Sudan University of Science and Technology

College of Graduate Studies

Analysis of Toxic Elements, Heavy and Radioactive in Kadugli Soil using Spectroscopic Techniques

تحليل العناصر السامة والثقيلة والمشعة في تربة كادقلي باستخدام تقنيات التحليل الطيفي

Thesis Submitted for the Fulfillment of the Requirements for the Degree of Doctor of the Philosophy (PhD) in Physics

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الآية

بسم الله الرحمن الرحيم

قال الله تعالي :

" قَالُواْ سُبْحَانَكَ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَّمْتَنَا إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ "

صدق الله العظيم

"البقرة:الاية:32"

Dedication

To those who brought me up and taught me and still carry from
their source the meaning of life
Fondler my Mother
Loving my Father
To the King of men's determination and brother's tenderness,
and loyalty to a friend
Dear husband
To my children who have born with obstacles of this journey

Acknowledgement

The beginning and end of gratitude is to God Almighty, by whose grace good deeds are accomplished and to Him all things Praise be to God, as it should be to his Majesty and His great authority, and prayers and peace be upon our master Mustafa, say: (Seek Knowledge from the cradle to the grave) , Thanks be to God who enabled me to complete this letter , I also extend my sincere thanks to sudan university of Science and Technology, beacon of science and Knowledge, I extend my sincere thanks, appreciation and respect to Dr . **Ahmad EL- Hassan** and **Abdel- Sakhi**, Candles that light our paths of Knowledge, and thanks to the savant **Professor Khaled Muhammad Haroun** To honors and favors him for supervising this study his advice and follow-up had a significant impact on the completion of this research.

Abstract

There is a clear interest in recent years to determine the concentrations of radioactive, toxic and heavy elements in the soil of areas of traditional mining, and find out if these concentrations are within the safe limit or exceed the safe limit, considers Laser Induced Breakdown Spectroscopy (LIBS) and Inducted Coupled Plasma (ICP) it is one of the most promising, fast and accurate methods for analyzing soil samples This study aimed, Spectroscopic techniques were applied to detect and determine the concentrations of different elements. The mean aim of this research was used Laser Induced Breakdown Spectroscopy (LIBS) and Inducted Coupled Plasma (ICP) to detect and calculate the concentrations of different elements. and to identify the toxic, heavy and radioactive elements in Kadugli city by Laser Induced Breakdown Spectroscopy (LIBS) and to determine the concentrations of toxic, heavy and radioactive elements in Kadugli city by Inductivity Coupled Plasma (ICP),and to calculate concentration of toxic, heavy and radioactive elements detected by LIBS system using calibration function, and to determine relative stander deviation and limit of detection of element in all samples. And to explain the reasons for the increase in the incidence of old humans' disease and providing the yellowish color of the teeth, and respiratory problems of newborns. fifteen surface soil samples that collected from Kadugli city, all samples were taken with a depth of ten centimeters at a distance of two linear Kilometers inside city, These samples were kept in plastic tubes with a tight lid After detection all samples contains four toxic elements (Sulfur(S), Arsenic (As), Cerium (Ce) and Iodine(I), five heavy elements (Sodium (Na), Magnesium (Mg), Phosphorus(P), Titanium (Ti) and Barium (Ba), Erath’s Metal elements (Titanium (Ti), Iron (Fe) , Manganese (Mn) ,Barium (Ba) and Magnesium (Mg)) in addition to one radioactive element (Rubidium (Rb).The average concentration for (Ti) was33.4 ppm , 6.4 ppm for (Fe) , 2.3 ppm for (Mn) , 3254 ppm for (Ba) , 53.2

ppm for (Mg) ,3521 ppm for (Na), 481.3 ppm for (Ce),4652 ppm for (P), 6241 ppm for (I) and 33.4 for (Rb) . The accuracy of LIBS system in range of (0.967 and 0.997). The concentration of detected elements presents in soil samples have low value, in a previous study in 2015, after analyzing the soil, it was found that it contains the following heavy metals (Nickel (Ni), Cadmium (Cd), Chromium (Cr), Lead (Pb)). in a previous study in 2002, after analyzing the soil, it was found that it contains the following heavy and toxic metals (Chromium (Cr), Lead (Pb), Zinc (Zn), Cobalt (Co), Mercuric (Hg)) and we found that LIBS system more accurate than ICP.

المستخلص

هناك اهتمام واضح في السنوات الاخيرة بتحديد تراكيز العناصر السامة والمشعة والثقيلة في تربة مناطق التعدين التقليدي ومعرفة اذا كانت هذه التراكيز في الحد الامن او تجاوزت الحد الامن يعتبر مطيافية انهيار البلازما وجهاز التحليل الطيفي لانبعاث البلازما الناتجة عن الحث و تعتبر من الطرق الواعدة والسريعة و الدقيقة والحساسة لتحليل عينات التربة. هدفت هذه الدراسة الى تطبيق تقنيات التحليل الطيفي لاكتشاف وتحديد تركيز العناصر المختلفة و ايضاً هدفت الىاستخدام مطيافية انهيار البلازما لتحديد العناصر السامة والمشعة والثقيلة . وهدفت الى استخدام جهاز التحليل الطيفي لانبعاث البلازما الناتجة عن الحث لتحديد تراكيز العناصر السامة والمشعة والثقيلة ، وحساب تراكيز العناصر السامة والمشعة والثقيلة في مطيافية انهيار البلازما باستخدام دالة المعايرة و حساب الانحراف المعياري والانحراف المعياري النسبي واقل تركيز للعنصر في كل العينات و توضيح اسباب زيادة امراض البيئة ومشاكل التنفس عند الاطفال حديثي الولادة. خمسة عشر عينة تربة سطحية تم جمعها من مدينة كادقلي جميع العينات اخذت بعمق 10سنتمتر وبعد كل عينة عن الاخرى 2 كيلومتر طولي من داخل المدينة تم حفظ العينات في انابيب بلاستيكية محكمة الغطاء . بعد عملية الكشف وجد ان كل العينات تحتوي على اربعة عناصر سامة (الكبريت S ، الزرنيخ As ، السيريوم Ce ، اليود I)،وخمسة عناصر ثقيلة (الصوديوم Na ، الماغنسيوم M g ، الفسفور P ، التيتانيوم Ti ، الباريومBa) وعناصر ارضية قلوية (التيتانيوم Ti ، الحديد Fe، المانجنيز Mn ، الباريوم Ba، الماغنسيوم Mg) بالإضافة لعنصر الربيديوم المشع Rb . كما وجد ان متوسط التركيز لعنصر التيتانيوم هو33,4 جزء من المليون و 6,4 جزء من المليون لعنصر الحديد و 2,3 جزء من المليون لعنصرالمانجنيز و 3254 جزء من المليون لعنصر الباريوم و 53,2 جزء من المليون لعنصر الماغنسيوم و 3521 جزء من المليون لعنصر الصوديوم ، كذلك دقة مطيافية انهيار البلازما في حدود 0,967 – 0,996 . وقورنت النتائج مع الدراسات السابقة وجد ان تراكيز العناصر التي تم الكشف عنها منخفضة. في دراسة سابقة في عام 2015 بعد تحليل التربة وجد انها تحتوي على العناصر الثقيلة (النيكل Ni ، الكادميوم Cd ، و السيريوم Cr ، الرصاصPb) في دراسة سابقة عام 2002 بعد تحليل عينات التربة وجد انها تحتوي على عناصر ثقيلة وسامة (الخارصين Zn ، الزئبق Hg ، الكوبالت Co ، السيريوم Cr ، الرصاصPb) بتراكيز عالية، نجد ان مطيافية انهيار البلازما ادق بكثير من جهاز ICP

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Chapter One

Introduction

1.1 Perface

spectroscopy has made an outstanding contribution to the present state of atomic and molecular physics, to chemistry, and to molecular biology. Information about structure and interaction of molecules with their surroundings may be derived in various ways from the absorption or emission spectra generated when electromagnetic radiation interacts with matter.

Wavelength measurements of spectral lines allow the determination of energy levels of the atomic or molecular system. The line intensity is proportional to the transition probability, which measures how strongly the two levels of a molecular transition are coupled [1].

Spectroscopy and photochemistry are both undergirded by the characteristic of matter to absorb radiation at specific wavelengths in the electromagnetic spectrum [2].

Spectroscopy is basically an experimental subject and is concerned with the absorption, emission or scattering of electromagnetic radiation by atoms or molecules. Electromagnetic radiation covers a wide wavelength rang, from radio waves to Gamma rays and the atoms or molecules may be in the gas, liquid or soil phase or, of great importance in surface chemistry, adsorbed on a solid surface [3].

1.2 Motivations

Negative consequences resulting from the local mining on the residents of the area, especially the newborns. The increase in environmental diseases resulting from pollution, which lead to the emergence of various diseases in the respiratory system. The spread environmental diseases are increasing in the population of the area especially the Kadugli area.

1.3 Objectives

1.3.1 General Objective

To detect and determine the concentration of toxic, heavy and radioactive elements by using spectroscopic techniques (LIBS and ICP) on the soil in Kadugli area

1.3.2 Specific Objectives

- To identify the toxic, heavy and radioactive elements in Kadugli city by Laser Induced Breakdown Spectroscopy (LIBS)

- To determine the concentrations of toxic, heavy and radioactive elements in Kadugli city by Inductivity Coupled Plasma (ICP).
- To calculate concentration of toxic, heavy and radioactive elements detected by LIBS system using calibration function.
- To determine relative stander deviation and limit of detection of element in all samples.
- To explain the reasons for the increase in the incidence of old humans' disease and providing the yellowish color of the teeth, and respiratory problems of newborns.

1.4 Methodology

Fifteen surface soil samples were collected from Kadugli city, all samples were taken from a depth of ten centimeters at a distance of two linear Kilometers. These samples were analyzed using laser Induced Breakdown Spectroscopy (LIBS) and Inductively Coupled Plasma (ICP) to calculate and measure the concentrations of toxic, heavy and radioactive elements respectively.

1.5 Thesis layout

This thesis consists of four chapters, chapter one introduction, chapter two showed theoretical background and previous studies, chapter three discussed the materials and method, finally chapter four Results, Discussion and recommendations.

Chapter Two

Theoretical Background and Previous Studies

2.1 Introduction

This chapter about elements (Toxic elements, Heavy elements, Radioactive elements) also including spectroscopy and previous studies have reviewed.

2.2 The Elements

Element is a pure chemical substance mode of one type of atom, which is known by atomic number. The elements are classified according to the effect on the environment and humans to toxic, heavy and radioactive elements [4].

2.2.1 Toxic elements

Toxic elements are chemicals and mixtures of chemicals group that put humans and other organisms at risk of death or disease or various injuries or even birth defects. Much of the definition of the main toxic elements includes at least cadmium, manganese, lead, mercury, radioactive metals and semiconductors such as arsenic and polonium. Elements that are good for plant life are Fe, Mo, Mn, Zn, Ni, Cu, V, Co, Cr but it becomes toxic if it reaches a certain level in the cell, all heavy elements are toxic if they are available in large concentrations it is the most important heavy metal associated with toxicity Pb, Cd, Ni, Hg, Cr, As [4]. The main types of toxins Corrosive toxins such as concentrated acids and alkalis. Mineral toxins such as mercury, lead, arsenic. Plant toxins such as alkaloids. Pyrotechnic toxins such as carbon monoxide, hydrogen sulfur and war gases. Animal toxins such as scorpions, snakes and spiders [5]. Toxins elements comes from different Sources such as air in our daily life, a person is exposed to inhaling many toxic compounds capable of causing harm and damage to the respiratory. The second sources sunshine although the sun is the basis of life on Earth, it is the main source of dangerous ultraviolet rays, and also Water the paint used to paint water pipes to prevent rust contains a lot of carcinogenic hydrocarbons [5]. Toxins enter the human body through the respiratory system. And the digestive system. And the skin and eyes. And fetal poison [6]. The Toxic Hazard Classification into extremely toxic, highly toxic, moderately toxic, slightly toxic, practically not toxic and relatively harmless [6]. Effect of Toxic Metals on Human Health. Metal ions such iron and copper are among the key nutrients that must be provided by dietary sources. In developing countries, there is an enormous contribution of human activities to the release of toxic chemicals, metals and metalloids into the atmosphere. These toxic metals are accumulated in the dietary articles of man. Numerous foodstuffs have been evaluated for their contributions to the recommended daily allowance both to guide for satisfactory intake and also to prevent over exposure. Further, food chain polluted with toxic metals and metalloids is an important route of human exposure and may cause several dangerous on human [7].

2.2.2 Heavy elements

Heavy elements are elements found in nature that have density greater than 5 jm\cm^3 and is non-toxic or toxic at low concentrations includes Mercury Hg, Cadmium Cd, Arsenic As, Chrome Cr, Titanium Ti, Lead Pb, Selenium Ce, Almonium AL, Barium Ba, Cadmium Cd, Copper Cu, Montanez Mn, Mercury Hg, Nickel [8]. Heavy metal pollution is often caused by human activities, it is used in various fields such as agriculture, medicine and industry. The human body contains some of these elements, such as copper and zinc, but at different rates that do not cause toxicity some elements such as Cu, Ce, Zn, are important for maintaining the metabolism of the human body [9]. copper and cesium are the most dangerous toxic elements that pollute the soil, the extraction of minerals from the mines and the resulting residues become a source of pollution to the surrounding soil. The danger of heavy elements is that they tend to accumulate. Despite the importance of heavy metals to humans, they become toxic if their concentration increases, such as Cu, Zn, Co, Ni, Cr, Mn, Cd or some other that are unnecessary and toxic at a lower concentration, such as Pb, Hg, As [10]. Cr, Fe, Cu its effect is limited to workplaces where prolonged exposure occurs to this in less danger than other elements. Magnesium is involved in bone mineralization, and protein synthesis enzymatic functions and normal muscle contraction, and neurotransmission. Arsenic is a carcinogenic and toxic element that enters the metabolism of metonin and is used for therapeutic purposes. [11]

2.2.3Radioactive elements

They are elements that contain an unstable nucleus that decays by emission of nuclear particles (alpha, beta, gamma) to reach a stable state. They are two types of radioactive elements, natural radioactive elements which are found in nature, industrial radioactive element, which are made by bombarding fixed elements with alpha or proton or neutron projectiles [12], Radioactive elements are divided into two categories according to their source. cosmic natural radioactive elements these elements are formed as a result of the interaction of cosmic rays with materials in space and this results in radioactive materials such as ^{3}H, ^{14}C, ^{7}Be, ^{22}Na,^{32}P, ^{35}S most of them are light elements and these elements are spread on the surface of the earth examples of these interactions are:

$$ {}^{1}_{1}H + {}^{1}_{1}H \rightarrow {}^{2}_{1}H + \beta^{+} + \gamma \qquad (2.1) $$

$$ {}^{2}_{1}H + {}^{1}_{1}H \rightarrow {}^{3}_{2}He + \gamma \qquad (2.2) $$

$$ {}^{3}_{2}He + {}^{3}_{2}He \rightarrow {}^{4}_{2}He + 2\,{}^{1}_{1}H \qquad (2.3) $$

$$ {}^{4}_{2}He + {}_{1}{}^{3}_{2}He \rightarrow {}^{6}_{4}Li + n \qquad (2.4) $$

$$ {}^{1}_{1}H + {}^{6}_{4}Li \rightarrow {}^{7}_{5}Be + \gamma \qquad (2.5) $$

$$ {}^{4}_{2}He + {}_{1}{}^{3}_{2}He \rightarrow {}^{6}_{4}Li + n \qquad (2.6) $$

from the previous interaction we conclude that light elements are naturally available [13] Earth's natural radioactive element, these element are found in the Earth's crust and include all materials with an atomic number greater than 83 these materials belong to the long-lived chains, the most important of these chains are the uranium 238 series and the thorium 232series, in addition to potassium40 which is found in the earth's crust with a proportion of 6% of stable potassium K^{39} Uranium 238 series This series begins with the element uranium and ends with the fixed element lead, interspersed with radon gas. Thorium 232 series This series begins with the element thorium and ends with the fixed element lead, interspersed with radon gas. Potassium 40 series The human body contains a high percentage of stable potassium K^{39} approximately equal 2.5 kjm the potassium element K^{40} is found in human body and animal and plant and is of great importance

2.2.4Industrial radioactive elements

These elements are made by bombarding non- radioactive elements with different shells, such as a neutron or a proton to turn into a radioactive element used for various purposes such as medicine, agriculture, industry and war, examples of elements that are used in medicine are ^{67}Ga, ^{201}Th, ^{123}I, ^{111}In, ^{81}Ru, ^{15}N, ^{18}F, ^{134}Cs, ^{95}Te [14]

2.3 Spectroscopy

Any matter in our universe is composed of atoms or molecules (or may be ions) or a collection of them. Each atom, molecule or ion has its unique states of energy (finger print). These energy states (levels) are, usually, represented by horizontal lines, each one represents certain probable state of energy of that matter. Actually these energy levels are the (identity) of the matter because one cannot find two matters with similar energy states. If, for any reason, the atom or the molecule exchanges energy with an external source of energy then its energy state will be changed. In this case the system suffered from (transition) in its energy states and the process is represented by vertical arrow. When the system gained external energy, the arrow is directed up and the process is named (absorption). While if the system loss energy the arrow is directed down and the process is known as (emission). Spectroscopy was originally the study of interaction between radiation and matter as a function of wavelength (λ). Historically it was referred to visible light dispersed according to its wavelength e.g. by a prism, later it expands to comprise any measurement of a quantity as a function of wavelength, frequency (υ) or energy (E) as a variable [15]

$$E = h\upsilon = \frac{hc}{\lambda} \tag{2.7}$$

Where: h : Plank's constant (6.626 x 10^{-34} J·s) υ : light wave frequency

c: speed of light (3 x 10^{8} m/s) λ : light wavelength

- **Bohr Atomic Model:** the idea that electrons move in elliptical orbits, since each orbit has a particular energy associated with it electron motion in the permitted orbits are fixed in values, i.e. quantized.
- **Electrons per shell:** the principles outlined by both the atomic Bohr model and the rules of the quantum number, only a certain amount of electron can occupy each orbital:

  $$\mathbf{e_N = 2.n^2} \tag{2.8}$$

  e_N: number of e/ shell

  n: principal shell number
- **Electromagnetic radiation (EMR)** is the most recognizable as visible light and as radiant heat ; less obvious spectra include $\gamma - ray$,X ray UV microwave ,and radio-frequency radiation

  $$p = h/\lambda = mv \tag{2.9}$$

  $$\lambda = \frac{mv}{h} \tag{2.10}$$

  h; plank constant = 6.62 ×10^{-34} J/s

  c: speed of light= 3 ×10^{8} m/s

  v: velocity m/s

  EMR require no supporting medium for in transmission and thus passes readily through vacuum. EMR is viewed as a stream of discrete particles or wave packets of energy of a photon being proportional to the frequency of the radiation, this dual views of radiation as particles and as waves are complementary this duality is also found in the behavior of

Strems of electrons and the elementary particles such as protons. And vice versa. it is completely rationalized by wave mechanics [15].

$$E= h.\nu = \frac{h.c}{\lambda} = h.c.V \tag{2.11}$$

ν: Frequency

V: wavenumber

There are two types of spectroscopy

- **Atomic spectroscopy:** The study of transitions, absorption or emission, between electronic states of an atom, is atomic spectroscopy. It deals with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state [4]. Atomic spectra involve only transitions of electrons from one electronic energy level to another. There are two types of atomic spectroscopy.

Atomic absorption spectroscopy (AAS). Atomic emission spectroscopy (AES).

