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Determination of Concentration of Trace Elements in Agricultural Soil (Fertile and Non-Fertile Soil) in Wad Hamid (River Nile State).

تحديد تركيز العناصر القليلة التركيز في التربة الزراعية (المخصبة وغير المخصبة) في ودحامد (ولاية نهر النيل)

A thesis submitted in fulfillment of the Requirements for the PhD degree in Physics

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Dedication

I dedicate this thesis:

To soul of my father, my mother, brother’s sisters and colleagues I dedicate this work and to all crewmen of administration, whose support me materially and morally.

Acknowledgment

I offer my sincere thanks to my family of university of Sudan and faculty of graduate studies and research of sciences physics and the loyal lecturer's. am heavily independent to my supervisor Dr. Mubarak dirar ali for his guidance, comments and encouragement. And co. supervisor dr. ahmed alfaki. I owe great debt to Eng. Mohamed abadlla for his unlimited support and encouragement. I commend this humble work to my great parents, god mercy and honored them and all my colleagues for their great help in providing information's, resources for me they all made my graduate experience memorable one by all sort of assistance I thank all persons who help me during the preparation of this work.

Abstract

Plants are very important for human life. recently it was observed thatplants using chemical fertilizers cause some times severe biological hazards. On the other hand, the elemental contents of the soil determine the suitable plants which can grow in it this encourages to do this work which aims to determine the elemental contents of clay and sand soil beside studying the effect of adding chemical fertilizer to them.

In this work 16 samples were prepared 5cm depth from clay soil region, 4 non-fertilized and 4 fertilized samples were taken in a powder form. From sand soil region 4 non-fertilized and chemical fertilized samples were also prepared. All samples were taken from Wad Hamid region near the River Nile.

The elemental contents of all samples were determined using x-ray fluorescence (XRF) and atomic absorption spectrometer (AAS) and laser induced break down spectroscopy (LIBS). The results obtained shows that for clay samples the concentration of Fe is higher in non-fertilized samples while the concentration of Cr, Mn, Ni, Au is higher in fertilized samples. for sand samples the concentration ofAu, Pb are higher in non-fertilized samples while the concentration of Cr, Mn, Ni is higher in fertilized samples.

This means that fertilization process added more Cr, Mn,Ni to the soil. the XRF technique looks more accurate than AAS and LIBS as for as it detects more elements with higher concentration (higher detection limit) than the other two techniques.

It can detect Mo, W, V in clay samples beside Co, Ti,Nb in sand samples which cannot be detected by AAS and LIBS. LIBS gives very poor results since it is unable to detect most of the elements detected by XRF and AAS.

Thus in soil elemental analysis XRF is more accurate in determining the soil elements while AAS can confirm the results of XRF.

المستخلص

النباتات مهمه جدا لحياة الانسان .فى الآونه الأخيره لوحظ أن النباتات يضاف اليها مخصبات كيميائيه تسبب حيانا أضرار بيولوجيه .وفي المقابل العناصر التي تحتويها التربة تحدد نوع النبات المناسب لزراعته بها وهذا ماشجعنا لعمل هذه الدراسه التي تهدف لتحديد العناصر الموجوده في التربة الطينية والرملية بجانب دراسه تاثير اضافه المخصب الكيميائي لها.

فى هذا العمل سته عشرعينه تم تجهيزها من عمقخمسه سنتمترات من منطقه ذات تربة طينية .أربعه عينات غير مخصبة وأربعه عينات مخصبة علي شكل بدره . ومن منطقه رملية أربعه عينات غير مخصبه وأربعه عينات مخصبة كيميائيا تم تجهيزها. اخذت كل العينات من منطقة ودحامد قرب نهر النيل.

العناصر اللتي تحتويها كل العينات تم الكشف عنها بواسطة الأشعة السينية الوميضية ومطيافية الأمتصاص الذري ومطيافية الليزر المستحث .

النتائج المتحصل عليها توضح أن التربة الطينية تركيز عنصر الحديد أعلي في العينات الغير مخصبة بينما نجد أن الذهب والنيكل والمنجنيزوالكروم تركيزها أعلي في العينات المخصبة وفي العينات الرملية تركيز الذهب والرصاص أعلي في العينات الغير مخصبةبينما تركيز الكروم والنيكل والمنجنيز أعلي في العينات المخصبة. هذا يعني أن عمليه التخصيب تضيف كثيرا من الكروم والنيكل والمنجنيز للتربة .

ظهر أن طريقه مطيافيه الأشعة السينية الوميضية أدق من طريقة مطيافية الأمتصاص الذري ومطيافية الليزر المستحث وذلك لاكتشافها عناصر أكثر بتراكيز عاليه (كفاءة اختبار عاليه) خلاف الطريقتين.

و يمكن تحديد الفولديوم والتنجستين والموليديوم فى عينات التربة الطينية بجانب الكوبالت والتيتانيوم والنوبيديوم فى العينات الرملية التي لا تكتشف بواسطة مطيافية الأمتصاص الذري ومطيافية الليزر المستحث .مطيافية الليزر المستحث نتائجها ضعيفه حيث لا يمكنها كشف العناصر التي تم تحديدها بواسطة مطيافية الأشعة السينية الوميضية ومطيافية الأمتصاص الذري . .

وعليه لتحديد العناصر الموجوده في التربة تعتبر مطيافية الأشعة السينيةالوميضية أكثردقة في تحديد العناصرالموجوده في التربة بينما مطيافية الأ متصاص الذري يمكن أن تؤكد نتائج مطيافية الأشعة السينية الوميضية.

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CHAPTERONE
INTRODUCTION

1.1Overview

Soil is not only a part of the ecosystem but also occupies a basic role for humans, because the survival of man is tied to the maintenance of its productivity. Soil functions as a filtering, buffering, storage, and transformation system protect against the effects of trace element pollution.Soil is the main source of trace elements for plants both as micronutrients and as pollutants. It is also a direct source of these elements to humans due to soil ingestion affected by “pica-soil”, geophagia, dust inhalation, and absorption through skin The soil-plant transfer of trace elements is a part of chemical element cycling in nature. It is a very complex process governed by several factors, both natural and affected by human. In the present study a total of 30 samples are collected from wed Hamid river Nile state Sampling of (two Fadden) of agricultural soil the samples are divide in two locations (fertile and non-fertilesoil) and measure of concentration trace elements in soil. The (XRF) spectrometer used to analysis of the trace elements in the soil samples. Soil analysis can provide important information about physical conditions, fertility (nutrient) status, and chemical properties that affect a soil’s suitability for growing plants. Four steps associated with soil testing include: 1) soil sample collection, 2) laboratory analysis, 3) interpretation of results, and 4) fertilizer or other management recommendations [1,2].

1.2 Soil Contamination:

Both terms, contamination and pollution, are used synonymously. According to the definition given by Knox et al. Trace element contaminated soils are not considered to be polluted unless a threshold concentration exist that be gusto affect biochemical and biological processes.

Soil pollution is as old as man’s ability to smelt and process ores, and goes back as far as the Bronze Age (2500 BC). Ernst comprehensively reviewed ancient metal contamination from the Bronze Age to Roman times. Almost all human activities have resulted in increased levels of trace elements in soils. The trace elements from anthropogenic sources exist mainly on the surfaces of soils as reactive forms and may occur as: water-soluble, exchangeable, associated with organic matter, carbonate, and oxides of Fe, Al and Mn and silicates. Sources of trace inorganic contaminants (TIC) [3].

1-3 Industrial Activities

There are many contamination activities due to industrial west which effect the soil as mentioned on the following

- Mining and smelting of metalliferous ores
- Brick and pipe manufacture
- Cement manufacture
- Others, e.g., ceramic, glass, chemical plants
- Power generation
- Burning of fossil fuel
- Nuclear reactors
- Incineration of municipal wastes
- Agricultural practices
- Soil amendment with sewage sludge
- Application of manure
- Mineral fertilizers
- Pesticides, fumigation
- Transport and urban-derived pollution
- Long-range transport of pollutants [4].

1.4 Contamination Due toFertilizing process

Fertilizes have contaminated effect due to using chemical fertilizers which effect the soil, plant, and human

1.4.1 Effectsof Chemical Fertilizers On Soil Pollution

According to the researches and studies the effects of chemical fertilizers on the soil is not immediatelyobvious. Because soils have strong buffering power due to their components. Over the time, it states thatemerged from the pollution, deterioration of soil fertility, soil degradation reactions occurring in the soil leads to deterioration of the balance of the current element. In addition, toxic substances accumulatewithin the vegetables and causing negative effects in humans and animals are fed.Soil structure in agricultural productivity are very important and it is regarded as an indicator.Unconsciously, the fertilizing, soil, just as in the deterioration of the structure is caused by industrialemissions. Especially Nano 3, NH 4NO 3, KCI, K 2SO 4, NH 4Cl demolish the structure, such as fertilizers,soil, soil structure, deterioration is difficult to obtain high-quality and efficient product.Particularly high level of sodium and potassium containing fertilizers, make a negative impact on soil,pH, soil structure deterioration and the increasing feature of acid irrigation or other agricultural operations or from the benefits derived from it is not possible or very scarce. Continuous use of acid-formingnitrogen fertilizers causes a decrease in soil pH, liming, if not carried to prevent the declining efficiencyof field crops. Basic use of fertilizers in the soil leads to an increase in ph.Increases in soil and plants,seedlings pH circuit of a sudden drop in the yield and quality drops, but causesHarmfulness [5]. In addition,expanding the size of soil pollution by accumulation in the soil.Research in the province of Rise in the territory of our country, one-way ammonium sulfatefertilization of tea, actually led to an increase in acidity of soils with low ph. Today 85% of the territory.

has dropped below pH 4 which is considered as the critical level. In Nevsehir over the last twenty-fiveyears as a result of nitrogen fertilization of potatoes grown in 100-fold increased acidity of the soil pH hasfallen to 2. Granting the land, excessive nitrogen fertilizers Rhizobium sp. activates, such as symbiotic

nitrogen fixing microorganisms is negatively affected. In this case, the part of the air plugs to benefit fromthe free nitro. In addition, more nitrogenous fertilizers limit the activities ofnitrifying bacteria. Thus, thecost of the second nitrogen source is damaged Given large amounts of potassium fertilizers in the soil of Ca and Fe with Zn disrupt the balance ofnutrients by the plants and prevent the receipt. However, the negative effects on organisms, given thevariety of worms and soil mite has been devastating and lethal effect [6].

1.4.2 Application ofOrganic Fertilizers

is one of important practical measures to improve soil fertility. In addition to providing necessary nutrients for crops and improving soil physio-chemical properties, organic fertilizers able to enhance soil microbial activity of soil, such as improving activity of soil enzymes and increasingsoil microbial biomass (Ren et al. 1996; Sun 2003; Lv et al. 2005). However, a lot of soil microbes are at nutrition-deficient or un-cultural levels under natural environmental conditions. The measurement of total microbial biomass with rich beef broth in the laboratory will introduce a great error due to the fact that a lotof nutrient-deficient microbes cannot grow. In general, traditional plate culture method can only separate 0.1%~1% of soil microbes present, and cannot reflect the original status of soil microbial diversity (CaiandLiao 2002; Vides and Lisc 2002; Luo et al. 2003). With the advances in the application of moleculartechniques, PCR-based techniques have been widely used (e.g. Bossio et al. 2005; Zhang et al. 2007). The objective of this study was to examine the effects of application of organic manures on peanut productionand the impacts on soil microbial biomass and diversity of soil microbe composition using combined platecounting and PCR-based Denaturing Gradient GelElectrophoresis (DGGE) methods [7].

pectoral analysis involves the calculation of waves or oscillations in a set of sequenced data. These data may be observed as a function of one or more independent variables such as the three Cartesian spatial coordinates or time. The spatial or temporal observation interval is assumed to be constant. Very few purely periodic data series exist, although monthly averages of a variable, such as number of births per 100,000 populations, taken over several years might be considered as such. The data for the individual years are no periodic.There are two reasons for calculating the spectrum. First, the periodic spectrum, regardless of whether the data are periodic or not, may be used to reduce empirical data to a simple mathematical expression containing far fewer terms than the original data, thus saving storage space and facilitating analytical manipulation. This kind of process is used for reducing the size of computer image files. Secondly, the spectrum is a fundamental component for describing statistically a single set of sequenced non-periodic data: it is a scale expansion of the variance. Similarly, it is necessary for investigating possible connections between several sets of similarly sequenced data: it provides scale expansions of regression parameters [8].

1.5 Spectral Analysis

Spectral analysis of the RR interval is an indirect, noninvasive measurement tool. Spectral analysis of heart rate variability is often referenced in the literature as an estimate of sympathetic and parasympathetic tone during sleep, otherwise termed the sympathy ova gal balance. High-frequency RR signal (greater than 0.15 Hz) is associated with increased parasympathetic tone, and low-frequency RR signal (0.04–0.15 Hz) is associated with increased sympathetic tone. The high frequency signal is most influenced by the vigil-mediated respiratory sinus arrhythmia of deep breathing, while the low frequency signal is most likely influenced by a barrel flex-mediated heart rate response to blood pressure. In short, a greater LF/HF ratio suggests greater sympathetic drive, and a lower LF/HF ratio suggests greater parasympathetic drive. As in PPG analysis, arrhythmias can invalidate results [9].

1.6 Research Problem

The research problem is related to the biological hazard caused by heavy and radioactive elements. And fertilizing process special chemical fertilizing which have serious effect on soil contamination.

1. 7 Aim ofThe Work

The aim of this work is to study the degree of soil contamination. This helps in determining the sources of contaminants and the concentration of elements and the effect of organic fertilizing.

1.8 Thesis of Layout

The thesis consists of 4 chapters the Chapter One consists on Introduction and Spectral Techniques and Research Problem and Aim of the Work andLiteratureReviewChapter Two consists on Theoretical Back ground and Introduction and Atomic Physics and Atomic Spectra and Atomic Absorption Spectroscopy and Laser Induced Break down Spectroscopy and X-ray Fluorescence Spectroscopy Chapter Three consists on Introduction and Materials and Instruments and Methodology Chapter Four consists on Introduction and Results and Discussion and Conclusions and Recommendations .

CHAPTER TOW

THEORATICAL BACKGROUND

2.1 Introduction

This chapter includes history of nuclear physics, radioactivity and soil. The beginning of nuclear physics may be traced to the discovery of radioactivity in 1896by Becquerel. Almost by accident, he noticed that well wrapped photographic plates were blackened when placed near certain minerals. To appreciate the significance of this discovery, it is useful to recall that the time was before the era of quantum mechanics [10].

2.2 Atomic Physics

Atomic energy is the source of power for both nuclear reactors and nuclear weapons. This energy comes from the splitting (fission) or joining (fusion) of atoms. To understand the source of this energy, one must first understand the atom.

An atom is a complex arrangement of negatively charged electrons arranged in defined shells about a positively charged nucleus. This nucleus contains most of the atom's mass and is composed of protons and neutrons (except for common hydrogen which has only one proton). All atoms are roughly the same size. A convenient unit of length for measuring atomic sizes is the angstrom (Å), which is defined as 1×10^{-10} meters. The diameter of an atom is approximately 2-3 Å.

In 1897, J. J. Thomson discovered the existence of the electron, marking the beginning of modern atomic physics. The negatively charged electrons follow a random pattern within defined energy shells around the nucleus. Most properties of atoms are based on the number and arrangement of their electrons. The mass of an electron is 9.1×10^{-31}kilograms [11].

One of the two types of particles found in the nucleus is the proton. The existence of a positively charged particle, a proton, in the nucleus was proved by Sir Ernest Rutherford in 1919. The proton's charge is equal but opposite to the negative charge of the electron. The number of protons in the nucleus of an atom determines what kind of chemical element it is. A proton has a mass of 1.67 x 10^{-27} kilograms.

The neutron is the other type of particle found in the nucleus. It was discovered by a British physicist, Sir James Chadwick. The neutron carries no electrical charge and has the same mass as the proton. With a lack of electrical charge, the neutron is not repelled by the cloud of electrons or by the nucleus, making it a useful tool for probing the structure of the atom.

Even the individual protons and neutrons have internal structure, called quarks. Six types of quarks exist. These subatomic particles cannot be freed and studied in isolation. Current research continues into the structure of the atom.

An atom is the smallest particle of an element that has the properties characterizing that element. Knowledge about the nature of the atom grew slowly until the early 1900s. One of the first breakthroughs was achieved by Sir Ernest Rutherford in 1911. He established that the mass of the atom is concentrated in its nucleus. He also proposed that the nucleus has a positive charge and is surrounded by negatively charged electrons, which had been discovered in 1897 by J. J. Thomson.

This theory of atomic structure was complemented by Niels Bohr in 1913. The Bohr atom placed the electrons in definite shells, or quantum levels. Understanding the atom continues to be a focus for many scientists [12].

2.3 Atomic Spectra

We know that in an atom, electrons have discrete and specific energies. There are more energy states in an atom than there are electrons. When an electron transitions from one energy level to another, it emits light or photon with a specific wavelength. In any given set of conditions, the collection of all these specific wavelengths is what constitutes the atomic spectrum. Hence, atomic spectra are the spectra of atoms.

The spectrum of the electromagnetic radiation emitted or absorbed by an electron during transitions between different energy levels within an atom.

When an electron gets excited from one energy level to another, it either emits or absorbs light of a specific wavelength. The collection of all these specific wavelengths of the atom in a given set of conditions like pressure, temperature, etc. is the atomic spectra of atoms. There are three types of atomic spectra and they are emission spectra, absorption spectra, and continuous spectra [13].

You might want to check the difference between emission and absorption spectra for better understanding.

Atomic spectroscopy is the study of the electromagnetic radiation absorbed or emitted by the atoms. There are three types of atomic spectroscopy and they are:

- Atomic emission spectroscopy: This involves the transfer of energy from the ground state to an excited state. The electronic transition can be explained in atomic emission.
- Atomic absorption spectroscopy: For absorption to take place there should be identical energy differences between the lower and higher energy levels. The

atomic absorption spectroscopy principle uses the fact that the free electrons generated in an atomizer can absorb radiation at specific frequency. It quantifies the absorption of ground-state atoms in the gaseous state.

- Atomic fluorescence spectroscopy: This is a combination of atomic emission and atomic absorption as it involves radiation of both excitation and de-excitation.

Uses of Atomic Spectroscopy

- It is used for identifying the spectral lines of materials used in metallurgy.
- It is used in pharmaceutical industries to find the traces of materials used.
- It can be used to study multidimensional elements [14].

2.4 Atomic Absorption Spectroscopy, Principles and Applications

when Sir Isaac Newton discovered that white light breaks up into its constituent spectral colors when directed through a glass prism.[1] From this work, he developed the corpuscular theory of light (the fact that light consists of particles), as opposed to only having a wave-like nature, which opened the door to several discoveries almost two centuries later[15].

2.5 Applications of Atomic Absorption Spectroscopy

The English chemist, Wollaston, was the first to observe dark lines in the solar spectrum that became known as Fraunhoffer lines. In 1832, Brewster concluded that atomic vapors in the atmosphere absorbed some of the radiation from the Sun resulting in the detection of these lines. Bunsen and Kirchoff demonstrated soon after that each chemical element had a characteristic color or spectrum when heated to incandescence (e.g., sodium (Na) yellow; potassium (K) violet). They were able to reproduce the black lines observed in the solar spectrum in the laboratory, thus allowing the identification of absorbing atoms in the corona through their emission spectra [16].

