

DATA ANALYSIS SOFTWARE DEVELOPMENT OF LASER INDUCED
BREAKDOWN SPECTROSCOPY (LIBS)



THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
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Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

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ABSTRACT

DATA ANALYSIS SOFTWARE DEVELOPMENT OF LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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Laser induced breakdown spectroscopy is a useful growing technique. The research's on LIBS is gaining importance in instrumentation and data analysis fields because it has a large number of applications in different fields especially in industrial, scientific investigation, medical, and many other fields. This study views a theoretical base of the LIBS technique as well as the setup of LIBS including new set up which are the portable LIBS set up which are getting more attention in recent works due to the ease of use and accurate results. From the analytical point of view, LIBS is usually characterized by direct laser ablation. And also the competition is made through a database which is explaining the different elements due to different wavelength and their intensities, which will refer in the end to the elements that the sample consist of: The database being used is coming from the laboratory with multiple experiences. Also, this work will focus on detecting specific elements which are FE, CU, ZN, AL and MG.

Key Words: laser, ablation, plasma, spectrometer, fiber optics, q.switch , lens.

ÖZ

DATA ANALYSIS SOFTWARE DEVELOPMENT OF LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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Lazerle indüklenen kırılma spektroskopisi faydalı bir büyüme tekniğidir. LIBS üzerinde yapılan araştırmalar, endüstriyel, bilimsel, tıbbi ve daha birçok alan gibi çeşitli özel alanlarda büyük uygulaması nedeniyle enstrüman teknolojisi ve veri analizi alanında önem kazanmaktadır. Bu çalışma, kullanım kolaylığı ve doğru sonuçları nedeniyle modern çalışmalarda daha fazla ilgi gören ve hazırlanmış taşınabilir kütüphaneler olarak yeniden kurulma dahil olmak üzere, liblerin teknik teorisinin temelini ortaya koymaktadır. Analitik bir bakış açısından, LIBS genellikle doğrudan lazer ablasyonu ile karakterize edilir. Ayrıca rekabet kuralı aracılığıyla ve rekabetinin yürütüldüğü, dalga boyu ve yoğunluktaki farktan dolayı farklı unsurları açıklayan veriler, sonuçta numuneyi oluşturan unsurlara atıfta bulunacaktır. Bunlar, birden fazla deney içeren laboratuvar veritabanıdır. Ayrıca bu çalışma, FE, CU, ZN, AL ve MG gibi belirli unsurları tespit etmeye odaklanacaktır.

Anahtar Kelimeler: lazer, ablasyon, plazma, spektrometre, fiber optik, q.switch, lens.

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To my family

TABLE OF CONTENTS

ABSTRACT	iii
ÖZ	iv
ACKNOWLEDGMENTS	v
TABLE OF CONTENTS	vii
LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER 1	1
1. INTRODUCTION	1
1.1 Libs in general	1
1.2 Basics of light and matter	2
1.3 Visible and uv light	3
1.4 ELECTRONIC STRUCTURE OF ATOMS	3
1.5 LASER ABLATION	4
1.6 Laser	4
1.7 Lasers types	5
1.8 Plasma	5
1.9 Radiation of the plasma	6
1.10 Uv-visible light spectrometers	7
1.11 basic idea of chemical spectroscopy	8
1.12 Analysis of Mixtures	8
CHAPTER 2	9
2. LIBS SET UP AND DETECTION THEORY	9
2.1 Typical libs set up	9
2.2 FOCUSING AND LIGHT COLLECTION	10
2.3 Lens	11
2.3.1 positive lens	11
2.3.2 Negative lens	11
2.4 Spectrometer	11
2.5 Optics	12
2.6 Q.switch	12

2.7 Compact libs systems	12
2.8 Detectors.....	13
2.9 Basic Signal-to-noise Theory	14
2.10.1 Noise in LIBS	15
2.10.2 Categories of libs noise includes:	16
2.11 Qualitative analysis	16
2.11.1-Emission line analysis	16
2.11.2- Host influence on emission line spectra and detection limits.....	16
2.12 Quantitative analysis	16
2.12.1 Software calibration techniques.....	16
2.12.2 Neighbor peak ratio comparison:.....	17
CHAPTER 3	18
3. LITERATURE SURVEY AND LIBS USES	18
3.1 Main Libs uses.....	18
3.1.1 LIBS in Archeology and Cultural Heritage	18
3.1.2 LIBS in Biomedical Applications. Biomedicine	18
3.1.3 LIBS in Industry	18
3.1.4 LIBS and Geological Samples	19
3.2 Literature survey.....	19
CHAPTER 4	24
4. EXPERIMENTAL.....	24
4.1 The theory of the analysis.....	24
4.2 AA dataset	27
4.3 bb data	28
4.4 CC data	29
CHAPTER 5	32
5. CONCLUSION AND TUTURE WORKS.....	32
5.1 Conclusions	32
5.2 Future works.....	32
6. REFERENCES.....	33

LIST OF TABLES

<u>Table 1.1(laser types)</u>	5
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LIST OF FIGURES

<u>Figure 1.1 basics of reflection, scattered of matter in general</u>	3
<u>Figure 1.2 Free and bound electrons and classification of transitions</u>	6
<u>Figure 1.3 mixture analysis components</u>	8
<u>Figure 2.1 typical libs set up</u>	9
<u>Figure 2.2 light collection</u>	10
<u>Figure 2.3 lens types</u>	11
<u>Figure 2.4 Hand held libs systems</u>	13
<u>Figure 2.5 micro-channel plate</u>	14
<u>Figure 2.6 signal to noise sources</u>	15
<u>Figure 4.1 FE spectrum</u>	24
<u>Figure 4.2 ZN spectrum</u>	25
<u>Figure 4.3 CU spectrum</u>	25
<u>Figure 4.4 AL spectrum</u>	26
<u>Figure 4.5 MG spectrum</u>	26
<u>Figure 4.6 AA.data set</u>	27
<u>Figure 4.7 BB result</u>	28
<u>Figure 4.8 CC results</u>	29
<u>Figure 4.9 noise for BB dataset</u>	30
<u>Figure 4.10 BB daata set signal after eliminating the noise</u>	30
<u>Figure 4.11 Raw ratio of BB data set</u>	31

