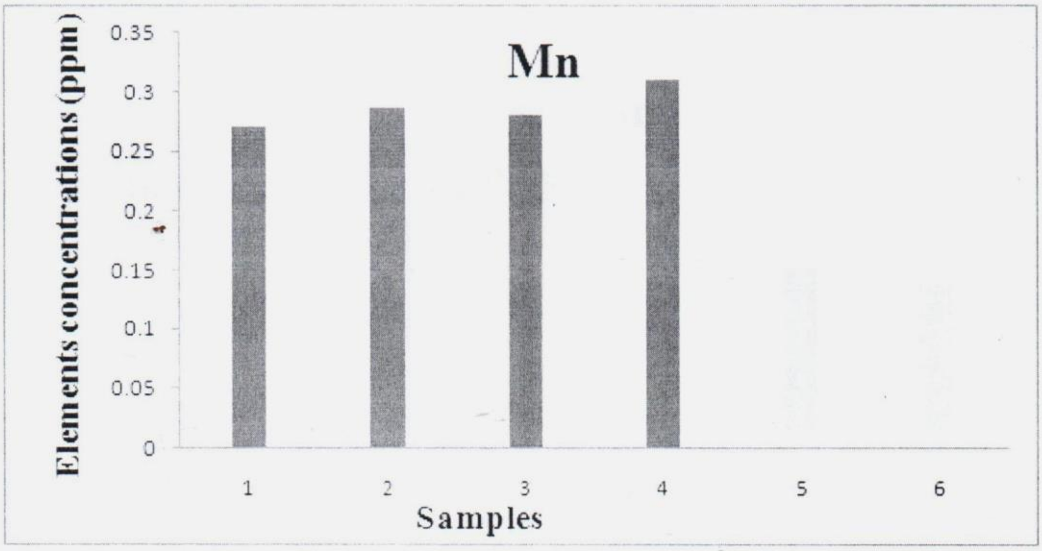

Figure 4.14 Mn concentrations in samples under investigation.

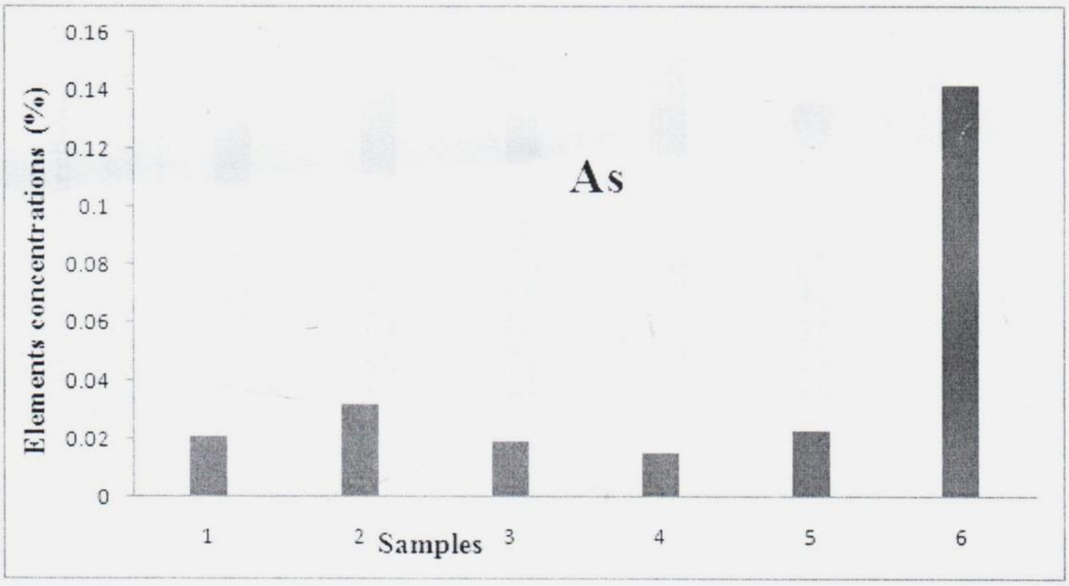

Figure 4.15 As concentrations in samples under investigation.