Atomic absorption spectroscopy (AAS).This spectroscopic technique makes use of the absorption of electromagnetic radiation by matter. Quantitatively, the absorption of radiation is expressed by Lambert – Beers low

$$I(\lambda) = I_0(\lambda) \exp[-L\sigma(\lambda)c] \tag{2.12 }$$

Where $I_0(\lambda)$ denotes the initial intensity emitted by some suitable source of radiation , While $I(\lambda)$ is the radiation intensity .after passing through a layer of thickness, L where the species to be measured is present at the concentration (number density) c, The quantity $\sigma(\lambda)$ denotes the absorption cross-section at the wavelength λ.

The absorption cross-section is a characteristic property of any species. the absorption cross-section $\sigma(\lambda)$ can be measured in the laboratory , while the determination of the light path length L is in many cases trivial. Once those quantities are known, the trace gas concentration c can be calculated from the measured ratio $I(\lambda)$ $I_0(\lambda)$

$$C= \log(\frac{(\frac{I0(\lambda)}{I(\lambda)})}{\sigma(\lambda)\ L}) = \frac{D}{\sigma(\lambda)\ L} \tag{2.13}$$

The expression

$$D = \log(\frac{I0(\lambda)}{I(\lambda)}) \tag{2.14}$$

D Is called the optical density of a layer of a given species [16].

Atomic Emission Spectroscopy, AES, is the measurement of light emissions from excited atoms. The concentration of an analyte element can be determined from the quantitative measurement of these emissions. A source such as a plasma, flame, or discharge is used to provide the energy to atomize and excite analyte atoms and promote them to higher energy levels. The optical emission corresponds to the excited atoms returning to lower energy level (s) and emitting light that is detected by a photon detector system. In AES, the process begins with sample introduction. Sample introduction techniques vary with AES but the usual procedure for liquid samples is to aspirate the sample solution and convert it into an aerosol to introduce small droplets of the analytic into the atomizer. This sample introduction method helps prevent the atomizer from being extinguished or from incompletely removing solvent. The heat of the atomizer desolvates or removes excess solvent/water from the sample droplets through volatilization and evaporation processes and dries the sample particles.1 In atomization, chemical bonds are broken and free atoms are produced. These free atoms become excited and gain energy from collisions in the atomizer. The atoms leave the ground state and are promoted to an excited state where they emit light upon returning to lower energy levels, the excited atoms return to lower energy states and eventually to the ground state due to the loss of energy. The relationship that exists between atoms in an excited state and atoms in a lower state is based on the Boltzmann equilibrium. The Boltzmann equilibrium is described in the following expression: Boltzmann Equation:

$$\frac{N_1}{N_0} = e^{-\frac{E}{kT}} \tag{2.15}$$

N_1 = number of atoms in the upper state

N_0 = number of atoms in the lower state

E = energy difference between upper and lower states, cm^{-1}

k = Boltzmann constant, J/K

T = absolute temperature, K , the equation is

$$\frac{N_1}{N_0} = \frac{g_1}{g_O} e^{-\frac{E}{kT}} [16] \tag{2.16}$$

- **Molecular Spectroscopy**: Thus far one can have been mainly concerned with emission from single atoms, I.e. spectra characterized by sharp lines arising from the emission of photons of particular energies when an electron makes a transition from an excited atomic state to a lower energy state. We wile no look at the spectrum of a simple diatomic molecular system. This separation is embodied more formally as the Boron – Oppenheimer approximation (briefly, that the vibrational motion is only slightly perturbed by the rotational motion and vice –versa). In this case we can treat the vibrational and rotational features of the spectrum as separate contributions superimposed on the overall electronic transitions between molecular states. A useful model for vibrational excitations is the quantum harmonic oscillator, which has energy levels given by:

$$En = h\,\omega(n + \tfrac{1}{2}) \qquad (2.17)$$

Where n is the vibrational quantum number, an integer, and ω_0 corresponds to the fundamental frequency of the simple harmonic oscillator (SHO).

Transitions in which Δn = -1 lead to an emission spectrum of equally spaced lines.Coming now to the rotational excitations, if you zoom in on one of the peaks in the comb of vibrational lines you will see some fine structure, this fine structure is replicated on top of each vibrational line. It arises from optical emission associate

$$E_{not} = h^2 J(J+1)/ 8\pi^2 I \qquad (2.18)$$

Where J= 0,1,2 …., h is Planck's constant, and I is the moment of inertia of the N_2 molecule. Note that the energy levels of the rotational states given by this expression are not equally spaced [17].

2.4 Lasers spectroscopy

Laser was developed in the early 1960s, spectrochemists began investigating its potential uses. An early observation was that a pulsed laser could produce a small plasma in air. The emission from that plasma from 1960 onwards, increasing availability of intense, monochromatic laser sources provided a tremendous impetus to a wide range of spectroscopic investigations.

Both absorption and fluorescence are used in many applications. However, because the laser needs to be tuned to a specific transition in a specific species, it is not as broadly useful as a hot plasma in which a variety of species can be excited and monitored simultaneously

A useful way of changing the wavelength of some lasers, for example the CO_2 infrared laser, is to use isotopically substituted material in which the wavelengths of laser transitions are appreciably altered . Such processes include fluorescence, dissociation, or pre-dissociation, and, following the absorption of one or more additional photons, ionization [17]. They are many types of application of laser in spectroscopy as like.

2.4.1Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

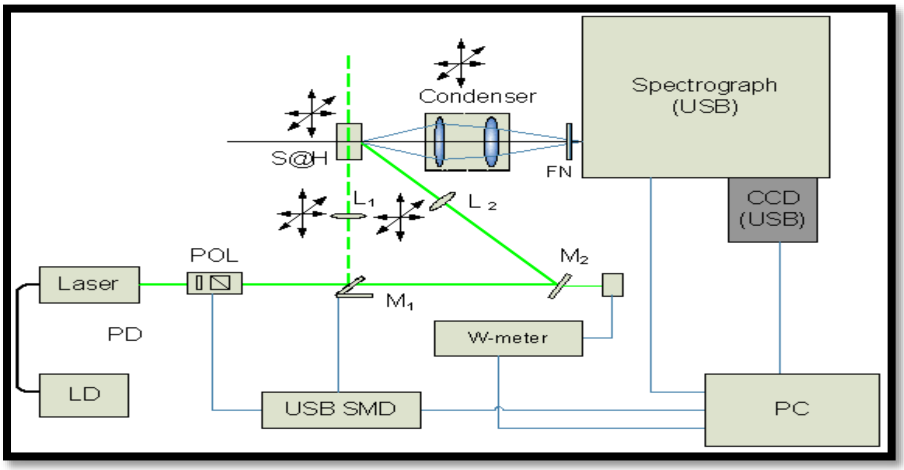


Figure (2.1): Laser Raman system

The Raman effect is based on molecular deformations in electric field E determined by molecular polarizability α. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency υm.

For many years Raman spectroscopy has been a powerful tool for the investigation of molecular vibrations and rotations. The introduction of lasers, therefore, has indeed revolutionized this classical field of spectroscopy. Lasers have not only greatly enhanced the sensitivity of spontaneous Raman spectroscopy but they have furthermore initiated new spectroscopic techniques, based on the stimulated Raman effect, such as coherent anti-Stokes Raman scattering (CARS) or hyper-Raman spectroscopy [18].

The research activities in laser Raman spectroscopy have recently shown an impressive expansion and a vast literature on this field is available. The most immediately obvious application of early, essentially non-tunable, lasers was to all types of Raman spectroscopy in the gas, liquid or solid phase. As a result, weaker Raman scattering can now be observed and higher resolution is obtainable. In addition to carrying out conventional Raman experiments with laser sources new kinds of Raman experiments became possible using Q-switched, giant pulse lasers to investigate effects which arise from the non-linear relationship between the induced electric dipole and the oscillating electric field. These are grouped under the general heading of non-linear Raman effects. For branches of spectroscopy other than Raman spectroscopy most laser sources may appear to have a great disadvantage, that of non-tunability. Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency υ_0 excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (Fig.2.1) when.

- A molecule with no Raman-active modes absorbs a photon with the frequency $\upsilon 0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\upsilon 0$ as an excitation source. This type if interaction is called an elastic Rayleigh scattering.
- A photon with frequency υ_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon’s energy is transferred to the Raman-active mode with frequency υ_m and the resulting frequency of scattered light is reduced to $\upsilon_0 - \upsilon_m$. This Raman frequency is called Stokes frequency, or just “Stokes”.
- A photon with frequency υ_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\upsilon_0 + \upsilon m$. This Raman frequency is called Anti-Stokes frequency, or just “Anti-Stokes”.

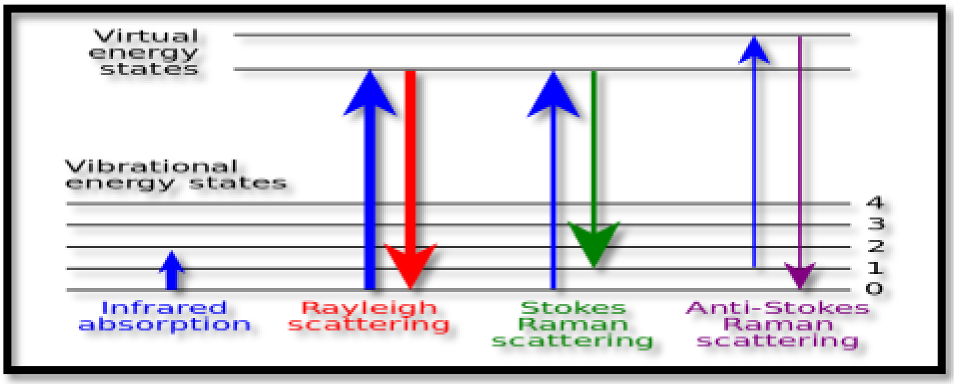


Figure (2.2): Stimulated Raman transitional schemes

About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $\upsilon_0 \pm \upsilon_m$. Spontaneous Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering.

Instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are used to reduce Rayleigh scattering and obtain high-quality Raman spectra [18].

2.4.2 Laser Induced Fluorescence (LIF)

Is an emitted from electronically excited levels that are populated by absorption of photons, typically in the ultraviolet and visible spectral region [19]. In Laser induced fluorescence (LIF) technique the laser beam is formed into a thin light sheet by a set of lenses, and this light sheet entering the observation volume. The fluorescence is captured by a collecting lens and imaged on to the detector surface; the data of the images is transferred from the camera to the control unit installed in a computer [20]. The emitted radiation is characteristic for the concentration and temperature of the regarded species. Fig (2.2) show the experiment use in this technique.

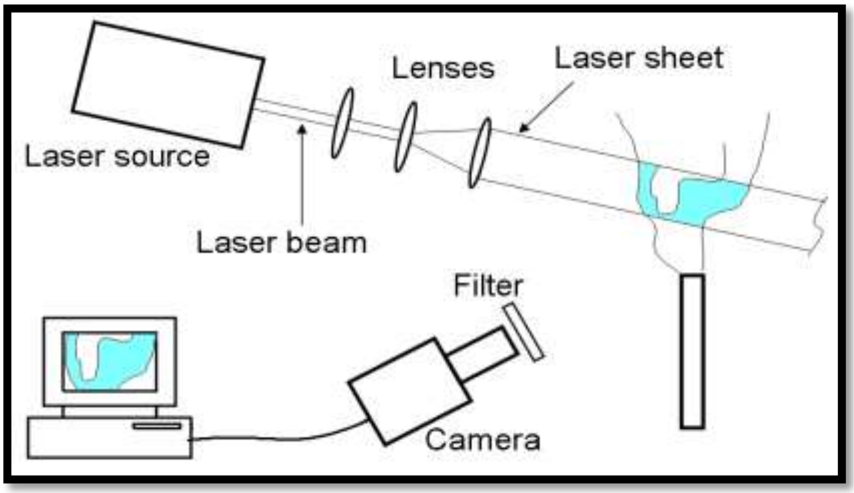


Figure (2.3): The experimental setup of LIF

2.4.3Mass spectroscopy

The basic principle of mass spectrometry (MS) is to generate ions from either inorganic or organic compounds by any suitable method, to separate these ions by their mass-to-charge ratio (m/z) and to detect them qualitatively and quantitatively by their respective *m/z* and abundance. The analyte may be ionized thermally, by electric fields or by impacting energetic electrons, ions photons. The ... ions can be single ionized atoms, clusters, molecules or their fragments or associates. Ion separation is effected by static or dynamic electric or magnetic fields.” Although this definition of mass spectrometry dates back to 1968 when organic mass spectrometry was in its infancy, it is still valid. However, two additions should be made.

First, besides electrons, (atomic) ions or photons, energetic neutral atoms and heavy cluster ions can also be used to effect ionization of the analytic. Second, as demonstrated with great success by the time-of-flight analyzer, ion separation by *m/z* can be effected in field free regions, too, provided the ions possess a well-defined kinetic energy at the entrance of the flight path. [21]. A mass spectrum is the two-dimensional representation of signal intensity (ordinate) versus m/z (abscissa). The intensity of a peak, as signals are usually called, directly reflects the abundance of ionic species of that respective m/z ratio which have been created from the analytic within the ion source. The mass-to-charge ratio, m/z, is dimensionless by definition, because it calculates from the dimensionless mass number, m, of a given ion, and the number of its elementary charges, z. The number of elementary charges is often, but by far not necessarily, equal to one. As long as only singly charged ions are observed (z = 1) the m/z scale directly reflects the m scale. However, there can be conditions where doubly, triply or even highly charged ions are being created from the analytic depending on the ionization method employed. The location of a peak on the abscissa is reported as at m/z. The distance between peaks on that axis has the meaning of a neutral loss from the ion at higher m/z to produce the fragment ion at lower m/z. Therefore, the amount of this neutral loss is given as “x u”, where the symbol u stands for unified atomic mass. It is important to notice that the mass of the neutral is only reflected by the difference between the corresponding m/z ratios. This is because the mass spectrometer detects only charged species, i.e., the charge-retaining group of a fragmenting ion. Since 1961 the unified atomic mass [u] is defined as 1/12 of the mass of one atom of nuclide 12C which has been assigned to 12 u exactly by convention [21].

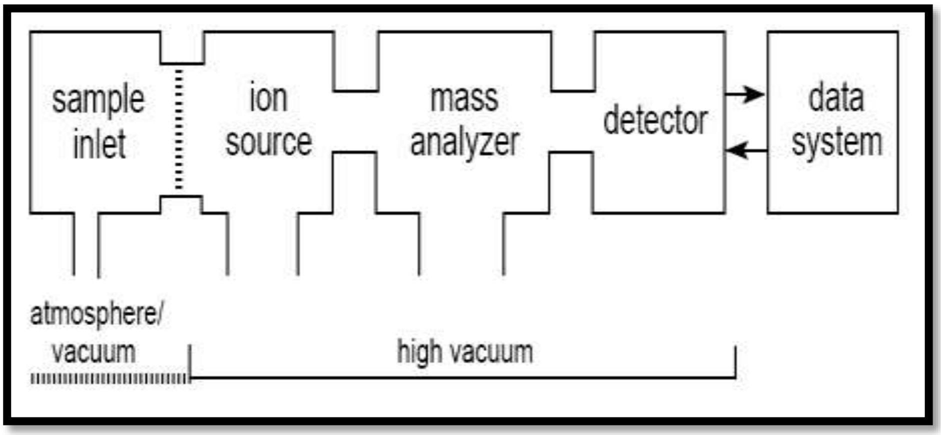


Figure (2.4) General scheme of a mass spectrometer

2.4.4Laser induced breakdown spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) is a spectrochemical technique which uses an intense laser pulse to determine the elemental composition of a sample and the relative quantities of the target′s constituent elements [22,23]. Understanding the plasma physics of LIBS is essential to provide an optimized setting for LIBS measurements [24]. A large number of environmental factors affect the plasma life time and features, changing the spectral emission and the performance of this technique for chemical analysis at the atomic level [25, 26, 27 and 28]. LIBS employ a low–energy pulsed laser in the order of tens to hundreds of mJ per pulse and focusing optics, in order to generate a plasma that vaporizes a small amount of target material [29,30]. The generated plasma contains the excited atoms and ions that were present in the target and sometimes molecules formed by recombination of those atoms. As the plasma cools, the atoms, ions, and molecules lose energy via the spontaneous emission of optical wavelength photons [31]. A spectroscopic analysis of the plasma light will thus yield the elements that are present in the target material. The positive identification of many elemental lines including both the wavelength and the intensity within the emission spectrum will form a unique spectral fingerprint of the target such as soil [32]. Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic technique utilizing high power ,laser pulses [33-37]. When a pulsed high power laser beam is focused on the material (Solid, Liquid, Gas and aerosols), a short lived (micro second) high temperature (few eV) and density (10^{16}-10^{19}cm^{-3}) plasma is produced and expands perpendicular to the target surface. Such laser produced plasmas, which contains a diversity of atomic and ionic species as well as free electron emit radiation over an extensive spectral range stretching from infrared to the X-ray region. Although different materials have different breakdown thresholds, the plasma is typically generated when the laser irradiance exceeds ~ 10^{8} MW/cm^{2} [38]. The LIBS system works and explains the major parts of LIBS to select specific functional requirements for its intended application. The three major parts of LIBS system are: Laser, sample and spectrometer are explained. LIBS employs the laser pulse to atomize the sample and leads to atomic emission. Compared to the conventional flame emission spectroscopy, LIBS atomizes 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 [39].

LIBS principles by the physics of laser-induced breakdown has been studied extensively. The minimum optical power density required to form a plasma is called the breakdown threshold;

different types of laser, samples, and ambient conditions will have different breakdown threshold [22]**.**

They are many application of LIBS for qualitative and quantitative elemental measurements in a wide range of samples such as various environmental sample, metallurgical and non-metallic solids, liquid samples, aerosols, gases samples, and advanced materials as well as in same miscellaneous applications. Among the application of LIBS, composition analysis of metallurgical samples has been most popular. Recent application, however, is more inclined to the environmental samples and liquid samples including biological samples.

LIBS have been applied to elemental analysis in the environmental samples such as air, soil, sewage sludge and solution. Environmental problems are among the most interesting and topical in application is a growing Interest in the in the in-situ analysis, on-line monitoring [40]. Strong efforts have been made to link this information with nutritional and environmental influences. The problem of reference stander, required for finally Quantitative analysis, is addressed [41]. In particular, publication about using LIBS on bio-matrix materials are relatively few. Overall, this is not very surprising, for a range of reasons. First biological tissue sample hard calcified tissue and soft cell materials are normally less tough in their texture than metals or minerals. Thus the ablation process destroys the sample area much more rapidly, which results in poor statistics and reproducibility. Second, in many cases, biological sample are rather inhomogeneous. Again, this makes selectivity, statistics, and reproducibility of results difficult, Third, traces of specific elements in the bio-mass are often of most interest at concentration levels that are close to or below the detection limits of LIBS. And finally, molecular species are of vita importance, and normally these are beyond the capabilities of LIBS [41] .

The use of LIBS for elemental analysis relies on some fundamental assumptions that must be verified, especially when semi-quantitative and quantitative analysis of samples is pursued. First of all the conditions of optically thin plasma and LTE are always the underlying premises for laser induced plasma studies by emission spectroscopy, both for fundamental studies and for analytical applications. The emission intensity I_{ul} of a peak of frequency v_{ul} is related to the number density of excited emitters, Nu by:

$$I_{ul} = \frac{1}{4\pi} N_u A_{ul} h v_{ul} G \tag{2.19}$$

Where A_{ul} is the spontaneous emission coefficient of the given transition, h is the Planck constant and G is an instrumental factor depending on the experimental set-up used. This relation is valid only when the considered u_l transition is optically thin, that is, not suffering from self-absorption, a condition that can severely affect low-energy and resonance lines, particularly for high-concentration elements. Several methods can be found in the literature to evaluate and correct self-absorption, and a good practice in analytical LIBS is to select accurately the emission lines to be used for analysis .All spectroscopic lines involving the ground state should be excluded, because they are the most severely affected by self-absorption phenomena, which alter the spectral line profiles and thus hinder the quantitative determination of major elements. For these elements, lines corresponding to transitions with lower energy level below 6,000 cm^{-1} should also be possibly excluded. [41].