Alan Walsh, a Lancashire-born physicist was working in his garden on a Sunday morning somewhere in the early 1950s when an idea that would solve a huge analytical chemistry puzzle popped up in his mind: how to accurately measure small concentrations of metallic elements by spectroscopy. The normal procedure in spectroscopy was to vaporize an element and measure the emission spectra, but this technique was flawed and produced inaccurate results. Walsh decided to measure absorption, not emission. By teatime on Monday morning, he showed that it could be done. It took him several more years to convince manufacturers to use atomic absorption spectroscopy (AAS) for the detection of metals, but he eventually succeeded. Today, most analytical laboratories will boast at least one atomic absorption spectrophotometerAAS is an analytical technique used to determine the concentration of metal atoms/ions in a sample. Metals make up around 75% of the earth's chemical elements. In some cases, metal content in a material is desirable, but metals can also be contaminants (poisons). Therefore, measuring metal content is critical in many different applications, which we will explore later in this article. Suffice to say for now that it finds a purpose in quality control, toxicology and environmental testing to name a few [17].

2.5.1 Principle of Atomic Absorption Spectroscopy

The basic principles of AAS can be expressed as follows. Firstly, all atoms or ions can absorb light at specific, unique wavelengths. When a sample containing copper (Cu) and nickel (Ni), for example, is exposed to light at the characteristic wavelength of Cu, then only the Cu atoms or ions will absorb this light. The amount of light absorbed at this wavelength is directly proportional to the concentration of the absorbing ions or atoms [18].

The electrons within an atom exist at various energy levels. When the atom is exposed to its own unique wavelength, it can absorb the energy (photons) and electrons move from a ground state to excited states. The radiant energy absorbed by the electrons is directly related to the transition that occurs during this process. Furthermore, since the electronic structure of every element is unique, the radiation absorbed represents a unique property of each individual element and it can be measured.

An atomic absorption spectrometer uses these basic principles and applies them in practical quantitative analysis. A typical atomic absorption spectrometer consists of four main components: the light source, the atomization system, the monochromatic and the detection system
In a typical experiment, the sample, either liquid or solid, is atomized in either a flame or a graphite furnace. The free atoms are then exposed to light, typically produced by a hollow-cathode lamp, and undergo electronic transitions from the ground state to excited electronic states. The light produced by the lamp is emitted from excited atoms of the same element that is to be determined, therefore the radiation energy corresponds directly to the wavelength absorbed by the atomized sample. A monochromatic is placed between the sample and the detector to reduce background interference. From here, the detector measures the intensity of the beam of light and converts it to absorption data.

While solid samples can be used for AAS this analysis is usually restricted to the more expensive graphite furnaces where the sample can be heated by controlled electrical heating as opposed to a direct flame. Also, AAS is normally only used to analyze metal atoms. The main reason for this is that metals have narrow, bright and clear single emission and absorption lines [19].

2.5.2 Atomizing Techniques - Flame Atomic Absorption Spectroscopy (FAAS)

FAAS is mainly used to determine the concentration of metals in solution in parts per million (ppm) or parts per billion (ppb) ranges. The metal ions are nebulizer as a fine spray into a high-temperature flame where they are reduced to their atoms and subsequently absorb light from an element-specific hollow cathode lamp.

While this method has proved to be a robust technique for routine metal determinations, it does have drawbacks. Firstly, it has limited sensitivity because of the spectral noise created by the flame. This aspect has, however, been improved as the technology has evolved. The main drawback is that one can only measure one metal at a time and as different lamps are required for each element, the lamp must be changed each time you want to analyze for something different. Also, a large part of the sample is lost in the flame (up to 90%) in FAAS, further influencing the sensitivity [20].

2.5.3 Atomizing Techniques - Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

In GFAAS, a type of electro thermal atomization, a sample is placed in a hollow graphite tube which is heated until the sample is completely vaporized. GFAAS is much more sensitive than FAAS and can detect very low concentrations of metals (less than 1 ppb) in smaller samples. Using electricity to heat the narrow graphite tube ensures that all of the sample is atomized in a period of a few milliseconds to seconds. The absorption of the atomic vapor is then measured in the region immediately above the heated surface. Naturally, the detection unit does not have to contend with spectral noise, leading to improved sensitivity [21].

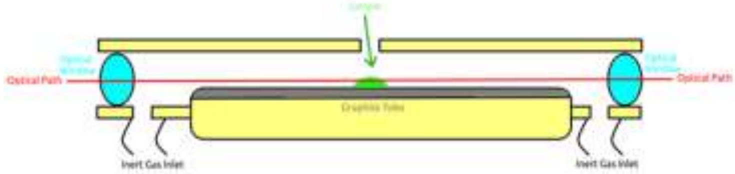

Fig (2.1):

A typical graphite tube atomization process.

2.5.4 Atomizing Techniques – Specialized Techniques

In glow-discharge atomizing systems, an atomized vapor is produced which can be swept into a cell for absorption detection. Glow-discharge cells can be used as an accessory to most FAAS systems. The solid-state sample is introduced onto a cathode after which high energy argon (Ar) ions, generated by an electrical current running from the anode to the cathode, are used to bombard and eject atoms into the path of radiation. The process is calledsputtering.

For this technique to work, samples must be electrical conductors or must be mixed with a conductor such as finely ground graphite or Cu The detection limits are in the low parts-per-million range for solid samples [22].

2.5.5 Hydride-Generating Atomizers

are mostly used for the analysis of heavy metal samples and even other elements like arsenic (As), tin (Sn), selenium (Se) and bismuth (Bi). Samples are diluted and acidified before being mixed with sodium borohydride ($NaBH_4$). A metal-hydride is generated and transferred to the atomization chamber by an inert gas like Ar. Here, the sample is introduced to a flame or furnace to produce the free metal atoms, ready for detection.

Mercury (Hg) is the only metal that does not atomize well in a flame or furnace. To analyze Hg, a special technique called, cold-vapor atomization is employed. The Hg sample is acidified and reduced before it is swept through by an inert gas. The absorption of the gas is then determined [23].

2.5.6 Radiation Sources In AAS And Signal Detection

There are two main sources of radiation available to AAS, namely, line source (LS) and continuum source (CS). CS is typically produced by deuterium lamps and emits light over a broad range of wavelengths, while LS, on the other hand, emits radiation at specific wavelengths, normally produced by a hollow cathode lamp.

To improve detection limits, monochromators are used to select the same wavelength of light absorbed by the sample and to exclude other wavelengths. This ensures that only the element of interest will be detected. The detector converts the light signal into an electrical signal proportional to the light intensity. Older equipment used photomultipliers for detection purposes, but nowadays they are replaced by charge-coupled device (CCD) detectors. The resolution per pixel in a CCD array detector is about 1.5 pm, small enough to use continuum light. Furthermore, if a CCD detector uses 200 pixels, for example, each of them makes its own measurement of absorbance or integrated absorbance, meaning that the equipment has 200 independent detectors providing better signal-to-noise ratio [24].

Until the late 1990s, LS spectrometerswere the only devices used in AAS. Walsh had already realized in the 1950s that the main difficulty of atomic absorption was "that the relations between absorption and concentration depend on the resolution of the spectrograph, and on whether one measures peak absorption or total absorption as given by the area under the absorption/wavelength curve He, therefore, excluded the use of continuum light sources (sources employing a wide range of wavelengths) because doing so would need a resolution of about 2 pm, something that could not be attained at the time.
In the meantime, many researchers saw the potential advantages of using a continuum radiation source. One such advantage would be that more than one analyses could be detected simultaneously. This led to the development of all kinds of radiation sources, mono- and polychromatous, detectors and evaluation principles for CS AAS. It was only in 1996 that a research group from Germany proposed a completely new spectrometer concept. They used a xenon (Xe) short-arc lamp, a high-resolution double monochromatic and a linear CCD array detector. In the early 2000s the first high-resolution-CS AAS (HR-CS AAS) spectrometer was manufactured by a German company.

HR-CS GFAAS has limitations, mainly because each element needs different atomization temperatures. In fast, sequential determination using HR-CS FAAS however, an unlimited number of analyses are available (atomized simultaneously) and can be detected by simply changing the wavelength to move from one analyses to the next. The equipment also makes it possible to adjust flame composition, stoichiometry and burner height within about a second. Previously, in LS AAS, these adjustments took up a long time, especially when several analyses were determined one after another.

There are several ways to do background corrections in LS AAS, most of which have limitations due to the use of a photomultiplier tube or solid-state detectors which integrate over the spectral range transmitted by the exit slit. In contrast, the software coupled to a CCD detector in HR-CS AAS automatically makes corrections on both sides of the analytical line. Any changes in radiation intensity are corrected automatically to the baseline, leading to extremely low noise levels [25].

2.5.7 Interpreting an Atomic Absorption Spectrometric Output

The interpretation of outputs in AAS is quite simple and follows Beer’s law, namely that absorbance is directly proportional to concentration. This means that the analyses’ concentration correlates with the electrical output received from the detector. One of the ways to determine the unknown concentration of an analyze is to use several solutions of known concentrations to calibrate the instrument. The curve shows radiation (absorbance) versus concentration and once the sample is measured, the concentration value could be obtained from the calibration curve.

In the analysis of lead (Pb) for example, light at 283.3 nm, corresponding to one of the spectral lines of Pb, is passed through the flame containing the sample. The beam contains light at 283.3 nm. The Pb atoms absorb light, and excitation of their electrons occurs. The absorption value is obtained and the unknown concentration of Pb in the sample can be read from the calibration curve. These days, all of this is done by the computer, but it is important to understand the principle of a calibration curve. there are four absorbance values of analyses solutions with known concentrations. The absorbance of the sample is measured and the concentration can be deduced from the graph [26].

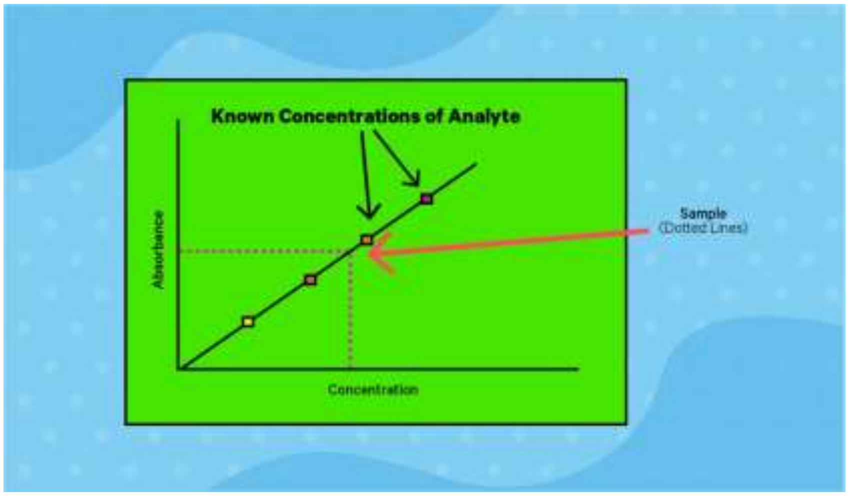

Fig (2.2):
A typical calibration curve.

a typical readout of absorbance versus wavelength is shown from analysis for Sn, cadmium (Cd) and iron (Fe) simultaneously, for example from a digested food sample. The spectral lines of the three elements, as indicated by the wavelength values, are close to each other which allows for simultaneous detection in this case.

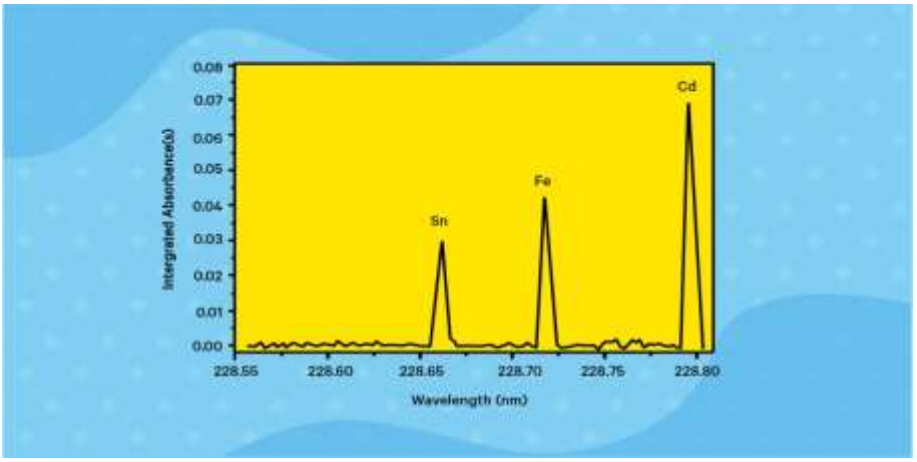

Fig (2.3):
Example of Sn, Fe and Cd detection in a food sample.

2.5.8 Background Correction

When obtaining absorption spectra, the detector might pick up signals from other particles in the flame, leading to background interference. This does not mean that the obtained spectrum is not representative of the sample, it simply results in a loss of spectral detail, such as peak broadening and the appearance of peaks in places where the sample does not absorb. Proper background correction techniques can minimize these deviations and enhance the signal from the analyses.

1) Koirtyohann and Pickett developed the first automatic background technique using a combination of a CS, such as a deuterium lamp, and a hollow cathode lamp (single LS). The radiation passing through the instrument alternates between the deuterium continuum and the analyses source and then subtracts background absorption from the total absorption measured with the hollow cathode lamp. This method has flaws though; the main one being the fact that deuterium is an ultraviolet source which limits the wavelength range available to the analyst [27].

2) Smith and Hefted introduced a background correction method based on the high and normal current pulsing of a hollow cathode lamp. The total absorbance, which includes interferences, is obtained when the normal current is in operation and the background is obtained with the high-current pulse. This technique only works well with volatile elements. In addition, it can only be used for FAAS and the continuous pulsing decreases the lifetime of the hollow cathode lamps.

3) The Zeeman-effect background correction method, which uses an alternating magnetic field to produce background versus sample data, is mostly used in LS GFAAS and has developed substantially over the years. However, it does have limitations when the sample contains another metal, different from the analyses,

with spectral lines close to the analyses wavelength, like Ni and Fe for example.

4) In HR-CS AAS, in contrast, the software of the instrument automatically selects correction pixels on both sides of the analytical line, which do not show any absorption lines. Any increase or decrease of the radiation intensity that is the same for all correction pixels will then be corrected automatically to the baseline. This means that the signal output is already corrected for lamp noise and any continuous background. This is also in contrast to LS AAS, where background corrections contribute significantly to the baseline noise (at least a factor two or more increase in noise). This in turn will influence the precision, limit of detection (LOD) and the limit of quantification (LOQ). Interested readers are directed to the review article of Reason et al. for more information [28].

The advantages of AAS most certainly outweigh the limitations as listed in the table below**.**

Table 2.1: Advantages and Limitations of AAS.

Advantages	**Limitations**
Low cost per analysis	Cannot detect non-metals
Easy to operate	New equipment is quite expensive
High sensitivity (up to ppb detection)	More geared towards analysis of liquids
High accuracy	Sample is destroyed
Mostly free from inter-element interference	
Wide applications across many industries	

2.5.9 Applications of Atomic Absorption Spectroscopy

AAS finds wide application in fields that vary from mining to pharmaceuticals, environmental control and agriculture. Most heavy metals are toxic and should be avoided as far as possible. If you ever had to use an antibiotic, chances are that the quality control process to ensure that the drug is free from the catalysts like palladium or platinum used to make them was performed by an AAS. Similarly, the food and health supplement industries make use of AAS to ensure that their products are safe for consumption. In mining, a lot of focus is on the recovery of precious metals like gold from old mining heaps. With the help of AAS, the amount of gold can be quantified to determine whether it would be profitable to extract it. The analysis of drinking water is probably one of the most important applications of AAS, especially in places where the environment is not properly cared for [29].

2.6 Laser Induced Breakdown Spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy. Atoms are excited from the lower energy level to high energy level when they are in the high-energy status. The conventional excitation energy source can be a hot flame, light or high temperature plasma. The excited energy that holds the atom at the higher energy level will be released and the atom returns to its ground state eventually. The released energy is well defined for the specific excited atom, and this characteristic process utilizes emissionspectroscopy for the analytical method. LIBS employ the laser pulse to atomize the sample and leads to atomic emission. Compared to the conventional flame emission spectroscopy,

LIBS atomize only the small portion of the sample by the focused laser pulse, which makes a tiny spark on the sample. Because of the short-life of the spark emission, capturing the instant light is a major skill to collect sufficient intensity of the emitting species. Three major parts of the LIBS system are a pulse laser, sample, and spectrometer. Control system is usually needed to manage timing and the spectrum capturing. illustrates those three major components and a computer in the conventional LIBS.

The LIBS has been used for the materials detection and analysis in various applications, such as steel and alloys, paints and coatings, wood pre-treatment, polymers, bacteria, molds, pollens, and proteins, and space exploration. The great majority of LIBS results were consolidated in the reviews. In spite of its advantage in analytical spectroscopy, LIBS application is still restricted with in certain areas and propagation of the technology is not very wide. Many laboratory LIBS systems are built in schools, research labs and companies with discrete optical parts. The irpi nearing approach in the new application seemed promising for a certain sample, but

actual use in the application field is usually very limited. We can explain the situation with other analytical techniques, for example, Gas Chromatography (GC). The GC can separate the volatile species. However, one GC setup can work for a narrow range of species grouped in the sample. For different applications, the user must change the GC column, detector,132 Advanced Aspects of Spectroscopy.

carrier gas or at least use a new column temperature cycle. The application of LIBS also needs case-by-case adjustment. Many new applications start with looking at the advantages of LIBS and choosing a LIBS setup, and it still needs a detailed investigation for successful analysis. This chapter describes how the LIBS system works and explains the major parts of LIBS to select specific functional requirements for its intended application. The three major parts: laser, sample and spectrometer are explained. The laser provides the breakdown energy and plasma generation. Analytical sample is the target of the laser shot and the source of emission species. The spectrometer comprises detection system with light detector and computer. Their disadvantages and limitations are discussed then suggesting how to select the equipment type and configuration to maximize the advantages of LIBS. This will provide a beginning inspiration of LIBS systems to install and apply the desired specific analytical purpose or application area [30].

2.6.1 Basic Principles &History of Laser Plasma Spectroscopy

Emission line spectroscopy is based upon "quantum" theory and was proposed over 140 years ago. LIPS (laser plasma spectroscopy) also known as Laser Induced Breakdown Spectroscopy (LIBS), is a relatively new type of atomic emission line spectroscopy made possible with the advent of the laser in 1961. LIBS was originally coined by Leon Radziemski and David Cremers at LANL (Los Alamos National Laboratory) in New Mexico (USA) in 1981. In the age of computer search engines, it became apparent that LIPS had too many alternative meanings outside the field of analytical spectroscopy. Therefore, LIBS has become the preferred acronym instead of LIPS for laser plasma spectroscopy. The LIBS designation was further promoted as an international standardized acronym for laser plasma spectroscopy by Andrzej MiziolekARL (U.S. Army Research Labs) during the first international LIBS conference held in Tirrenia, Pisa (Italy) in 2000.

In the early 1960’s Lloyd Cross of Trion Instruments (Ann Arbor, MI, USA) and Fred Breech of Jarrell-Ash Company (Waltham, MA, USA) developed the first LIBS in atomic line spectroscopy system. The initial “MARK I Optical Microprobe” device utilized the “third” ruby laser ever built and became the first commercially available analytical instrument to use a laser. For more information, the reader is referred to chapter. The MARK I was arranged so that a Q-switched ruby laser pulse (0.4joule 694 nm red) was focused down onto the sample surface, ablating the sample and creating a vapor of the material. The vaporized material was subsequently ionized between high voltage electrodes. The ionized sample emission was then spectrographically collected and measured on photographic plates as atomic line intensities. Following the MARK, I, the MARK II employed a Q-switched neodymium glass laser demonstrated by John Myers of Lear-Sigler Systems Center, (AnnArbor, MI USA). Lear-Sigler purchased Trion Instruments in 1962. The MARK IINd: glass laser proved to be less temperature sensitive and it provided higher pulse energies than the MARK I Ruby laser. It provided more than 0.5 joules 1062nm in the Lasers in Chemistry [31].