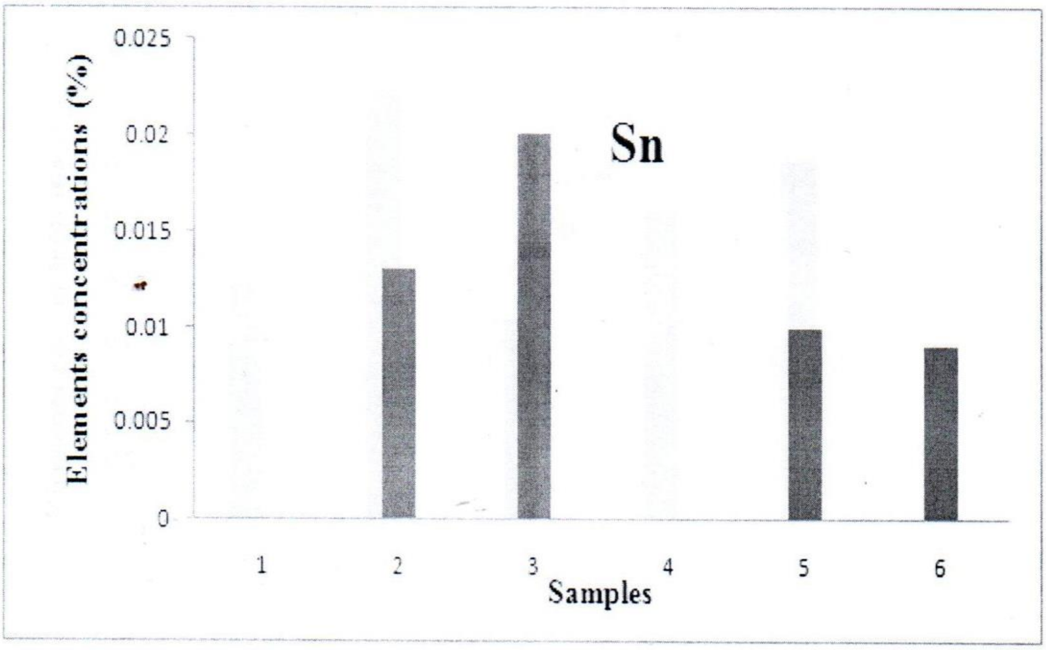

Figure 4.16 Sn concentrations in samples under investigation.