2. 5 Calculation LIBS

If the energy levels of two atomic or ionic states are in local thermodynamic equilibrium (LTE), then population density of upper-level Nj is related to ground level number density (N_i) by the Boltzmann equation.

$$N_j = N_i g Q^{-1} \exp\left(\frac{E_j}{kT}\right) \qquad (2.20)$$

Here gj and Ej are the statistical weight and energy of upper-level j respectively, Q is the partition function of relevant species, K is the Boltzmann's constant, and T is the electron temperature of the plasma. The total intensity of a spectral line 'I' from an excited atom or ion in homogenous and optically thin plasma for a transition from state j→i is given by [42].

$$I = h\nu_{ji} A_{ji} N_j \qquad (2.21)$$

where ν_{ji} = frequency of the transition from state j→i; A_{ji} = Einstein coefficient for spontaneous emission; Nj = population of the upper level j; h = Planck's constant. So from above two equations, we get

$$I = h\nu_{ji} A_{ji} N_i g Q^{-1} exp\left(\frac{E_j}{kT}\right) \qquad (2.22)$$

From Eq. (3), one can determine the population density of the relevant species (atoms or ions) for an element in plasma from a measurement of the absolute intensity of corresponding transition and the knowledge of the excitation temperature and atomic constants. However, it is not possible to derive a theoretical expression relating N and the concentration of the particular element (in samples) under investigation. Hence, in practice, an empirical relationship is required between the observed line intensity (Ij) and corresponding concentration (C), i.e.

$$I_i = F(C) \tag{2.23}$$

Here F (C) is called analytic calibration function and the graph between the LIBS intensity of a line of specific element and the concentration is called the calibration curve.

Limit of detection (LOD)

Detection limit means the lowest concentration of particular element or compound and it is commonly used as evidence of the quality of the sensors, LOD can be estimated using the equation

$$LOD = \frac{2\sigma_b}{S} \tag{2.24}$$

Where (σ_b) is the standard deviation of the background and S is the sensitivity which is given by the ratio of the intensity to the concentration. The relative standard deviation (R.S.D.) is defined as the deviation of values around the mean and is calculated as the ratio of standard deviation to the mean given.

$$RSD(\%) = \frac{standerd\ deviation}{mean} x100 \tag{2.25}$$

The relative standard deviation decreased with the number of shots but no improvement in R.S.D. was noticed after laser shots.

$$RA = \frac{|d| + SDxt_{0.96386}/\sqrt{n}}{M} \quad [43] \tag{2.26}$$

2.6 LIBS advantages and disadvantages

LIBS advantages and disadvantages are able to detect all elements and have the ability to provide simultaneous multi-element detection capability with low absolute detection limits. In addition, because the laser spark uses focused optical radiation to form the plasma, LIBS exhibits numerous appealing features that distinguish it from more conventional AES-based analytical techniques like inductively coupled plasma mass spectroscopy. These are: simple and rapid or real time analysis, the ablation and excitation processes are carried out in a single step; little-to-no sample preparation, which results in increased throughput and reduction of tedious and time-consuming sample digestion and preparation procedures (this, however, can lead to a loss of accuracy through contamination). LIBS allow in situ analysis requiring only optical access to the sample. It can also be performed over a great distance, a technique referred to as remote sensing. Unlike remote analysis, in which some part of the LIBS system is close to the sample is the method of stand-off analysis. Here, the laser pulse is focused on to the sample at a distance using a long focal length optical system [44-45]. Virtually any kind of sample can be analyzed: solids, liquids, aerosols, or gases. LIBS has the ability to analyze extremely hard materials which are difficult to digest such as ceramics, glasses and superconductors. It is a non-destructive method, very small amount of sample (0.1 µg – 0.1 mg) is vaporized. It provides good sensitivity for some elements (e.g. Cl, F) difficult to monitor with conventional AES methods. In addition, LIBS has adaptability to a variety of different measurement scenarios, e.g. underwater analysis, direct and remote analysis, compact probe with the use of miniature solid state lasers, stand-off analysis [20]. We can summarize LIBS advantages and disadvantages below:

- Very small amount of sample (about 0,1Mg – 0.1 mg) is vaporized, (same time is called nondestructive method).
- All states of matter can be analyzed, as well as conductive and nonconductive samples. [20].
- Local analysis in micro regions offers a Spatial resolving power of about 1-100$\mu\, m$ Possibility of simultaneous [21].
- Ability to analyze extremely hard materials which are difficult to digest or dissolve and Easy analysis of refractory materials such as ceramics.
- Micro analysis is possible with spatial resolution of 1-10 µm.
- Capability of remote analysis in harsh environment and Capability of simultaneous multi element analysis.
- Simple and rapid analysis (ablation and excitation processes are carried out in a single step) [22].

Disadvantages are :

- Variation in the mass ablated caused by changes in the bulk matrix.
- Difficulty in obtaining matrix matching standards.
- Detection limits higher (poorer) than standard solution techniques (i.e. ICP-OES) [20].
- Poor precision, typically 5 – 10 % depending on the sample homogeneity sample matrix, and excitation properties of the leaser.
- Standard emission disadvantages such as spectral interference and self-absorption. [33].
- Possibility of optical component damage from high energy density lasers.
- Increased cost and Complexity of the system [20].

2.6 Inductively Coupled Plasma (ICP)

It is considered one of the best devices technique or spectroscopic method used in the world in the analysis of the various mineral elements in all materials, whether food or water, with extreme accuracy and speed in performance. It can measure from 1to 73 metallic elements in a single sample through only one injection. Among the most important elements that our laboratories examine with this device are heavy metal elements. Its presence in food and water is a serious threat to human health and safety, they are calcium, magnesium, silicon, arsenic, cadmium, Lead, chromium, iron, zinc, copper, titanium, Mercury, sodium potassium, Nickel, manganese. ICP spectroscopy utilizes a plasma as the atomization and excitation source. A plasma is an electrically neutral, partially ionized gas made up of ions, electrons, and atoms. Plasmas are characterized by their electron density and temperature. The temperature of a plasma in ICP usually ranges from 4000-8000 K. Plasmas in acquire their energy from an electric or magnetic field and this energy must be maintained for the plasma to be used for. ICP, the energy is acquired from electrical currents produced by electromagnetic induction. Plasmas and their properties will be discussed in further detail in the section of Laser-Produced Plasma-ICP. In ICP, the stable, high temperature plasma is formed by an ICP torch. The ICP is a continuous plasma meaning it does not form and quickly decay. The density and temperature of the plasma decrease from the core of the plasma outward.

The ICP torch is made of three concentric tubes and is partially enclosed by a water-cooled coil that is powered by a radio frequency generator. The field becomes magnetically activated when the power is turned on and an inert gas such as Argon flows through the torch. The flowing gas becomes electrically conductive when a tesla coil ignites the gas and a plasma is formed. A diagram in fig (2.1) shows the details of an ICP torch. In ICP, the sample is introduced (solid, liquid, or gas) directly inside the plasma and atomization and excitation occur as previously discussed in Flame-AES. An advantage of ICP-AES is the sensitivity of the technique due to the high temperature plasma source. This sensitivity results in good emission spectra for most elements.

Device installation**,** by three concentric quartz tubes, flame, spectroscopic and optical, radio frequency surrounding generator, glass plasma coil and output device**.**

The Principle of ICP torch is placed inside the coil that passes through with an electric current with a drop on the radio plasma and then argon atoms flow in which the gas supply usually 14 to 18 liters per minute between the two outer tubes of the torch and the electric spark where it is normalized for a short time to introduce free electrons in to the gas stream as the electrons interact with the radiofrequency magnetic field of the induction coil it accelerates first in one direction and then in the other since changes in the field of electrical frequencies are usually 12/20000 cycles per second where the accelerated electrons collide with the argon atoms and sometimes due with the argon atoms and sometimes due to this collision give up one of the electrons this process continues until the rate of release of new electrons when colliding with the argon atoms is balanced and a fireball is produced.[45]. Uses ICP to measurement of metals and heavy metals concentration in water and effluents, and also measuring the concentration of heavy metals in sludge and soil after digestion of the sample by conventional methods. The device is distinguished by its accurate measurements of heavy elements.

Applications in many filed like , environment to determine the percentage of mercury in water and fish to determine the mercury pollution of lakes and determining the percentage of heavy metals in industrial wastewater and determining the percentage of lead in gasoline, mining and petroleum to determining the proportions of the various elements in the crude to determine the quality of the crude and to determine the percentage of impurities in crude oil and lubricating oils and determine the percentage of different minerals in solid samples and at last medical and nutritional fields. Estimation of the amount of calcium, potassium, and phosphorous in the blood and the determination of the amount of contamination with heavy metals for different foods, determining the ratios of active substances in nutritional supplements such as iron phosphorous, zinc and other elements. Advantages of ICP are simultaneous with solid state detector, bench top model, Water re-circular and that re-circular have the ability to be situated at a distance from the instrument, or water chiller, viewing of the plasma is computer controlled and spectrum range from 167 to 847 nm or more [46].

2.7 Previous Studies:

There have been several publications in the last decade which have reviewed laser induced breakdown spectroscopy either as a unique method of elemental analysis or as a member of the family of atomic emission techniques. LIBS have also been addressed in reviews on laser applications process monitoring, and materials processing. Many spectroscopic studies of laser plasmas have also appeared in the physics journals.

M.A GONDAL, were applied Laser Induced Breakdown Spectroscopy (LIBS) technique to determine the concentrations of different toxic elements like lead, chromium, cadmium and zinc in four different lipstick brands sold at local markets in Saudi Arabia. These samples contain toxic elements, the maximum concentration detected in four lipstick brands was much higher than the permissible safe limits for human use and could lead to serious health problems. Which is carcinogenic dermatitis, allergic and eczematous [47]

Gondal, et al. in 2007 Developed laser induced breakdown spectroscopy for determination of toxic metals in wastewater collected from local point manufacturing plant. A pulsed Nd**: YAG** laser at 106nm was focused on the solid residue from wastewater**.** The concentration of different element of environmental significance like Pb, Cu, Cr, Ca, S , Mg ,Zn ,Ti , Sr , Ni , Si , Fe , Al , Ba , Na , K and Zr , in paint wastewater were 6, 3, 4, 301, 72, 200, 20 ,42, 4, 1, 35, 120, 133, 119, 173, 28, and 12 mg kg^{-1} respectively. The potential capabilities of LIBS as a rapid tool for paint industry effluent characterization was discussed in details. Optimal experimental conditions were evaluated for improving the sensitivity of LIBS system through parametric dependence study. The laser induced breakdown spectroscopy (LIBS) results were compared with the results obtained using standard analytical technique such as inductively coupled plasma emission spectroscopy (ICP). The relative accuracy of LIBS system for various elements as compared with ICP method was in the range of 0.03 – 0.6 at 2.5% error confidence. Limits of detection (LOD)of LIBS system were also estimated for the above mentioned elements. [48]

Sensei, et al in 2009 have demonstrated the capability of LIBS technique to provide reliable qualitative and quantitative analytical evaluation of several heavy metals in soils especially chromium (Cr) and with reference to the concentrations measured by conventional inductive coupled plasma spectroscopy (ICPS). A number of element including Al, Ca, Cr, Cu, Fe, Mg**,** Mn, Pb, Si, Ti, V and Zn have been detected in five soil samples and one sewage sludge sample. [49]

Majidi and others published "Spectroscopic Applications of Laser-Induced Plasmas" in 1992. This publication has perhaps had the most influence in terms of style and content on the review that follows. Majidi and Joseph reviewed analytical results on solids, liquids, gases, and mixed phase systems for the years 1987-1992. Emphasis was on applications of LIBS such as determination of hazardous elements in air toxic elements in wastewater. LIBS required only optical access to samples [50] They has other previous reviews under title generation of pulsed Fe plasma and study of its physical parameters done by Naseer M. Hadi. In this work, a pulsed Fe plasma generation by Q-switched Nd: YAG laser. The energy per pulse at the target surface was fixed at a level of (475 mJ, 6 ns), focused on Fesoli dtar getatatmo spheric pressure and vacuum pressure (1×10^{-1} mbar). The plasma temperature was measured from Boltzmann plot using six Fe I spectral lines at the wavelengths (501.2, 534.1, 556.9, 576.2, 602.4 and 623.07) nm. The electron density was measured by means of Stark broadening formula (FWHM) for spectral lines Fe I at line transition 576.2 nm and for Fe I at line transition 556.9 nm as the reference electron density, at atmospheric pressure and vacuum pressure. The density was $8.2x10^{18}$ cm^{-3} and electron temperature 1.466 eV at atmospheric pressure, the electron density was $9x10^{18}$ cm-3 and the electron temperature 1.711 eV at pressure ($1×10^{-1}$) mbar. Measurements were done based on theory of local thermodynamic equilibrium (LTE) in the range (500-650 nm) of emitted spectrum [51]. Analysis of cosmetic products using different IR spectroscopy techniques this other previous study doing by Sylwia Pasieczna- Patkowska. This article describes the application of IR spectroscopic methods in the study of the composition of finished cosmetic products. Four spectroscopic techniques: TS (transmission spectroscopy), PAS (photo acoustic spectroscopy), ATR (attenuated total reflectance) and DRS (diffuse reflectance spectroscopy) were used for this purpose. Tested cosmetic products were of different consistency and application. The choice of spectroscopic techniques was dictated by the physical state and consistency of the sample [52]

KHALID A, and others Swere applied atomic absorption spectrophotometer to determination of heavy metals (Lead, Cadmium, Chromium and Nickel) samples of six most popular brands of lipsticks sold at local markets in Faisalabad. The ranges of averages for all samples analyzed were: Pb, 0.286- 6.234 ppm; Cd, 0.200-0.500 ppm; Cr, 0.222-5.430 ppm and Ni, 0.600-5.947 ppm. From all colors in dark brown and shocking pink colors the metals concentration were higher, while in baby pink color the metal contents were low [53]. Reuland and Trinler (1980) their stated that HPLC contribute itself well to the separation of many components found in lipstick. Andrasko (1981) analyzed lipstick stain by a combination of several techniques. In addition to color comparison and TLC analysis in a scanning electron microscope and HPLC analysis also been chosen. The finding showed that the discrimination between lipsticks was achieved by color comparison [54].

Other study was Laser Induced Breakdown Spectroscopy of Diesel Particulate Matter Exhaust Emissions Generated from on Road Diesel Engine: Light Duty Vehicles, by Richard Viskup. This research was applying Laser Induced Breakdown Spectroscopy (LIBS) technique for high resolution spectrochemical analysis of Diesel Particulate Matter - DPM exhaust emissions. DPM has been collected from real, on road - Light - Duty Vehicles, driven by combustion Diesel engine. We have been concerned with the main chemical elements, presents in various type of real Diesel particulat matter from LIBS measurements, it has been shown, that the plasma electron density can be use for the basic classification of different types of DPM matrices. The excitation temperatures of atoms and ions in plasma can be used for further quantitative analyses of diverse Diesel Particulate Matter. The aim of this study is to reveal the compounds, which are mostly dominant in the Diesel engine exhaust emissions and can affect the overall composition of the DPM. The presence of these elements in exhaust emission may point to different processes, mainly to fuel quality, insufficient engine combustion process, incomplete catalytic reaction, inefficient Diesel particulate filtering technique, or failure of the Diesel engine [55].

Double-Pulse and Calibration-Free Laser-Induced Breakdown Spectroscopy (LIBS) on quantitative analysis this other study done by Victor Ulises Lev Contreras Loera. This study content Laser-induced breakdown spectroscopy (LIBS) represents a powerful tool for qualitative analysis and can achieve quantitative results with acceptable accuracy and precision. Nevertheless, due to the high laser pulse energies used in LIBS, sample damage represents a drawback for some applications. In recent years, novel techniques, such as Double Pulse LIBS (DP-LIBS), have been developed to overcome main LIBS drawbacks. In order to diminish sample damage, this dissertation studies the use of signals from orthogonal DP-LIBS obtained at low ablative energies for quantitative analysis by a self-calibrated method called Calibration Free (CF)-LIBS. Before testing DP-LIBS with CFLIBS, this dissertation presents the implementation of conventional single pulse LIBS (LIBS or SP-LIBS) as well as orthogonal DP-LIBS approaches. For optimal implementation of quantitative analysis, two problems are solved by different techniques (calibration curves and CF-LIBS). In the first case, a series of experiments, based on calibration curves technique, were conducted to quantify the Active Pharmaceutical Ingredient (API) in commercial pellets by estimating their Cl content. Results from LIBS were compared and validated with those obtained by High Performance Liquid Chromatography (HPLC). In the second problem, CF-LIBS is presented as a technique capable of determining the chemical composition of multi-elemental samples. Fe, Cr, Mn, and V elements from a steel sample were successfully quantified. Results obtained by CF-LIBS satisfactorily agree with microprobe technique results and certified elemental values in the sample. After successful DP-LIBS and CF-LIBS implementation we demonstrated, for the first time to the best of our knowledge, that CF-LIBS can be successfully applied to spectral lines obtained from orthogonal DP-LIBS configuration. The great improvement in atomic emission, signal-to-noise ratio (SNR), signal-to background ratio (SBR) and reproducibility offered by DP-LIBS has been tested in CFLIBS in order to reduce the use of high energies. As a consequence, when DP-LIBS is applied to CF-LIBS instead of conventional SP-LIBS, the mass removed by laser ablation is reduced by a factor of 13 without losing signal intensity. This is a remarkable finding that can be exploited in critical applications where sample damage represents a drawback [56].

Laser Induced Breakdown Spectroscopy (LIBS) applied to stratigrafic elemental analysis and Optical Coherence Tomography (OCT) to damage determination of cultural heritage Brazilian coins, study by Marcello M. Amaral. In this study a compositional characterization of 1939's Thousand "Réis" and 1945's One "Cruzeiro" Brazilian coins, forged on aluminum bronze alloy. The coins were irradiated by a Q-switched Nd: YAG laser with 4 ns pulse width and energy of 25 mJ emitting at 1064 nm reaching 3.1010Wcm-2 (assured stoichiometric ablation condition), forming a plasma in a small fraction of the coin. The plasma emission was collected by an optical fiber system connected to an Echelle spectrometer. The capability of LIBS to remove small fraction of material was exploited and the coins were analyzed ablating layer by layer from patina to the bulk. The experimental conditions to assure reproductively were determined by evaluation of three plasma paramethers: ionization temperature using Saha-Boltzmann plot, excitation temperature using Boltzmann plot, plasma density using Saha-Boltzmann plot and Stark broadening. The Calibration-Free LIBS technique was applied to both coins and the analytical determination of elemental composition was employed. In order confirm the Edict Law elemental composition the results were corroborated by Neutron Activation Analysis (NAA). In both cases the results determined by CF-LIBS agreed to with the Edict Law and NAA determination. Besides the major components for the bronze alloy some other impurities were observed. Finally, in order to determine the coin damage made by the laser, the OCT (Optical Coherence Tomography) technique was used. After tree pulses of laser 54μg of coin material were removed reaching 120μm in depth [57].

Other study done by Vinicius C. Costa under title Calibration Strategies Applied to Laser-Induced Breakdown Spectroscopy: A Critical Review of Advances and Challenges. In this study laser-induced breakdown spectroscopy (LIBS) has been reported in the literature as an alternative to traditional methods of analysis, becoming well established among electroanalytical techniques. LIBS is a technique widely used for qualitative approaches; however, it is necessary considerable effort for use in quantitative analysis, mainly due to severe matrix effects. These limitations make it difficult to broaden the application of LIBS in quantitative analysis. In this sense, this review discusses recent advances in calibration strategies applied in LIBS for minimizing matrix effects and enabling determination with satisfactory accuracy and precision. Applications, advantages, and limitations of the calibration strategies, such as matrix matching calibration (MMC), internal standardization (IS), standard addition (SA), multi-energy calibration (MEC), one-point gravimetric standard addition (OP GSA), one-point and multi-line calibration (OP MLC), slope ratio calibration (SRC), two-point calibration transfer (TP CT), single-sample calibration (SSC), multiple linear regression (MLR), principal component regression (PCR), partial least squares (PLS) and artificial neural networks (ANN) are discussed[58].