2.6.2 LIBS System Design withModern Technology.

a Laser as a breakdown energy sourceLIBS uses pulsed-laser light and focuses it onto the sample surface to make a plasma plume that contains the highly excited species of the sample composition. For generatingplasma, there is a threshold value of the energy density. The threshold level will depend on the absorption coefficient of the sample surface of the laser wavelength, which is highly different by the sample phase. Gas and liquid need more energy to make breakdown. Solids with a dark color surface easily make a strong breakdown compared to clear or highly reflective solids. Figure 2 shows the effect of laser energy to make breakdown by the relation of laser power and focusing. Starting with a laser beam as 1 cm diameter, this light beam can be condensed by a convex lens. The focused beam density becomes 160 J/cm2. Also, the laser is operating in the pulsed mode, assuming a10 nsecduration, totalpower per unit of time will be 16 GWatt/ cm2 [32].

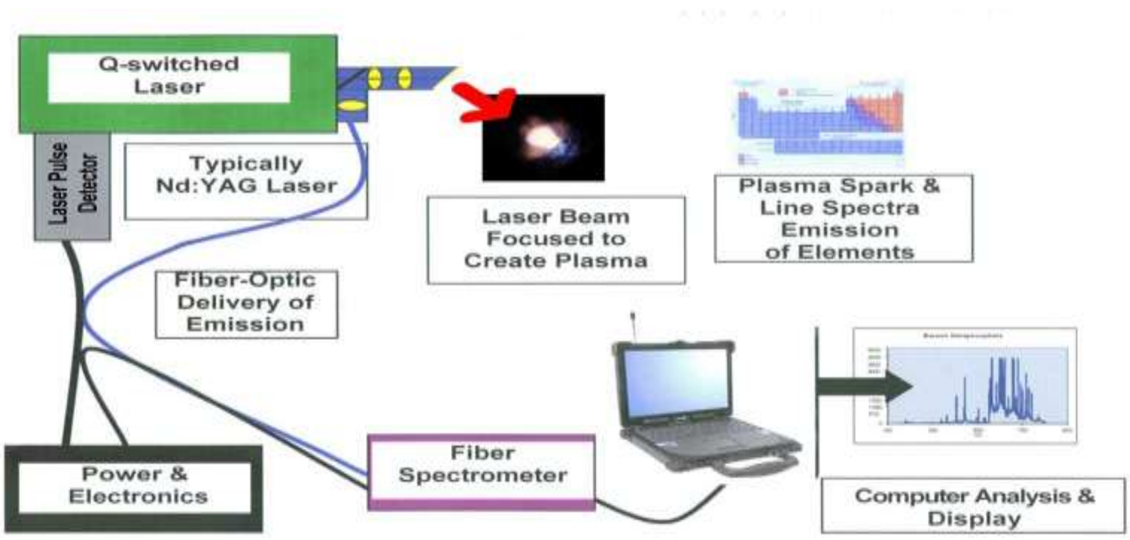

Fig (2.4): LIBS System

2.6.3 Basic Principles &History of Laser Plasma Spectroscopy

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Early Q-switched ruby and ND: glass laser systems were used to evaluate various laser-material interactions. These included the power density effects in laser producedcraters, the thrust producing capabilities of lasers and the evaluation of the laser'spotential use in directed energy weapons and nuclear fusion reactors. During the 1980's, Neodymium doped**Y**ttrium**A**luminum **G**arnet (Nd: YAG) lasers became the most common laser system used in most applications including LIBS. Nd: YAG crystal laser became popular for LIBS because they were easily configured to produce the megawatt peak power levels required for reliable laser plasma generation. During the 1980's and 1990's the relatively high expense and large size associated with lasers and spectrophotometers insured that Ion

Conductive Plasma and other laboratory instruments remained more attractive for most commercial chemical analysis applications.

A number of portable LIBS systems were developed for field-testing environments during the 1990s. One example is a US Army LIBS sensor for subsurface in-situ soil classification and heavy metal contamination detection. This system is part of the SCAPS (site characterization analysis penetrometer system) The cone penetrometer system consists of a steel cone that is hydraulically pushed into the ground while in-sit measurements are continuously collected and transported to the surface for data interpretation and visualization. The U.S. Army Engineer Waterways Experiment Station field-portable LIBS system included a rugged compact (1.25” diameter x 14” long) 17-Megawatt Nd: YAG laser probe and fiber-optic delivery system. The system’s remote LIBS probe was lowered into deep wells and used to measure trace amounts of heavy metals contaminants in soil and water. Scientists at LANL, developed portabellas systems for the determination of metals in soils that led to LIBS for use on Mars Rovermission [33].

This became an important development for the National Aeronautic Space Administration (NASA). A thin dust layer covers everything on the Martian surface. It was found that the Mars Rover x-ray analysis system was not able to provide chemical composition data on underlying Martian rock and soil. LANL developed space qualified portable LIBS technology for NASA in order to penetrate the coated Martin surface.

This LIBS system is expected to provide an extremely versatile and portable method of determining the elemental composition of Martian gases, liquids, and solids on future space missions [34].

After 2001, Homeland Security and the war on terror sparked interest in LIBS as
a promising portable technology for detecting explosives, landmines, biological weapons and chemical contamination. LIBS studies at ARL (U.S Army Research

Labs) during the 1990s led to the development of portable backpack-based LIBS systems for field measurements of potentially hazardous substances and devices Portable LIBS chemical analysis also provides many advantages for use in fieldtestingfor environmental pollutants. The advantages of LIBS include rapid, reliable, multi-elemental in-situ analysis with little or no sample preparation.

The integration of miniature fiber optic spectrometers with small high peak power laser transmitters lead to the development of compact portable analytical equipment assembled with commercial “off-the-shelf” components. In a typical modern LIBS system, a high peak power pulsed 1064nm Nd: YAG laser is focused to produce a plasma on a targeted material. For more information, the reader is referred to chapter Elemental line spectra is created, collected and analyzed for the elements present. LIBSanalysis data is processed and displayed with nearly instantaneous speed on laptop computers. A schematic of a modern LIBS system It iscomprised of the following basic elements:

1) *A high peak power Q-switched laser output (~1-50 ns pulse width)
2) Delivery optics to focus the laser pulse onto the target surface
3) Laser pulse emission and detection timing circuitry
4) Optics to gather plasma emission and transfer to the spectrometer
5) A spectrophotometer to separate the emission line spectra
6) A computer for wavelength analysis of the emission line spectra

* Note: A Q-switch is a device that is similar to a shutter that controls the laser resonator's ability to oscillate. This shutter effect allows one to spoil the resonator's "Factor,” keeping it low to prevent lasing action. Under these conditions, the laser gain material is able to store higher levels of energy. The extra stored energy is subsequently extracted as laser light emission in the form of extremely short pulse width, high-peak power pulses [35].

2.6.4 Laser Plasma Generation

3.1 Detector Timing & Multiple Pulse LIBS

The optimization of LIBS system event timing is important for efficient capture of high resolution line spectra. During the first microseconds after the focused laser pulse initiates a plasma “spark”, the resulting plasma energy is dominated by a strong “white light” continuum also described as broadband black body or bremsstrahlung radiation emission. Bremsstrahlung is from the German bremsen, to brake and strahlung, radiation, thus, "braking radiation" or "deceleration radiation". This is essentially electromagnetic radiation that is produced by the acceleration and collision of charged particles (read electrons) with other charged particles such as atomic nuclei [36].

The initial few microseconds after plasma ignition is followed by a longer period when elemental line spectra emission shows up as the dominating broadband emission decays.

The optimum “gate” time for turning on the spectrometer, and avoiding the masking broadband bremsstrahlung emission, is typically one or two microseconds after the plasma initiation.

For electro-optic Q-switched lasers, the Q-switch timing electronics are used to establish T0 laser/plasma ignition mark. For passive or satiable absorber Q-switched lasers a photo-diode is required to “pickoff” the laser output as a T0 laser/plasma ignition timing mark. In either case, the T0 is used to start the system electronics clock and set spectrophotometer gate. [37].

2.7 X-Ray Fluorescence (XRF):

X-ray fluorescence spectrometry is a powerful technique for elemental analysis. When it was introduced on a commercial scale about 30 years ago, the main research efforts were devoted to the developments of instrumentation and practical applications, with only moderate attention to fundamental conditions. Generally, the continuing interest in trace elements has stimulated the developments of several powerful analytical techniques for their detection and quantitative determination, one of these is X-Ray Fluorescence (XRF), where a source of x-ray photons is used to study the elemental composition of materials. Absorption of these photons by the photoelectric effect produces vacancies in the inner electron shells of the atoms of material, followed by the emission of characteristic x-rays of the elements present.

The peaks in x-rays spectrum indicate what kind of atoms are present, while the number of counts (the area underthepeaks) is related to the number of the atoms in the sample, allowing the quantitative measurements to be made. Moreover, the method gives information about the elements present in the sample irrespective of their state of chemical combinations or the phases in which they exit Energy – Dispersive X-rays Fluorescence (EDXRF) spectrometry is an established technique for qualitative and quantitative elemental analysis. It is presently routinely used in the analysis of various samples, including environmental samples, chemical analysis particularly in the investigation of metal, glass, and for biological samples such as plants, human and animal tissues, and for geological samples…. etc.

X-ray fluorescence analysis (XRF) is a powerful analytical technique for qualitative and quantitative determination of chemical elements in a sample. The operating principle of XRF is based on the irradiation of the sample with ionizing radiation, thus inducing excited states of the atoms in the analysis. The response of the atoms during the de-excitation process is the emission of X-rays having well defined energies or wavelengths characteristic for an element It usually provides elemental analysis for all the elements with atomic number eleven or higher. This analytical method plays an important role in environmental monitoring [38,39].

2.7.1 Principles:

XRF spectrometry is based on particular interactions of electromagnetic radiation with matter. The relative occurrence of these phenomena depends on the energies of photons of the primary radiation and on the composition of the irradiated substance. When an X-ray beam interacts with a given substance, it suffers an attenuation of its original intensity due to different processes that can occur in the inner structure of the material. The nature and magnitude of these interactions are directly influenced by: The energy of the incident X-ray beam. The nature of the impinging X-rays (degree9of monochromaticity).

The elemental constituents of the sample (average atomic number). The excitation source for XRF can be any type of ionizing radiation, either electrically charged particles or high-energy photons. Accelerators or radioactive isotopes are used to deliver electrons, protons, α-particles; X-ray tubes, radioactive isotopes or synchrotron storage rings act as photon emitters. First steps are currently being taken to establish X-ray lasers and plasma sources for excitation of light elements. If a sample is excited by an appropriate source, a number of characteristic lines are emitted for each element, forming a spectrum in terms of counts versus either wavelength or energy, depending on the detection system. Wave length and energy are equivalent and can be correlated by:

$E\ (\text{Kev}) = 1.2398/\ \lambda\ (\text{nm})$

Where, the energy E is in kilo electron volts (Kev) and the wavelength λ in nanometers (nm).

The spectrum contains the analytical information to determine the elements qualitatively and quantitatively. The wavelength or energy of a characteristic line corresponds; according to Moseley; to the atomic number Z of the emitter and thus enables the determination of the investigated. The count rate of the characteristic line is related to the concentration of the element. With appropriate excitation techniques, element can be made to emit characteristics x-ray from different type of sources; 55Fe, 57Co, 109Cd, 241Am. These radiations can be used analytically for qualitative, semi-quantitative and quantitative analysis for a wide range of element. The characteristics x-rays of the elements presented in the sample are produced during the irradiation and detected by a Si (Li) detector. The charge collected by the detector provides an electrical signal proportional to the x-ray energy emitted. The amplified signal is processed and displayed by a Multi-Channel Analyzer (MCA) which is connected, via interference, to a computer where x-ray spectrum is analyzed using appropriate software. The intensity of the detected x-ray lines can be related to the concentration of the specific element in the sample through the simplified following equation:

$Ii = Si\ Ci\ T$

$Ii \equiv$ intensity emitted from the element i; $Si \equiv$ sensitivity of the system from the element i which comprises atomic constant, system geometry and detector efficiency;

$T \equiv$ absorption correction term [40,41].

2.7.2 Interaction of X-rays with Matter:

There are four modes through which x-rays interact with an atom. These modes are:

- Photoelectric interaction.
- Radiation less transition (Auger effect).
- Photon Scattering (Coherent and incoherent Scattering).
- Pair production.

2.7.3 Photoelectric Interaction

If a photon strikes a bound electron in an atom and the energy of the photon is greater than the binding energy of the electron, an interaction is produced between the photon and the electron.

The incident photon is completely absorbed and its energy is converted in the ejection of an electron. The electron (photoelectron) is ejected with an energy E which is the difference between the original photon energy and the binding energy of the electron in its shell. The removal of a bound electron creates a vacancy and an unstable atom, which result in rearrangement processes to reach the normal state through transitions of electrons from outer to inner shells. The potential energy lost in each transition is emitted as an x-ray photon that can either escape from the atom, with a characteristic energy of the emitting element, or be absorbed in the atom and transferred to an outer electron producing Auger electron.

Excitation is followed by relaxation. If the **k** shell was ionized, the most probable electron transition in the K hole ←LIII, which is associated with emission of a K α 1 photon, followed in probability ranking by k ← LII (K α 2). K ← MIII (K β I) and so forth..

2.7.4 Auger Electron:

Auger absorption occurs predominantly in light atomic number elements, because the electrons are more loosely bound and the characteristic photons more readily absorbed. For high atomic number elements, the emission of characteristic X-rays in the more probable phenomenon.

There are two ways of looking at an Auger process:

1. It is a process of radiation less reorganization of an atom ionized in an inner shell because of a direct interaction of two electrons.

2. A quantum of x-rays is first produced, then absorbed by an outer electron of the atom in which it originates, and finally the outer electron is ejected from the atom (internal conversion).

2.7.5 Coherent Scattering (or Rayleigh Scattering):

It is a process by which photons are scattered by bound atomic electrons and in which the atom is neither ionized nor excited, also the photon energy remains unchanged. A more detailed view is, however, an excitation or induced oscillation of the total electron system, and subsequent re-radiation in phase with coherent the incident radiation**.**

Therefore, it can be accepted that the coherent (Rayleigh) scattering occurs when a low energy photon scattered from a high atomic energy number (Z) target. Coherent scattering induces no change in the energy or the momentum of the system. (11)

2.7.6 Compton Effect (In-Coherent Scattering):

Principle of Compton scattering involves the interaction of the X-ray incident photon with a weakly bounded atomic electron (approximately free electron).

The electron takes a part of the photon energy and the remainder is scattered as a new photon with different energy and wavelength. The relationship between the incoherent scatter (λc) and the incident ($\lambda 0$) wavelength is:

$$\lambda c - \lambda 0 = 0.0243(1- \cos\theta)$$

Where (θ) is the angle through which the radiation is scattered.

2.7.7 PairProduction:

Pair Production process occurs for X-ray or gamma-ray photons of energy equal or more than 1.022 MeV. When a photon of energy 1.022 MeV is passing near the atomic nucleus, the photon will disappear and a pair an electron and a positron will be created.

The relation between the photon energy (Ep) and the kinetic energies of both electron and positron is:

Ep= 2 m0c2 + m0v2

Where (c) is the speed of light, (m0) is the electron (or positron) (v) is its now velocity [42,43].

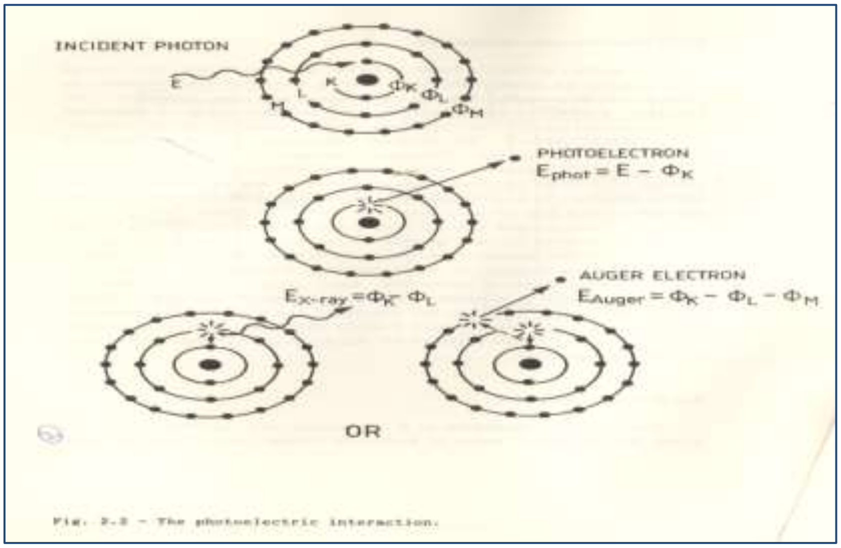


Fig (2.5): The photoelectric interaction

2.8 Literature review

1.determination of heavy metals in soil using XRF techniqueAntonella ENE, Alina Bosnia L. Grorgescu (September 14,2009).

The main objective of this paper is to determine the level of soil pollution with heavy metals, in the vicinity of Iron and Steel Integrated Works (ISIW) at Galati, Romania, whose activity lasted from 1965, being one of the most important metallurgical complexes in the South-East of Europe and representing a great potential of environmental contamination.

The main goal of the present research was to use XRF technique in order to assess the heavy metals distribution in some areas near the industrial complex of Galati and to compare the soil heavy metal concentrations with the maximum values admitted by the Romanian guideline [18]. This study is part of a partnership project funded by National Plan of Research, Developing and Innovation, of implementation of high precision and sensibility methods for the bio-monitoring of the environmental pollution.

in South XRF technique has been employed in order to evaluate the pollution of soil with heavy metals (As, Cr, Cu, Ni, Pb, V and Zn) in the vicinity of Iron and Steel Integrate.Works (ISIW) at Galati, Romania. This is one of the first published studies on soil pollution realized in this region related with the industrial activity. The experimentalresults indicate that the concentrations of heavy elements decrease with the distancefrom the metallurgical works and they are greater than the levels detected in the controlsoil collected from a zone situated far from traffic and industrial activity. For themmajority of metals, pronounced maximum concentrations for all depths were detectedin the sites located in influence zones of industrial objective with ferrousprocessing activities. Anthropogenic releases give rise to higher concentrations ofthe metals relative to the normal background values and in some locations theirlevels exceed the alert level admitted by the Romanian guideline [44].

2-**Determination of Cr, Zn, As and Pb in soil by X-ray fluorescence spectrometry based on a partial least squareregression model.**

Axing Lu, Xiangyang Qin, Jihua Wang, Jiang Sun, Dazhou Zhu, Ligang Pan (Jul 2017).

Soil samples were collected from five provinces over China, including Beijing, Xinjiang, Heilongjiang, Yunnan, and Jiangsu. Heavy metalCr, Zn, Pb and As in soils were analyzed by a portable X-ray fluorescencespectrometry (XRF). For predicating metal concentration in soils, a partial leastsquare regression model (PLSR) was established. After cross-calibration, the correlation coefficients for validation (R) of value predicted by PLSR model

against that measured by AAS and A FS for Cr, Zn, Pb and as was 0.984, 0.929, 0.979, and 0.958, square error of validation (SEP)was 108 mg kg-1, 117 mg kg -1, 116 mg kg-1, and 167 mg kg -1 for metals concentration from about 100 to 1500 mg kg -1, and the relative square error of validation(RSEP) was about 14.5 %, 15.6 %, 14.9 %, and 21.0 %. These results indicated XRF based on PLSR model could be applied for determination of Cr, Zn, Pb and As in soil, and would be an effective tool for rapid, quantitative monitoring of metal contamination.