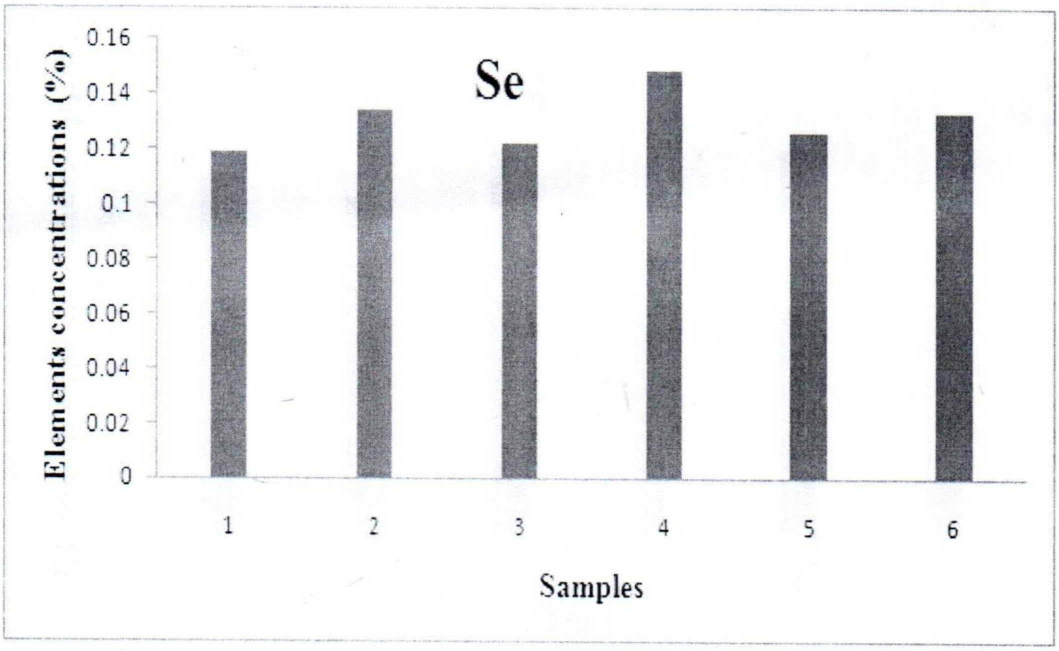

Figure 4.17 Se concentrations in samples under investigation.

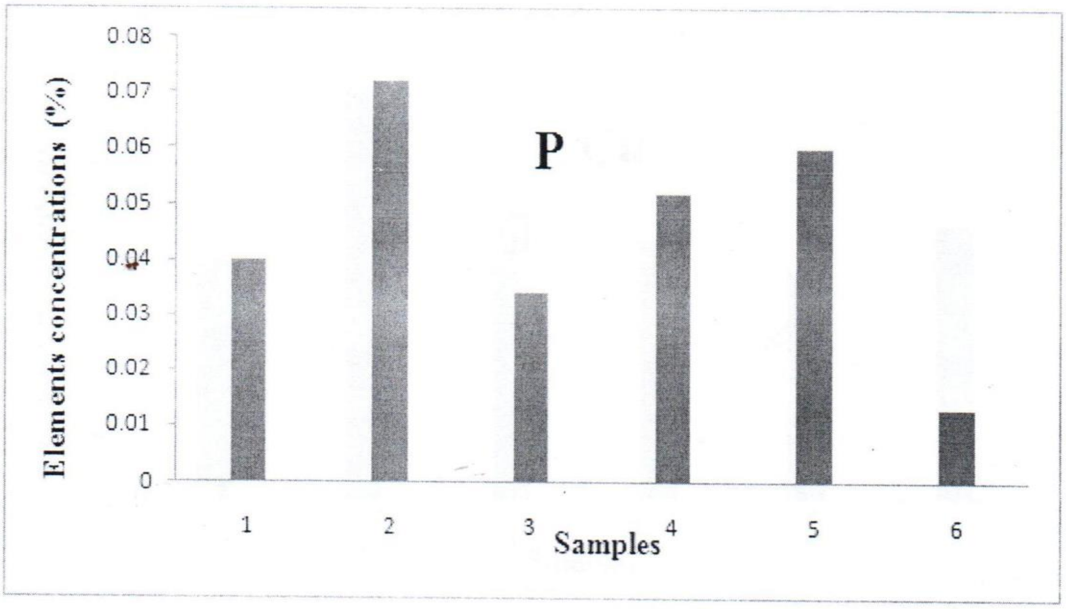

Figure 4.18 P concentrations in samples under investigation.