Gondal et al (2002) LIBS experiments are based on the study of plasma resulting from interaction of intense laser radiation with sample medium. The laser source serves to vaporize, atomize and excite the sample material and the light emitted from plasma is spectrally resolved and analyzed identification and concentration of the trace elements present in the sample LIBS have been applied successfully for the analysis of gases, liquids, solids solid aerosols, liquid aerosol and soils. Heavy and toxic trace such as Co, Cr, Hg, Pb, and Zn can be detected by LIBS in soil and water samples at ppb-level detection limits remotely. The unique features of LIBS are: low analysis cost per sample, ability to analyze large number of samples in short amount of time measurement precision sufficient for screening many elements of interest, high sensitivity and possibility of in situ detection from remotely- located samples. Thus study show that LIBS can be applied in many applications, covering a wide variety of areas of interest such as pollution monitoring (contaminants in liquids, solid and gaseous samples) trace element analysis of soil and water, immediate determination of or grades during mining and prospecting and industrial chemical process control [59].

GAUDIOSO, (2010) were applied laser induced breakdown spectroscopy to soils and aqueous samples, meteorites and terrestrial samples simulating extraterrestrial planets, and cultural heritage samples including buildings and objects of various kinds. [60] Gobran, et al. In 2018 is one of the pioneering works on laser induced breakdown spectroscopy where the pollution of water and soil for different samples in some gold mining areas in sudan [61]

In 2017 Mohammed. A. EL- and Khalid M. H. published an overview of Measurements for Radioactive Materials at the East and West banks of the River Nile. Soil sample were collected along the East and west banks of the River Nile region starting from Bait AL- mal in the west side and the second East bank of the River Nile shambat. Gamma measurements wear performed using high resolution HPGe detector with low background PC multichannel spectrometer. The gamma measurements of the soil revealed the presence of the natural long –lived radioisotopes U^{238}, $Th^{232}$and $Ka^{40.}$ Th.3±2.1 Bqkg^{-} 10.76 ± 2.13Bqkg^{-1} ±11.6 Bqkg^{-1} , respectively .the other factors controlling the distribution of the detected natural radioisotopes have been discussed.Absorbe.07 ± 1.53 nGyh^{-1} . Also the estimated activity utilization indexes have been presented. The ratios between the detected radioisotopes have been calculated. [62] in 2014 Abedelrazig. M. A. and salwa. M. I and Ahmed. H. El published an overview of Determination of Heavy Metals Exposure to Environmental in Fingernails of Females in Port Sudan The purpose of volunteer's female students were collected to determine their levels of this study is determining the usefulness of imposed guidelines for exposures to elements level in district of eastern Sudan in Port Sudan city. Elements calcium (Ca), copper(Cu), nickel (Ni),zinc (Zn), and lead(Pb) concentration in fingernails sample of contamination in hands fingernails. The samples were measured using graphite furnace atomic absorption spectroscopy (Perkin-Elmer, Spectrophotometer) to analyze the heavy metals in females' fingernails of ages 14 to 16 years and children of 4to 5years old. Different methods are used for data assessment and source identification such as correlation

principal component analysis, eigenvalue and variance confirming that the sources of Ca, Cu, and Zn exposure to environmental from locality contamination such as soil dispersion and underground drinking water, while Ni and pb are connected to other sources expose by environmental contamination factors [63].

Chapter Three

Materials and Method

3.1 Introduction

This chapter shows the study area and equipment that have been used in experiments in addition to the method that has been applied

3-2 Study area

Kadugli is a city located in the state of south Kordofan in sudan, on the foothills of a mountain bearing its name, at an altitude of 499 meters above sea level it is about 589 km away from Khartoum and it is capital of south kordofan state it is located in an area rich in natural agricultural and mineral resources [64].

In recent years a new activity has appeared in this area, which is traditionalistic mining which has affected the environment and human

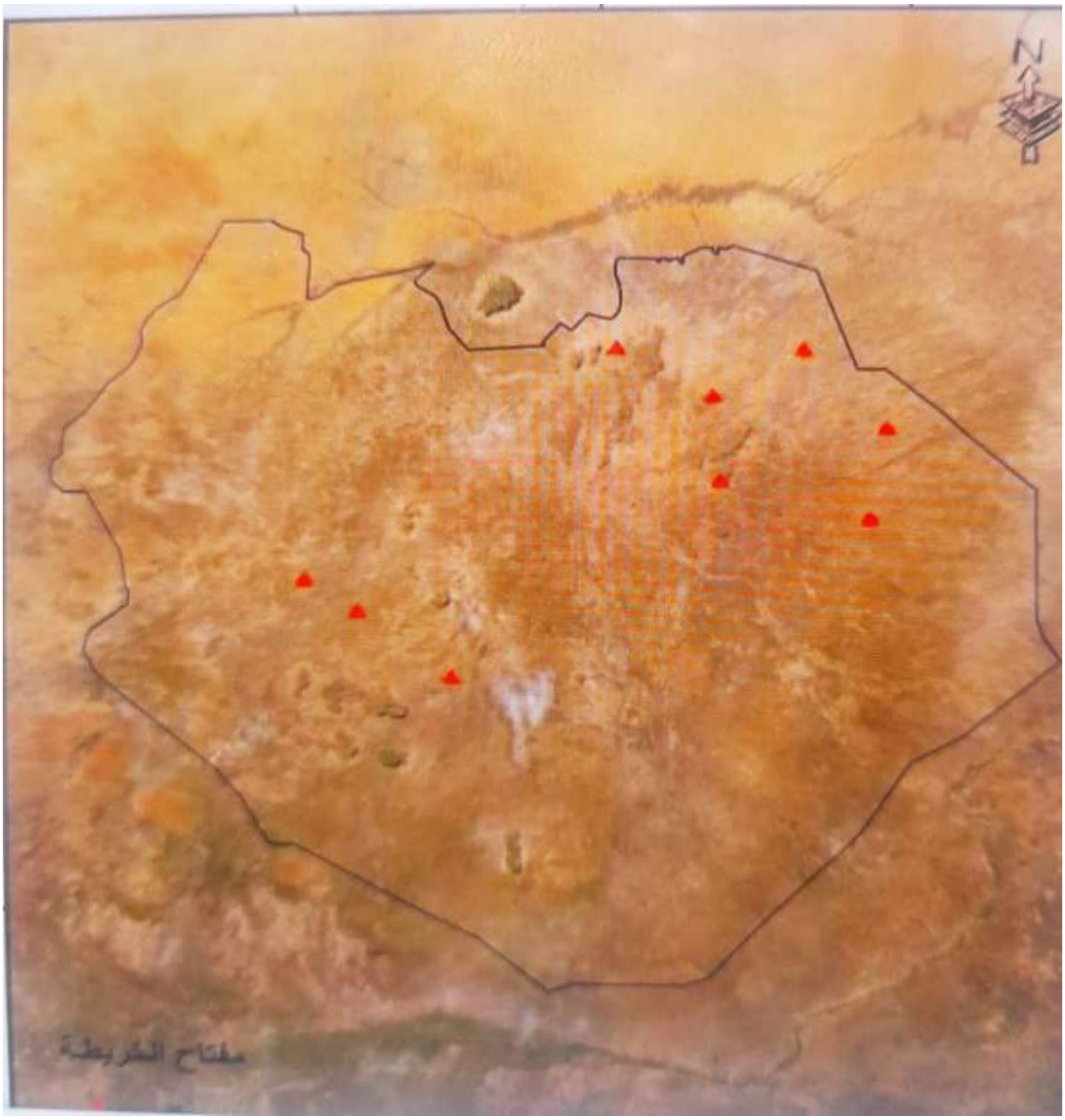


Figure (3.1) Mining areas in Kadugli

3.3 Materials

3.3.1 Sample

3-3-1 LIBS and N_2 – laser: N_2 laser was used as excitation source with the following parameters

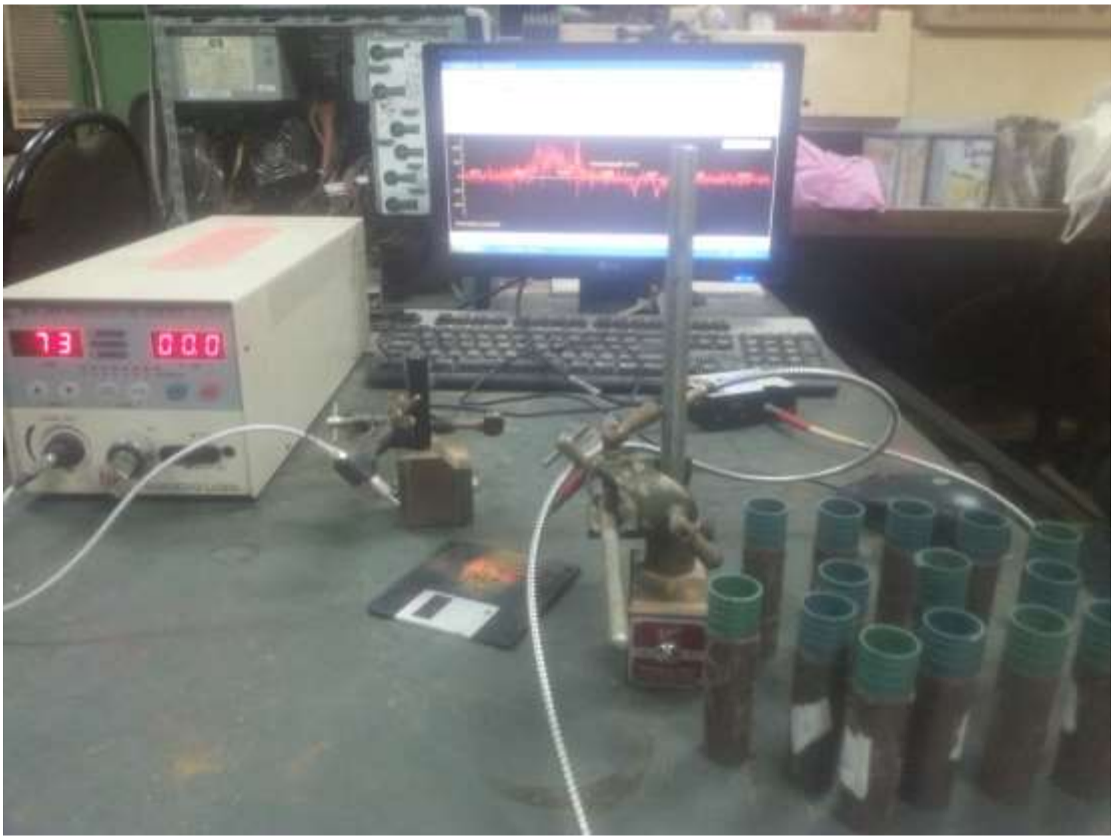
Table (3.1): N_2- laser parameters

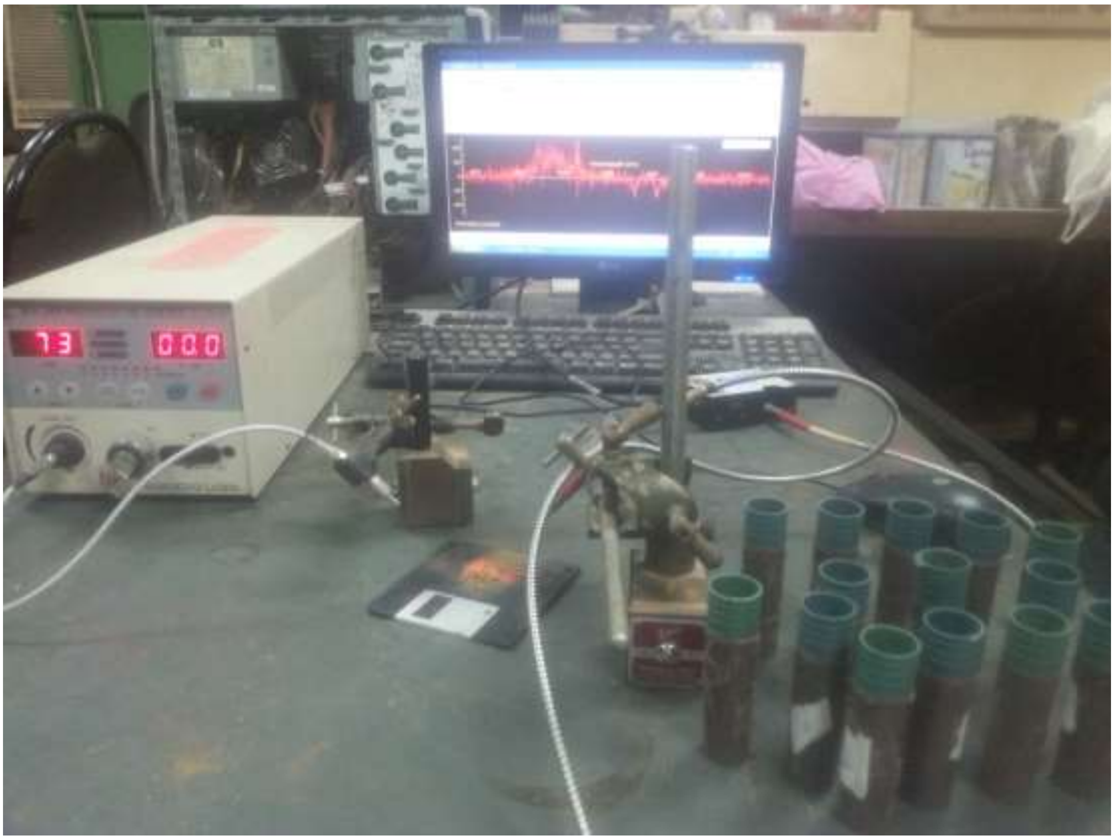
Wavelength	337.3nnm
Frequency	88Hz
Energy	100mj
Pulse duration	6nns

3-3 2 USB 2000 Spectrometer

Table (3.2) shows the USB 2000 Spectrometer

Detector	Liner silicon CCD array
Optical resolution	0.30 – 10nnm FWHM
Dynamic Range	$2*10^8$ – 2000
Sensitivity	400 – 90 photons/ count 600 - 41 photons/ count 800- 203 photons/ count
Integration time	3 ms





Figuer (3.2) LIBS system

Materials and methods

In this papers, this study was focused on the analysis of soil, utilizing LIBS for the detection of Erath's Metal elements present in samples collected from Kadugli City. Fig (1) Schematic diagram of the experimental setup applied for the analysis of soil samples. Fifteen surface soil samples were collected from Kadugli city; all samples were taken with a depth of ten centimeters at a distance of two linear Kilometers. These samples were analyzed using laser Induced Breakdown Spectroscopy (LIBS) to calculate the concentrations of Erath's Metal elements respectively. This is the first study of its kind where LIBS technique has been applied for the measurement of Erath's Metal in Kadogly City soil. The concentration of each Erath's Metal determined with LIBS technique.

3-4 Inductive Coupled plasma (ICP)

3-4-1 ICP device installation

- Three concentric quartz tubes.
- The flame
- Ultimate and visual.
- Radio Frequency Surrounding Generator.
- Glass plasma coil.
- Output device.

3-4-2 The mechanism of action of the device

A torch is placed inside an induction coil supplied with an electric current with a di on the radio plasma. Then the argon atoms flow in which the gas width usually (14 to 18) liters per minute between the two outer tubes of the torch and the electric spark, it is normalized for a short time to introduce free electronics into the gas stream .As the electronics interact with the radio frequency magnetic field of the induction coil the first acceleration in one direction and then in the other, as changes in the field of electrical frequencies are usually 27/2000 cycles per second, Where the accelerated electronics collide with the atoms of Argentina and sometimes because of this collision give up one of the electrons this process continues until the rate of release of new electrons is balanced in the collisions with the atoms of the argon ions resulting in fireballs E– 900 shimadzu Plasma atomic Emission Spectrometer

Plasma	ON
Temp in stand	OK
Stand Door	Closed
Coolant Water	ON
Ar Gas P (KPa)	428.48
Power (k w)	120
Plasma	10.01
Auxiliary	0.60
Carrier	0.70
Ar purge	Low
Direction	Axial
Nozzle Dest	013
Settings	Low
Speed (r.p.m)	20
Spectro Temp (c)	38.00
CCD Temp(C)	-14.89
CCD Coolant	ON
Condensation	OK
Vacuum Level (p a)	6.9
FAN	OK

Figure (3:3) ICP devices

3-4 Methods

In work fifteen samples from gold mining activity from (Kadugli area south Kordofan)

Use Laser Induced Breakdown Spectroscopy (LIPS) Technique, which is an atomic emission Spectroscopy that can analyses any sample successfully and can be applied to soil samples.

Samples were collected from mining areas in Kadugli city at a distance of tow linear Kilometers between each sample and the next Ten centimeters deep. This sample will be put in plastic sample holder

The first sample was taken from inside Al- Bardab After wearing gloves, use a spoon of steel. This sample will be put in plastic sample holder with fifteen samples .sample were analyzed using an ICP device and LIPS device and calculate element concentration.

Chapter Four

Results and Discussion

4.1 Introduction

This chapter contains results obtained by LIBS system and ICP in addition to analysis, discussion, conclusion and recommendation.

4.2 Results

A number of 15 soil samples collected from Kadugli City were analyzed using (LIBS) and ICP to measurements the concentration of obtained element's as shown below.