Quantitative or semi-quantitative analyses for Cr, Zn, As and Pb in soil can be performed using XFR with a calibration model established by the method of PLSR. Creating PLSR calibration models for XRF especially useful if suitable well characterized reference standards are not available or the fundamental parameter method is inaccessible or unsatisfactory. As demonstrated, this model is suitable for soil samples of different types without a set of standards for each site. Certainly, Reith PLSR model approach can be considered as a useful tool for fast screenings, field testing and rapid identification of heavy metals in soil [45].

3-Laser-Induced Breakdown Spectroscopy (LIBS) to Detect of Remains Uranium Metals in the Basra Soil.AlaaH. Ali, Radhi M. Chyad, AhmedA. Hamed, NoonK. Chya(2019).

The laser-induced breakdown spectroscopy system (LIBS) had been designed for analysis of two samples of Iraqi soil in Basra (Zubair and Faw) via analysis of induced plasma emissions that generated via high peak power laser pulse, the system that design consist of Nd:YAG laser passively Q-switched with output laser pulse energy (120mJ@1064nm) and (10ns) pulse duration, the laser beam was focused via converging lens with a focal length (100mm) that had generated ($15.28*10^6 W/mm^2$) power intensity, optical spectrum analyzer with spectrum range of (320-740 nm) and (0.2nm) optical resolution had been used to analysis of emitted plasma spectrum, three emission lines had been recorded (383.96, 393.40

and 394.44 nm) which are compared with NIST database, the research had focus on Uranium element in the soil, that is considered as the most dangerous pollutants on the environment and a major cause of cancer in Basra.

In this work, we have constructed a LIBS system by using a portable commercial spectrometer from Throats Inc. equipped with CCD detector to identify spectral lines emitted from the soil, the database from NIST and ocean-optics also used to select and detect the element according to emission lines, the sample Lab laser we also had use to completed the system that offer fast and low cost technology, for develop the system we will go to wide range and higher resolution spectrometer and faster CCD detector to get more spectrum and increase the limit of detection, for the developing of the system to calculate the concentration of uranium element in the soil we must get the emission parameters from references as (Aki, ΔE, g_k and g_i) that is main part to calculate the plasma parameters and concentration via (CF-LIBS) technology [46].

4-Laser-Induced Breakdown Spectroscopy Coupled with Multivariate Chemometrics for Variety Discrimination of Soil. Ke-Qiang Yu, Yan-RuZhao, FeiLiu, Yong He (June 2016).

The aim of this work was to analyze the variety of soil by laser-induced breakdown spectroscopy (LIBS) coupled with chemo metrics methods. 6 certified reference materials (CRMs) of soil samples were selected and their LIBS spectra were captured. Characteristic emission lines of main elements were identified based on the LIBS curves and corresponding contents. From the identified emission lines, LIBS spectra in 7 lines with high signal-to-noise ratio (SNR) were chosen for further analysis. Principal component analysis (PCA) was carried out using the LIBS spectra at 7 selected lines and an obvious cluster of 6 soils was observed. Soft independent modeling of class analogy (SIMCA) and least-squares support vector machine (LS-SVM) were introduced to establish discriminant models for classifying the 6 types of soils, and they offered the correct discrimination rates of 90% and 100%, respectively. Receiver operating characteristic (ROC) curve was used to evaluate the performance of models and the results demonstrated that the LS-SVM model was promising. Lastly, 8 types of soils from different places were gathered to conduct the same experiments for verifying the selected 7 emission lines and LS-SVM model. The research revealed that LIBS technology coupled with chemo metrics could conduct the variety discrimination of soil.

This research focused on investigating the characterization of soil utilizing LIBS technology combined with chemo metrics methods. Based on the features of soil's LIBS curves and PCA on full spectra, several characteristic lines were identified. In order to simplify the discriminant model, 7 emission lines (Si I 390.55 nm, Al I 394.40 nm, Fe I 404.58 nm, Mg I 518.36 nm, Na I 588.99 nm, Ca II 393.36 nm, and K I 766.49 nm) with high SNR were selected to conduct the further next analysis. PCA was carried out on the LIBS spectra at the 7 selected emission lines. An obvious cluster was observed and analyzed. Then, SIMCAand LS-SVM discrimination models were established, and their performances were evaluated by ROC curve. Results demonstrated that the LS-SVM model was the optimal model for discriminating the different types of soils. Moreover, the 7 selected emission lines and the LS-SVM model were applied to the other 8 types of soil samples, which also achieved outstanding discrimination results. To improve the extendibility of our application, more samples and a diversified analytical data set should be taken into account to obtain enough spectrum data in further investigations. It could provide a theoretical guidance for establishing agrotype system and farmland management [47].

5-**Analysis of Heavy Metal in Soil through Atomic Absorption Spectroscopy for Forensic Consideration. AshutoshMaurya, LavKesharwani,Munish Kumar Mishra (June 2018).**

As we know that the soil is the most important component of earth ecosystem, which has four key functions: it is a means for the growth of plants, is a means of storage, supply and purification of water, is a modifier of the earth's atmosphere. Soils can be infected by the accumulation of heavy metals and metalloids through the emissions of industrial waste, elimination of high quality metal waste, application of soil fertilizers, sludge purification, pesticides, sewage irrigation, coal combustion residues, petrochemical spills and atmospheric storage. Even though heavy metals are naturally found in the soil, geological and anthropogenic activities increase the concentration of heavy metals in harmful quantities which is dangerous for both plants and animals. In forensic science heavy metal analysis of soil Heavy metal is providing a unique fingerprint of any soil. The goal of this study will to determine if there is a correlation between land use type and concentrations of heavy metals in soil and characterization of soil. Atomic absorption spectrometry (AAS) is a technique which is helpful to measuring the quantities of trace elements present in soil samples.

From this study it was concluded that the variation of soil at different sites of river, institutional regions, urban areas, and industrial areas can be very useful during the investigation of various types of crimes. This experiment proves that heavy metal analysis of soil samples are valuable evidence for forensic purpose. The growth of urbanized regions is occurring worldwide, and, as a result, research in the area of soil contamination by heavy metals has become increasingly important excessive amounts of these elements can become harmful to organisms. Significantly large concentrations of toxic metals not only diminish soil quality, but also can lead to human intake through the tropic food web. Heavy metal is providing a unique fingerprint of any soil. it gives unique soil profile from one region to another region which is helpful in forensic investigation. Soil can be very helpful in various type of crime like murder, poisoning cases, hit and run, burglary, poisoning cases etc [48].

6-Heavy metals concentrations in selected soil samples of Al –Diwaniyah governorate, Southern Iraq.Anees A. Al-Hamzawi (July 2019).

Heavy metals’ origin, accumulation, and distribution in soil samples have been the focus of much attention by many researchers to monitor soil pollution. The objective of this study is to determine the levels of the heavy metals such as lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) in the soil samples collected from different areas residential, industrial and agricultural of Al-Diwaniyah governorate southern Iraq using the effective technique of atomic absorption spectroscopy AAS, so that the degree of pollution could be ascertained. The results show that the mean values of Pb, Cd, Cu and Zn concentrations in soil samples are 31.75, 1.804, 18.51 and 29.82 mg/l, respectively. The results show that the heavy metals concentrations were found to be higher in industrial regions than the other locations. Mean values of Pb and Cd in soils studied were generally higher than the acceptable limits, suggesting some degrees of pollution with heavy metals.

The heavy metals concentrations in soil samples collected from different areas residential, industrial and agricultural of Al-Diwaniyah governorate, southern Iraq have been determined by using AAS technique. The metals Pb and Cd are most abundant in the soil samples of the study area due to human activities. The results indicated that the industrial areas are more polluted than the agricultural and residential regions due to the industrial activities. The results of heavy metals concentrations in the present study show that the soil samples are not polluted by Cu and Zn [49].

7-Analysis of cadmium and lead using atomic absorption spectrophotometer in roadside soils of Jimma town. BihonegnSisay, Eyob Debebe, AsfawMeresa, TigistAbera (July 2019).

Cadmium and lead are pollutants of great concern to human health. The analysis of Cadmium and lead content in our environment is crucial for policy makers to make decisions concerning the environment and to secure the wellbeing of the inhabitants. In this study lead and cadmium in roadside soil was analyzed. The soil sample was collected at the distance of 18m, 20m, 25m, 26m and from the roadside. The collected sample was digested on hot plate. The concentration of lead and cadmium was measured by flame atomic absorption spectroscopy (FAAS). Lead concentrations in soil samples varied from 36.47 to 43.42mgkg^{-1}. Lead analyses showed that there was a considerable contamination in soil affected from traffic intensity. Cadmium and lead were determined using AAS in the surface layer (0.0-5.0cm) of soils, situated in areas under different impact of traffic contamination. The Concentration cadmium in soil samples lies between 0.505mg/kg to 1.745mg/kg. The obtained results of Cadmium and concentration in the soil around Jimma, Ethiopia; 1.745mg/kg and 43.42mg/kg respectively, were compared with WHO and EPA. The maximum contaminate level according to WHO, for lead and cadmium in soil is 100 and 3.00mg/Kg respectively and appropriate recommendation and conclusion was forwarded. From this site the concentration of lead is higher than cadmium. The average lead and cadmium concentration in soil samples from the four sites of Jimma were all found to be below the maximum tolerable limit according to WHO standards.

As the study result indicated there is no sampling sites recorded a lead and cadmium concentration beyond the world health organization (WHO) permissible limit of 100 and 3.12mg/kg respectively. An average soil lead and cadmium concentration in these studied sites was in the estimated natural concentration 35mg/Kg to 50mg/Kg and 0.5mg/Kg to 5mg/Kg. However, the concentration of such a heavy metal in these sampling sites were below the world health organization permissible limit the soil sample taken from sampling site of roadside exposed to gasoline and vehicular emission shows a considerable difference in concentration of lead and cadmium in relative to the soil of non-gasoline area. This shows that the level of lead and cadmium in these sites were primarily due to vehicular emission and goals line effluent. In this study the concentration of lead is higher than cadmium in the roadside soil in Jimma south west Ethiopia.

Generally, for this study the concentration of lead and cadmium in around Garage area and bajajtera soil in Jimma town is almost very slightly affect human and animal health. Even if the result is below the limit, certain precautionary measures must be conducted in order to prevent possible ingestion of soil containing lead and cadmium. Finally, we recommend further study on this area by increasing the sample size to make it more representative. Ratio can be used to differentiate between lead-contaminated and non-contaminated soils are presented [50].

8-Estimation and Bio-Availability of Toxic Metal between Soils and Plants. Al Saad Mohammed Ali, Hatem AbdMoniem Ahmed, HananAbd El Azim Emara, MuhammedNaeemJanjua, Nada Alhafez (2019).

Heavy metals contamination of soil is one of the most alarming concerns in the debate about food security and food safety all over the world because it determines the possible composition of food and feeds at the root level of the food chain. Simultaneously, plants are important components of the ecosystem as they transfer elements from abiotic and biotic environments. The primary sources of elements from the environment to plants are air, water, and soil. The aim of this study was to determine the accumulation levels of trace toxic heavy metals in soils and plant samples in the garden of the Al-Nadwa-Riyadh area. Lead and cadmium were measured in the soil and plants by graphite atomic absorption spectrometry, while arsenic and mercury were measured using hydride generation atomic absorption spectrometry. Plant samples were digested by 8 ml of nitric acid followed by 2 ml hydrogen peroxide, while soil samples were digested by 6 ml concentrated nitric acid followed by 2 ml hydrofluoric acid and 2 ml hydrogen peroxide.

In soil samples, results presented here showed that levels of lead were within the set of all standards, while cadmium exceeds the limits of FAO and EC standards. Arsenic was found to be above the FAO standard

but within the set of all other standards. On the contrary, mercury was investigated far above all the set standards. All levels of the heavy metals in all plant samples were below the maximum permissible limit standard values of FAO/WHO, except mercury. The results demonstrated that mean content of Hg uptake by the plants was higher than the contents of each trace metals under test. Concentrations of trace heavy metals in our studied soil samples show that Pb was within the set of all standards, while cadmium exceeded that of FAO/WHO and EC, but fell within all other standards (Ling-Zhi,Austria, Germany, Poland, USA). Arsenic was by far the within FAO/WHO limits, but within the set of all other standards. On the contrary, mercury was far above all these standards (Table 6). The mean content of all heavy metals in all our tested plant samples were below the maximum permissible standard values except for Hg, which was above the standard limits set by FAO/WHO (Table 5). The detection of this toxic metal in our tested plant sample clearly indicates a persistent exposure of plants to soil contaminated with abnormally high concentrations ofHg. Con5sumption of such contaminated edible plants for prolonged durations causes the accumulation of this highly neurotoxic substance in the human body, posing serious health hazard to humans as well as animals.

Based on the results of this study, it is highly recommended that concerned authorities should carryout routine screening of soil as well as crops for the presence of toxic heavy metals [51].

9-**Evaluation of trace elements in clay sediments products of tatikolocality using x-ray fluorescence technique.NjingaR.L, Baba Alfa, Okoh Sunday, Muhammad T. A (2011).**

Clay products in Tatiko village, Paikoro local government area in North central part of Nigeria with coordinates 9°26′N 6°38′E / 9.433°N 6.633°E have been major instruments of cooking, drinking of water, eating of meals, decorations and exportations for decades, thus the need to ascertain the level of trace heavy elements. Samples of red clay sediments were taken at vertical depth of 150 cm and a horizontal depth of 100cm beneath the earth surface at site 1, and labeled Tat. A1. Also, Brown clay sediments were taken at a vertical depth 200 cm and horizontal depth of 100cm beneath the earth surface at site 2 and labeled Tat. B1. Clay sediments products with sample identification: Tat. A2, Tat. M2, Tat. F3 and Tat. M3 were analyzed using Energy Dispersive X-RayFluorescence(EDXRF) technique (mini pal 4 PW 4030 X-ray Spectrometer) for the determination of sixteen elements of interest; Al, Ba, Ca, Cr, Cu, Fe, Ga, K, Mn, Mo, P, Rb, Si, Ti, V, and Zn. The concentration of Al, Si, and Fe which were the major elements in the samples ranged from 6.56% to 11.1%, 18.77 to 29.43% and 8.39 to 17.04%

respectively for all the analyzed samples. The concentration of the following which constitute the trace elements; Ba, Ni, V, Cu, Ga, P, Ti, and Zn were within the range of 0.15% to 0.47%, 0.011% to 0.0463%, 0.03% to 0.066%, 0.008% to 0.0567%, 0.0005 to 0.0896%, 0.1264% to 0.2005%, 0.6591% to 1.049% respectively. The concentrations of elements obtained were outside the range of toxic and hazardous permissible criteria recommended by Federal Environmental Protection Agency (FEPA) of Nigeria 1998.

The obtained results have shown that application of the XRF method gave an array of the elemental composition of clay sediments product in Tatiko village, Paikoro local government Area, Niger State-Nigeria. This work showed seventeen different elements which were neither toxic nor hazardous to humans as classified by the reports of the FEPA, Nigeria,Thiswork showed clearly that the toxic elements; Ba, Cr, Ga, V and Zn were below the limit recommended by the report of the committee on substances in relation to human health, by Federal Environmental Protection Agency (FEPA), Nigeria. These results gave the information on the main contents of the clay products, anthropogenic activities which influence clay sediments, natural clay-forming processes and hazards, connected with changes of elements chemical form under environmental conditions and their influence on living organisms [52].

10-**Principles, developments and applications oflaser-induced breakdownspectroscopy in agriculture: A review. Keqiang Yu, Jie Ren, YanruZhao (July2020).**

Considering the diversity of soil contents, quality and usability, a systematic scientific study on the elemental andchemical composition (major and minor nutrients elements, trace elements, heavy metals, etc.) of soil is very important.

Rapid and accurate detection and prevention of soil contamination (mainly in pollutants of heavymetals) is deemed to be a concerned and serious central issue in modern agriculture and agricultural sustainabledevelopment. In order to study the chemical composition of soil, laser induced breakdown spectroscopy (LIBS)has been applied recently. LIBS technology, a kind of atomic emission ceroscopy, is regarded as a future“Superstar” inthefield of chemical analysis and green analytical techniques. In this work, the research achievements

and trends of soil elements detection based on LIBS technology were reviewed. The structural composition andoperating principle of LIBS system was briefly introduced. The paper offered a review of LIBS applications, including detection and analysis of major element, minor nutrient element and heavy metal element. Simultaneously, LIBS applications to analysis of the soil related materials, plants-related issues (nutrients, pesticide residues, andplants disease) were briefly summarized. The research tendency and developing prospects of LIBS in agriculturewere presented at last. At present, LIBS technology is undergoing a rapid technical development for using laboratorial, man-portable, robotic-based, and standoff methods in chemical analysis field.

Further research could focus on several aspects as follows: (1) noveltechniques (data processing or signal enhancement) should be developed to enhance LIBS signal and improve the reliability, accuracy and repeatability of LIBS analytical results; (2) LIBS technology should be combined with other analytical techniques (Raman, fluorescence, etc.) to reinforce the analytical ability of laser spectrometer and extend theapplicability of the chemical apparatus; (3) portable and customized LIBS instrument should be developed to cope with the in situ, online detection in emergencies, environmental monitoring, history cultural heritage, and so on; (4)

LIBS core parts must be researched and developed,Contributing to the rapid development of the LIBS industry [53].

11- Elemental Analysis of Soils Using Laser-Induced Breakdown Spectroscopy (LIBS). Ning fang Yang (August 2009).

Laser-induced breakdown spectroscopy (LIBS) has been applied for the quantitative analysis of various samples, but it is controversial for chemically-complex soils. In order to study the effect of delay time, gate width, and repetition rate on the LIBS signal in soil, the emission line at 396.84 nanometer was selected. The results indicated that repetition rate, delay time, and gate width significantly affected the LIBSsignal, delay time was more important than gate width in controlling the LIBS signal. The optimum instrumental parameters for soil analysis was obtained when repetition rate, delay time, and gate width equaled 10 hertz, 1 microsecond, and 10 microseconds, respectively. In order to compare the analytical ability of univariate and multivariate approaches in analyzing the LIBS spectral data and to quantitatively determine copper and zinc concentrations in soils, 12 samples with different copper and zinc concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and LIBS, respectively. The univariate and the partial least square (PLS) regression were coupled with LIBS to build the calibration models and to predict copper and zinc concentrations. The background-subtracted signal intensity at 324.75 nanometer (copper) and 334.59 nanometer (zinc) were used for the univariate analysis, and

the full spectral range 200-600 nanometer and the reduced spectral ranges 250-450 nanometer and 300-350 nanometer were used for the PLS analysis. Copper and zinc concentrations predicted by LIBS were compared with those measured by ICP-OES. The results demonstrated that (1) the PLS regression was powerful in analyzing the LIBS spectral data, and compared to the univariate regression, it improved the normalized root mean square error of calibration (NRMSEC) about 15% and the normalized root mean square error of prediction (NRMSEP) about 10% respectively; (2) The PLS regression using the reduced spectral range (300-350 nanometer) containing copper and zinc peaks producedthe best resultsamongall the spectral ranges, which indicated that use of the suitable spectral range in the PLS regression improved the LIBS analytical ability; (3) The implementation of multivariate approaches in analyzing the LIBS spectral datamade the quantitative analytical ability of LIBS promising and comparableto that of ICP-OES.The effect of instrumental parameters (td, tw, and repetition rate) on the LIBS signal intensity, the RSD% of signal, and SNR were analyzed using soilsamples (SRM-2586), and the optimum set of instrumental parameters for soil sample analysis were determined according to the standards that “to maximize the signal intensity and SNR, and to minimize the RSD% of signal”. The results of this study indicated that (1) repetition rate, td, and towsignificantlyaffected the LIBS signal intensity; (2) tdwas more important than twin controlling the LIBS signal intensity, the RSD% of signal intensity, and SNR; (3) the optimum instrumental parameters for soil analysis were obtained when repetition rate, td, and twoequaled 10 Hz, 1 μs, and 10 μs, respectively [54].