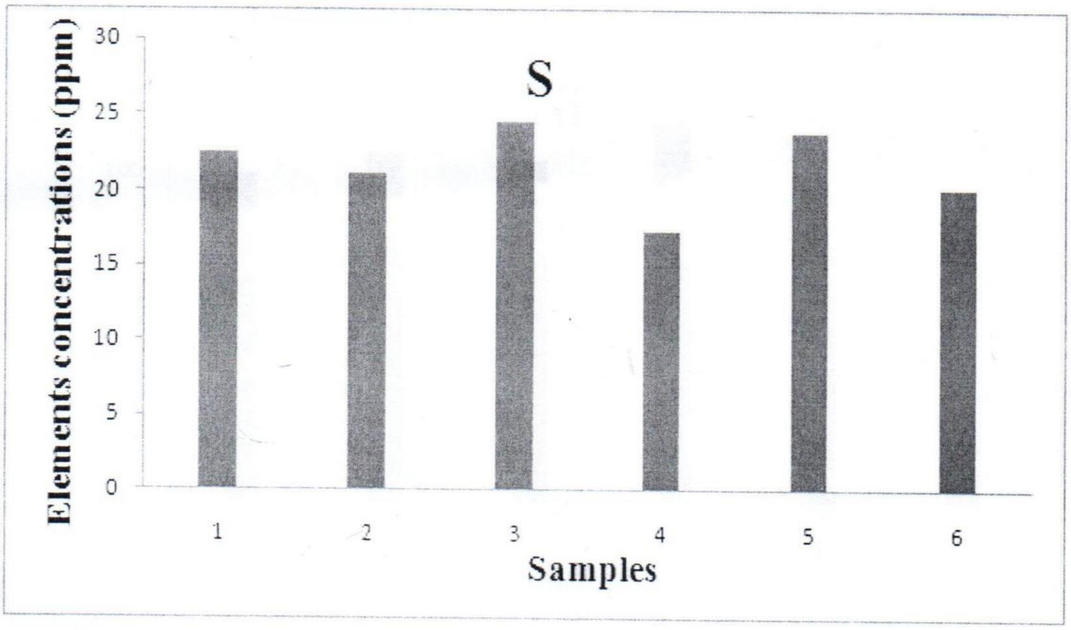

Figure 4.19 S concentrations in samples under investigation.

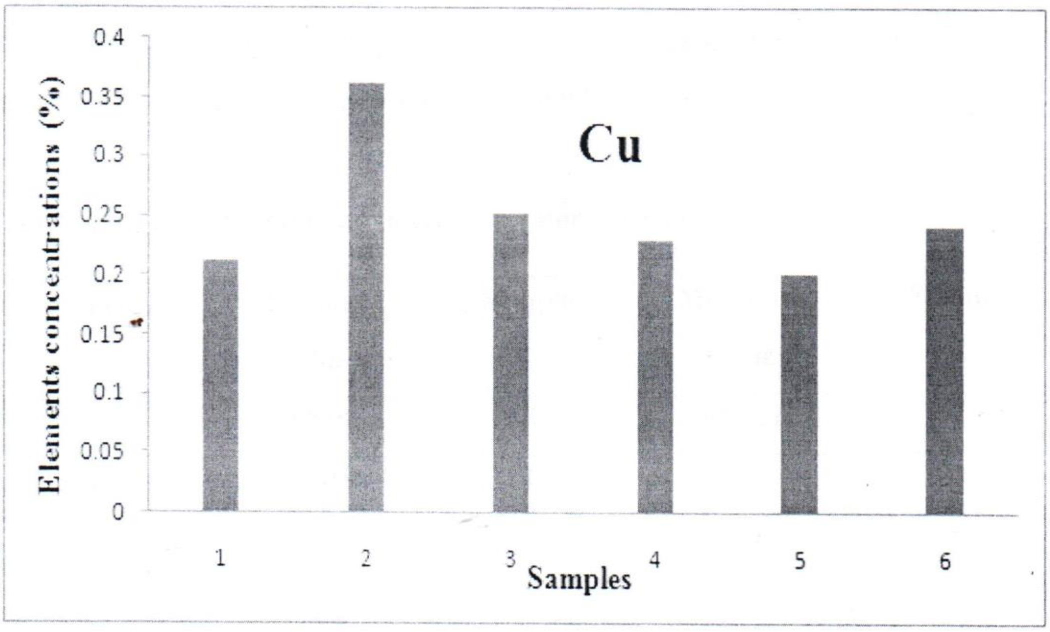

Figure 4.20 Cu concentrations in samples under investigation.