4.2.1 Laser-Induced Breakdown Spectroscopy (LIBS) Results

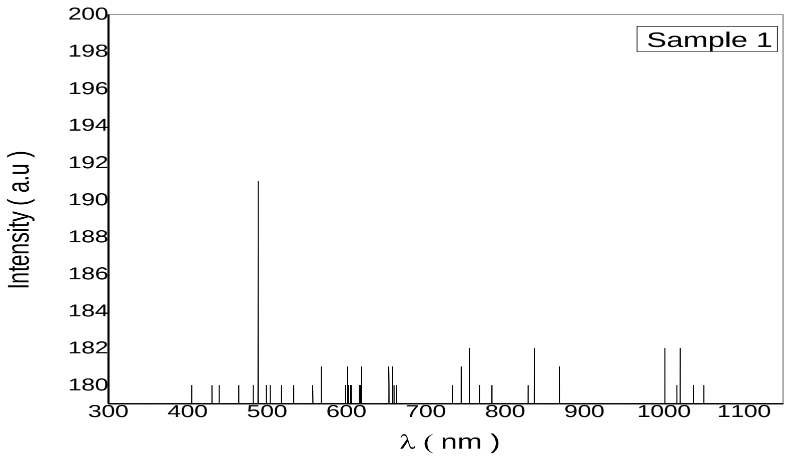


Figure (4.1) Typical LIBS spectra of sample 1 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40

Table (4.1) analyzed data of LIBS spectra sample 1 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	191	TI I
568.894	181	Na I
600.641	181	AL I
602.404	181	Mn I
625.668	180	Ba I
654.303	180	Mg I
836.563	182	Pa
969.471	181	SII

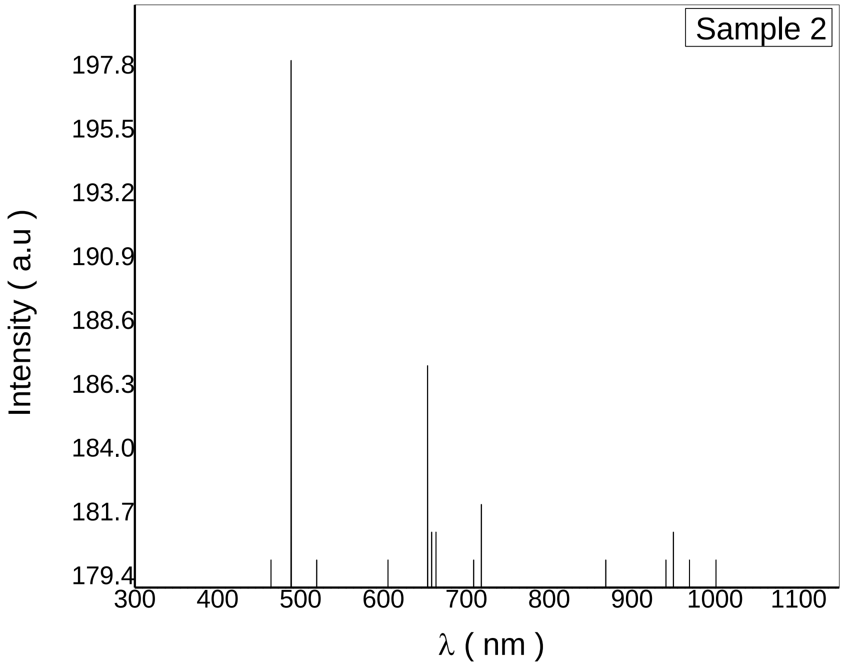


Figure (4.2) Typical LIBS spectra of sample 2 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.2) analyzed data of LIBS spectra sample 2 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
462.242	180	Rb II
488.594	198	Ti I
604.312	180	P II
653.070	187	Na II
654.597	182	Mg II
655.562	180	Rb II
869.471	180	S II
941.497	180	Mg II
963.899	180	P I
968.905s	180	Rb II
1002.401	180	As I

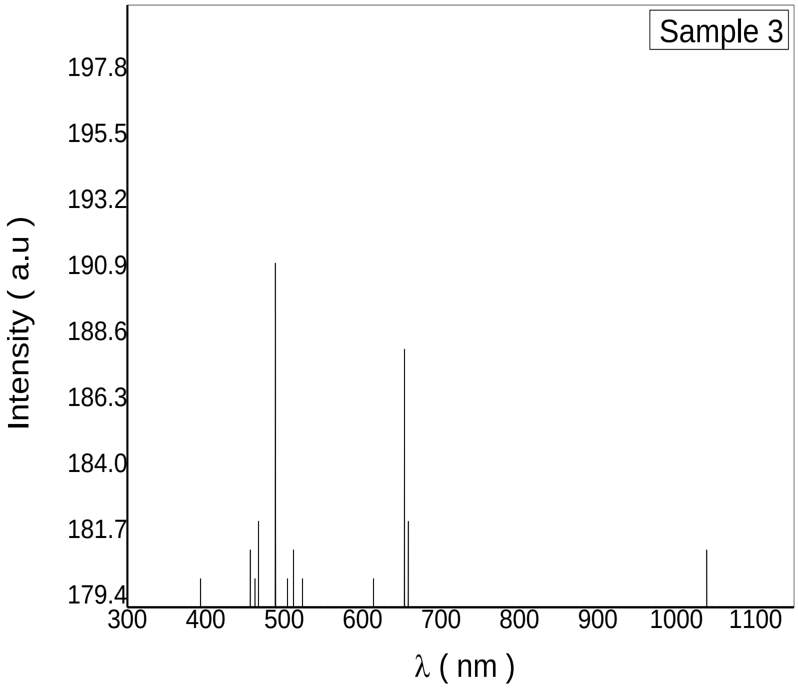


Figure (4.3) Typical LIBS spectra of sample 3 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.3) analyzed data of LIBS spectra sample 3 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
394.401	180	Al I
457.177	180	Rb II
466.680	182	Al I
466.856	182	Na I
488.594	191	Ti I
504.103	180	Si II
511.225	181	K I
522.715	180	Fe I
615.513	180	Si II
653.07	187	Na II
1045.51	181	S I

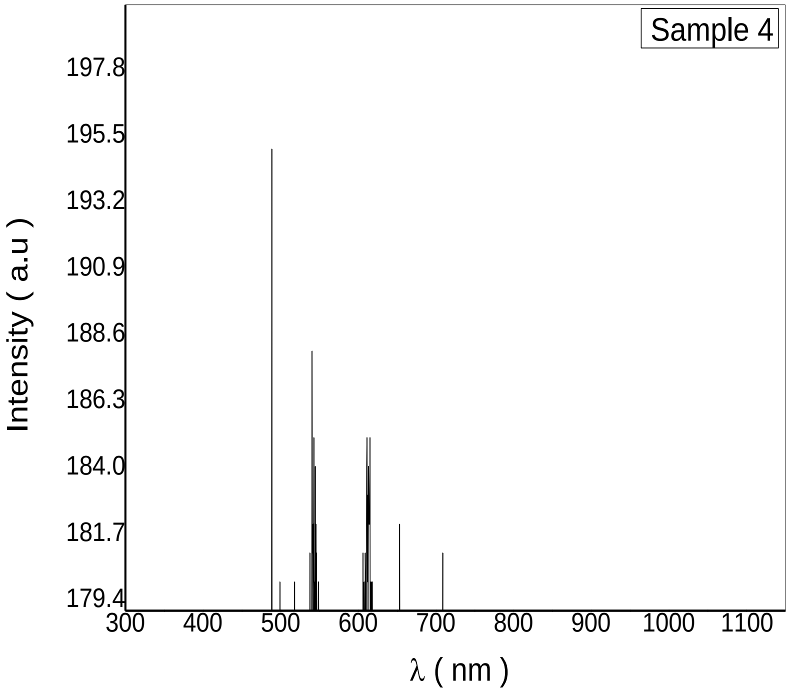


Figure (4.4) Typical LIBS spectra of sample 4in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.4) analyzed data of LIBS spectra sample 4 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	195	Ti I
498.281	180	Na I
515.208	180	Rb II
517.159	180	Fe I
541.455	185	Na I
543.153	184	Rb II
607.078	181	Rb I
607.319	180	Al II
608.044	180	B II
614.171	184	Ba I
615.513	186	Si II
652.731	182	Ba II
653.07	182	Na II

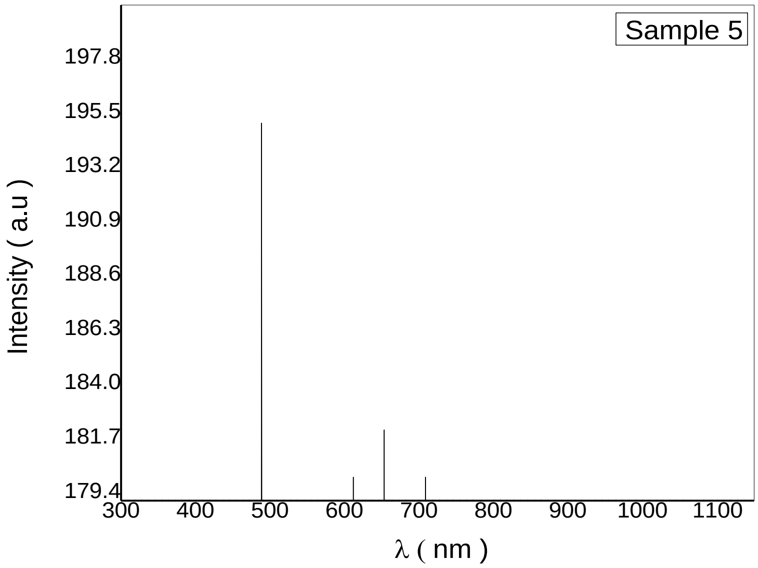


Figure (4.5) Typical LIBS spectra of sample 5 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.5) analyzed data of LIBS spectra sample 5 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	195	Ti I
612.416	180	Ca I
652.668	182	Ba I
709.417	180	Hg I

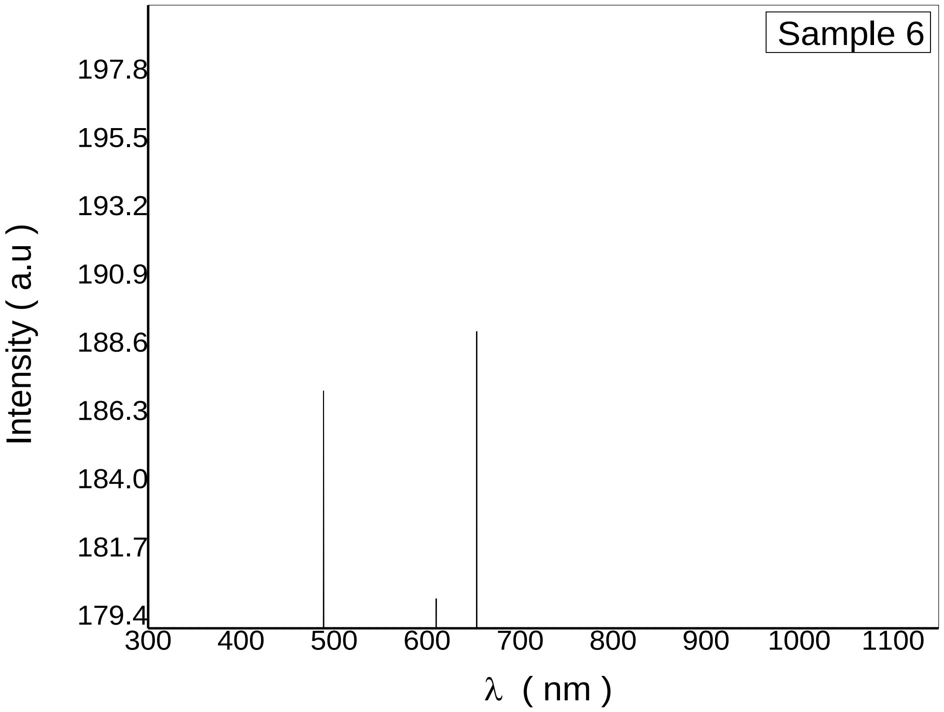


Figure (4.6) Typical LIBS spectra of sample 6 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ

Table (4.6) analyzed data of LIBS spectra sample 6 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	188	Ti I
609.147	180	V I
652.668	189	Ba I
654.303	185	La I

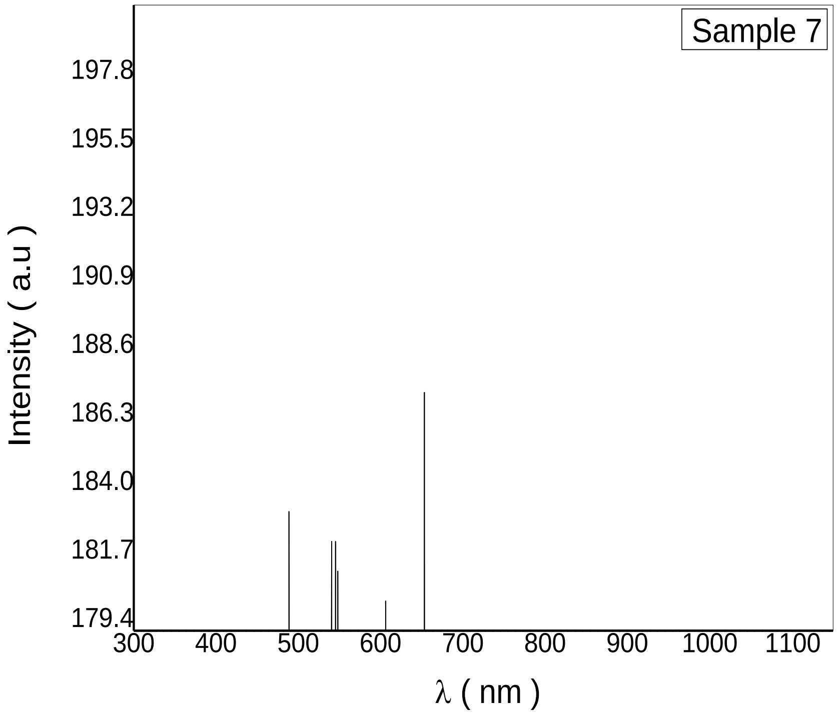


Figure (4.7) Typical LIBS spectra of sample 7 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.7) analyzed data of LIBS spectra sample 7 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	183	Ti I
540.594	182	Ra I
546.681	181	I II
548.450	181	Li I
605.673	180	Al I
652.668	187	Mg II

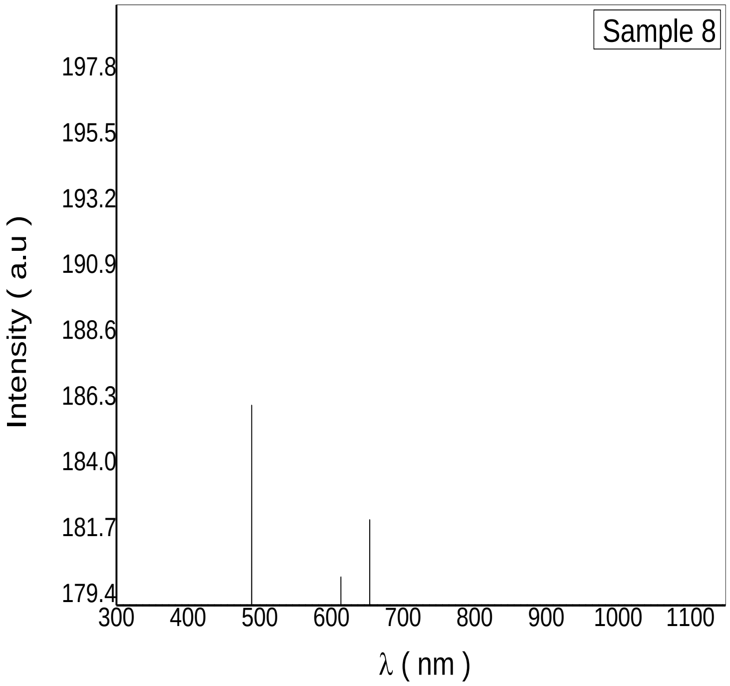


Figure (4.8) Typical LIBS spectra of sample 8 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.8) analyzed data of LIBS spectra sample 8 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	185	Ti I
612.416	181	Ce I
614.050	180	Ba I
652.668	182	Ba I

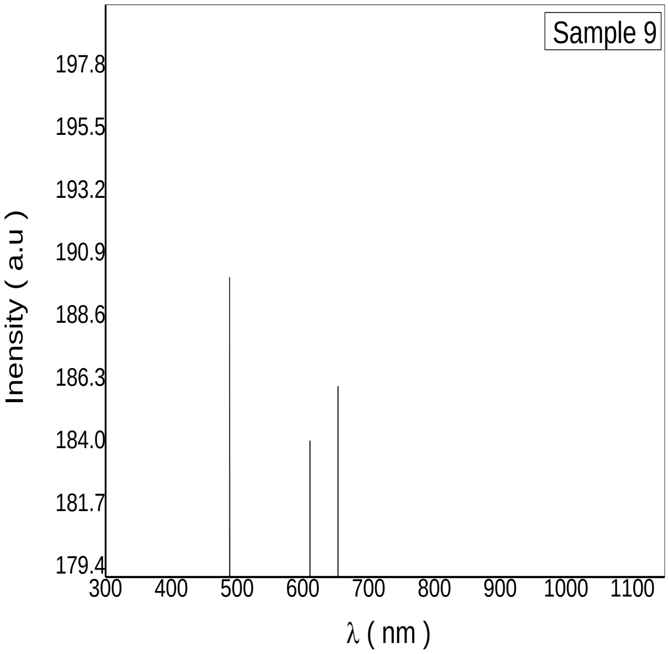


Figure (4.9) Typical LIBS spectra of sample 9 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.9) analyzed data of LIBS spectra sample 9 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	189	Ti I
610.781	184	Ca I
652.668	185	Ba I
654.302	181	La I

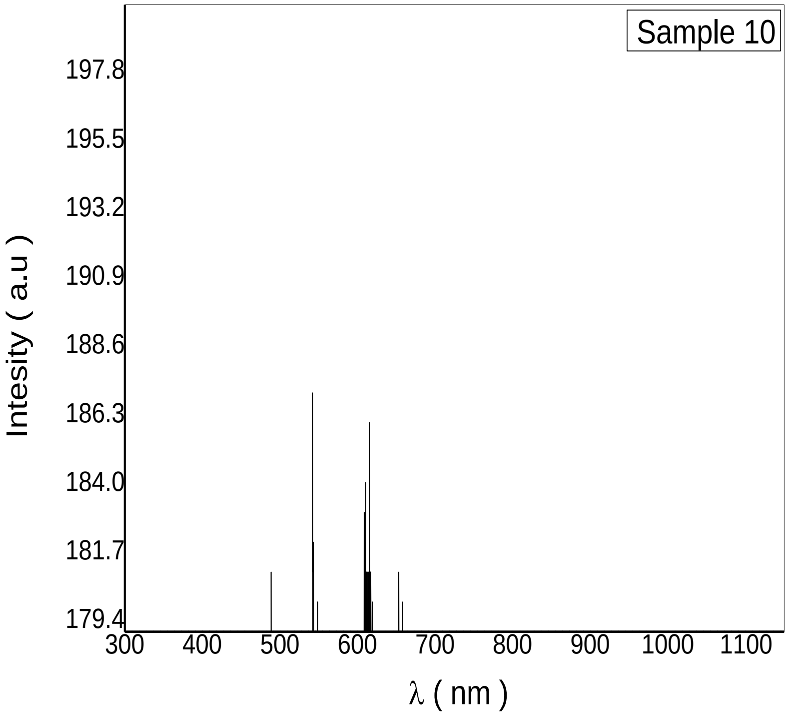


Figure (4.10) Typical LIBS spectra of sample 10 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.10) analyzed data of LIBS spectra sample 10 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	181	Ti I
542.127	187	Ce I
543.762	181	Y I
548.870	179	Eu I
609.147	183	V I
610.781	184	In II
614.050	181	Ba I
615.889	185	O I
619.159	180	Y I
652.668	181	Ba I
612.459	181	Ce I
654.303	180	La I
657.572	180	Ca I

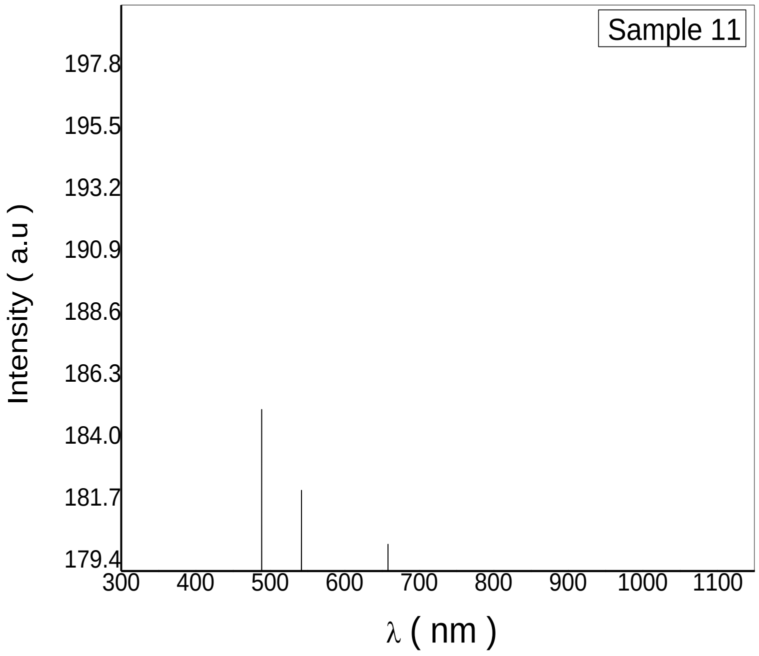


Figure (4.11) Typical LIBS spectra of sample 11 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.11) analyzed data of LIBS spectra sample 11 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	184	Ti I
542.127	181	Ce I
657.180	180	C II