CHAPTER 1

1. INTRODUCTION

1.1 Libs in general

Laser Induced Breakdown Spectroscopy (LIBS) is a beneficial material categorization technique in terms of elemental composition and quantification. Because of its relatively rapid measurement, LIBS can be used for factual time in-situ analysis without the difficulty of exporting the target sample back to the laboratory [2]. In addition, LIBS is convenient for non-destructive and non-invasive testing of materials because a slight amount of mass and surface area is frequently interrogated by the laser [2][3]. LIBS for field employment requires no complicated equipment set-up and sample preparation. LIBS analysis generally involves the identification of atomic components of a sample (qualitative analysis) and determining its relative concentration (quantitative analysis) [2]. The wavelength position of the emission line fingerprints the element and when correctly calibrated, the intensity of the line authorizes quantification. However, as LIBS process involves atomization of the sample, it is not convenient to determine the nature of compounds [3][18]. The target sample explored by the laser can be in any state of matter i.e., solids, liquids, gases, aerosols, hydrosols. For this rationale, LIBS is considered as widely used technique as it can be applied to a diversity of sample composition. Over time, LIBS has been used for stand-off and distant measurements to discover elements present in non-reachable and dangerous areas [3]. This has made LIBS valuable in a number of applications ranging from process monitoring in industries, medical operations, and soil sample testing to underwater learning of geological and archaeological structures [3]. As an analytical technique LIBS has many special benefits. It doesn't require preparing the sample, which can avoid more contamination of the material to be analyzed [10][11]. The analysis procedure is quick and can be utilized for all samples conducting and non-conducting, despite their physical states, i.e. aerosols, gases, liquids or solids. LIBS is analysis prosperity of very rigid materials that are not so easy to digest or

dissolve, like ceramics and semi or super-conductors [1]. Its tendency to simultaneous multi-element determination, localized microanalysis, and surface analysis is also of huge value and it has been used effectively in dangerous and difficult environmental conditions to study remotely situated samples for online and real-time information about their spectra. In element processing monitoring and in a portable analysis of the field LIBS has been so functional for in situ trace metal analysis of real samples where exactness and precision are not the chief requirements [1]. Also, the LIBS found to be able to be applied in many military and security of homeland [1]. Nowadays these applications has a significant role because the jeopardy of chemical and biological terrorist acts have enlarged the demand for precise and rapid determination of chemical and biological warfare (CBW) agent species [1][18]. Its hard to recognize this biological and chemical agents because of different states existence such as liquid, vapor and fine powders [1][3]. These agents are present in low concentration comparative to background interfering such as powder, soil or painted surfaces in addition to air. managing these agents are not simple so LIBS has been originated as an appropriate technique for the identification and recognition of chemical and biological warfare (CBW) agents. Libs applications as handy and easy portable to use CBW agents needs to develop and optimize a ways which are static for rapid analyzing complex spectra existed in the field [2][18]. Numerical approaches have been utilized to interpret information of spectroscopic in numerous of applications [16]. recently some groups of investigators have demonstrated the likelihood of biomaterial identification by LIBS coupled through chemo metric methods [16]. This item explains the technical feature of LIBS in brief as well as the different uses it, which will be precious in understanding the environmental conditions of the planet Earth [33].

1.2 Basics of light and matter

The ablation of an object can be produced when it has been hit by a beam of radiation, and causing scattered, transmitted, reflected signal or can be excite by fluorescence as well [3]. These processes are shown in Figure (1) [31]. In scattering process it can be believed that the radiation is primarily absorbed then almost instantaneously totally re-emitted uniformly in whole directions, but otherwise unchanged [20]. With fluorescence, absorption is happening to the photon in first place and a high state energy is stimulated, then the molecule drops back to a middle energy state by re-

emitting a photon. as a part of energy of the incident photon is maintained in the molecule (or is missed by a non-radiative process for instance collision with another molecule) the emitted photon has less energy therefore a longer wavelength than the absorbed photon. Resembling scatter, fluorescent radiation is also emitted regularly in different directions [20].

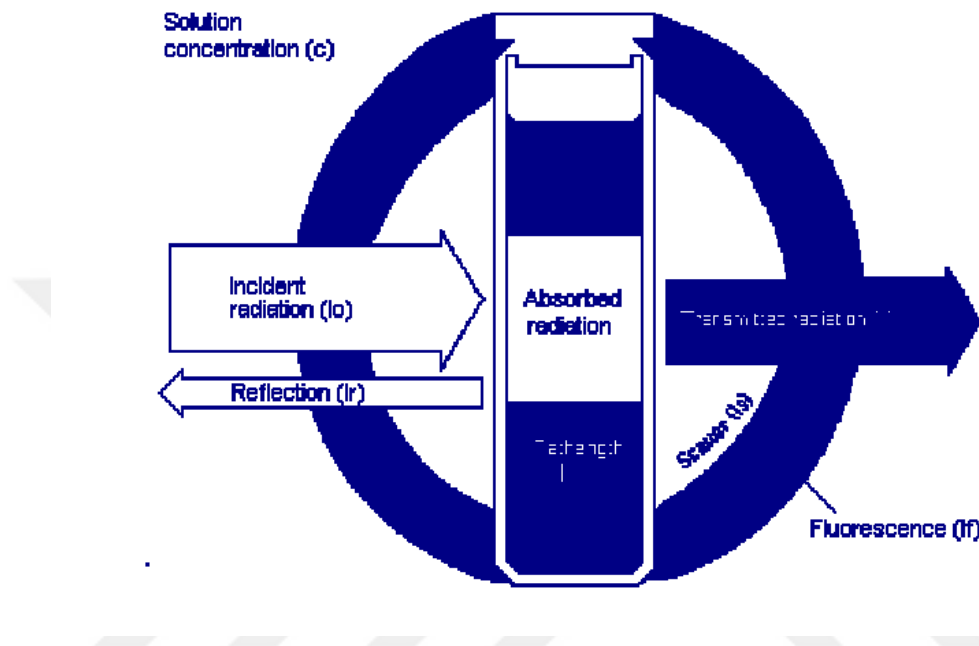


Figure 1.1 basics of reflection, scattered of matter in general[15]

1.3 Visible and uv light

The part of electromagnetic spectrum which can be detected and visible for human's eyes is call the visible spectrum [21]. And it named visible light or simply named as light [4]. The wavelength which human eyes can respond to is varied from 380-740 nanometers [4]. Whether the UV is electromagnetic radiation with wavelength starting from 10 nm (the frequency is approximately (30 PHz) to 400 nm (750 THz), less than that of the visible light but more long than X-rays [21][4].