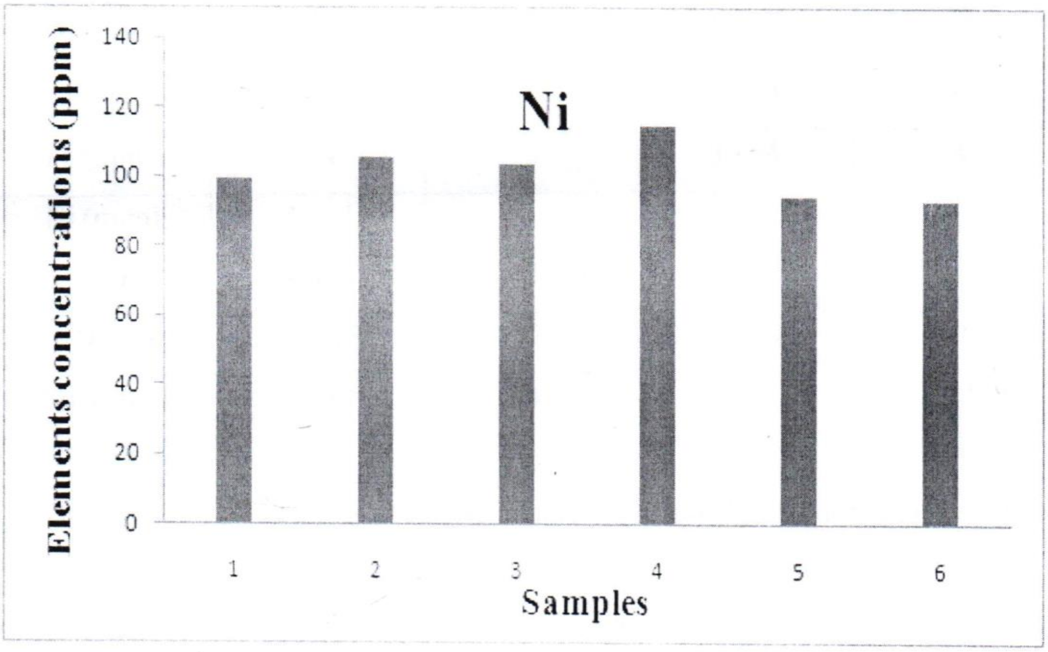

Figure 4.21 Ni concentrations in samples under investigation.

Considering the previous Figures we can find the concentrations of minimum and maximum values of concentrations in every sample. The results are listed in Table (4.5):

Table (4.5) The minimum and maximum values in each sample.

Elements	Maximum	Sample	Minimum value	Sample
TI (%)	0.048	5	0.0021	1
Si (%)	0.0019	1	0	3.6
Zn (%)	0.5021	2	0.4162	6
As (%)	0.142	6	0.015	4
Sn (%)	0.02	3	0	1.4
Se (%)	0.119	1	0.149	4
P (%)	0.072	2	0.013	6
CU (%)	0361	2	0.201	5
Al (PPm)	4.443	2	2.469	6
Fe (PPM)	36.47	2	19.94	4
Ni (PPm)	114.7	4	93.09	6
Al (PPm)	4.443	2	2.469	6
S (PPm)	24.625	3	17.38	4
Mn (PPm)	0.310	4	0	6.5

The analytical elements as obtained in this study can be divided into two groups depending on their concentration in samples:

1-Major elements (High concentration in samples:

Or greater than 0.1 % by weight of the sample, which are Zn, Cu.

2- Trace elements (Low concentration elements): are elements with concentration less than 0.1 % by weight which are Ti, pb, Fe, Al, Mn, As, Sn, Se, P, S, and Ni.

4.3 The credibility of the result

To ensure the credibility of the results, two different samples were selected randomly to repeat the measurements five times for each sample at the same measurement conditions.