12- **ICP/XRF Analysis for Trace Elements in Soil Samples from Gezira and Suki Schemes, Sudan.Marwa M. Adam, Mustafa. M. Osman, Ahmed. S. Elhag, Mohamed. A. Elsheikh (2021).**

In the present study, soil samples have been collected from two different agriculture areas: Gezira and Suki schemes in Sudan. The elementalconcentrations for Cr, Ni, Cu, Zn, and Pb have been determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP -OES) and X-ray Fluorescencespectrometry (XRF). The accuracy of measurements has been investigated by using ISE (PT) 1&4 and fortifiedsamples for ICP, IAEA-Soil-7 for

XRF, respectively. A good agreement was found between certified and measured values.

The average elemental concentrations by ICP of these elements Cr, Ni, Cu, Zn, and Pb in loc1werefoundas follows: 84.7, 48.15, 33.5, 65.43, and 12.57 ppm, respectively. While the results obtained in loc2 were found as follows: 105, 65.1, 41.3, 55.4, and 12.74 ppm, respectively. The average elemental concentrations by XRF of these elements Cr, Ni, Cu, Zn, and Pbin loc1 were found as follows: 77.21, 43.72, 27.62, 86.96, and 18.74 ppm, respectively. While the results obtained in lock2 were found as follows: 123.33, 57.41, 35.99, 98.85, and 16.43 ppm, respectively.A statistical test (t-test) was applied to the data of both methods without any significant difference between.

the two techniques.The results obtained were compared to WHO permissible limits. Correlations between different elements were performed. Hierarchical cluster analysis was done for the data. The average elemental concentrations were calculated and compared with data from the literature.

Elemental concentrations of Cr, Ni, Cu, Zn, and Pb were analyzed in soil samples using ICP and XRF techniques. The results obtained show no significant difference between both techniques. The elemental concentration of Cr, Ni, and Cu in the Suki scheme was found higher than their concentration in the Gezira scheme. While the concentration of Pbwas found to be similar in both locations. The elemental concentration of Zn in the Suki scheme was found lower than their concentration in the Gezira scheme. The elemental concentrations were found to be within the WHO permissible limits for analyzed elements insoil except for Ni. XRF spectrometeremployed is a promising tool that may beusedforquickscreeninganalysis of environmental samples without the need for time-consuming sample preparation procedures. Whereas in the case of ICP-OES, sample pretreatment methods depend on the type of soil and the chemical method itself [55].

Chapter Three
Material and Methods

3.1 Introduction

This chapter include material, methods I examined 16 sample of soil located at Wad Hamid locality at River Nile State from deferent depths deferent sorts (sand& clay soil) fertilized and unfertilized with three deferent methods.

3.2 Material

16 sample of soil are sand and clay from different depths 4 samples at depth (5cm - 10cm), 4samples at depth (20cm-25),4samples at depth (30cm-35) and four samples at depth (40cm-45cm) wait of each sample 1gram from random directions through two feddan.

3.3 Instruments

Synchronized with the output of the laser pulse. Data acquisition and analysis were performed using a personal computer. The gate delay time

And gate width were adjusted to maximize the signal-to-background (S/B) and signal-to-noise(S/N) ratios. Emission spectra were recorded mainly using a 2400-L/mm grating for better spectral resolution. Around 100 pulses were accumulated to obtain one spectrum and 30 such spectra were recorded for each experimental condition to increase the sensitivity of the system and to reduce the standard deviation in the recorded data.

major parts: (1) a laser to generate the LIP; (2) a sample container (ablation chamber) to house the samples in an inert gaseous environment under a vacuum or simply in air; and (3) a detection system to collect, resolve, and measure the atomic emission lines from the LIP. The detection system usually consists of a dispersing element (a monochromatic or a grating), an optical detector, detection electronics, and a computer.

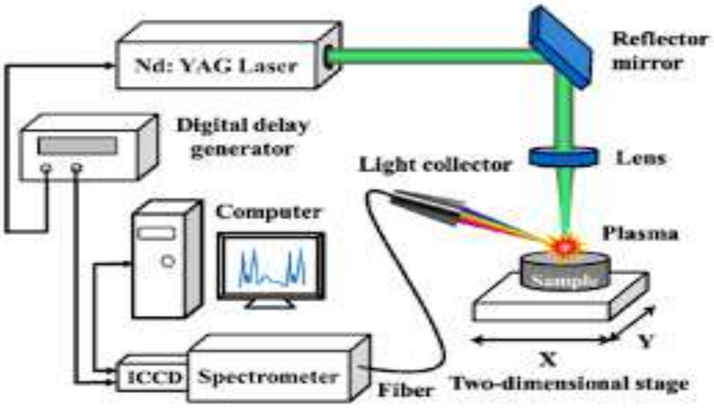


Fig (3.1): parts of LIBS

3.4 Sample Preparations

Three deferent methods are used in analyzing the above samples so as to achieve maximum accuracy of detection. +

16samples were taken from wad Hamid area near river Nile from one farm having area (2fadan) four were taken from clay non-fertilized and from fertilized at depth of 5cm similarly 4 samples were taken from non-fertilized sand and 4from fertilized sand at the same depth the samples were put in small plastic capsule. they were drayed for three days at room temperature. then they were milled and then refined using grids.

3.5 Laser Induced Break Down Spectroscopy:

Laser-induced breakdown spectroscopy (LIBS) is an extremely versatile spectroscopic technique which can be used to analyze the composition of almost any material. It is a favored technique in situations where rapid analysis is required, as most samples do not need any preparation, and the full spectrum of elements present in a sample is reported in a single experiment.

3.5.1 LIBS Work

The operating principle of LIBS is quite simple. An intense, highly focused laser pulse is fired at a sample, creating a small plume of plasma consisting of electronically excited atoms and ions. As these atoms decay back into their ground states, they emit characteristic wavelengths of light.

The emitted light is picked up by lenses and/or a fiber optic system on the instrument, and focused onto a detector such as a CCD. The spectrum of the emitted light is then analyzed for the presence of atomic emission lines to indicate which elements are present.

A number of different types of laser can be used for LIBS, as the most important parameter for a successful reading is the spot size of the laser on the material - this typically has to be on the order of micrometers. The most common laser used is exciters and Nd: YAG lasers. The laser pulse used to create the plasma is very short - typically 5 - 20 nanoseconds long. Some LIBS equipment includes filters to remove the incident laser wavelength from the received light. This is rarely necessary, however, as there is most often a significant gap between the laser blast and the spectral lines becoming visible.

Immediately after the laser pulse, the light received by the spectrometer is white, as the plasma bubble is small and very hot. The conditions in the plasma break down the vast majority of chemical bonds, leaving the constituent elements as free atoms, which are often ionized. As the plasma expands and cools, the ions and atoms relax from their excited states, emitting the useful spectral lines - these can typically be detected around 1 µs after the initial laser pulse. To make sure that the reading is as clear as possible, the detector is usually shut off until this point.

3.5.2 LIBS Used for:

LIBS are versatile in application, as the samples rarely need any preparation at all. It is popular for in situ analysis on manufacturing lines, and field work where less robust analytical equipment is impractical. Some common applications include:

- Environmental monitoring (e.g. soil contamination)
- Rapid material characterization in R&D
- Analysis of teeth and bones in forensic studies
- Analysis of vessels, tubing and radioactive waste in the nuclear industry
- Characterization of minerals and ores in mining exploration

3.6 Met 5000 Instrument

The device X-met 5000 based on florescent x-ray and detect heavy elements concentration only. It detects sample informs of powder, liquid. And solid .

Fig (3.2): Parts of XRF

3.6.1 XRF spectroscopy methodology

XRF is an analytical method to determine the chemical composition of all kinds of materials. The materials can be in solid, liquid, powder; filtered or other form.XRF can also sometimes be used to determine the thickness and composition layers and coatings. The method is fast, accurate and non-destructive, and usually requires only a minimum of sample preparation. Applications are very broad and include the metal, cement, oil, polymer, plastic and food industries, along with mining, mineralogy and geology, and environmental analysis of water and waste materials. XRF is also a very useful analysis technique for research and pharmacy. Spectrometer system s can be divided into two main groups: energy dispersive systems (EDXRF) and wavelength dispersive systems (WDXRF), explained in more detail later. The elements that can be analyzed and their detection levels mainly depend on the spectrometer system used. The elemental range for EDXRF goesfrom sodium to uranium (Na to U). For WDXRF it is even wider, from beryllium to uranium (Be to U). The concentration range goes from (sub) ppm levels to 100%. Generally speaking, the elements with high atomic numbers have better detection limits than the lighter elements.

The precision and reproducibility of XRF analysis is very high. Very accurate results are possible when good standard specimens are available, but also in applications where no specific standards can be found.

The measurement time depends on the number of elements to be determined and the required accuracy, and varies between seconds and 30 minutes. The analysis time after the measurement is only a few seconds.

Figure 1 shows a typical spectrum of a soil sample measured with EDXRF – the peaks are clearly visible. The positions of the peaks determine the elements present in the sample, while the heights of the peaks determine the concentrations.

3.7 Atomic Absorption Spectroscopy

Spectroscopy is the study of how radiated energy and materials interact. Matter absorbs energy, which will create some sort of change in its state.

The atomic part refers to the atoms in a material, which will absorb radiated energy from a light source.

These atoms will each have their own characteristics when it comes to absorbing energy because each element has a unique electronic structure.

Therefore, using AAS, you can measure for a specific element in a material, based on the amount of light absorbed at a defined wavelength, which corresponds to the known characteristics of the element you are testing for.

3.7.1Typical calibration curve for an element measured by AAS

Note: AAS is also referred to as atomic absorption spectrometry. The difference between spectroscopy and spectrometry is that spectroscopy is the study of how energy and materials interact, while spectrometry refers to how you apply this as a measuring technique. For practical purposes, it doesn't really make any difference which term you use.

3.7.2 History of Atomic Absorption Spectroscopy

As a phenomenon, atomic absorption spectrometry was first discovered in 1802, when the English scientist William Hyde Wollaston observed and described dark lines in the sun's spectrum. In 1817, the German physicist Josef von Fraunhofer carefully mapped out these spectral absorption lines, which are now named after him. A theory of spectra chemical analysis then developed with the work of the scientists Gustav Kirchhoff and Robert Bunsen in 1860.Kirchhoff and Bunsen developed the spectroscope, splitting light into wavelengths. It was not until the 1930s that this technique became more widely used. However, atomic absorption spectroscopy as a modern technique for chemical analysis dates from 1955, when the Lancashire-born scientist Alan Walsh published his significant paper on the potential for AAS in Melbourne, Australia. Walsh's breakthrough came with the realization that he needed to be measuring absorption of light rather than emission. This led to the development of new techniques for AAS. The first commercially available instruments appeared in the 1960s.As AAS has developed since this time, with the continuing application of new technology, including automation and computers, it has become an extremely reliable analytical technique. It is fast, sensitive, specific and user-friendly.

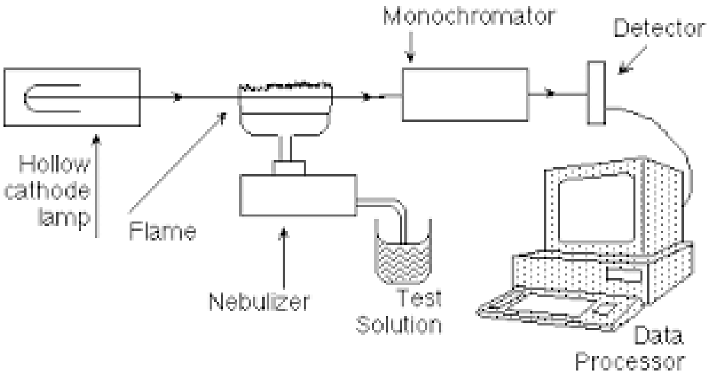


Fig (3.3) : Device AAS

3.7.3 Instrument

In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electro thermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromaticin order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.

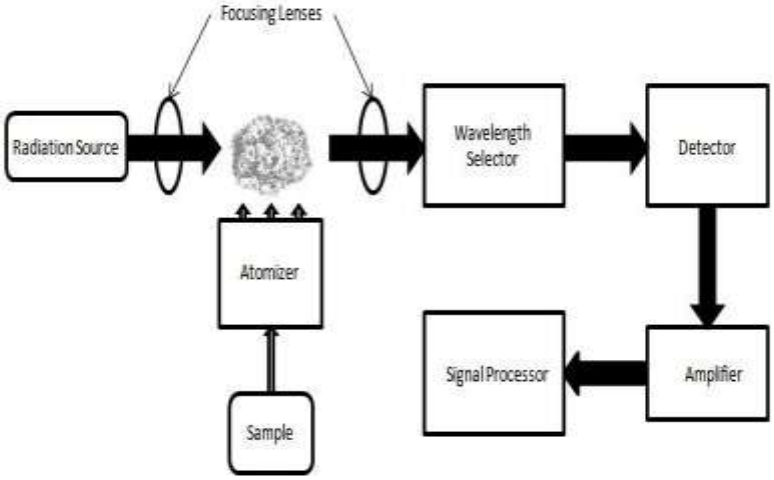


Fig (3.4): part of AAS

3.7.4 Atomizers

The atomizers most commonly used nowadays are (spectroscopic) flames and electro thermal (graphite tube) atomizers. Other atomizers, such as glow-discharge atomization, hydride atomization, or cold-vapor atomization, might be used for special purposes.

3.7.5 Flame Atomizers

The oldest and most commonly used atomizers in AAS are flames, principally the air-acetylene flame with a temperature of about 2300 °C and the nitrous oxide[1] system (N_2O)-acetylene flame with a temperature of about 2700 °C. The latter flame, in addition, offers a more reducing environment, being ideally suited for analyses with high affinity to oxygen.

A laboratory flame photometer that uses propane operated flame atomizer

Liquid or dissolved samples are typically used with flame atomizers. The sample solution is aspirated by a pneumatic analytical nebulizer, transformed into an aerosol, which is introduced into a spray chamber, where it is mixed with the flame gases and conditioned in a way that only the finest aerosol droplets (< 10 μm) enter the flame. This conditioning process reduces interference, but only about 5% of the aerosolized solution reaches the flame because of it.

On top of the spray chamber is a burner head that produces a flame that is laterally long (usually 5–10 cm) and only a few mm deep. The radiation beam passes through this flame at its longest axis, and the flame gas flow-rates may be adjusted to produce the highest concentration of free atoms. The burner height may also be adjusted, so that the radiation beam passes through the zone of highest atom cloud density in the flame, resulting in the highest sensitivity.

The processes in a flame include the stages of desolation (drying) in which the solvent is evaporated and the dry sample Nano-particles remain, vaporization (transfer to the gaseous phase) in which the solid particles are converted into gaseous molecule, atomization in which the molecules are dissociated into free atoms, and ionization where (depending on the ionization potential of the analyze atoms and the energy available in a particular flame) atoms may be in part converted to gaseous ions.

Each of these stages includes the risk of interference in case the degree of phase transfer is different for the analyze in the calibration standard and in the sample. Ionization is generally undesirable, as it reduces the number of atoms that are available for measurement, i.e., the sensitivity.

In flame AAS a steady-state signal is generated during the time period when the sample is aspirated. This technique is typically used for determinations in the mg L^{-1} range, and may be extended down to a few μg L^{-1} for some elements.

3.7.6 Electro Thermal Atomizers

Electro thermal AAS (ET AAS) using graphite tube atomizers was pioneered by Boris V. Lvov at the Saint Petersburg Polytechnic Institute, Russia, since the late 1950s, and investigated in parallel by Hans Mossman at the Institute of Electrochemistry and Applied Spectroscopy (ISAS) in Dortmund, Germany.

Although a wide variety of graphite tube designs have been used over the years, the dimensions nowadays are typically 20–25 mm in length and 5–6 mm inner diameter. With this technique liquid/dissolved, solid and gaseous samples may be analyzed directly. A measured volume (typically 10–50 μL) or a weighed mass (typically around 1 mg) of a solid sample are introduced into the graphite tube and subject to a temperature program. This typically consists of stages, such as drying – the solvent is evaporated; paralysis – the majority of the matrix constituents are removed; atomization – the analyze element is released to the gaseous phase; and cleaning – eventual residues in the graphite tube are removed at high temperature.

The graphite tubes are heated via their holmic resistance using a low-voltage high-current power supply; the temperature in the individual stages can be controlled very closely, and temperature ramps between the individual stages facilitate separation of sample components. Tubes may be heated transversely or longitudinally, where the former ones have the advantage of a more homogeneous temperature distribution over their length. The so-called stabilized temperature platform furnace (STPF) concept, proposed by Walter Slaving, based on research of Boris Lvov, makes ET AAS essentially free from interference. The major components of this concept are atomization of the sample from a graphite platform inserted into the graphite tube (Lvov platform) instead of from the tube wall in order to delay atomization until the gas phase in the atomizer has reached a stable temperature; use of a chemical modifier in order to stabilize the analyze to a paralysis temperature that is sufficient to remove the majority of the matrix components; and integration of the absorbance over the time of the transient absorption signal instead of using peak height absorbance for quantification.

In ET AAS a transient signal is generated, the area of which is directly proportional to the mass of analyze (not its concentration) introduced into the graphite tube. This technique has the advantage that any kind of sample, solid, liquid or gaseous, can be analyzed directly. Its sensitivity is 2–3 orders of magnitude higher than that of flame AAS, so that determinations in the low μg L^{-1} range (for a typical sample volume of 20 μL) and ng g^{-1} range (for a typical sample mass of 1 mg) can be carried out. It shows a very high degree of freedom from interferences, so that ET AAS might be considered the most robust technique available nowadays for the determination of trace elements in complex matrices.

3.7.7 Specialized Atomization Techniques

While flame and electro thermal vaporizers are the most common atomization techniques, several other atomization methods are utilized for specialized use.

3.7.8 Glow-Discharge Atomization

A glow-discharge device (GD) serves as a versatile source, as it can simultaneously introduce and atomize the sample. The glow discharge occurs in a low-pressure argon gas atmosphere between 1 and 10 torr. In this atmosphere lies a pair of electrodes applying a DC voltage of 250 to 1000 V to break down the argon gas into positively charged ions and electrons. These ions, under the influence of the electric field, are accelerated into the cathode surface containing the sample, bombarding the sample and causing neutral sample atom ejection through the process known as sputtering. The atomic vapor produced by this discharge is composed of ions, ground state atoms, and fraction of excited atoms. When the excited atoms relax back into their ground state, a low-intensity glow is emitted, giving the technique its name.

The requirement for samples of glow discharge atomizers is that they are electrical conductors. Consequently, atomizers are most commonly used in the analysis of metals and other conducting samples. However, with proper modifications, it can be utilized to analyze liquid samples as well as non-conducting materials by mixing them with a conductor (e.g. graphite).