1.4 ELECTRONIC STRUCTURE OF ATOMS

An atom contains a number of negatively charged electrons and a positively charged nucleus [4]. If the entire negative charge of the electrons is equal to the entire positive charge of the nucleus then this atom is known as neutral atom. These forces which holding atom are overall predominantly electrostatic, composed of attractions between

all the electron and the nucleus and repulsions between all the atomic electrons [1][4]. A plain theory of electrostatics, however, fails to account for the stability of atoms and for the characteristics of their spectra. The early attempts of Bohr and de Broglie to provide a plausible theory of atomic structure led to the much more sophisticated, probabilistic quantum mechanics of Heisenberg, Schrödinger, and others. The object of the theory of atomic structure is the study of stationary states of isolated atoms [5]. At the primary scene, such a study appears to be unrealistic since an atom is never been isolated in total and it should interact with photons so it will observe it[22]. Though, in low pressure and low photon density condition, the effects of atom-atom and photon-atom interaction are weak enough to be ignored. Even in the case of an isolated atom, its energy relies not only on the charge of the nucleus but on its volume and the charge distribution within this volume[22].

1.5 LASER ABLATION

Ablation scenarios are reliant on a multi-dimensional matrix of parameters including laser properties and material properties[4]. Laser fluencies of micro joules to mill joules for each square centimeter able to cause desorption of ions and atoms with no apparent physical alter to the surface[4]. At elevated fluencies, alternative mechanisms come into play as, for subsequent pulses, the laser energy is incident upon melted and recompensed matter[3]. The surface reflectivity changes with an ablation crater, with or without elevated walls, forms. The elements of the original sample may have been electively evaporated so that the redeposited material no longer exhibits the original composition. Essential concerns in ablation are the minimum power density to start vaporization; the effects of shorter or longer laser pulse lengths; the rate at which ablation proceeds; and the objective of retaining the composition of the sample after ablation into the plasma. We talk about each of these in turn [4].

1.6 Laser

The first laser has been invented by Theodore Maiman in the year 1960[4]. Laser action is started by stimulating the electrons of the atoms in a laser medium from the ground state into a higher energy level by means of optical amplification, creating a population inversion [4]. This is attained by pumping the laser medium via the application of a great amount of energy in the form of broadband light [1][4]. The electrons emit radiation while they make transitions back to the ground state. The

majority of energy transitions emit a phonon, however, some transitions result in the emission of a photon. as a photon is emitted it is trapped in the laser cavity[2][3]. This photon passes through the medium and stimulates more emissions from the population inversion [3]. The light which being emitted by a laser will contain dissimilar optical frequencies related to the different modes of the optical resonator. These resonator modes are identified as transverse and longitudinal modes. The laser longitudinal modes rule the characteristic of the spectral, for instance, line width and coherence length. The transverse modes direct the beam diameter, beam divergence, and energy distribution [20].

1.7 Lasers types

There are different sorts of lasers with dissimilar characteristics and different wave Lengths and also different operating parameters [3]. these days thousands of laser lines are there of range from a very ultraviolet to the far-infrared section .the recent studies have made it achievable that many laser wavelengths to be used for the function of libs measurements and also to figure their effect of the measurements of libs [3][4]. the lasers which are generally used in libs and also some characteristics of them are in this table[3].

Table 1.1 laser types [4]

Laser Type	Wavelength	Pulse Duration	Energy/Pulse
CO ₂ , Repetitive	10.6μm	10 – 100μs	0.1 – 5 J
CO ₂ Q-switched	10.6μm	200 ns	0.1 J
Er:YAG Q-switched	2.94μm	170 ns	25 mJ
Nd:YAG	1.06μm	5 – 10 ns	1 – 3 J
Ruby Normal Pulse	694.3nm	0.2 – 10 ms	1 – 500 J
Ruby Q-switched	694.3nm	5 – 30 ns	1 – 50 J
Ruby Picosecond Pulse	694.3nm	10ps	0.01 – 0.5 J
Nd:YAG Second Harmonic	532.0nm	4 – 8 ns	0.5 – 2 J
Nd:YAG Third Harmonic	354.7nm	4 – 8 ns	0.2 – 0.7 J
N ₂ Laser	337.1nm	3 – 6 ns	0.1 – 0.6 mJ
XeCl Excimer	308nm	20 – 30 ns	0.5 – 1 J
Nd:YAG Fourth Harmonic	266nm	3 – 5 ns	0.1 – 0.3 J
KrF Excimer	248nm	25 – 35 ns	0.5 – 1 J
ArF Excimer	193nm	8 – 15 ns	8 – 15 mJ
CO ₂ , Repetitive	10.6μm	10 – 100μs	0.1 – 5 J

1.8 Plasma

The local assembly of atoms, ions and free electrons is called plasma and the plasma is electrically equal (neutral) in which charged species are act together [3]. The

distinguishing of the plasma relies on different parameters, the most fundamental being the ionization degree [4]. The plasma which has the ratio of electrons to another species is to be less than 10% is known as weakly ionized plasma. On the other hand, highly ionized plasmas might have atoms stripped of several of their electrons, leading to a very high electron to atom/ion ratios. LIBS plasmas characteristically fall in the category of weakly ionized plasmas. To create a spark in air or a gas requires laser intensities of the order of 10^{11} Wcm^{-2} . Sparks are produced by the breakdown of the gas due to the electric field accompanied by the light wave analogy with the electrical breakdown of gases [20]. The breakdown is due to strong ionization and absorption by gases that are habitually transparent to light [4]. The breakdown is marked by a threshold irradiance below which nearly no effects are noticed. The beginning of the breakdown is an abrupt, dramatic phenomenon happening in a simply determined threshold. Its spatial in addition to temporal profiles compose an interesting study [4].

1.9 Radiation of the plasma

The radiation from cooling plasma may be classified into three classes that rely on the formation mechanism [3]. These mechanisms are demonstrated in Figure 2. The free-bound and the free-free mechanisms contribute to the continuous background spectrum which extends from deep-UV to the infrared while the bound-bound transitions make the optical line spectrum [3].