The measurements were as follows:

1-Zn in sample 1 (Ginger + Anise)

Table (4.6) Concentrations of Zn in a sample 1 measured five times

Trials	Concentrations of Zn (%)
1	0.442
2	0.451
3	0.449
4	0.453
5	0.455
Average	0.45

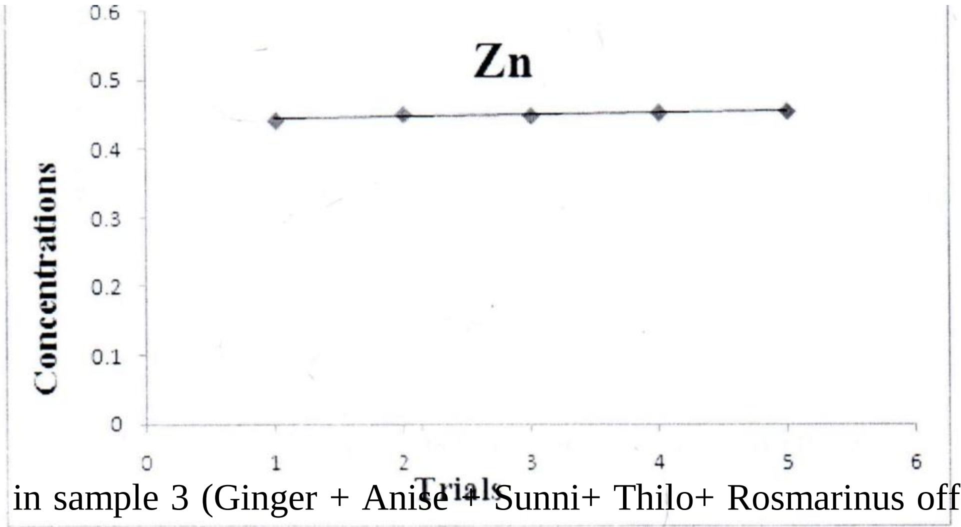

Figure 4.22 Concentrations of Zn in a sample 1 measured five times

2-As in sample 3 (Ginger + Anise + Sunni+ Thilo+ Rosmarinus officinalis+ Hyssop leaves).

Table 4.7 concentrations of As sample 3 measured five times

Trials	Concentrations of As (%)
1	0.039
2	0.0395
3	0.04
4	0.0389
5	0.0388
Average	0.03924

Comparing the concentration of some samples of medicinal herbs with concentrations of some samples of anticancer- medicinal herbs [26], we found the average mean concentrations of these elements are approximately matched and examples of this:

1-Average value concentration of Al in samples of anticancer- medicinal herbs (cinnamon) is 3.91 ppm and average concentration of Al in medicinal herbs samples 5 is 3.79 ppm and the percentage errors of Al concentration is 0.0316 %.

2-Average value concentration of pb in samples of anticancer- medicinal herbs (Nigella sativa) is 36.6 PPm and the average concentration of Pb in medicinal herbs samples 5 is 36.79 ppm, therefore, percentage error of pb concentration is 0.00516 %

3-Average value concentration of se in samples of anticancer- medicinal herbs (Cinnamon) is 0.137% and average concentration of Se in medicinal herbs sample 2 is 0.134 % and the percentage errors of Se concentration is 0.02239%

4- Average value concentration of Ti in samples of anticancer- medicinal herbs (Nigella sativa) is 0.0261 % and the average concentration of Ti in medicinal herbs sample 4 is 0.026 %, therefore, percentage error of Ti concentration is 0.00384 %.

5-Average value concentration of P in samples of anticancer- medicinal herbs (Garlic) is 0.0596 % and the average concentration of P in medicinal herbs sample 4 is 0.052 %, therefore, percentage error of P concentration is 0.146 %
6-Average value concentration of Cu in samples of anticancer- medicinal herbs (Nigella sativa) is 0.37 % and the average concentration of Cu in medicinal herbs sample 2 is 0.361 %, therefore, percentage error of Cu concentration is 0.025 %.
7- Average value concentration of Si in samples of anticancer- medicinal herbs (Cloves tree) is 0.0113% and the average concentration of Si in medicinal herbs sample 4 is 0.012 %, therefore, percentage error of Si concentration is 0.058 %.

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