3.7.9 Hydride Atomization

Hydride generation techniques are specialized in solutions of specific elements. The technique provides a means of introducing samples containing arsenic, antimony, selenium, bismuth, and lead into an atomizer in the gas phase. With these elements, hydride atomization enhances detection limits by a factor of 10 to 100 compared to alternative methods. Hydride generation occurs by adding an acidified aqueous solution of the sample to a 1% aqueous solution of sodium borohydride, all of which is contained in a glass vessel. The volatile hydride generated by the reaction that occurs is swept into the atomization chamber by an inert gas, where it undergoes decomposition. This process forms an atomized form of the analyze, which can then be measured by absorption or emission spectrometry.

3.7.10 Cold-Vapor Atomization

The cold-vapor technique is an atomization method limited to only the determination of mercury, due to it being the only metallic element to have a large enough vapor pressure at ambient temperature. Because of this, it has an important use in determining organic mercury compounds in samples and their distribution in the environment. The method initiates by converting mercury into Hg^{2+} by oxidation from nitric and sulfuric acids, followed by a reduction of Hg^{2+} with. The mercury, is then swept into a long-pass absorption tube by bubbling a stream of inert gas through the reaction mixture. The concentration is determined by measuring the absorbance of this gas at 253.7 nm. Detection limits for this technique are in the parts-per-billion range making it an excellent mercury detection atomization method.

Two types of burners are used: total consumption burner and premix burner.

3.7.11 Radiation Sources

We have to distinguish between line source AAS (LS AAS) and continuum source AAS (CS AAS). In classical LS AAS, as it has been proposed by Alan Walsh, the high spectral resolution required for AAS measurements is provided by the radiation source itself that emits the spectrum of the analyze in the form of lines that are narrower than the absorption lines. Continuum sources, such as deuterium lamps, are only used for background correction purposes. The advantage of this technique is that only a medium-resolution monochromatic is necessary for measuring AAS; however, it has the disadvantage that usually a separate lamp is required for each element that has to be determined. In CS AAS, in contrast, a single lamp, emitting a continuum spectrum over the entire spectral range of interest is used for all elements. Obviously, a high-resolution monochromatic is required for this technique, as will be discussed later.

3.7.12 Hollow Cathode Lamp (HCL)

Hollow cathode lamps (HCL) are the most common radiation source in LS AAS. Inside the sealed lamp, filled with argon or neon gas at low pressure, is a cylindrical metal cathode containing the element of interest and an anode. A high voltage is applied across the anode and cathode, resulting in an ionization of the fill gas. The gas ions are accelerated towards the cathode and, upon impact on the cathode, sputter cathode material that is excited in the glow discharge to emit the radiation of the sputtered material, i.e., the element of interest. In the majority of cases single element lamps are used, where the cathode is pressed out of predominantly compounds of the target element. Multi-element lamps are available with combinations of compounds of the target elements pressed in the cathode. Multi element lamps produce slightly less sensitivity than single element lamps and the combinations of elements have to be selected carefully to avoid spectral interferences. Most multi-element lamps combine a handful of elements, e.g.: 2 - 8. Atomic Absorption Spectrometers can feature as few as 1-2 hollow cathode lamp positions or in automated multi-element spectrometers, a 8-12 lamp positions may be typically available.

3.7.13 Electrode less Discharge Lamps

Electrodeless discharge lamps (EDL) contain a small quantity of the analytic as a metal or a salt in a quartz bulb together with an inert gas, typically argon gas, at low pressure. The bulb is inserted into a coil that is generating an electromagnetic radio frequency field, resulting in a low-pressure inductively coupled discharge in the lamp. The emission from an EDL is higher than that from an HCL, and the line width is generally narrower, but EDLs need a separate power supply and might need a longer time to stabilize.

3.6.14 Deuterium Lamps

Deuterium HCL or even hydrogen HCL and deuterium discharge lamps are used in LS AAS for background correction purposes. The radiation intensity emitted by these lamps decreases significantly with increasing wavelength, so that they can be only used in the wavelength range between 190 and about 320 nm.

Xenon lamp as a continuous radiation source

3.7.15 Continuum Sources

When a continuum radiation source is used for AAS, it is necessary to use a high-resolution monochromatic, as will be discussed later. In addition, it is necessary that the lamp emits radiation of intensity at least an order of magnitude above that of a typical HCL over the entire wavelength range from 190 nm to 900 nm. A special high-pressure xenon short arc lamp, operating in a hot-spot mode has been developed to fulfill these requirements.

3.7.16 Spectrometer

As already pointed out above, there is a difference between medium-resolution spectrometers that are used for LS AAS and high-resolution spectrometers that are designed for CS AAS. The spectrometer includes the spectral sorting device (monochromatic) and the detector.

3.7.17 Spectrometers for LS AAS

In LS AAS the high resolution that is required for the measurement of atomic absorption is provided by the narrow line emission of the radiation source, and the monochromatic simply has to resolve the analytical line from other radiation emitted by the lamp. This can usually be accomplished with a band pass between 0.2 and 2 nm, i.e., a medium-resolution monochromatic. Another feature to make LS AAS element-specific is modulation of the primary radiation and the use of a selective amplifier that is tuned to the same modulation frequency, as already postulated by Alan Walsh. This way any (unpopulated) radiation emitted for example by the atomizer can be excluded, which is imperative for LS AAS. Simple monochromators of the Littre or (better) the Czerny-Turner design are typically used for LS AAS. Photomultiplier tubes are the most frequently used detectors in LS AAS, although solid state detectors might be preferred because of their better signal-to-noise ratio.

3.7.18 Spectrometers for CS AAS

When a continuum radiation source is used for AAS measurement it is indispensable to work with a high-resolution monochromatic. The resolution has to be equal to or better than the half-width of an atomic absorption line (about 2 pm) in order to avoid losses of sensitivity and linearity of the calibration graph. The research with high-resolution (HR) CS AAS was pioneered by the groups of O'Haver and Harnly in the US, who also developed the (up until now) only simultaneous multi-element spectrometer for this technique. The breakthrough, however, came when the group of Becker-Ross in Berlin, Germany, built a spectrometer entirely designed for HR-CS AAS. The first commercial equipment for HR-CS AAS was introduced by Analytic Jena (Jena, Germany) at the beginning of the 21st century, based on the design proposed by Becker-Ross and Florek. These spectrometers use a compact double monochromatic with a prism pre-monochromatic and an echelon grating monochromatic for high resolution. A linear charge-coupled device (CCD) array with 200 pixels is used as the detector. The second monochromatic does not have an exit slit; hence the spectral environment at both sides of the analytical line becomes visible at high resolution. As typically only 3–5 pixels are used to measure the atomic absorption, the other pixels are available for correction purposes. One of these corrections is that for lamp flicker noise, which is independent of wavelength, resulting in measurements with very low noise level; other corrections are those for background absorption, as will be discussed later.

3.7.19 The Reason of use Atomic Absorption Spectroscopy

*AAS provides a high degree of accuracy.

*Normally results fall within a range of 0.5 per cent to 5 per cent accuracy, but this may improve further depending on the standards set for testing and analysis.

*It is a highly sensitive method of analysis.

*In a given material, it can measure parts per billion of a gram.

*In applications such as medicine and pharmaceuticals, AAS has helped revolution is practices, detecting things such as trace toxins.

*In some sectors, this method has been able to detect elements which people were previously unaware existed in certain material, such as cobalt and molybdenum in soil.

*It is a technique that is well-suited to reaching otherwise inaccessible places, such as mines, to test rocks to see if they are worth mining.

*Modern AAS systems are a comparatively inexpensive means to accurately detect specific elements.

3.7.20 Status of Using Atomic Absorption Spectroscopy

Atomic absorption spectroscopy has different laboratory and testing applications in industrial, clinical and research settings, as a crucial component in various processes.

These processes include**:**

- Quality control
- Toxicology
- Environmental tee

3.7.21Work Structure of Atomic Absorption Spectroscopy

Elements exist on an electromagnetic spectrum, and their atoms will absorb wavelengths of light that relate to their particular characteristics.

During the atomic absorption spectroscopy process, these atoms will absorb electromagnetic radiation at a specific wavelength. This produces a measurable signal.

By looking at these signals, it is then possible to determine the parts per million, or ppm, levels of specified metals in the material that is being tested.

3.7.22 Creation of Signals

Within an atom, there are electrons at various energy levels. During the spectroscopy process, the absorbing of energy moves electrons to a more energetic level.

The radiant energy the electrons absorb is directly related to the transition that occurs during this process. The atoms absorb light in an excited state. Atomic absorption measures the amount of light at a resonant wavelength, which passes through a cloud of atoms and is absorbed by them.

Once the excited electrons start to relax again, they emit energy in the form of photons.

Every element has its own unique electronic structure. Therefore, the radiation absorbed represents a unique property of each individual element.

Chapter Four

Result, Discussion, Conclusion And Recommendation

4.1 Introduction

This chapter exhibits the results of soil analysis beside discussion conclusion and recommendation.

4.2 Results

The number of examined samples are16 samples with three methodologies XRF, LIBS and AAS for more comparative

4.2.1 XRF results

The table and figures below shows the XRF analysis and data forall samples

Table (4.1): the table below shows the concentration of elements in clay non-fertilized sample (1-1)

ELE	Conc.	STD
Cr	1.04	1.000
Mn	3.04	1.000
Fe	69.87	1.000
Ni	0.01	1.000
Au	3.4	1.000
Zn	3.88	1.000
Pb	7.34	1.000

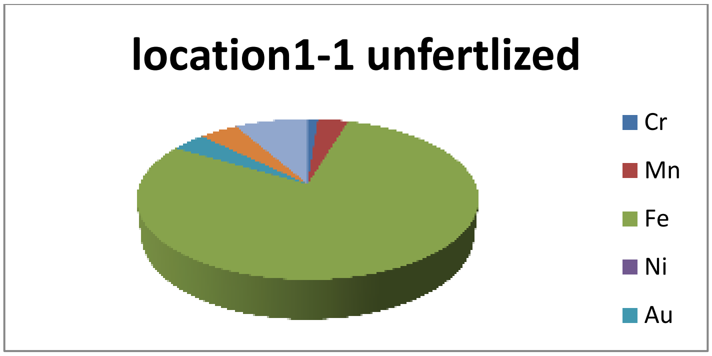


chart (4.1): location (1) – sample (1) in clay non-fertilized sample

Table (4.2):the table below shows the concentration of elements in clay non-fertilized sample (1-2)

ELE	Conc.	STD
Cr	0.23	0.217
Ni	0.90	0.528
Mo	2.91	0.141
Cu	4.23	0.233
W	9.13	1.365
V	0.57	0.289
Mn	0.56	0.335
Fe	84.24	1.028

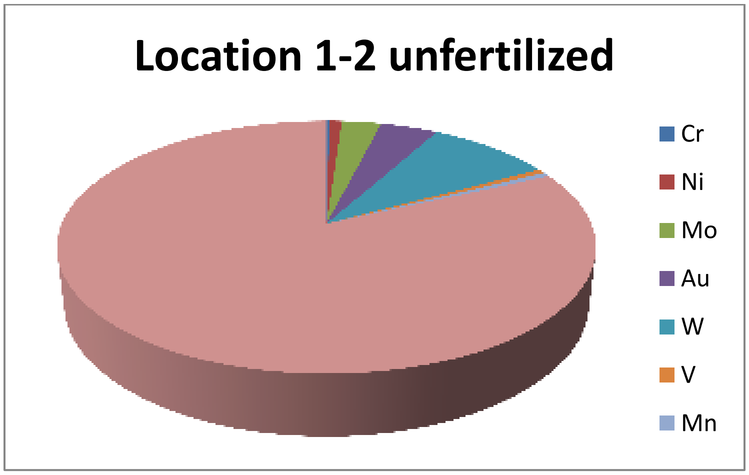


chart (4.2): location (1) – sample (2) in clay non-fertilized sample

Table (4.3): the table below shows the concentration of elements in clay non-fertilized sample (1-3)

ELE	Conc.	STD
Cr	2.23	0.74
Ni	1.14	0.390
Mo	1.85	0.091
Au	1.25	0.158
W	4.96	0.699
V	1.50	0.187
Mn	1.69	0.224
Fe	80.43	0.667

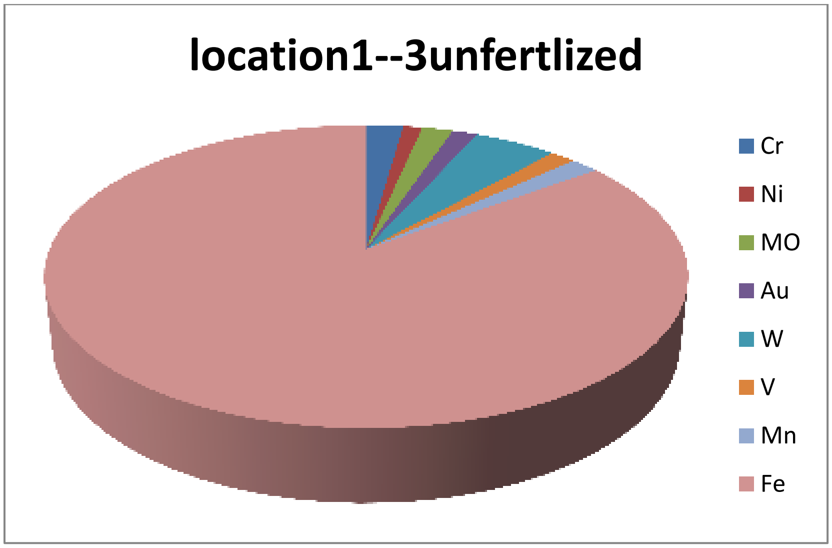


chart (4.3): location (1) – sample (3) in clay non-fertilized sample

Table (4.4):the table below shows the concentration of elements in clay non-fertilized sample (1-4)

ELE	Conc.	STD
Cr	2.03	0.103
Ni	1.20	0.351
Mo	1.00	0.120
Au	6.23	0.114
W	4.49	0.891
V	1.48	0.223
Mn	1.63	0.382
Fe	80.02	0.858

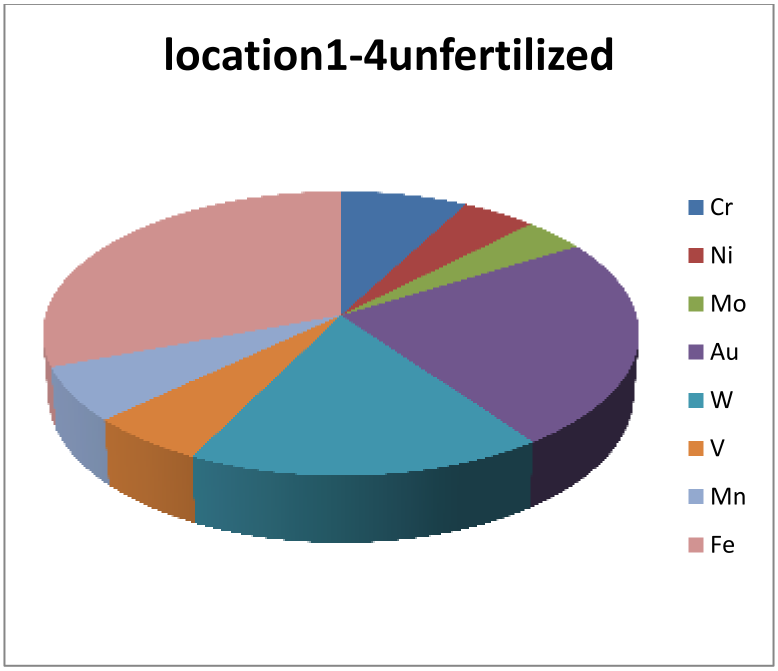


chart (4.4): location (1) – sample (4) in clay non-fertilized sample

Table (4.5): the concentration of elements in clay fertilized sample (2-1)

ELE	Conc.	STD
Cr	0.55	0.155
Ni	2.50	0.227
MO	1.11	0.144
Au	2.32	0.252
W	7.55	0.086
V	6.24	0.414
Mn	1.60	0.321
Fe	75.66	0.866

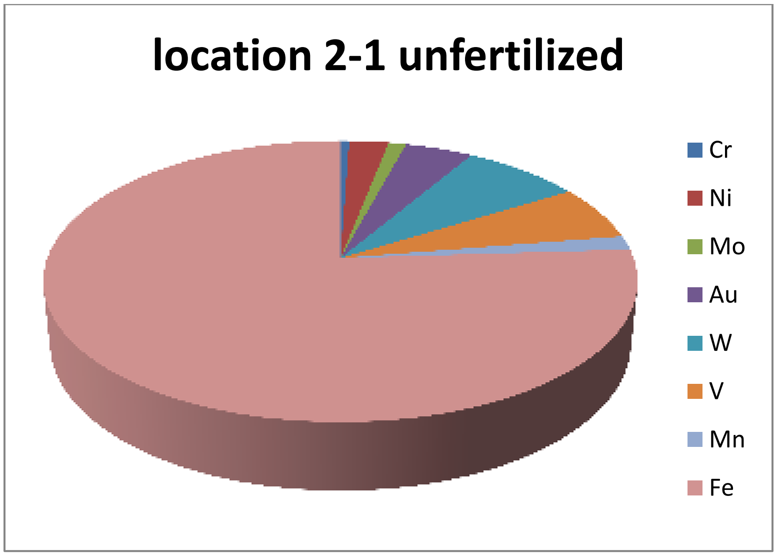


chart (4.5): location (2) – sample (1) in clay fertilized sample

Table (4.6): the table below shows the concentration of elements inclay fertilized sample (2.2)

ELE	Conc.	STD
Cr	9.33	0.018
Mn	3.02	0.018
Fe	46.72	0.050
Ni	2.88	0.002
AU	4.77	0.004
Zn	0.54	0.001
Pb	8.82	0.003

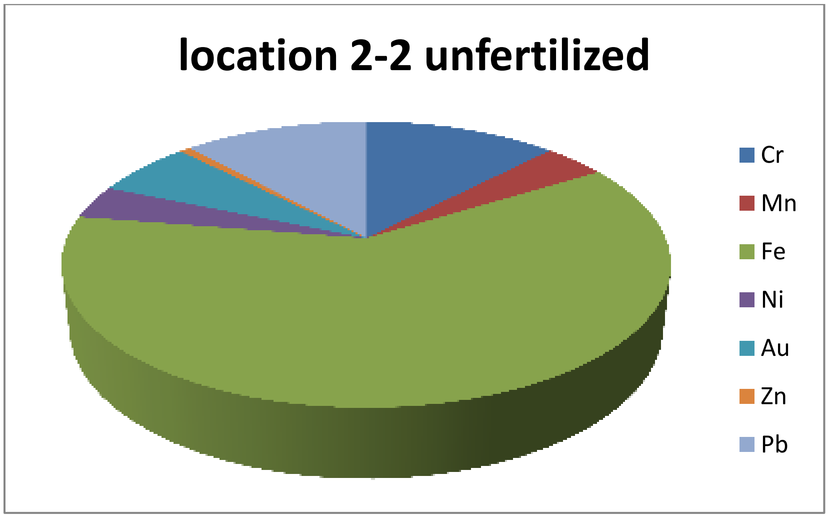


chart (4.6): location (2) – sample (2) in clay fertilized sample

Table (4.7): the table below shows the concentration of elements in clay fertilized sample (2.3)

ELE	Conc.	STD
Cr	0.55	0.037
Ni	0.90	0.276
Mo	2.26	0.115
Au	2.23	0.176
W	8.23	0.895
V	1.65	0.240
Mn	9.42	0.228
Fe	73.95	0.682