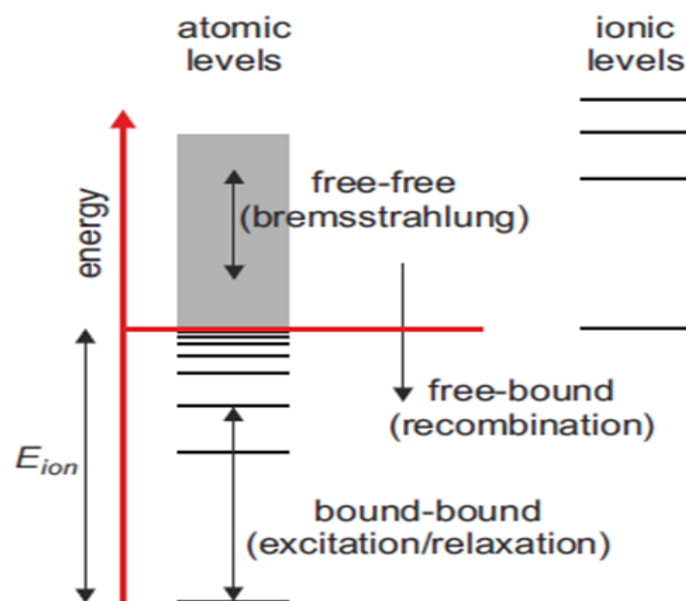


Figure 1.2 Free and bound electrons and classification of transitions[15]

The free-bound continuum is more distinct in the shorter wavelengths of the spectrum. In radiative recombination linking an electron e and the ion X^+ , the resulting atom or ion stays in an excited state X^*



$$h\nu = E(\text{ion}) - \delta E(\text{ion}) - Ek + \frac{1}{2}m_e v_e^2 \quad (1.2)$$

Where the very last term is the kinetic energy of the electron. The recombination also can occur non-radioactively in the course of three-body recombination in which a part of the neutralization energy is given to a third particle, habitually to another electron. The free-free radiation or bremsstrahlung occurs when free electrons drop part of their kinetic energy in the interaction with positive ions and neutral atoms [4][21][23]. The total background emission spectrum may be created by summing up the contributions from the free bound with the free-free radiation. At wavelengths shorter than about 500 nm, the resultant spectral volumetric emission coercion for the entire continuous emission differs with the wavelength and has a saw tooth structure owing to the recombination[4][21]. At longer wavelengths, the emission is practically not rely on the frequency till the plasma turned optically thick at several micrometer wavelengths and begins to radiate as a black body[4]. The accurate spectral shape of the background varies in accordance with the concentration of every chemical species, the electron density and plasma temperature [4].

Bound-bound transitions take place between separate energy states. Electronic transitions in an ion or an atom are usually the most prominent in a LIBS spectrum however, molecular band systems also are detected. The observed spectrum of lines at frequencies or wavelengths given by Equations produce the preferred LIBS signal. At the other extreme, characteristic emission comes from the sample matrix or ambient air participate to the background [21][23].

1.10 Uv-visible light spectrometers

In the last 35 years, the ultraviolet spectrometers and visible light spectrometers have been coming in to general utilize and more than this period have to turn into the greatest significant analytical instrument in the laboratory of the modern times other

techniques can be employed in various applications but none rival UV-Visible spectrometry for its ease, accuracy, rapidity, versatility and reasonable cost [3][4].

1.11 basic idea of chemical spectroscopy

If white light is falling on a sample it can be fully reflected, in this case the substance will be appears in color of white or we can be considered that all light is absorbed , so that the substance will look as black. If only a portion of the light being absorbed and reflection will be for a balanced amount then in this case there is the ability to detect the color, the reflected light will decide the color then. Thus, if yellow is absorbed, the sample color will be blue and if violet is absorbed, the color will be yellow-green[4]. Colors are expressed as complementary. However, many substances that appear without color do have absorption spectra. In this case, the absorption will occur in the infra-red or ultraviolet and not in the visible region.[4][21].

1.12 Analysis of Mixtures

It's not common to discover a practical problem in which one has a mixture to be analyzed with a single component which absorbs radiation [21]. When there are numerous such components which the absorption is in the same wavelength their absorbance put in together, and it is no longer to be proper that the absorbance of the sample is proportional to the concentration of one component (see Figure (3))[4][21]. So in these cases, numerous approaches can be adopted with the most important being chemical reaction and multi-wavelength measurements [21].

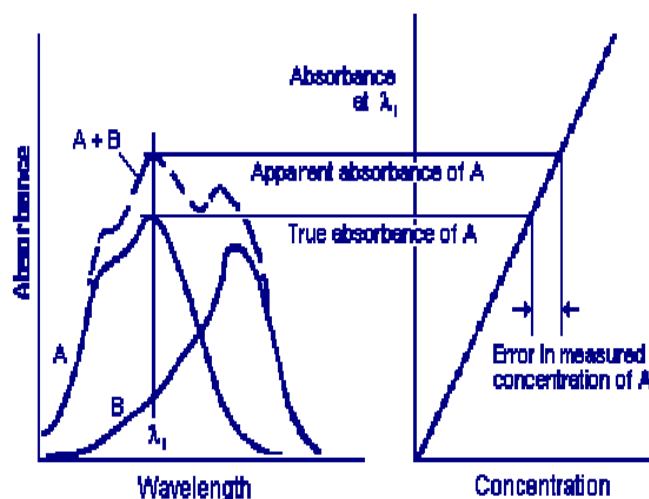


Figure 1.3 mixture analysis components[15]

CHAPTER 2

2. LIBS SET UP AND DETECTION THEORY

2.1 Typical libs set up

The main devices which forming the LIBS set are shown in Figure (4) high-energy pulsed laser (usually in the nanosecond range) is directed at the sample [3][4] .the sample is vaporized due to this high energy and plasma is stimulate [14] the diffracting of the light gathered is a responsibility of the spectrometer with a more or less complex optical system, so to get the spectral signature. after that, the light is detected by means of using devices such as a photomultiplier tube(PMT), a photodiode array (PDA), or a charge-coupled device (CCD) [3].at last, the acquired spectrum is processed through a computer for extra analysis[2][3]. LIBS set-ups require accurate time management to stay away from some plasma life stages and to progress the spectral signature. The choice of the laser merged with the set spectrometer-detector and time control, adapted to environmental circumstances, are able to decide whether the experiment is successful [2].