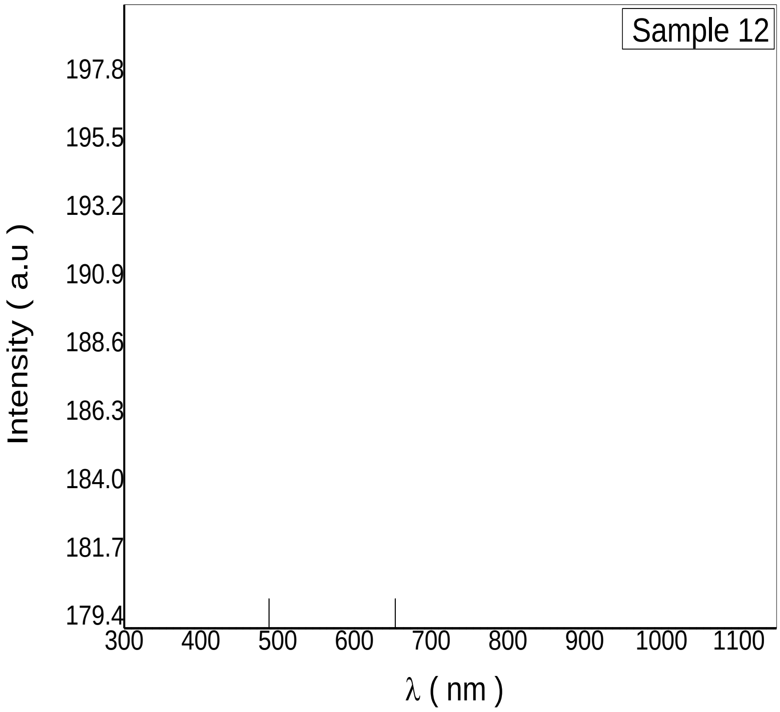


Figure (4.12) Typical LIBS spectra of sample 12 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.12) analyzed data of LIBS spectra sample 12 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	180	Ti I
652.668	180	Ba I

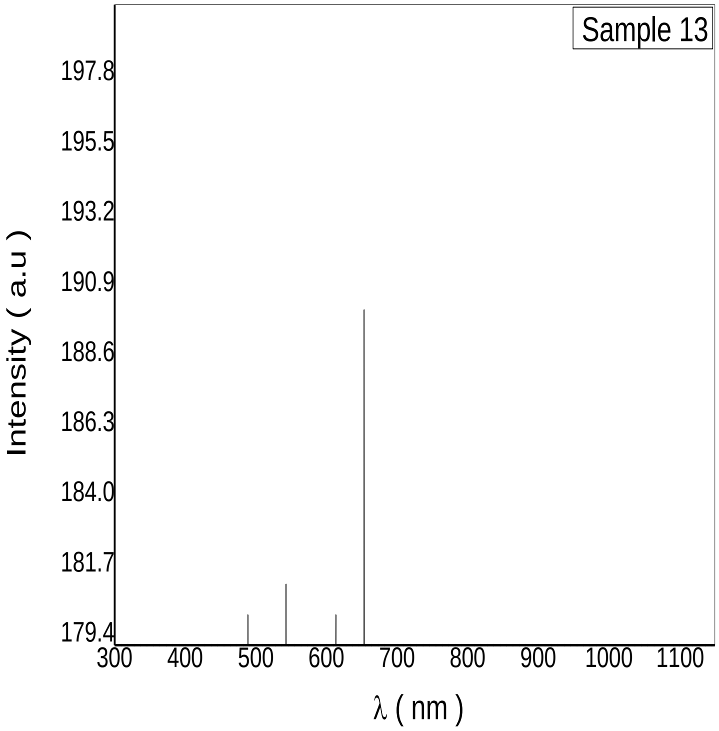


Figure (4.13) Typical LIBS spectra of sample 13 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.13) analyzed data of LIBS spectra sample 13 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	180	Ti I
542.127	181	Ce I
612.415	180	Ce I
614.050	180	Ba I
652.668	189	Ba I
654.303	185	La I

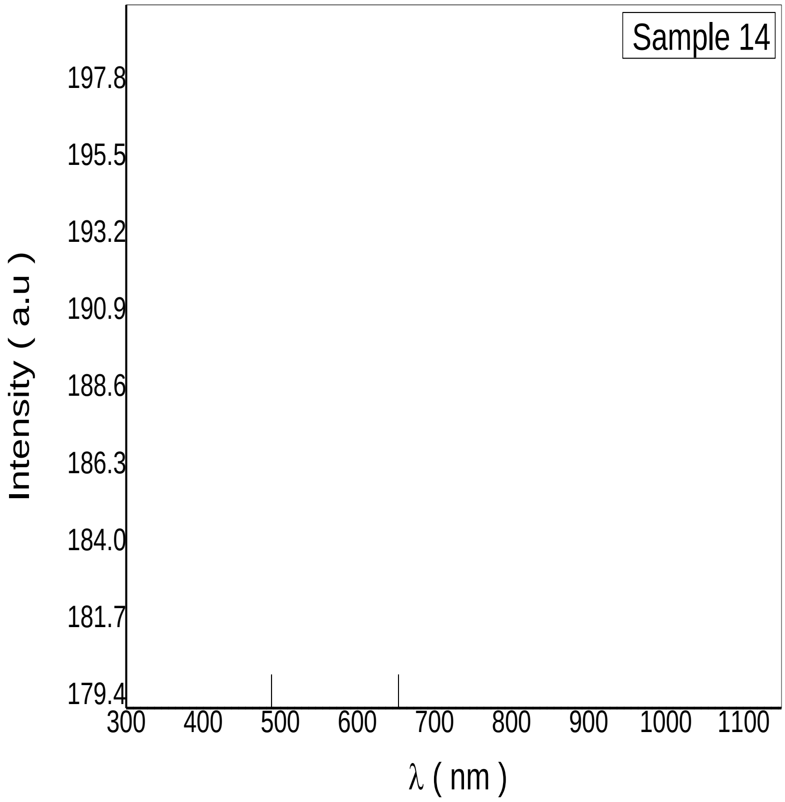


Figure (4.14) Typical LIBS spectra of sample 14 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.14) analyzed data of LIBS spectra sample 14 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.594	179	Ti I
652.668	170	Ba I

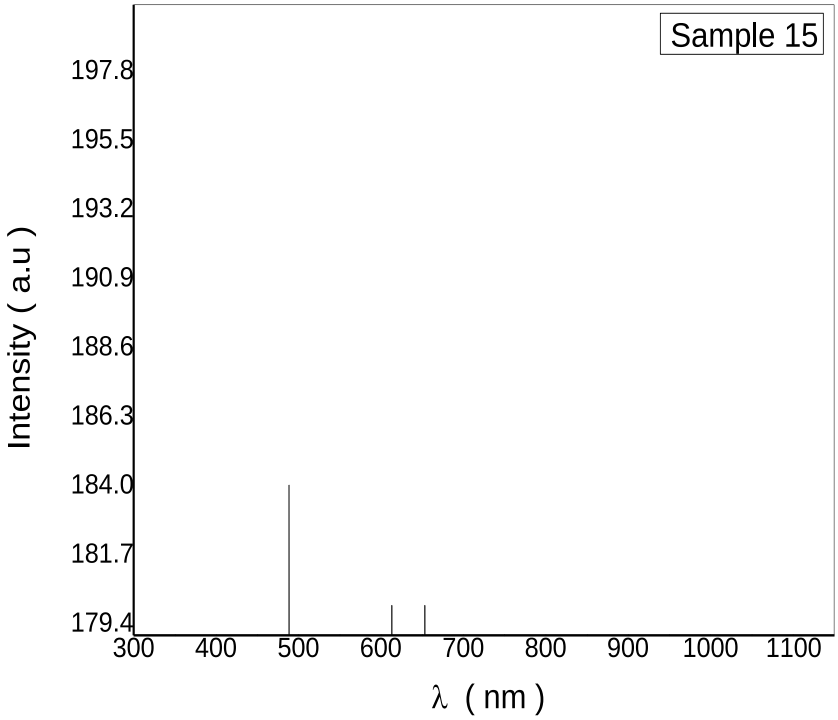


Fig (4.15) Typical LIBS spectra of sample 15 in the region of (100 -1100) nm recorded at delay time of 0.5s and laser pulse energy 40 mJ.

Table (4.15) analyzed data of LIBS spectra sample 15 at irradiated by 40 mJ

Measured λ (nm)	Intensity (a.u)	Elements
488.593	184	Ti I
612.416	179	Ce I
652.668	179	Ba I
614.050	179	Ba I

4.3 Inductively Coupled Plasma (ICP) Results

Table (4.16) analyzed data of sample (1) by Inductively Coupled Plasma

1000mg/L	AL 26+	Fe 40	Mg 1.3	Mn 2.0	Na 3.9
1mg/L<=	S 9.6				
1ug/L<=	Ba 180	Be 1.4	Ca 880	Co 130	Cr 120
	Cu 120	Er 54	I 110	K130	Si 170
	Ni 40	P 320	Ru 100	Sc 6.4	Zn 18
<1ug/L	Sr 20	Ti 23	V 19	Y13	
Not detected ug/L	Ag <45	As <84+	Au< 18	B<17	Bi <76
	Cd <6.8	Ce < 160	Cs <14000	Dy <30	Eu <6.2
	Ga <48	Gd <50	Ge <45	Hf <75	Hg <6.0
	Ho <36	In <340	Ir <330	La <28	Lu <4.0
=	Mo<70	Nb <59	Nd <79	Os <170	Pb <57+
	Pd <130	Pr <110	Pt <240	Rb <86000+	Re <57
	Rh <230	Sb <81	Se <140	Sm <110	Sn <150
	Ta <110	Tb <63	Te <160	Th <540	Ti <280
	Tm <30	U <470	W<150	Yb <2.0	Zr <23

Table (4.17) analyzed data of sample (2) by Inductively Coupled Plasma

1000mg/L						
1 mg/L	Na14	Rb25				
1 ug/L	AL230	K38	P45	S60	Si55	Zn 8.9
<1ug/L	Mg0.52					
Not detected ug/L	Ag<30	As<39	Au<9.8	B <44	Ba<18	Be<0.29
	Bi<37	Ca<0.39	Cd<3.6	Ce<110	Co<15	Cr<16
	Cs1000	Cu<40	Dy<20	Er<23	Eu<40	Fe<16
	Ga<31	Gd<33	Ge<24	Hf<44	Hg<2.9	Ho<24
	I<23	In<160	Ir<180	La<19	Li<0.98	Lu<2.1
	Mn<2.1	Mo<31	Nb<36	Nd<56	Ni<28	Os<85
	Pb<27	Pd<88	Pr<37	Pt<130	Re<27	Rh<150
	Ru<40	Sb<41	Sc<3.2	Se<70	Sm<73	Sn<92
	Sr<0.92	Ta<45	Tb<43	Te<82	Th<90	Ti<7.5
	Ti<150	Tm<20	U<250	V <2.9	W<77	Y<4.4
	Yb<1.2	Zr<15				

Table (4.18) analyzed data of sample (3) by Inductively Coupled Plasma

1000mg/L						
1 mg/L	Rb25					
1 ug/L	Al220	Fe23	K24	Mg2.5	Na590	S180
<1 ug/L	Si400	Zn3.1				
Not detected ug/L	Ag<30	As<36	Au<8.9	B<4.5	Ba<1.8	Be<0.29
	Bi<37	Ca<0.36	Cd<3.6	Ce<110	Co<15	Cr<16
	Cs<1000	Cu<40	Dy<20	Er<23	Eu<4.0	Ga<31
	Gd<34	Ge<24	Hf<44	Hg<2.9	Ho<24	I<23
	In<160	Ir<170	La<19	Li<0.98	Lu<2.1	Mn<2.1
	Mo<31	Nb<36	Nd<57	Ni<28	Os<89	P<46
	Pb<27	Pd<88	Pr<74	Pt<130	Re<27	Rh<150
	Ru<40	Sb<41	Sc<3.2	Se<69	Sm<73	Sn<92
	Sr<0.39	Ta<25	Tb<43	Te<85	Th<91	Ti<7.6
	Ti<150	Tm<20	U<250	V<2.9	W<76	Y<4.4
	Yb<1.2	Zr<15				

Table (4.19) analyzed data of sample (4) by Inductively Coupled Plasma

1000mg/L	Al 3.8	Fe 5.8	Na 1.0	Rb 29		
1 mg/L	B9.3	Ba23	Ca410	K100	Mg330	Mn450
1 ug/L	S350	Si94	Sr 12	Th120	Zn9.9	
Not detected ug/L	Ag <31	As<43+	Au <9.9	Be<0.35	Bi<41	Cd<4.0
	Ce <120	Co<16	Cr <17	Cs<11000	Cu <44	Dy <21
	Er<24	Eu <4.2	Ga<33	Gd<35	Ge <26	Hf<48
	Hg <3.2	Ho <25	I<27	In<190	Ir<190	La<20
	Li<0.99	Lu <2.2	Mo<40	Nb<39	Nd <59	Ni<21
	Os<93	P <50	Pb <31+	Pd <92	Pr<77	Pt<140
	Re<31	Rh<160	Ru <46	Sb <45	Sc<3.4	Se<77
	Sm<77	Sn<98	Ta <52	Tb <45	Te<92	Ti<8.0
	Ti<160	Tm<21	U<270	V<3.1	W<86	Y<4.6
	Yb <1.3	Zr<16				

Table (4.20) analyzed data of sample (5) by Inductively Coupled Plasma

1000mg/L	Al 9.0+	Fe 5.5				
1 mg/L	Ba 31	Ca 93	C0 33	Cr 38	Cr 38	Cu 72
1 ug/L	K 120	Mg 150	Mn 160	Na 730	Na 730	S 190
	Si 130	Sr 7.0	V 7.0	Zn 4.5	Zn 4.5	
Not detected ug/L	Ag <33	As<51+	Au <11	B<11	B<11	Be <0.42
	Bi<47	Cd<4.4	Ce<130	Cs <11000	Cs 11000	Dy <22
	Er <25	Eu<4.5	Ga <35	Gd<37	Gd <37	Ge <29
	Hf <52	Hg<3.5	Ho <26	I<30	I< 30	In< 210
	Ir<210	La<21	Li <1.0	Lu<2.6	Lu <2.6	Mo<44
	Nb<43	Nd<62	Ni <23	Os <100	Os <100	P<56
	Pb<36+	Pd<96	Pr <80	Pt <150	Pt<150	Rb 39000+
	Re<36	Rh<170	Ru<58	Sb <50	Sb <50	Sc<3-6
	Se<85	Sm<81	Sn <110	Ta <67	Ta<67	Tb <47
	Te<100	Th<380	Ti <8.4	Ti <180	Ti<180	Tm <22
	U<310	W<92	Y <4.9	Yb<4.9	Yb<1.4	Zr<17

Table (4.21) analyzed data of sample (6) by Inductively Coupled Plasma

1000mg/L	Al 63+	Ca 1.9	Fe 69	Mg 1.4	Mn 1.7
1 mg/L	Ba 120	Be 2.7	Cd 91	Co 80	Cr 220
1 ug/L	Cu 200	Er 71	Gd 53	Hf 82	I 61
	K 120	Li 1.7	Na 320	Nb 53	Ni 86
	P 250	Re 130	Ru 150	S 720	Sc 13
	Si 100	Sr 36	Th 510	Ti 31	V37
	Y17	Zn 34			
Not detected ug/L	Ag <25	As <86+	Au <16	B<13	Bi <66
	Ce <88	Cs <7600	Dy <16	Eu <3.6	Ga <30
	Ge <35	Hg <4.4	Ho <20	In <200	Ir <260
	La <15	Lu <3.4	Mo <54	Nd <45	Os <130
	Pb <58	Pd <69	Pr <57	Pt <180	Rb <14000
	Rh <120	Sb <65	Se <100	Sm <59	Sn <120
	Ta <100	Tb <35	Te <130	Ti <230	Tm <17
	U<330	W<120	Yb <1.3	Zr <12	

Table (4.22) analyzed data of sample (7) by Inductively Coupled Plasma

1000mg/L<=	Al 14	Ca 3.6	Cs 2.9	Fe 31	Mg 1.8
Not detected ug/L	Mn 4.7	S 9.4			
1 ug/L<=	Ba 560	Be 1.4	Cd 3.4	Ce 180	Co 180
	Cr 55	Cu 420	Dy 39	Er 12	Eu 3.8
	Gd 33	Hf 47	I 60	In 370	Ir 280
	K 200	La 95	Li 3.4	Lu 1.9	Na 410
	Nb 19	Nd 1000	Ni 98	P 220	Pr 21
	Re 76	Ru 32	Sc 5.8	Si 58	Sm 25
	Sr 130	Th 210	Ti 9.7	U210	V15
	Y47	Yb 1.5	Zn 50	Zr 3.9	
Not detected ug/L	Ag <4.0	As<52+	Au <7.0	B<4.7	Bi <35
	Ga <7.8	Ge <15	Hg <3.3	Ho <3.9	Mo <29
	Os <85	Pb <29+	Pd <12	Pt <100	Rb <92000+
	Rh <21	Sb <37	Se<59	Sn <36	Ta <37
	Tb <7.4	Te < 64	Ti <88	Tm<3.3	W 67

Table (4.23) analyzed data of sample (8) by Inductively Coupled Plasma

1000mg/L<=	Al 39+	Ba 1.3	Cs85	Fe 43	Mn 7.0
1 mg/L<=	Ag 3.3	Be 3.5	Ca 990	Ce270	Co 380
1 ug/L<=	Cr 140	Cu 250	Dy 78	Er 17	Eu 1.8
	Gd 55	Hf 68	I 46	In 820	K 230
	La 28	Li 14	Lu 2.9	Mg 890	Na 250
	Nd 100	Ni 73	P 180	Pb 62 +	Pr 12
	Re 99	Ru 76	S 460	Sc 12	Si 38
	Sm 18	Sn 27	Sr 31	Th 350	Ti 12
	U330	V 14		Y13	Yb 2.9
	Zr 16	Zr 9.9	W70		
Not detected ug/L	As <42+	Au <7.6	B<5.8	Bi <38	Cd <2.4
	Ga <7.0	Ge < 16	Hg < 2.2	Ho<2.5	Ir < 120
	Mo <26	Nb <4.7	Os <57	Pd <7.7	Pt <89
	Rb <140000+	Rh <14	Sb <32	Se <49	Ta <39
	Tb <4.8	Te <71	Ti <59	Tm <2.1	

Table (4.24) analyzed data of sample (9) by Inductively Coupled Plasma

1000mg/L<=	Al 38+	Ba 1.4	Ca1.3	Cs 9.3	Fe 41
1 mg/L<=	Mu 7.3				
1 ug/L<=	Ag 3.7	Be 3.4	Ce 240	Co 420	Cr 210
	Cu 220	Dy 80	Er 24	Eu 1.8	Gd 52
	Hf 67	I 97	In 850	K 170	L7a 2
	LI 1.5	Lu 2.7	M0g 95	Na 200	Nb 21
	Nd 93	Ni 130	P 330	Pb 58+	Pr 12
	Re 97	Ru 10	S 650	Sc 8.9	Si 64
	Sm 17	Sr 37	Th320	Ti 15	U31
	V 23	W 69	Y16	Yb 3.1	Zn31
	Zr 7.5				
Not detected ug/L	As< 46+	Au< 7.7	B< 5.7	Bi <38	Cd <2.4
	Ga<7.2	Ge< 16	Hg< 2.3	Ho <2.8	Lr<120
	Mo<26	Os<61	Pd<7.9	Pt<87	Rb<140000+
	Rh< 15	Sb<32	Se<52	Sn<66	Ta<40
	Tb<4.9	Te <57	Tl<58	Tm<2.2	