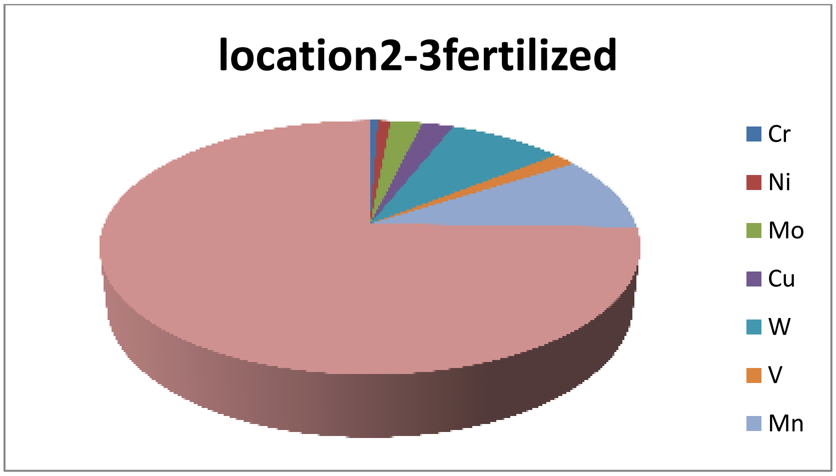


chart (4.7): location (2) – sample (3) in clay fertilized sample

Table (4.8): the table below shows the concentration of elements inclay fertilized sample (2-4)

ELE	Conc.	STD
Cr	5.26	0.170
Ni	3.00	0.298
Mo	2.54	0.139
AU	7.38	0.259
W	8.98	1.130
V	0.40	0.243
Mn	1.00	0.396
Fe	71.03	0.936

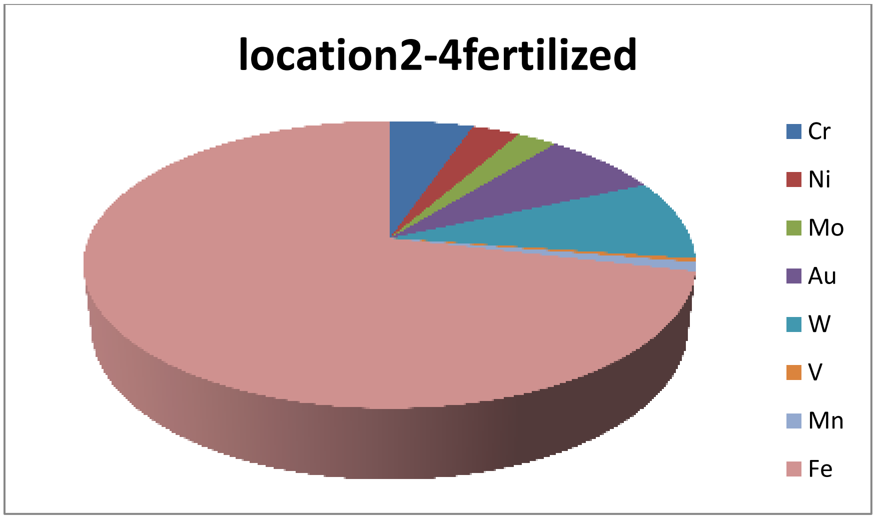


chart (4.8): location (2) – sample (4) in clay fertilized sample

Table (4.9): the table below shows the concentration of elements in sand fertilized sample (3.1)

ELE	Conc.	STD
Cr	2.09	0.158
Ni	3.75	0.428
Mo	2.11	0.129
Au	1.05	0.212
W	6.22	1.008
V	1.89	0.317
Mn	2.91	0.334
Fe	68.77	0.883

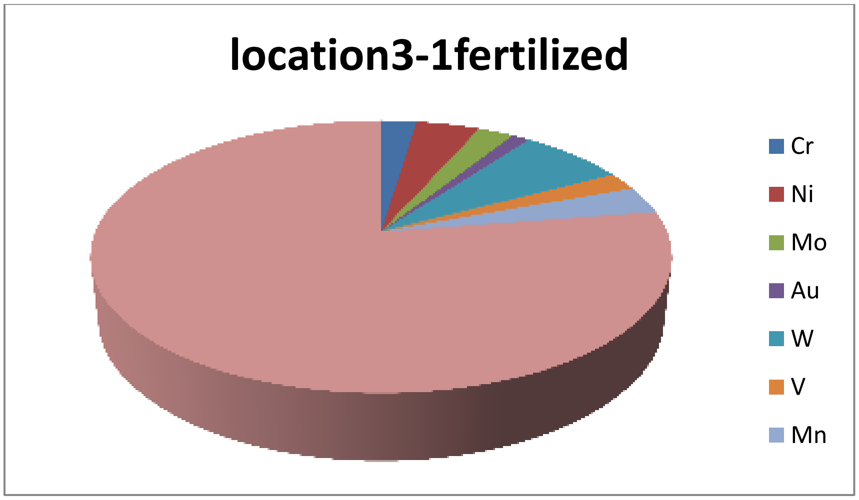


chart (4.9): location (3) – sample (1) in sand fertilized sample

Table (4.10):the table below shows the concentration of elements in sand fertilized sample (3.2)

ELE	Conc.	STD
Cr	2.09	0.156
Ni	3.33	0.539
Mo	5.00	0.157
Au	0.21	0.265
W	4.52	1.246
V	0.31	0.449
Mn	0.92	0.363
Fe	80.09	1.056

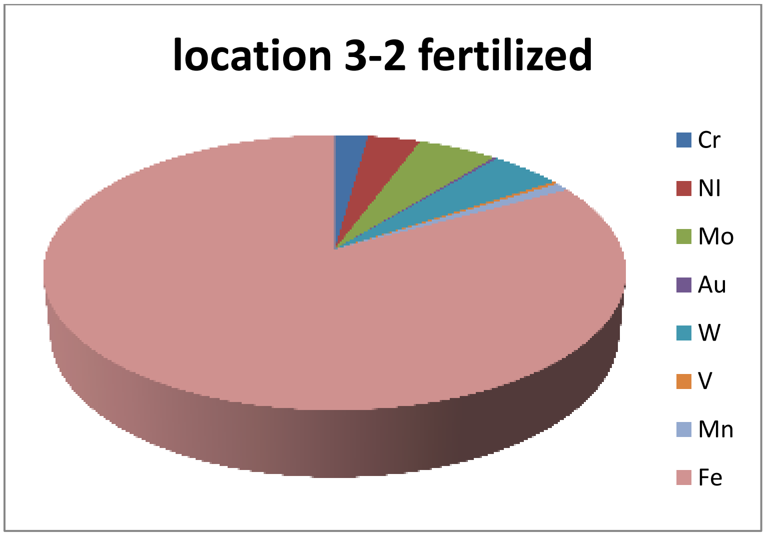


chart (4.10): location (3) – sample (2) in sand fertilized sample

Table (4.11): the table below shows the concentration of elements in sand fertilized sample (3.3)

ELE	Conc.	STD
Cr	50.31	1.022
Ni	4.62	0.500
Mo	1.26	0.041
Au	2.02	0.057
W	5.37	0.304
V	7.24	0.164
Mn	2,56	0.553
Fe	36.48	1.034
Co	2.83	0.272
Nb	1.25	0.043
	0.21	0.187

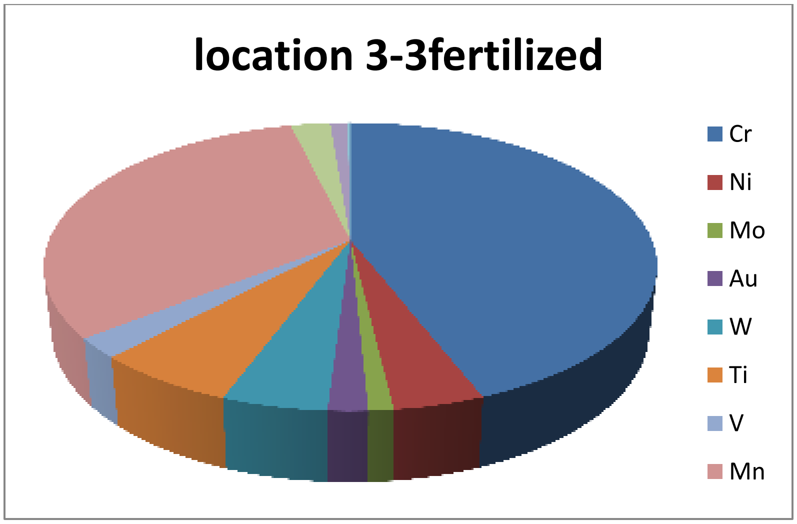


chart (4.11: location (3) – sample (3) in sand fertilized sample

Table (4.12): the table below shows the concentration of elements in sand fertilized sample (3.4)

ELE	Conc.	STD
Cr	0.07	0.028
Mn	0.00	0.018
Fe	0.45	0.018
Au	2.33	0.002
Zn	0.43	0.002
Pb	1.25	0.002

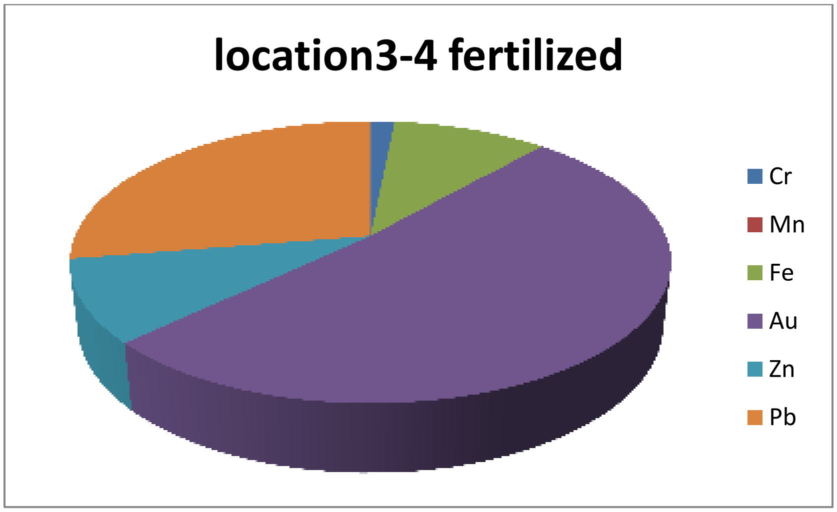


chart (4.12): location (3) – sample (4) in sand fertilized sample

Table (4.13): the table below shows the concentration of elements in sand non-fertilized sample (4.1)

ELE	Conc.	STD
Cr	0.04	0.021
Mn	0.00	0.013
Fe	1.63	0.042
Ni	1.27	0.001
Au	4.2	0.001
Zn	0.23	0.002
Pb	2.99	0.002

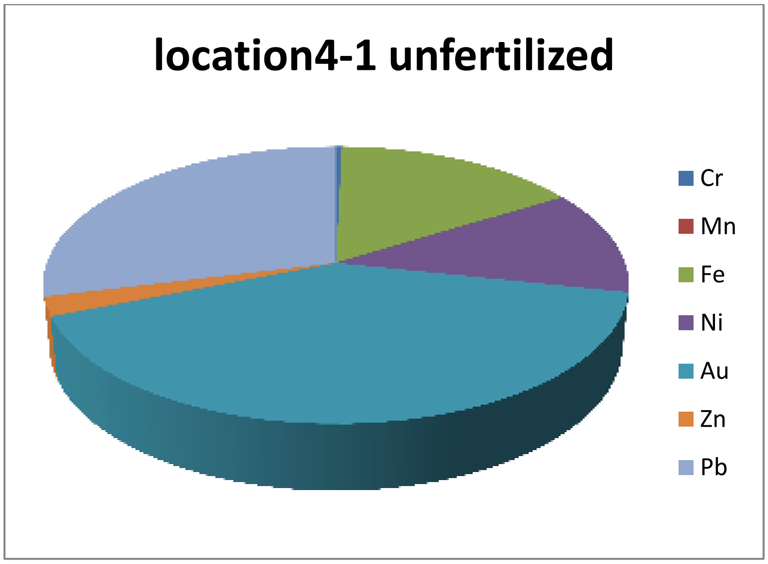


chart (4.13): location (4) – sample (1) in sand non-fertilized sample

Table (4.14): the table below shows the concentration of elements in sand non-fertilized sample (4.2)

ELE	Conc.	STD
Cr	0.00	1.#00
Ni	0.59	1.#00
Mo	1.70	1.#00
Au	5.34	1.#00
W	8.62	1.#00
V	0.93	1.#00
Mn	0.90	1.#00
Fe	80.37	1.#00
Pb	3.01	1.#00

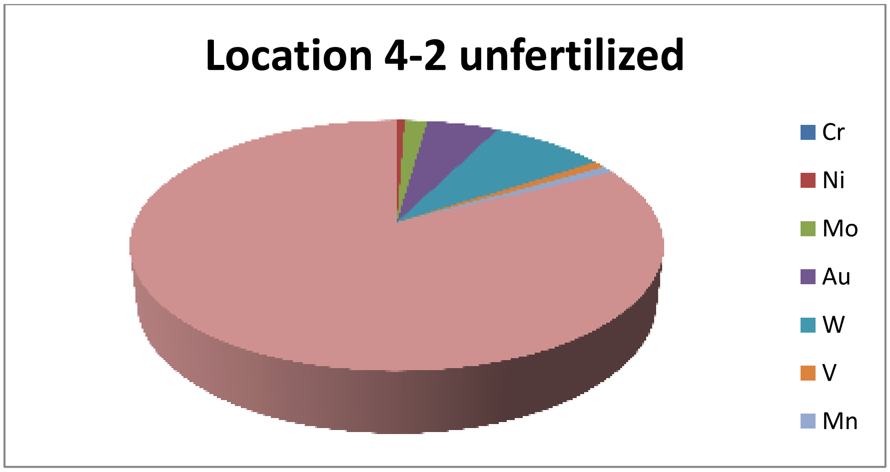


chart (4.14): location (4) – sample (2) in sand non-fertilized sample

Table (4.15):the table below shows the concentration of elements in sand non-fertilized sample (4.3)

ELE	Conc.	Std
Cr	0.00	1.#00
Ni	0.00	1.#00
Mo	2.02	1.#00
Au	3.22	1.#00
W	10.83	1.#00
V	1.22	1.#00
Mn	0.52	1.#00
Fe	86.21	1.#00
Pb	2.01	1.#00

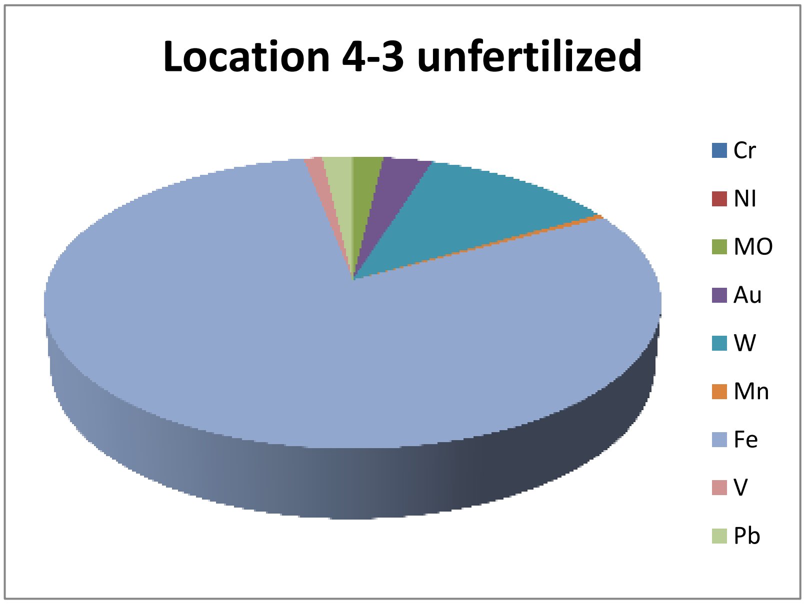
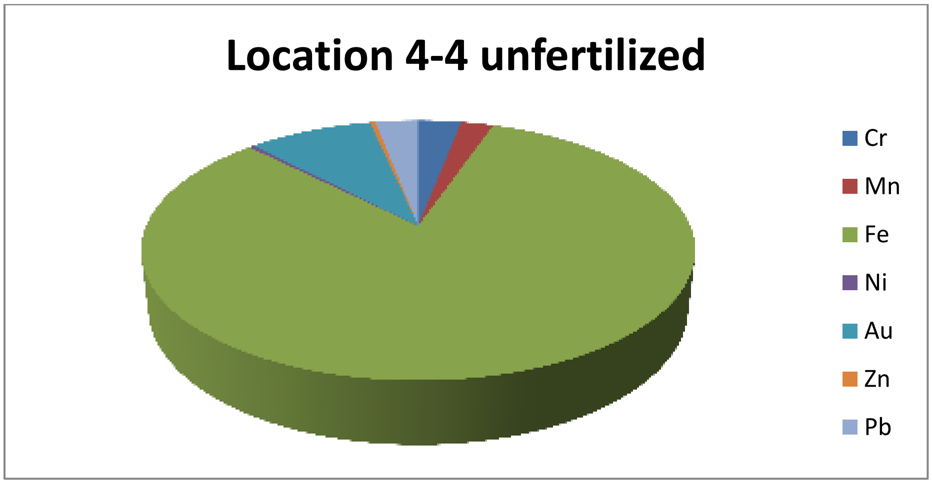


chart (4.15): location (4) – sample (3) in sand non-fertilized sample

Table (4.16):the table below shows the concentration of elements in sand non-fertilized sample (4.4)

ELE	Conc.	STD
Cr	0.08	0.001
Mn	0.06	0.026
Fe	2.19	0.051
Ni	0.01	0.003
AU	0.23	0.002
Zn	0.01	0.001
Pb	0.08	0.003



chart(4.16): location (4) – sample (4) in sand non-fertilized sample

4.3 LIBS results: The Table Below Shows the Data of Concentration the Intensity of Line Spectrometer for Elements

Table (4.17)the table below shows the Intensity of elements in (fertilized)clay sample (2.1)

ƛ	Intensity	Elements
4062.5	143	U II
4105.142	143	V I
4211.7475	142	Dy I
4830.0585	141	Mo I
4894.6217	145	Cl II
6283.445	143	Xe II
6542.8812	150	Xe II
6585.493	141	C II
7566.263	141	Pb II
7655.100	141	Mg I

Table (4.18)the table below shows the Intensity of elements in (un-fertilized) clay sample (1.1)

ƛ	Intensity	Elements
4062.531	142	U II
4068.629	142	Au I
4234.134	142	Mn I
48689. 591	149	Cl II
5012.620	142	AgII
6283.533	141	Xe II
6543.028	144	NaII
7581.009	141	F I
8851.923	142	Xe I
10478.36	141	Ar I
10547.76	142	CuII

Table (4.19) the table below shows the Intensity of elements in (un-fertilized) clay sample (1.3)

ƛ	Intensity	Elements
4916.586	153	Ar II
5106.661	141	Cu II
6496.033	143	Xe I
6567. 548	149	Au I
6661.538	144	Ca I
6849.519	141	Pt II
8191.947	141	Cl I
9489.423	142	F I
10478.36	141	Ar I
10547.78	142	Cu II

Table (4.20) the table below shows the Intensity of elements in (un-fertilized) clay sample (1.2)

ƛ	Intensity	Elements
4115.625	143	Dy II
4234.13	142	Mn I
4800.120	141	N I
4916.586	145	Ar II
6283.533	143	Xe II
6308.052	141	K II
6543.028	152	Rb II
6520.552	143	Na II
6590.024	141	C II
7556.490	142	Pb II
7650.48	141	Mg I

Table (4.21) the table below shows the Intensity of elements in (un-fertilized) clay sample (1.4)