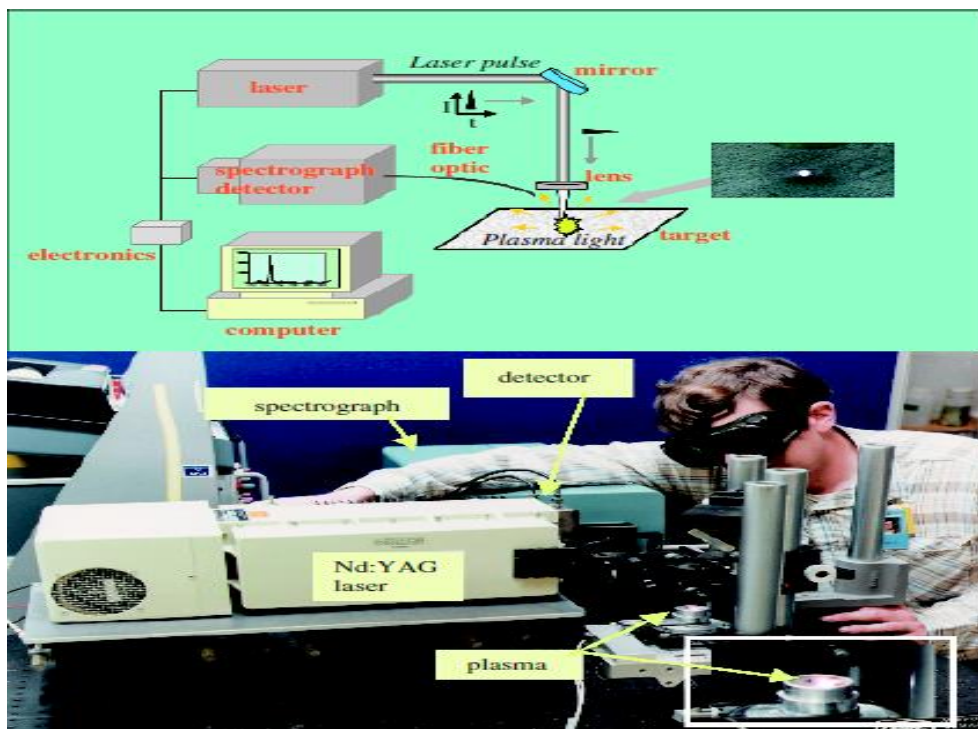


Figure 2.1 typical LIBS set up[4]

2.2 FOCUSING AND LIGHT COLLECTION

In LIBS, we can use mirrors or lenses so that to focus the laser pulses as shown in (Figure 5)usually, to focus the laser pulse a single lens could be used to an adequately small spot to attain an analytically useful plasma (a)[6]. For systems demanding an adjustable focus, for instance, industrial process monitoring in which the lens-to-sample distance may be varying, a multi-lens system may be needed with the relative locations of the lenses adjusted to locate the focal point on the target (b). as well as the pulses of the laser can be focused using a mirror (c)[6]. A lens of a mirror system can accumulate the light of the plasma and that due to the equipment, which is after that focused into the detection system (e.g. spectrograph and detector). The simplest optical system to collect the plasma light is a lens even though multiple lenses can be used in definite cases [1][6]. Unless constructed particularly to remove the effect, lens systems will show chromatic aberration such that the focal position of the lens system is wavelength-dependent (Figure 5 d)[1][9]. This is owing to the dependence of the refractive index of optical materials on wavelength [9].

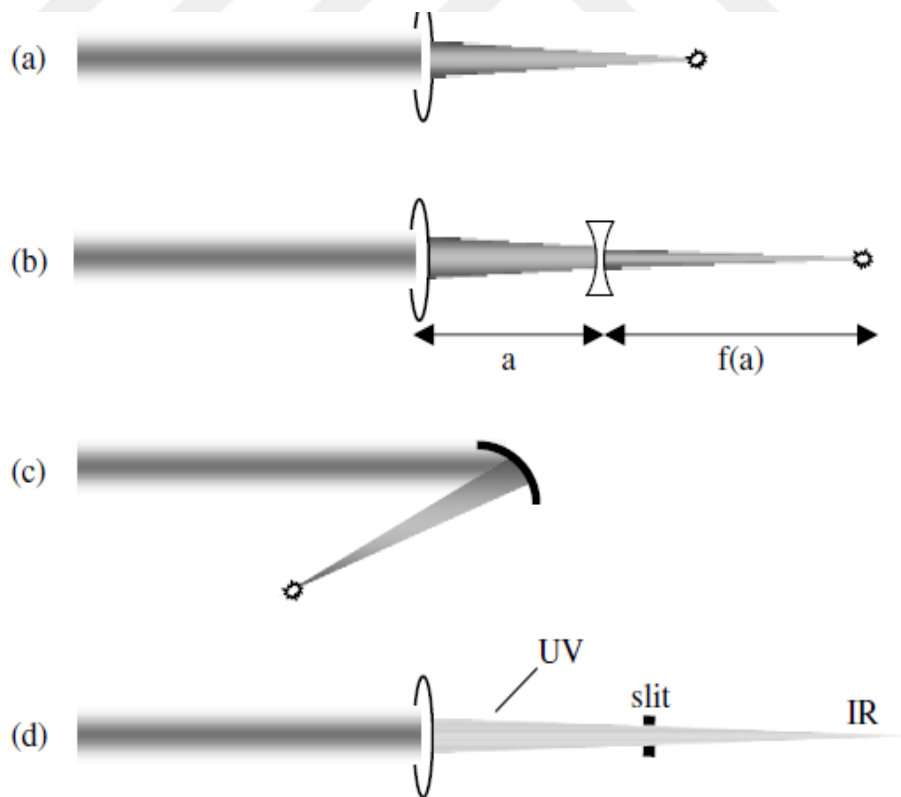


Figure 2.2 light collection [4]

2.3 Lens

The lens is an instrument made from a transparent material (might be glass as an example), the lens has two surfaces which light can cross through [22][24].lens can be convex or concave or can be concave from one side and convex from other, also can be flat from some side or both.

2.3.1 positive lens

A positive (converging) lens is believed to have a positive focal length. A converging lens leads to be more convergent through exiting rays in coming out than they were income in the lens [22].

2.3.2 Negative lens

A negative or a (diverging) lens is believed to have a negative focal length. A diverging lens causes exiting rays to be more divergent coming out than they were incoming in the lens [22].