Table (4.25) analyzed data of sample (10) by Inductively Coupled Plasma

1000mg/L<=	Al 33+	Ca 1.1	Cs 3.9	Fe 35	Mn 2.8
1 mg/L<=	P 1.5				
1 ug/L<=	As 47+	Ba 340	Be 6.1	Ce 290	Co 42
	Cr 42	Cu 84	Dy 25	Er 390	Eu 1.2
	Gd 42	Hf 55	I 390	In 210	K560
	La 46	Li 2.8	Lu 2.3	Mg 260	Na 260
	Nd 130	Ni 44	Pr 10	Re 86	Ru 22
	S 400	Sc 4.4	Si 33	Sm 19	Sr 25
	Th 250	Ti 240	U 230	V 7.2	W 65
	Y 27	Zn 69	Zr 20		
<1ug/L	Yb 0.93				
Not detected ug/L	Ag <2.7	Au <5.8	B <4.4	Bi < 28	Cd <1.9
	Ga <5.1	Ge <12	Hg <1.8	Ho <2.4	Ir <97
	Mo <20	Nb <4.7	Os <50	Pb <23+	Pd <6.9
	Pt <68	Rb <1000	Rh <13	Sb <26	Se <41
	Sn <22	Ta <30	Tb <4.4	Te <46	Ti <51
	Tm <1.9				

Table (4.26) analyzed data of sample (11) by Inductively Coupled Plasma

1000mg/L<=	Al 23+	Ca 1.1	Cs 6.0	Fe 30	Mn 5.9
1 mg/L<=	As 40+	Ba 620	Be 4.6	Bi 30	Ce 470
1 ug/L<=	Co 150	Cr 36	Cu 86	Dy 54	Er 83
	Eu 1.3	Gd 38	Hf 45	I 190	In 520
	K 270	La 62	Lu 1.9	Mg 180	Mo 19
	Na 270	Nb 9.2	Nd 200	Ni 140	P 700
	Pr 13	Re 74	Ru 21	S 430	Sc 2.4
	Si 45	Sm 19	Sr 25	Th 210	Ti 5o
	U 170	V 8.2	W 52	Y 26	Yb 2.1
	Zn 45	Zr 19			
<1ug/L	Li 0.84				
Not detected ug/L	Ag <2.6	Au <5.6	B<4.0	Cd <1.7	Ga <5.4
	Ge <11	Hg <1.7	Ho <2.3	Ir <88	Os <44
	Pb <21+	Pd <7.0	Pt <63	Rb <81000+	Rh <13
	Sb <24	Se <38	Sn<20	Ta <29	Tb <4.3
	Te <40	Ti <50	Tm <1.8		

Table (4.27) analyzed data of sample (12) by Inductively Coupled Plasma

1000mg/L<=	Al 44+	Ca 1.4	Cs 1.7	Fe 22	I12
1 mg/L<=	K 1.2	Mn 1.4	Na 1.1	P 34	S20
1 ug/L<=	As 58+	Ba 170	Be 4.8	Cd 3.1	Ce 110
	Co 31	Cr 47	Cu 210	Dy 18	Er 100
	Eu 1.5	Gd 32	Hf 41	In 120	Ir 150
	La 50	Li 3.1	Lu 1.8	Mg 580	Nb16
	Nd 91	Ni 57	Pr 13	Re 66	Ru 26
	Sc 5.8	Si 63	Sm 17	Sr 110	Th 190
	Ti 63	U 170	V10	W 57	Y33
	Zn 180	Zr 20			
< 1ug/L	Yb 0.54				
Not detected ug/L	Ag <2.7	Au <5.1	B<3.6	Bi <24	Ga <5.1
	Ge <11	Hg <2.1	Ho <2.5	Mo <22	Os <55
	Pb <22+	Pd <7.4	Pt <71	Rb <74000+	Rh <13
	Sb<26	Se <43	Sn <26	Ta <27	Tb <4.6
	Te <49	Ti <56	Tm <2.0		

Table (4.28) analyzed data of sample (13) by Inductively Coupled Plasma

1000mg/L<=	Al 14+	Fe 1.2			
1 mg/L<=	Ba 15	Ca 36	Co 23	Cu 92	Er 160
1 ug/L<=	I110	K 170	La 16	Li 1.1	Mg 32
	Mn 77	Na 150	Nb 20	P 420	S 150
	Si 30	Sr 3.5	Ti 67	Y 5.3	Zn 12
	Zr 9.4				
<1 ug/L	Be 0.79				
Not detected ug/L	Ag < 15	As <46+	Au <9.3	B< 7.9	Bi <41
	Cd <3.7	Ce <77	Cr <12	Cs <8300	Dy <11
	Eu <2.4	Ga <18	Gd <17	Ge <20	Hf <30
	Hg <3.2	Ho <13	In <130	Ir <190	Lu <1.7
	Mo <40	Nd <38	Ni <21	Os <92	Pb <32+
	Pd <47	Pr <46	Pt <140	Rb <29000+	Re <30
	Rh <76	Ru <40	Sb <46	Sc <1.9	Se <76
	Sm <41	Sn <58	Ta <56	Tb <25	Te <84
	Th <210	Ti <120	Tm <11	U <210	V<1.7
	W<85	Yb <0.78			

Table (4.29) analyzed data of sample (14) by Inductively Coupled Plasma

1 mg/L<=	B 4.2	Ba 3.2	Ca 480	Er 4o	I 62	K 35
1 ug/L<=	Mg 240	Mn 51	Na 140	Nb 17	P 230	S 77
	Si 7.2	Sr 12	Th 58	Ti 17	Y2.4	Zn 4.6
< 1ug/L						
Not detected ug/L	Ag < 11	As <26+	Au <5.8	Be <0.21	Bi <25	Cd <2.4
	Ce <57	Co <9.5	Cr 7.8	Cs <6100	Cu <28	Dy <7.8
	Eu <1.7	Ga <13	Gd <13	Ge <13	Hf <20	Hg <1.9
	Ho <9.4	In <93	Ir <120	La <9.5	Li <0.69	Lu <1.1
	Mo <20+	Nd <28	Ni <13	Os <61	Pd <19+	Pd <34
	Pr <34	Pt <89+	Re <19	Rh <56	Ru <27	Sb <30
	Sc <1.4	Se <49	Sm <29	Sn <40	Ta <31	Tb <18
	Te <53	Ti <75	Tm <7.9	U<130	V<1.2	W<53
	Yb <0.55	Zr < 5.6				

Table (4.30) analyzed data of sample (15) by Inductively Coupled Plasma

1000mg/L<=	Al 16+	Cs 1.7	Fe 21	Mn <12	P 1.9
1 mg/L<=	S 1.9				
1 ug/L<=	Ba 60	Be 2.7	Ca830	Ce 150	Co 9.3
	Cr 13	Cu 42	Dy 13	Er 360	Eu 1.0
	Gd 26	Hf 35	I 530	In 89	K380
	La 54	Li 1.4	Lu 1.3	Mg 490	Na 210
	Nb 9.0	N d 97	Ni 6.7	Pr 12	Re 56
	Sc 2.0	Si 71	Sm 15	Sr 7.3	Th 140
	Ti 210	Ti 50	U 130	V1.2	W 39
	Y 20	Zn 59	Zr 34		
1ug/L	Yb 0.41				
Not detected ug/L	Ag <2.0	As <23+	Au <3.5	B <2.7	Bi <17
	Cd < 1.2	Ga <3.3	Ge<7.2	Hg <1.2	Ho< 1.8
	Ir <61	Mo <13	Os <32	Pb <15+	Pd <5.5
	Pt <44	Rb< 57000+	Rh <9.4	Ru <26+	Sb <17
	Se <25	Sn <13	Ta <18	Tb <3.2	Te <29
	Tm <1.4				

4.4 Calculation Concentration Results by LIB and ICP methods

Table (4.31) Concentration ppm By ICP and Concentration ppm By LIB sample 1 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti I	2300	2500
Na I	3.9	4.1
AL I	26	24.2
Mn I	2	2.3
Ba I	18000	18563
Mg I	1.3	2.1
S I	4.6	4.72

Table (4.32) Concentration ppm By ICP and Concentration ppm By LIB sample 2 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Rb	25	27.2
Ti	< 7.5ppt	9.31
P	4500	4621
Na	1400	1502
Mg II	52	53.2
Rb	25	27.1
S	6000	6124
Mg	52	54.3
P	4500	4652
Rb	25	27.4
As	< 39 ppt	40.35

Table (4.33) Concentration ppm By ICP and Concentration ppm By LIB sample 3 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
A Lǀ	2200	2310
Rbǁ	25	27.3
AL ǁ	2200	2421
Na ǀ	59000	59332
Tiǀ	<706 ppt	724.1
Si ǁ	40000	40115
K ǀ	2400	2451
Fe ǀ	2300	2401
Si ǁ	40000	42134
Na ǁ	59000	59614
Si ǀ	40000	42153

Table (4.34) Concentration ppm By ICP and Concentration ppm By LIB sample 4 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti ǀ	< 160 ppt	166.1
Na ǀ	1	0.93
Rb ǁ	29	31.2
Fe ǀ	5.8	6.4
Na ǀ	1	1.22
Rb ǁ	29	31.2
Rb ǀ	29	33.4
AL ǁ	3.8	4.12
B ǀ	9.3	10.2
Ba ǀ	23	24.3
Si ǀ	4900	4935
Ba ǀ	23	25.1
Na ǀ	1	0.97

Table (4.35) Concentration ppm By ICP and Concentration ppm By LIB sample 5 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti ǀ	< 180 ppm	213.4
Ca ǀ	9300	9532
Ba ǀ	3100	3254
Zr ǀ	< 3.5 ppm	5.12

Table (4.36) Concentration ppm By ICP and Concentration ppm By LIB sample 6 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti ǀ	3100	3312
V ǀ	3700	3942
Ba ǀ	120	124.2
Na ǀ	32000	3521

Table (4.37) Concentration ppm By ICP and Concentration ppm By LIB sample 7 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti ǀ	970	987
I ǁ	6000	6241
L i ǁ	340	352
AL ǁ	14	17.5
M g ǁ	1.8	2.21

Table (4.38) Concentration ppm By ICP and Concentration ppm By LIB sample 8 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti ǀ	120	12.4
Ce ǀ	270	283.2
Ba ǁ	1.3	2.31
Ba ǀ	1.3	1.72

Table (4.39) Concentration ppm By ICP and Concentration ppm By LIB sample 9 at irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti I	150	162.3
Ca I	1.3	2.11
Ba I	1.4	1.81
La I	270	309

Table (4.40) Concentration ppm By ICP and Concentration ppm By LIB sample 10sat irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti I	24000	25134
Ce I	29000	29752
Y I	2700	2841
Eu I	120	124.3
V I	720	782.4
InII	21000	22431
Ba II	34000	35216
Y I	2700	2812.1
Ba I	34000	35124
Ce I	29000	31241
La I	4600	4712
Ca I	1.1	2.01

Table (4.41) Concentration ppm By ICP and Concentration ppm By LIB sample 11sat irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti I	5000	5421
Ce I	470	481.3

Table (4.42) Concentration ppm By ICP and Concentration ppm By LIB sample 12 sat irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti I	6300	6421
Ba I	17000	18245

Table (4.43) Concentration ppm By ICP and Concentration ppm By LIB sample 13 sat irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti Ⅰ	6700	6852
Ba Ⅱ	15	17.2
Ba Ⅰ	15	18.34
La Ⅰ	1600	1732

Table (4.45) Concentration ppm By ICP and Concentration ppm By LIB sample 15sat irradiated by 40 mJ

Elements	Concentration ppm By ICP	Concentration ppm By LIB
Ti Ⅰ	1700	1852
Ba Ⅰ	3.2	4.12

4.5 Discussion

A number of 15 soil samples collected from Kadogly were analyzed uses Inductively Coupled Plasma (ICP), and Laser-Induced Breakdown Spectroscopy (LIBS), all samples were taken with a depth of ten centimeters at a distance of two linear Kilometers inside city, These samples were kept in plastic tubes with a tight lid detection some elements like Titanium (Ti), Sodium (Na), Cesium (Ce), Iodine (I), Phosphorus (P), Sulfur , Rubidium (Rb), Barium (Ba), Magnesium (Mg) and Arsenic (As) assessment.

4.5.1 Most Elements repeated on Kadugli City Soil sample that detected by LIBS and ICP methods

Table (4.46) metal elements that all most appear in all samples collected from Kadugli city

λ (nm)	Intensity (a.u)	Elements	A_{jk} (10^8 s^{-1})	E_i (cm^{-1})	E_f (cm^{-1})	Concentration ppm
488.594	190	Ti I	0.018	0.000	23792.59	33.4
515.208	180	Rb II	0.015	0.000	23715.081	33.4
546.681	181	I II	0.030	7603.15	56092.88	6241
568.894	180	Na I	0.616	0.000	16973.368	3521
600.769	180	Ce I	0.422	3764.008	20591.937	481.3
602.404	180	P II	0.71	18722.71	57876.574	4652
652.668	180	Ba I	0.33	9215.501	24531.513	3254
654.303	180	Mg I	0.575	21911.178	41197.403	53.2
969.471	181	S I	0.28	52623.640	63446.065	6124
1000.637	179	As I	0.55	18186.328	53135.750	40.35

For the above tables it observed that and all samples contains four toxic elements (Sulfur(S), Arsenic (As), Cerium (Ce) and Iodine(I), five heavy elements (Sodium (Na), Magnesium (Mg), Phosphorus(P), Titanium (Ti) and Barium (Ba) in addition to one radioactive element (Rubidium (Rb). It is clear that all detected elements have low concentration.

4.5.2 Erath’s Metal in Kadugli City Soil as compared to safe limit

The soil samples were collected from Kadugli city contain Erath’s Metal elements (Titanium (Ti), Iron (Fe), Manganese (Mn), Barium (Ba) and Magnesium (Mg)). And used Calibration curve to calculated concentration by LIBS method.

Table (4.47) the concentrations of earth’s metal elements collected in surface soil samples collected from Kadugli city, and comparison of LIBS results

λ (nm)	Intensity (a.u)	Elements	A_{jk} (10^8 s^{-1})	E_i (cm^{-1})	E_f (cm^{-1})	Concentration ppm
488.594	190	Ti I	0.018	0.000	23792.59	33.4
522.715	180	Fe I	0.500	11976.238	34782.419	06.4
602.404	181	Mn I	0.787	17052.29	41789.48	02.3
652.668	180	Ba I	0.33	9215.501	24531.513	3254
654.303	180	Mg I	0.575	21911.178	41197.403	53.2

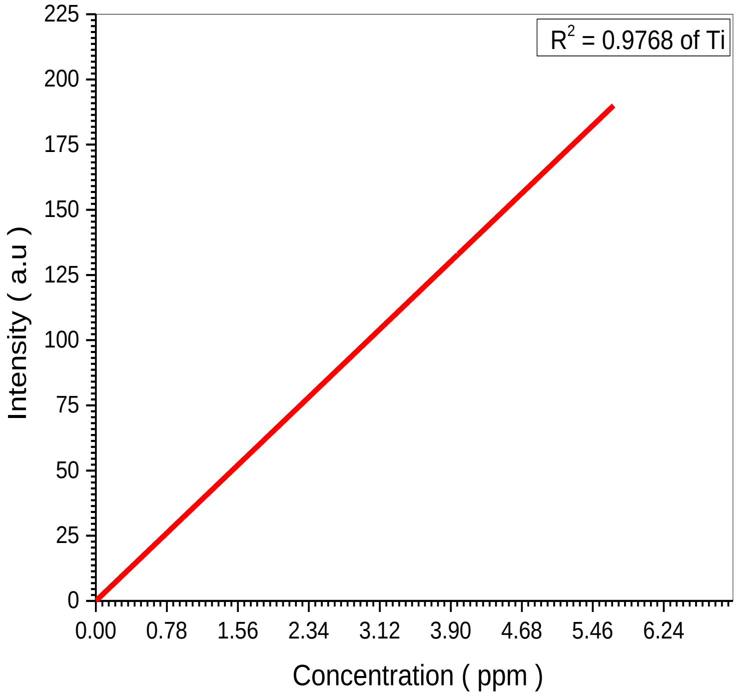


Figure (4.16) Calibration curve for Titanium (Ti) obtained by using analytic calibration function of (Ti) with known concentration.

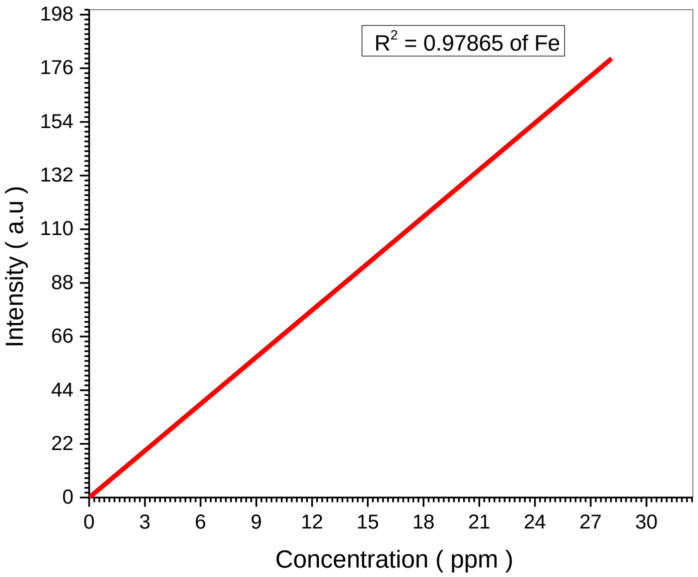


Figure (4.17) Calibration curve for Iron (Fe) obtained by using analytic calibration function of (Fe) with known concentration.

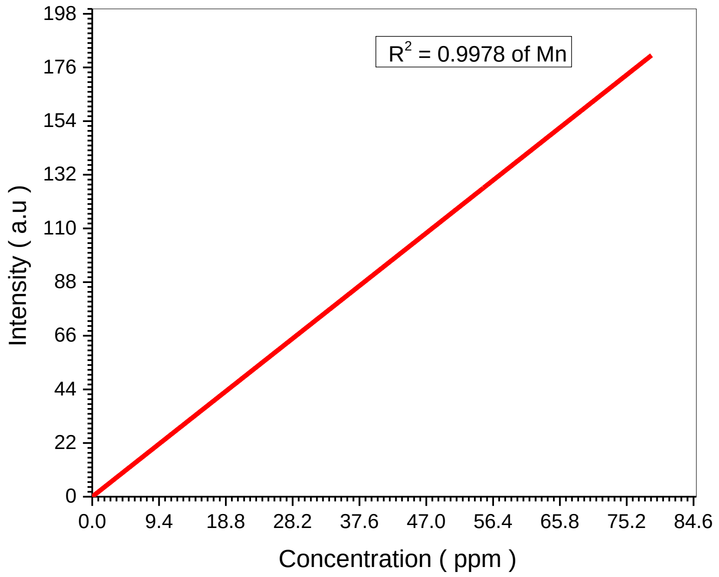


Figure (4.18) Calibration curve for Manganese (Mn) obtained by using analytic calibration function of (Mn) with known concentration.