ƛ	Intensity	Elements
4728.605	142	Ar II
4847.115	141	Be II
4894.110	149	Ca I
6142.548	141	C I
6543.028	146	Rb II
6567.548	153	Au I
661.538	142	Xe I
6849.519	143	Pt I
7603.485	142	K I
8851.923	142	Xe I
10572.355	141	U I

Table (4.22) the table below shows the Intensity of elements in (fertilized) clay sample (2.2)

ƛ	Intensity	Elements
4894.110	150	Ti I
4988.100	143	TL II
6283.533	142	Xe II
6543.028	144	Na II
6496.033	143	XeI
6684.014	142	Y I
7343.990	143	Br I
7603.485	142	Ca II
10547.836	141	Cu II

Table (4.23) the table below shows the Intensity of elements in (fertilized) clay sample (2.3)

ƛ	Intensity	Elements
4115.625	142	Dy II
4916.586	155	Ar II
6543.028	144	Na II
6590.024	141	C II
7109.014	142	Pt I

Table (4.24) the table below shows the Intensity of elements in (fertilized) clay sample (2.4)

ƛ	Intensity	Elements
4894.110	150	Cl II
5012.620	142	Ag II
5176.081	141	Sm I
5129.086	140	Pm I
6567.548	156	Au I
6520.552	148	Na II
6661.538	144	Ca I
6827.043	143	Cs I
7082.019	146	Pt I
7581.009	141	F I
8334.975	142	Cl I
10572.355	143	U I

Table (4.25)the table below shows the Intensity of elements in (fertilized) sand sample (3.1)

ƛ	**Intensity**	**Elements**
4068.629	143	Au II
4162.620	145	U I
4115.625	146	Dy II
4916.586	158	Ar II
5176.081	141	Sm I
6283.533	141	Xe II
6520.552	145	Na II
6567.548	150	Au I
7062.019	143	Hg I

Table (4.26)The table below shows the Intensity of elements in (fertilized) sand sample (3.2)

ƛ	**Intensity**	**Elements**
4068.629	142	AU I
4062.531	142	U II
4234.134	142	Mn I
4258.653	142	Ar I
4869.591	149	Cl II
6283.533	141	Xe II
6567.548	142	Au I
6661.538	141	Ca I
7343.990	141	Br I
10547.836	142	Cu II

Table (4.27)The table below shows the Intensity of elements in (fertilized) sand sample (3.3)

ƛ	Intensity	Elements
4894.110	144	Cl II
6283.533	142	Xe II
6543.028	142	RbII
6567.548	142	Au I
6661.538	143	Ca I
7062.019	142	Hg I
7603.485	142	Ca II
7628.004	141	Ar I

Table (4.28) the Intensity of elements in (fertilized) sand sample (3.4)

ƛ	Intensity	Elements
4258,653	141	Ar I
4916.586	147	Ar II
6283.533	141	Xe II
6543.028	144	Rb II
7084.495	142	Pt I
7581.009	142	F I
8169.471	141	N I
8169.471	141	N I
10384.357	141	Xe II

Table (4.29)The table below shows the Intensity of elements in (un-fertilized) sand sample (4.1)

ƛ	Intensity	Elements
4916.586	152	Ar II
5294.591	141	Fe I
6543.028	144	Xe II
6567.548	150	Au I
6661.538	144	CaI
6849.519	143	Pt I
7084.495	148	Pt I
8169.471	143	N I
8191.947	141	Cl I
10572.355	142	U I

Table (4.30)The table below shows the Intensity of elements in (un-fertilized) sand sample (4.2)

ƛ	Intensity	Elements
4916.586	149	Ar II
4988.100	144	Tl II
5106.610	142	Cu I
5129.086	142	Pm I
6283.533	143	Xe II
6567.548	142	AuI
6637.019	141	Br I
6084.495	144	Pt I
7603.485	144	Ca II
8160.471	142	N I
8160.471	142	N I
9489.423	142	F I

Table (4.31)The table below shows the Intensity of elements in (un-fertilized) sand sample (4.3)

ƛ	Intensity	Elements
4115.625	141	Dy II
4140.144	142	Fe I
4894.110	151	Ti I
5106.610	146	Cu I
5129.086	143	Pm I
6283.533	141	Xe II
6543.028	149	Na II
6567.548	145	Au I
6614.543	142	N II
6614.543	142	N I
7368.509	141	Mg I

Table (4.32)The table below shows the Intensity of elements in (un-fertilized) sand sample (4.4)

ƛ	Intensity	Elements
4046.153	141	Au I
4115.625	143	Dy II
4115.625	143	Dy II
4728.605	141	Ar II
4894.110	153	Ti I
5460.069	141	Si I
6520.552	141	Xe II
6567.548	141	Au I
6661.538	142	Ca I
7109.014	141	Pt I
10547.836	141	Cu II

4.4 AAS: The Results of AAS Which Shows the Concentration of Elements AreShown Here

Table (4.33)The table below shows the concentration of elements in (un-fertilized) clay sample (1.1)

Element	Concentration per PPM
Au	3,8
Fe	62.87
Ni	0.01
Pb	6.52

Table (4.34)The table below shows the concentration of elements in (un-fertilized) clay sample (1.2)

Element	Concentration per PPM
Cu	4.14
Fe	81.27
Ni	0.90
W	9.14

Table (4.35) The table below shows the concentration of elements in (un-fertilized) clay sample (1.3)

Element	Concentration per PPM
Au	1.14
Fe	81.20
Ni	1.24
W	4.9.

Table (4.36) The table below shows the concentration of elements in (un-fertilized) clay sample (1.4)

Element	Concentration per PPM
Au	6.25
Fe	79.20
Ni	1.22
W	4.4

Table (4.37)The table below shows the concentration of elements in (fertilized) clay sample (2.1)

Element	Concentration per PPM
Au	2.20
Fe	75.33
Ni	2.35
W	6.52
Cr	1.46

Table (4.38) The table below shows the concentration of elements in (fertilized) clay sample (2.2)

Element	Concentration per PPM
Au	4.73
Fe	42.33
Ni	2.80
Pb	8.76
Cr	9.36

Table (4.39)The table below shows the concentration of elements in (fertilized) clay sample (2.3)

Element	Concentration per PPM
Au	2,26
Fe	72.03
Ni	0.93
Pb	8.72
Cr	0.54
W	8.21

Table (4.40)The table below shows the concentration of elements in (fertilized) clay sample (2.4)

Element	Concentration per PPM
Au	7,36
Fe	62.87
Ni	3.01
W	8.96
Cr	5.25

Table (4.41)The table below shows the concentration of elements in (fertilized) sand sample (3.1)

Element	Concentration per PPM
Au	1,08
Fe	67.87
Ni	3.77
Pb	6.52
Cr	2.0 6
W	6.21

Table (4.42)The table below shows the concentration of elements in (fertilized) sand sample (3.2)

Element	Concentration per PPM
Au	0.24
Fe	80.07
Ni	3.30
W	4.44
Cr	2.03

Table (4.43)The table below shows the concentration of elements in (fertilized) sand sample (3.3)

Element	Concentration per PPM
Au	2.04
Fe	37.20
Ni	4.64
W	5.39.
Cr	5.62

Table (4.44) The table below shows the concentration of elements in(fertilized)sand sample (3.4)

Element	Concentration per PPM
Au	2.35
Fe	0.63
Cr	0.04

Table (4.45)The table below shows the concentration of elements in (un-fertilized) sand sample (4.1)

Element	Concentration per PPM
Au	4,01
Fe	22.03
Ni	1.33
Pb	2.82
Cr	0.06

Table (4.46) The table below shows the concentration of elements in (un-fertilized) sand sample (4.2)

Element	Concentration per PPM
Au	5,36
Fe	80.7
Ni	5.51
W	8.55
Cr	0.00

Table (4.47)The table below shows the concentration of elements in (un-fertilized) sand sample (4.3)

Element	Concentration per PPM
Au	3.20
Fe	85.33
Ni	0.35
W	10.72
Cr	0.00

Table (4.48) The table below shows the concentration of elements in (un-fertilized) sand sample (4.4)

Element	Concentration per PPM
Au	0.21
Fe	42.33
Ni	0.03
Pb	0.06
Cr	0.06

Table (4.49) Comparison Between XRF, AAS and LIBS

In the table below comparison was made between XRF, AAS and LIBS

Sample	Method	Fe	Cr	Mn	Ni	Au	Zn	Mo	Cu	W	V	Pb
1-1	**XRF**	69.87	1.04	3.04	0.01	3.4	3.88	_	_	_	_	7.34
	AAS	62.87	_	_	0.01	3.8	_	_	_	_	_	6.52
1-2	**XRF**	84.24	0.23	0.56	0.90	_	_	2.91	4.23	9.13	0.57	_
	AAS	81.27	_	_	0.90	_	_	_	4.14	9.14	_	_
1-3	**XRF**	80.43	2.23	1.69	1.14	1.25	_	1.85	_	4.96	1.50	_
	AAS	81.20	_	_	1.24	1.14	_	_	_	4.9	_	_
1-4	**XRF**	80.02	2.03	1.63	1.20	6.23	_	1.00	_	4.49	1.48	_
	AAS	79.20	-	_	1.22	6.25	_	_	_	4.4	_	_
2-1	**XRF**	75.66	0.55	1.60	2.50	2.32	_	1.11	_	7.55	6.24	_
	AAS	75.33	1.46	_	2.35	2.20	_	_	_	6.52	_	_
2-2	**XRF**	46.72	9.33	3.02	2.88	4.77	0.54	_	_	_	_	8.82
	AAS	42.33	9.36	_	2.80	4.73	_	_	_	_	_	8.76
2-3	**XRF**	73.95	0.55	9.42	0.90	2.23	_	2.26	_	8.23	1.65	_
	AAS	72.03	0.54	_	0.93	2.26	_	_	_	8.21	_	8.72
2-4	**XRF**	71.03	5.26	1.00	3.00	7.38	_	2.54	_	8.98	0.40	_
	AAS	62.87	5.25	_	3.01	7.36	_	_	_	8.96	_	-

Sample	Method	Fe	Cr	Mn	Ni	Au	Zn	Mo	Cu	W	V	C0	Ti	Nb	Pb
3-1	**XRF**	68.77	2.09	2.91	3.75	1.05	-	2.11	_	6.22	1.89				-
	LIBS														
	AAS	67.87	2.0 6	_	3.77	1.08	_	_	_	6.21	_				6.52
3-2	**XRF**	80.09	2.09	0.92	3.33	0.21	_	5.00	-	-	0.31				_
	LIBS														
	AAS	80.07	2.03	_	3.30	0.24	_	_	-	4.44	_				_
3-3	**XRF**	36.48	5.31	2.56	4.62	2.02	_	1.62	_	5.37	7.24		0.21		_
	LIBS														
	AAS	37.20	5.62	_	4.64	2.04	_	_	_	5.39	_	-	-	-	-_
3-4	**XRF**	0.45	0.07	0.00	-	2.33		-	-	-	-	-	-	-	
	LIBS														
	AAS	0.63	0.04			2.35	_	_	_	4.4	_	-	-	-	_
4-1	**XRF**	1.63	0.04	0.00	1.27	4.2	0.23	-	_	-	-	-	-	-	2.99
	LIBS														
	AAS	22.03	0.06	_	1.33	4.01	_	_	_	-	_	-	-	-	2.82
4-2	**XRF**	80.37	0.00	0.90	0.59	5.43	-	1.70	_	8.62	0.93	-	-	-	3.01
	LIBS														
	AAS	42.33	9.36	_	2.80	4.73	_	_	_	_	_				8.76
4-3	**XRF**	86.21	0.00	0.52	0.00	3.22	_	2.02	_	10.83	1.22	-	-	-	2.01
	LIBS														
	AAS	85.33	0.00	_	0.35	3.20	_	_	_	10.72	_				
4-4	**XRF**	2.19	0.08	0.06	0.01	0.23	0.01	-	_						0.08
	LIBS														
	AAS	80.7	0.00	_	5.51	5.36	_	_	_	8.55	_				-

Table (4.50) the concentration of elements in (un-fertilized) clay sample (1.1)

sample	method	U!!	Au !	Mn!	Cl!!	Ag!!	Xe!!	Na!!	F!	Xe!	Ar!	Cu!!
1-1	**LIBS**	9.05	9.05	9.05	9.50	9.05	8.99	9.18	8.99	9.05	8.99	9.05

Table (4.51) the concentration of elements in (un-fertilized) clay sample (1.2)

sample	method	Dy!!	N!	Mn!	C!!	K!!	Xe!!	Na!!	Rb!!	Pb!!	Ar!!	Mg!
1-2	**LIBS**	9.08	8.96	9.02	8.96	8.96	9.08	9.08	9.65	9.02	9.21	8.96

Table (4.52) the concentration of elements in (un-fertilized) clay sample (1.3)

sample	method	Cu!!	Au!	Ca!	Pt!	Cl!	Xe!	F!	Ar!	Cu!!	Ar!!
1-3	**LIBS**	9.81	10.3	10.02	9.8	9.8	9.95	9.08	9.8	9.8	10.64

Table (4.53) the concentration of elements in (un-fertilized) clay sample (1.4)

sample	method	Be!!	Ca!	Xe!	C!	K!	Xe!	Au!	Rb!!	Pt!	Ar!!	U!
1-4	**LIBS**	8.91	9.4	9.9	8.91	8.97	8.97	9.6	9.22	9.03	8.97	8.91

Table (4.54) the concentration of elements in (fertilized) clay sample (2.1)

sample	method	U!!	Dy!	C!!	Pb!!	Xe!!	Xe!!	Mo!	Cl!	Mg!	V!
2-1	**LIBS**	10	9.9	9.8	9.86	10	10.4	9.8	10.1	9.86	10

Table (4.55) the concentration of elements in (fertilized) clay sample (2.2)

sample	method	Ti!	Tl!!	Xe!!	Na!!	Xe!	Y!	Br!	Ca!!	Cu!!
2-2	**LIBS**	11.6	11.08	11	11.1	11.08	11	11.08	11	10.9

Table (4.56) the concentration of elements in (fertilized) clay sample (2.3)

sample	method	Dy!!	Ar!!	Na!!	C!!	Pt!
2-3	**LIBS**	19.6	21.4	19.8	19.4	19.6

Table (4.57) the concentration of elements in (fertilized) clay sample (2.4)

sample	method	Cl!!	Ag!!	Sm!	Pm!	Au!	Na!!	Ca!	Cs!	Pt!	F!	U!	Cl!
2-4	**LIBS**	8.6	8.1	8.12	8.06	8.9	8.5	8.29	8.2	8.4	8.1	8.23	8.17

Table (4.58) the concentration of elements in (fertilized)sand sample (3.1)

sample	method	Au!	U !	Dy!!	Ar!!	Sm!	Xe!!	Na!!	Au!	Hg!
3-1	**LIBS**	10.8	11	11.1	12	10.7	10.7	11.05	11.4	10.8

Table (4.59) the concentration of elements in (fertilized) sand sample (3.2)

sample	method	Au!	U!!	Mn!	Ar!	Cl!!	Xe!!	Au!	Ca!	Br!	Cu!!
3-2	**LIBS**	9.9	9.97	9.9	9.9	10.4	9.9	9.9	9.91	9.9	9.91

Table (4.60) the concentration of elements in (fertilized) sand sample (3.3)

sample	method	Cl!!	Xe!!	Rb!!	Au!	Ca!	Hg!	Ca!!	Ar!
3-3	**LIBS**	12.6	12.4	12.4	12.5	12.6	12.5	12.4	12.3

Table (4.61) the concentration of elements in (fertilized) sand sample (3.4)

sample	method	Ar!!	Ar!!	Xe!!	Rb!!	Pt!	F!	N!	N!	Xe!
3-4	**LIBS**	11	11.4	11.1	11.2	11	11.1	11	11	11.1

Table (4.62) the concentration of elements in (un-fertilized) sand sample (4.1)

sample	method	Ar!!	Fe !	Xe!!	Au!	Ca!	Pt!	Pt!	N!	Cl!	U!
4-1	**LIBS**	10.4	9.7	9.9	10.3	9.9	9.8	10.2	9.8	9.7	9.8

Table (4.63) the concentration of elements in (un-fertilized) sand sample (4.1)

sample	method	Ar!!	Tl!!	Cu!	Pm!	Xe!!	Au!	Br!	Pt!	Ca!!	N!	F!	N!
4-2	**LIBS**	8.6	8.3	8.2	8.1	8.3	8.2	8	8.4	8.3	8.1	8.2	8.1

Table (4.64) the concentration of elements in (un-fertilized) sand sample (4.2)

sample	method	Dy!!	Fe!	Ti!	Cu!	Pm!	Xe!!	Na!!	Au!	N!!	Nr!!	Mg!
4-3	**LIBS**	8.9	8.91	9.5	9.2	9	8.9	9.4	9.1	8.9	8.9	8.9

Table (4.65) the concentration of elements in (un-fertilized) sand sample (4.3)

sample	method	Au!	Dy!!	Dy!!	Ar!!	Ti!	Si!!	Xe!!	Au!	Ca!	Pt!	Cu!!
4-4	**LIBS**	8.9	9.1	9.1	8.9	9.7	8.99	8.9	9	9.1	8.9	9.1

4.5 Discussion

In this work it is desired to compare between the concentration of non-fertilized and fertilized clay and sand samples for two regions. the first region soil is clay while the second region soil is sand one also needs to compare between three spectrometer techniques which are XRF, AAS and LIBS.

In view of tables (4.13) and (4.15) the average concentration ofCr,Mn, Ni,Au is more in fertilized than non-fertilized according to XRF and AAS results.However, the average concentration of Fe in non-fertilized clay samples is higher than fertilized. This may be attributed to the fact that clay, sand is rich in Fe while the fertilizers itself consists mainly of organic material thus is poor in Fe. thus it addition to clay samples to become fertilized decrease Fe concentration.

In some clay samples Pb appear but with higher concentration in fertilized clay samples according to XRF and AAS spectrometer results. This may be attributed to the fact that fertilizers are produced in side industrial areas which are highly contaminated with Pb.

The results of LIBS for non-fertilized and fertilized clay samples gives concentration of almost all elements in the range of 8-12. there are no elements common for most fertilized and non-fertilized clay samples. most elements detected by LIBS are absent in XRF and AAS results also most detected elements by XRF and AAS does not exist in LIBS.

This make LIBS analyses less reliable and less accurate results. table (4.14) shows the results of XRF and AAS for fertilized and non-fertilized sand samples. the average concentration of Cr, Mn, Ni in fertilized sand are higher that of non-fertilizedsand.

However, for Au, Pb the average concentration of them is higher in non-fertilized sand compared to fertilized sand samples. This means that the fertilizer is poor in Au and Pb.

The LIBS again gives less reliable andless accurate results as shown by table (4.16).

In view of tables (4.13) and (4.14) a direct compare on between XRF and AAS spectrometers indicates that XRF techniques gives more accurate results compared to AAS results. The XRF spectrometer detect elements like Mo, W, V, Co, Ti, Nb which cannot be detected by AAS. It is very interesting to note that some elements like Co, Ti, Nb are detected in sand samples only.

4.6 Conclusion

The results of XRF, AAS and LIBS shows that the fertilization process only produce small change in the elements content of clay and sand samples.

Sand samples consists of elements like Co, Ti, Nb which does not exist in clay samples. The study indicates that XRF is more sensitive than AAS and LIBS techniques.

The poorest technique is LIBS one

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4.7 Recommendations

1-XRF is the most powerful technique for determination of concentration of elements.

2-AAS can be utilized as a confirming technique to the XRF.

3-the fact the use of chemical fertilizer does not change the chemical structure of the soil desiccates using organic fertilizers.

4-clay soil is rich in important vital elements thus are more suitable to be used for better plant growing.

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