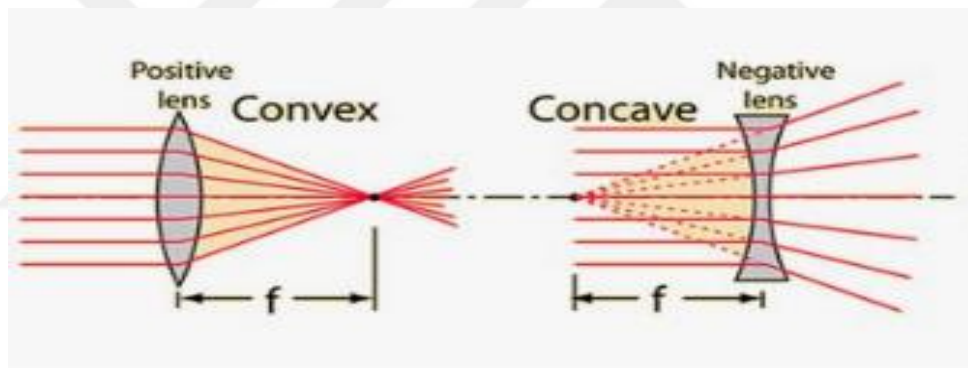


Figure 2.3 lens types[4]

2.4 Spectrometer

Spectrometers are instruments that are used to spread light out into wavelengths named "spectra," that resemble something similar to rainbow-colored bars. By using the spectra, scientists are able to seek and study the "emission lines" and "absorption lines" that are kind of fingerprints of atoms and molecules that can be present. Each atom has a unique fingerprint since each can just emit or absorb specific wavelengths of energy. Therefore, the fingerprint -- as seen in the location and spacing of spectral lines -- is unique for each atom[3]. Spectrometers are instruments that engineers build to reveal

fingerprints .there are visible light and invisible light spectrometers as well there are further kinds of spectrometers like mass spectrometers, magnetic spectrometers [3].

2.5 Optics

Optics usually made of plastic or glass. The majority are approximately a human hair diameter, and in the length of many miles [2][22]. Light is transmitted from one end to the other end of the fiber optic through its central part, and a signal is imposed. Fiber-optic systems are superior to metallic conductors in numerous applications. The most significant benefit is bandwidth. due to the light wavelength, it is likely to transmit a signal that contains significantly more information than is achievable with a metallic conductor even a coaxial conductor .a fiber optic consist of three main parts: The core is typically made of glass or plastic, even though further materials are sometimes used, relying on the transmission spectrum preferred [1][2][22]. The core which transmission light. the cladding is made of material the same which the core is made of, except with a little lower index of refraction (usually about 1% lower). The coating often comprises one or more coats of plastic material to shield the fiber from the physical environment. Occasionally metallic sheaths are added to the coating for additional physical protection [22].

2.6 Q.switch

a method for achieving active pulses from lasers via modulating the intracavity losses. involving two kinds those are active Q switching, passive Q switching. Q-switching leads to fewer pulses with more energy for each pulse [3][22].

2.7 Compact libs systems

there are novel generations of compact (one piece) libs systems that can be held in any environment simply and work efficiently .this systems probably connected to the new devices including pcs and wife in addition it offers results in nearly no time and also it has the setup codes and calculations within its fabrication thus it can be used with simply trained workers and gives the results in extremely competent way .besides using such instrument provides a short and rapid general picturing in an undistracted test for the important machines or environment being tested[1][3] . it can assist the fabrication or geological uses and also in military uses[22][30]. Compact, inexpensive, rugged laser/computer/fiber spectrophotometer components are readily incorporated

into a wearable eye-safe in-situ LIBS field chemical analysis system. Wearable LIBS systems may be brought together from commercially obtainable components and are proper for qualitative and semi-quantitative analysis field-testing of a number of different materials. These systems are being interesting for employ in several applications involving mining, anthropology, geology, oil exploration, remote medical diagnostics and in chemical and biological weapons detection Eye-safe in-situ LIBS provides the operator with improved real-time sensitivity, awareness and association with targeted materials in field environments. It permits instantaneous evaluation of a material's texture and color with simultaneous exposure of the materials chemical composition with no sample preparation [3][4].

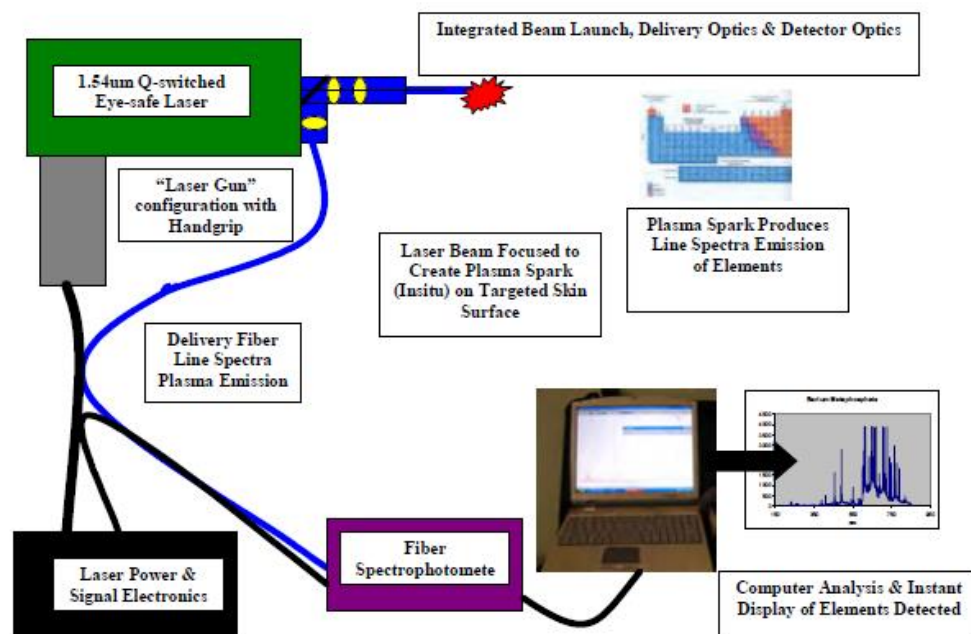


Figure 2.4 Hand held libs systems[11]

2.8 Detectors

The intensified Charged-Coupled Device (ICCD) is the base of the detection system of the LIBS. The ICCD works by coupling a CCD detector to a micro-channel plate (MCP) to make the gain of the system larger. The MCP is intimately associated with a photomultiplier tube, making the electron cascade more increased as shown in figure 8 [10][12].