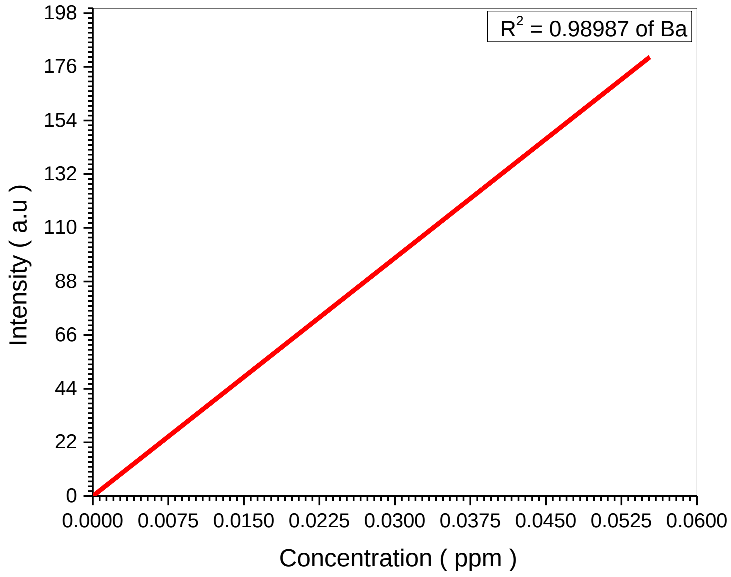


Figure (4.19) Calibration curve for Barium (Ba) obtained by using analytic calibration function of (Ba) with known concentration

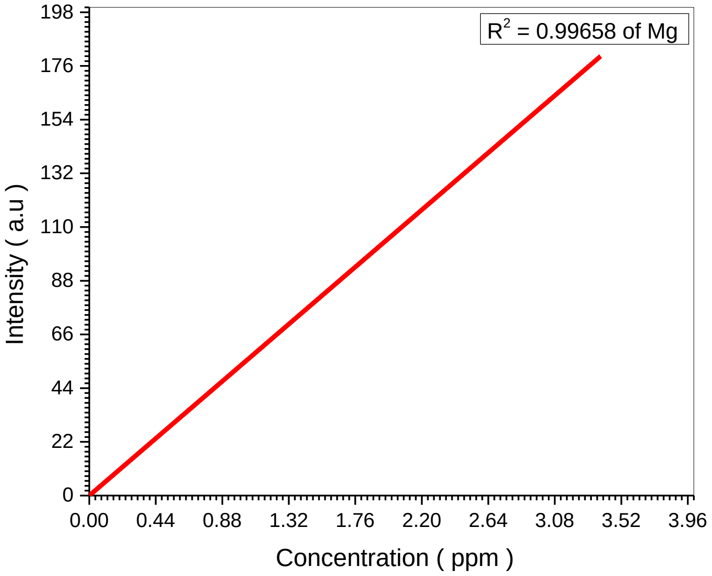


Figure (4.20) Calibration curve for Magnesium (Mg) obtained by using analytic calibration function of (Mg) with known concentration

The calibration curves for each element under investigation were established by plotting the LIBS signal intensity of specific transition of each element as a function of the concentration. A typical calibration curve for (Titanium (Ti), Iron (Fe), Manganese (Mn), Barium (Ba) and Magnesium (Mg)) inside the surface soil samples were presented from Fig (4.16) to Fig (4.20), similar calibration curves were drawn for other elements under study for quantification of their concentration present in surface soil samples. The LIBS spectra were recorded for these different concentrations of each element for its calibration. The LIBS signal intensity showed linear dependence on the concentration of Titanium (Ti) which was 33.4 ppm with accuracy 0.9798, Iron (Fe) was 6.4 ppm with accuracy 0.97865, Manganese (Mn) was 2.3 ppm with accuracy 0.9978, Barium (Ba) was 3254 ppm with accuracy 0.9898 and Magnesium (Mg) was 53.2 ppm with accuracy 0.99568, all samples concentration was obtained by using calibration equation. The LIBS signal intensity showed linear dependence on the concentration of Titanium (Ti) which was 33.4 ppm with accuracy 0.9798, Iron (Fe) was 6.4 ppm with accuracy 0.97865, Manganese (Mn) was 2.3 ppm with accuracy 0.9978, Barium (Ba) was 3254 ppm with accuracy 0.9898 and Magnesium (Mg) was 53.2 ppm with accuracy 0.99568.

4.5.3 Assessment Concentration of some elements in Kadogly City Soil

laser-induced breakdown spectroscopy (LIBS) has been applied for the determination levels of (Limit of detection (LOD), relative standard deviation (R.S.D.) and relative accuracy (RA) describe) in soil samples and the results have been compared with inductively coupled plasma emission spectroscopy (ICP).

Table (4.48) elements detected in all samples with the limit of detection and maximum detected concentrations and maximum permissible concentration safe limit (MPC).

Elements	Λ (nm)	LIB Concentration (ppm)	ICP Concentration (ppm)	I(a.u)	S.D	LOD	RSD	RA
Al I	394.401	2310	2200	180	2.484013	63.75634	0.107533	0.050001
Rb II	457.177	27.3	25	180	0.051938	0.015755	0.190251	0.092001
Si II	504.103	40115	40000	180	2.596923	1157.506	0.006474	0.002875
K I	511.225	2451	2400	181	1.151679	31.19077	0.046988	0.02125
Fe I	522.715	2401	2300	180	2.280776	60.84603	0.094993	0.043914

As clear from Table (4.48), the relative accuracy is in the range of 0.2875 to 0.92001 which is quite acceptable for any good instrument. In order to achieve the better accuracy and precision with our method, following additional precautions were undertaken. The R.S.D. value in our case was (0.1 %). The all samples results with LIBS method were comparable to the results obtained by inductively coupled plasma emission spectroscopy (ICP). The limit of detection for some elements under investigation is given in Table (4.48). In this study, the limit of detection calculated using above mentioned method for (element's ppm) which are higher than safe permissible limit and therefore LIBS might not be a technique of choice for the assessment of safety limits. Comparison of the data from two detection systems and the accuracy of LIBS The accuracy and precision for the all sample under investigation obtained from these two detection systems (LIBS and ICP) are compared in table (4.48).

4.6 Conclusions

In this research, Laser Induced Breakdown Spectroscopy (LIBS) was used to survey 15 soil samples collected from Kadogly City, this sample putting in plastic tuob, in this samples we find four toxic elements, five heavy elements, five earth's metal in addition to one radioactive element. The concentration of detected elements presents in soil samples were Low, we found that LIBS system more accurate than ICP.

4.7 Recommendations

- Study heavy metal in all state area.
- Detection elements on same area using different techniques (gamma spectroscopy, and XRF).
- Built up database for elements after survey all area.

References:

[1] wolfagang Demoted, leaser spectroscopy, Springer, 2003.

[2] Ronald w, Waynant Editor, Marwood N, Edige, Electro-optics handbook, Ch. 20.1 New York,2000.

[3] Michael Hollas, J Modem, spectroscopy, Wiley and sons England, 2004.

[4] Agency, A basic toxicity classification of radionuclides international atomic energy, Vienna, 1963.

[5] Fathi, afify, basics of toxicology, house of Knowledge,2000.

[6] Abdu alaziz, fathi, basics of toxicology, AL-Fajr publishing house, 2001.

[7] Abdu Almonem. Toxic element produce and effect to environment,2007.

[8] Albyati. Firas Abbas fabel. Environmental pollution is a hindrance to development and a threat to the population. university of al Mosu.2010.

[9] Al- Hadithi. Khaled Ibrahim. Study of selected heavy elements phosphorous and fluoride in the muddy part of the sediments of the Qadisiyah Dam reservoir.2010.

[10] Alhelo. Majed Ragheb. Environmental protection Low in the Light of Sharia. the new university house, Alexandria.2009.

[11] Alsadi. Hussein Ali . Basics science Environmental and pollution. Alyazory house. Oman.2006.

[12] Alali. Wedad. Awareness Environmental in states councils' cooperation alkhaligy.2005.

[13] Aldama. Mohamad shehata. Nuclear physics .2005.

[14] Hammed. Mamduoh. radioactive effect. 2003

[15] Svanberg, sune, Atomic and Molecular Spectroscopy, editions- springer verlag Berlin Heidelberg,2004.

[16] platt, U and J. Stutz, interaction of Molecules with radiation in : U, Platt and. Stutz, Deferential optical absorption spectroscopy, physics of Earth and Space Environments,2008.

[17] http:// WWW.oceanoptics.com/products. 2Atomic and Molecular Spectroscopy University of Michigan physics, p$^{441-442}$ Advanced physics Laboratory February,(2006) Hameed, Sood, 2004, Basics of Leaser, . Umm Al Qura University.

[18] Sensor Kristine Eland Zeigler, Robert J , Lascola ,and Laura, Tovo, Fiber –optic Laser Raman Spectroscopy, Westinghouse savannah River Company Aiken,2003.

[19] Schulz, Christof, Leaser and its applications. Umm Al Qura University, 2004.

[20] Miziolek. A, V. Plleschi and I. Schechter, Leaser-induced Breakdown Spectroscopy, Cambridge University press, 2006,

[21] Joseph sneddon,1998, Leaser-induced Breakdown Spectroscopy, Spring New York.

[22] Capitelli. M, A. Casavla, G. Colonna, Laser-induced Plasma expansion, theoretical and experimental aspects, Spectrochim Acta Part,2004.

[23] Mahmoud Al-Salihi, Rongxing Yi, Shiqi Wang, Qiang Wu, Fangrui Lin, Junle Qu, And Liwei Liu, Quantitative laser-induced breakdown spectroscopy for discriminating neoplastic tissues from non-neoplastic ones, Optics Express, Vol. 29, No. 3,4159-4173, 2021.

[24] Daniel Diaz, Alejandro Molina and David W. Hahn, Laser-Induced Breakdown Spectroscopy and Principal Component Analysis for the Classification of Spectra from Gold-Bearing Ores, Applied Spectroscopy, Vol. 74(1) 42–54, 2020.

[25] Vinicius C. Costa, Diego V. Babos, Jeyne P. Castro, Daniel F. Andrade, Raimundo R. Gamela, Raquel C. Machado, Marco A. Sperança, Alisson S. Araújo, José A. Garcia and Edenir R. Pereira-Filho, Calibration Strategies Applied to Laser-Induced Breakdown Spectroscopy: A Critical Review of Advances and Challenges, Sociedade Brasileira de Quimica, J. Braz. Chem. Soc., Vol. 31, No. 12, 2439-2451, 2020.

[26] X. Li, S. Yang, R. Fan, X. Yu, D. J. O. Chen, and L. Technology, "Discrimination of soft tissues using laser-induced breakdown spectroscopy in combination with k nearest neighbors (kNN) and support vector machine (SVM) classifiers," Opt. Laser Technol. 102, 233–239 ,2018.

[27] H. Fu, J. Jia, H. Wang, Z. Ni, and F. Dong, "Calibration Methods of Laser-Induced Breakdown Spectroscopy," in Calibration and Validation of Analytical Methods-A Sampling of Current Approaches Intech Open, 2017.

[28] Gondal, M.A.; Nasr, M.M.; Ahmed, Z.; Yamani, Z.H. J. Environ. Sci. Health, Part A, 44, 528. 2009.

[29] M. Gondal, R. Aldakheel, M. Almessiere, M. Nasr, J. Almusairii, B. J. J. o, P. Gondal, and B. Analysis, "Determination of heavy metals in cancerous and healthy colon tissues using laser induced breakdown spectroscopy and its cross validation with ICP-AES method," J. Pharm. Biomed. Anal. 183, 113153, 2020.

[30] F. Mehari, M. Rohde, R. Kanawade, C. Knipfer, W. Adler, F. Klämpfl, F. Stelzle, and M. J. J. o. b. Schmidt, "Investigation of the differentiation of ex vivo nerve and fat tissues

using laser-induced breakdown spectroscopy (LIBS): Prospects for tissue-specific laser surgery,″ J. Biophotonics 9(10), 1021–1032 ,2016.

[31] Ran Zhou, Ke Liu and et al, Determination of micronutrient elements in soil using Laser induced breakdown spectroscopy assisted by Laser-induced breakdown spectroscopy fluorescence, Journal of Analytical Atomic Spectrometry, Vol 36, No3, 2021.10. Gondal, M.A.; Hussain, T.; Yamani, Z.H.; Baig, M.A. J. Hazard. Mater, 163, 1265, 2009

[32] Gondal, M.A.; Nasr, M.M.; Ahmed, M.M.; Yamani, Z.H.; Alsalhi, M.S. J. Environ. Sci. Health, Part A, 46, 42, 2011.

[33] M.A. Gondal, T. Hussain, Determination of poisonous metals in wastewater collected from paint manufacturing plant using laser-induced breakdown spectroscopy, Talanta71(2007)73–80.

[34] Qingyu Lin, Pengkun and et al, Quantative Multiple-element simultaneous analysis of seaweed fertilizer by laser induced breakdown spectroscopy, Optics Express, Optical SocietyofAmerica,Vol28,No.10,2020.

[35] Paullino R. Villas-Boas and et al, Application of Laser-induced breakdown spectroscopy for Soil analysis, part 1: Review of fundamental and chemical and physical properties, European Journal of Soil Science, Welly, 2019.

[36] Zaitun,S Prasetyo, M Suliyanti, Isnaeni and Y Herbani, Quantitative analysis of titanium concentration using calibration-free laser-induced breakdown spectroscopy (LIBS),IOPConf.Series:JournalofPhysics,2018

[37] German Marcos-Robredo, Miguel Angle Rey-Ronoco and Teresa Alonso-Sanchez, Analysis Technique by laser induced breakdown spectroscopy, Mineral and Slurry Samples ,Journal of Proceedings, MDPI, 2018.

[38] Ran Zhou, Ke Liu and et al, Determination of micronutrient elements in soil using LaserinducedbreakdownspectroscopyassistedbyLaserinducedbreakdownspectroscopyfluorescence, Journal of Analytical Atomic Spectrometry, Vol 36, No3, 2021.

[39] Yueh. F, Evolution of Leaser-induced Breakdown Spectroscopy as Technetium Monitor, waste Manage, Assoc, 2000.

[40] LEE.Y and J. sneddon, Recent Development in Leaser-induced Breakdown Spectroscopy P$^{129-136}$ ISIJ International 2002.

[41] https// biophysics.sbg.ac.at,2019

[42] Knadel, M., Gislum, R., Hermansen, C., Peng, Y., Moldrup, P., de Jonge, L. W., & Greve, M. H, Comparing predictive ability of laser-induced breakdown spectroscopy to visible near-infrared spectroscopy for soil property determination. Biosystems Engineering, 156, 157–172, 2017.

[43] Qingyu Lin, Pengkun and et al, Quantative Multiple-element simultaneous analysis of seaweed fertilizer by laser induced breakdown spectroscopy, Optics Express, Optical Society of America, Vol 28, No.10, 2020.

[44] Cecile Faber, Nour Eddine Ourti and et al, Analysis of Li-Rich Minerals Using HandheldLIBSTool,DataDescriptor,MDPI,2018.

[45] Gibaek Kim and et al, Development of Aerosol-LIBS (Laser-Induced Breakdown Spectroscopy)for Real-time Monitoring of Process-induced Particles, Aerosol and Air Quality Research, 2019.

[46]https// www.piactton.com,2018

[47] M.A. Gondal Z.S. SEDDIGI, M.M. NASR, B. GONDALIN. determine the concentrations of different toxic elements like lead, chromium, cadmium and zinc in four different lipstick brands sold at local markets in Saudi Arabia. Physics department E-mail address:magonal@Kfupm.edu.sa 2009.p^{727}

[48]Gondal, M, A & Hussain, T. Determination of poisonous metals in wastewater collected from paint manufacturing plant using laser induced breakdown spectroscopy. Talanta, 2007 71(1), 73-80.

[49]Senesi, G. S., Dell Aglio, M., Gaudiuso, R., De Giacomo, A., Zac cone, C., De Pascale, O., … & Capitelli, M. Heavy metal concentration in soils as determined by laser induced breakdown spectroscopy (LIBS), with special emphasis on chromium. Environmental research, 2009, 109(4), 413-420.

[50] Colin E Webb, Julian D C Jones: Handbook of laser technology and applications vol 1 - principles - (iop, 2004).

[51] Naseer M. Hadi1, Sabah H. Sabeeh 2 and Mustafa M. R. Sabhan3, Generation of Pulsed Fe Plasma and Study of Its Physical Parameters, International Journal of Innovative Research in Science, Engineering and Technology (An ISO 3297: 2007 Certified Organization) Vol. 4, Issue 1, January, 2015

[52] Sylwia Pasieczna-Patkowska and Tomasz Olejnik - Analysis of cosmetic products using different IR spectroscopy techniques – Annales Universitatis Mariae Curie-Skłodowska Lublin – Polonia Vol. Lxviii, 1-2 Sectio Aa 2013.

[53] KHALID A, BUKHARI IH*, RIAZ M, REHMAN G, AIN QU, BOKHARI TH, RASOOL N, ZUBAIR M AND MUNIR S, Department of Chemistry, Government College University, Faisalabad, 38000, Pakistan,2013.

[54] Reuland DJ, Trinler WA . Comparison of Lipstick Smears by High Performance Liquid Chromatography. Journal of the Forensic Science Society 20:111-120.1980

[55] Richard Viskup, Christoph Wolf and Werner Baumgartner-Laser Induced Breakdown Spectroscopy of Diesel Particulate Matter Exhaust Emissions Generated from on Road Diesel Engine: Light Duty Vehicles- Viskup, R., Wolf, C. and Baumgartner, W. DOI: 10.5220/0007618203080314 In Proceedings of the 7th International Conference on Photonics, Optics and Laser Technology (PHOTOPTICS 2019

[56]Victor Ulises Lev Contreras Loera- Double-Pulse and Calibration-Free Laser-Induced Breakdown Spectroscopy (LIBS) on quantitative analysis - A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy-Oracio - Centro de Investigations en Óptica A.C. January 2013]

[57] Marcello M. Amarala, Marcus P. Raelea, Anderson Z. de Freitasa, Guilherme S. Zahna, Ricardo E. Samada, Nilson D. Vieira Jr. a, Luiz V. G. Tarelhob -Laser Induced Breakdown Spectroscopy (LIBS) applied to stratigrafic elemental analysis and Optical Coherence Tomography (OCT) to damage determination of cultural heritage Brazilian coins- National Institute of Metrology, Standardization and Industrial Quality – INMETRO, Av. N. Sra. Das Graças, 50 –Duque de Caxias – RJ , BR – ZIP: 25250-020]

[58] Vinicius C. Costa, a Diego V. Babos,b Jeyne P. Castro,b Daniel F. Andrade,b Raimundo R. Gamela,b Raquel C. Machado, b Marco A. Sperança,c Alisson S. Araújo,b José A. Garciab and Edenir R. Pereira-Filho *,b- Calibration Strategies Applied to Laser-Induced Breakdown Spectroscopy: A Critical Review of Advances and Challenges- J. Braz. Chem. Soc., Vol. 31, No. 12, 2439-2451, 2020Printed in Brazil - ©2020 Sociedade Brasileira de Química https://dx.doi.org /10.21577/0103-5053.20200175]

[59] Gondal. M. A, Zulfiqar Ahmad, 2002, Leaser-induced Breakdown Spectroscopy of geological samples P$^{340-341}$ Dhahran.

[60] Gaudiuso, R., Dell Aglio, M., Pascale, O. D., Senesi, G. S., & Giacomo, A. D, laser induced break down spectroscopy for elemental analysis in environmental, cultural heritage and space applications: A review of methods and results. Sensors, 2010 10(8), 7434-7468.

[61] Gobran, Ph.D. Determination of Soil Pollution in Some Gold Mining Areas in Sudan and Tuti Island, Al-Neelain University,2018

[62] Mohammed Aidarous El-Tayep, Kh. M. Haroun . Measurements for Natural Radioactive Material sat the East& West banks of The River Nile. Science Journal of Analytical Chemistry. 2017.

[63] Abedelrazig. M. Abdelbagi, Salwa. M. Ibrahim, Ahmed. H. Elfaki The Determination of Heavy Metals Exposure to Environmental in Fingernails of Females in Port Sudan International Journal of Physics and Applications. ISSN 0974-3103 Volume 6, Number 1 (2014), pp. 7-13