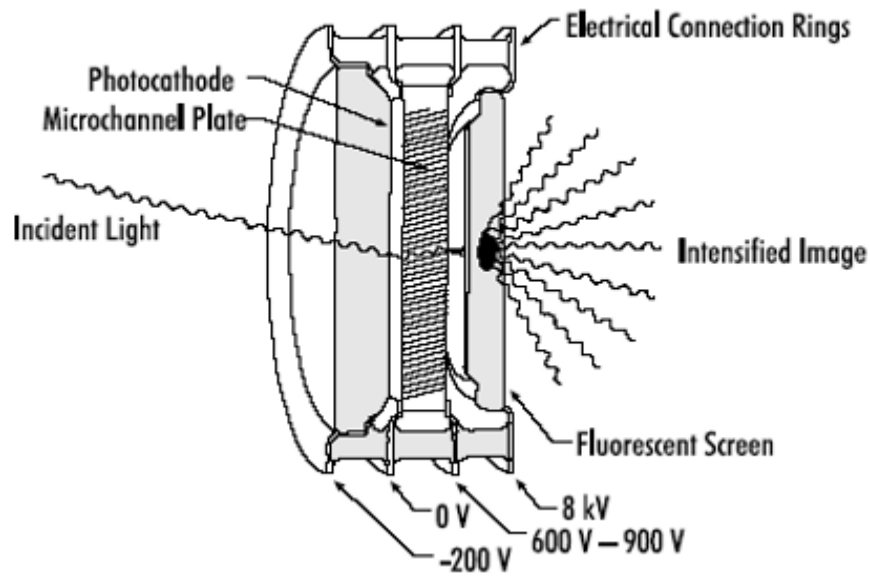


Figure 2.5 micro-channel plate[22]

The photons which are incident to the photocathode will be absorbed and then get the electrons are to be free, which after that multiplied into a charge cloud by a cascade in the MCP and lastly is incident on the fluorescent screen[1][10]. The MCP can be gated with little time constants by controlling the voltage across the system. The CCD works as a sensor of the image through the mixing of an array of photoactive capacitors. In reading the device every capacitor transfers its charge to a coupled capacitor and so on till the transferring of the charge to the system's final capacitor in the system. This after that transfers the charge to an amplifier to be changed to voltage for the line by line reading of the array [10][21].

2.9 Basic Signal-to-noise Theory

A signal is defined as a measured value in an experiment, while noise can be known as fluctuations in the measured signal. Both the noise and the signal have contributions from a diversity of sources [24]. The signal of concern, the true analytical signal, is the part of the measured signal that is due to the existence of the analytic [21]. A background signal, which is the signal that is measured in the absence of analytic, and a dark signal, which is the signal measured when there is no light hitting the detector, also can be defined. Each of these signals appears with a corresponding noise [3][21]. A schematic of these three signal sources is offered in Figure 1-2. Noise as well comes

from a diversity of sources [21]. When considering the appearance of photons at a detector, the Poisson likelihood distribution can often be applied [21][24]. This is applicable as long as the emission of photons from an emission source is random. In this case, the signal noise could be defined as the square root of the number of photon counts and is termed shot noise.[3][21].though, the fluctuations in the signal can be larger than those predicted by shot noise[21]. In this case, the noise is comparative to the magnitude of the signal instead of the square root. This kind of noise is named the flicker noise [20]. Other kinds of noise can include but are not limited to, digitization noise, detector noise, and sampling noise [21].

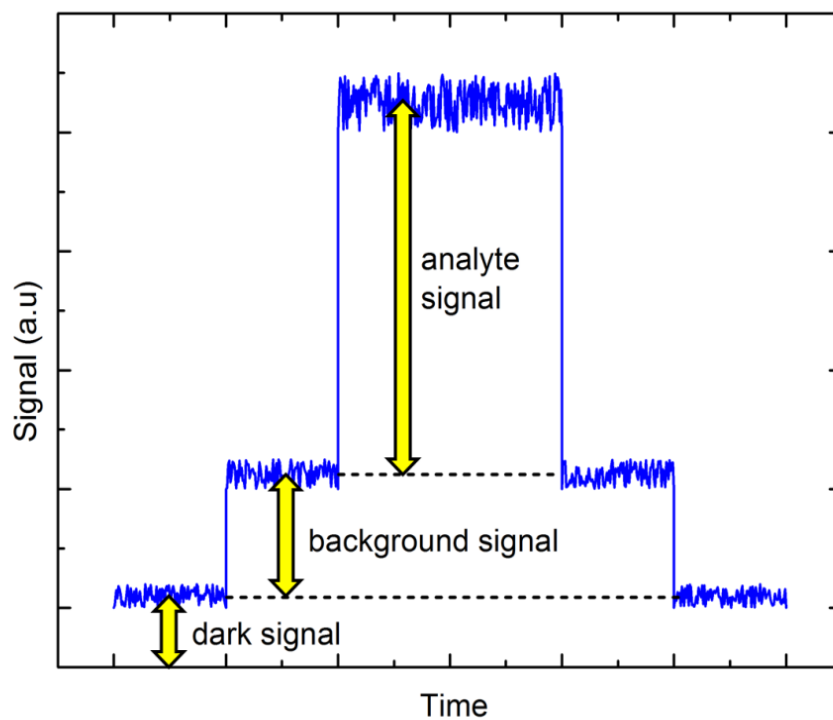


Figure 2.6 signal to noise sources[15]

2.10.1 Noise in LIBS

Most available LIBS work reports at least a various effort in minimizing the noise in experiments, but relatively small has been finished in the field of investigating the limiting noise in LIBS experiments. As the LIBS sampling procedure is extremely complex, the complete characterization of the laser-induced plasma is hard [21]. Often work is done with respect to reduce the noise between measurements for one or two precise experimental parameters, but never by considering every single one.[24].

2.10.2 Categories of libs noise includes:

- 1-Effect of the Laser Source
- 2- Effect of the Optics, Gating Parameters, and Detection System
- 3- Effects of the Sample and Sampling area
- 4-Effects of Post Experimental Data Analysis

2.11 Qualitative analysis

2.11.1-Emission line analysis

The qualitative analysis basically started when finding the essential lines which are taken from the spectra of libs also one should search the fixed lines values from different databases so that to assign the lines which specific study interest in.[5][11]. ARL and the NIST (U. S. National Institute of Standards and Technology) gives a good and repayable databases [5].

2.11.2- Host influence on emission line spectra and detection limits

Adverse effects which can be caused rather from the environment or from some chemical composition of the sample we are targeting, this can cause a real affect in unpredictable way [20]. Matrix effect is the effect produced through the host element which is added to the analyze during the reaction of the plasma. Matrix effects are an adverse host influence on LIBS resulting in inconsistent line spectra intensity due to chemical composition and material properties [20]. Every time we shot a pulse of laser on our target the substance which we are studying is being shifted or changed via responses with its surroundings [20].

2.12 Quantitative analysis

2.12.1 Software calibration techniques

The spectrometer's operation are being controlled and being set up through computer softwares [5]. This software's include mathematical algorithms that identify and compare and contrast the data resulting from spectroscopic. The computer software find the concentration through comparing the lines of the results with matched lines from databases and then applied the relative intensities for implementing that purpose [5].

2.12.2 Neighbor peak ratio comparison:

An alternative method of quasi-quantitative analysis with LIBS depends on the observation through this method we are focusing on intensity of neighboring peaks [15][30].



CHAPTER 3

3. LITERATURE SURVEY AND LIBS USES

3.1 Main Libs uses

LIBS is being used in many different fields, specifically, the fields which can get benefits of through fast analysis of atomic-level chemical analyses, thus no need for sample preparation here, or even in the field[1][2]. So this part will review the most important applications on this instant[2].

3.1.1 LIBS in Archeology and Cultural Heritage

Samples with archeological or cultural worth are difficult to be analyzed by normal methods [1]. These samples is forbidden in most cases to be moved or destroyed for the sake of analyses, and most number of analysis and some experience in a controlled environment is required. For these reasons and preferably the portable LIBS set ups can be used for, and that can minimize the difficulties when the sample cannot be moved[35]. Secondly the LIBS technique does not need to be in touch with the sample, avoiding injure in precious samples [35].even though LIBS ablates a quantity of the sample, the craters almost microscopic and practically invisible to the eye besides, this microscopic ablated surface advances the spatial resolution, providing perfect spatial analysis and also a depth profile analysis of the sample [35]. Also here we need no preparation for the sample ; therefore we get a fast and clean analysis .as well, LIBS probes with fiber optics permit to analyze the samples with has complex access[35].

3.1.2 LIBS in Biomedical Applications. Biomedicine

This field may offer a big development in few years [36]. LIBS can analyze chemical compositions of biological samples such as human tissues, bones and fluids [36].

3.1.3 LIBS in Industry

The use of LIBS in industry has been growing for long time, meanwhile, LIBS is a really fast analytical tool to control some manufacturing processes. Moreover, libs can be applied to work through large distances as well, permitting sample analysis in risky

and environments which are known to be hard and harsh. For example, remote detecting of dangerous chemicals such as explosives has been assessed with LIBS even at trace levels. In the industry of nuclear energy, the influences of radiation on living beings and machines are widely identified. Libs can work at a certain distance from reactors or nuclear waste , through the use of fiber optics, avoiding hazardous radiation levels .In the metallurgical industry, smelters, and final products can achieve high temperatures, and LIBS be able to analyze the alloy compositions in the production line or detect impurities in further production sectors, as the automotive industries[22][35]. LIBS can also be functional in detecting toxic products such as heavy metals in industrial wastes [35] .These waste products supposed to be recycled or stored, and knowing the elements in them can supply key data to decrease the environmental impact of the process. In the renewable energy field, analysis and detection of impurities in solar cells can be a valuable tool to progress the manufacturing processes or to attain high-efficiency solar panels. There are new research works in this field although there is an enormous amount of work to do [14][15].

3.1.4 LIBS and Geological Samples

Towards Extraterrestrial Limits. Analysis of some types of minerals is achievable using LIBS, in particular, of soils and geological samples in situ Sample features can powerfully affect the experimental conditions and decrease the accuracy, but quantitative analysis remains possible [3][21] .LIBS analysis can distinguish traces of toxic material in soils, water, or rocks with no need for sample preparation and in the normal environment, the sample exists in[3].

3.2 Literature survey

F. Anabitarte 2012[1] focused on the technique as a method that can be used for chemical analyses with no need for the sample preparation .with giving definitions for the basics like plasma and ablation as well it indicated the chemical signature of the different elements and how can we explore the element from its spectral signature. As well as it focused on the fields that this technique used, or can be used for in future like: Archeology and Cultural Heritage, Biomedical Applications, in Industry and Geological Samples more ever it indicated the libs challenges as well as an example it referred to the most important challenge which is(as a standard recognition in chemical

quantitative analysis. A good approximation for this purpose can be offered through the free algorithms, but didn't get enough perfect results yet).

Osayuwamen Ogboghodo 2015[2] focused on underwater experiments, basically the underwater LIBS uses like directly from the environment, or wastewaters from industries. In this paper it compared the results of the steel samples in air, submerged steel samples, corroded steel samples in air, corroded steel samples underwater and Effects of pressure on signal characteristics from submerged steel samples.

D. A. Cremers and L 2006[4]: in their handbook of the LIBS they indicated the whole idea and also the history of the early tries as well as the last up to their date tries of the LIBS and here is some important highlights that indicated in this book:

- 1990 Australia, Grant et al. provided detection limits for minor components in iron mineral this is a development of field-based technique.
- Sabsabi and Cielo (Canada in 1992 and 1995) published their works in aluminum.
- In 2002 prototype Martian rover which is called K9 rover with the LIBS sensor unit on the Mars.
- Anglos et al., 1997 diagnostics of painted artworks using LIBS for identifying pigment
- Georgiou et al., 1998 laser restoration of artworks and painted artworks.
- Eppler et al., 1996 focused on the Determination of the composition of soils and contaminants and also showed matrix effects in the detection of Pb and Ba in soil
- Theriault et al., 1998 described A real-time fiber-optic LIBS probe for the in situ detection of metals in soils
- Vadillo et al., 1996 who reported on space and time-resolved LIBS using CCD detection
- Zayhowski, 2000 A passively Q-switched Nd:YAG microchip laser was described
- Yamamoto et al., 1996..to the 1998 started to study and then designed a portable LIBS systems in a size of a small suitcase which used for first for analysis of contaminants in soils and lead in paint

(These mentions are the most important mentions of the early LIBS works in the nineties period)

Michael J. Myers(Lasers in Chemistry)[5]:this study focused the methods of analyze the results including Qualitative analysis which includes: Emission line analysis, Host influence on emission line spectra and detection limits and also Quantitative analysis which includes: Software calibration techniques, Neighbor peak ratio comparison. and also highlighted the advantages of using the libs as portable and the huge capabilities of getting good results with many examples of using these types of libs systems with examples like:

- Sensor based on LIBS for subsurface in-situ soil classification and heavy metal contamination detector which prevented of US army. This is a part of SCAPS which means (site characterization analysis penetrometer system) .

- Scientists at LANL, a portable system for determining the metals in soils that led to LIBS to be used in mars rover mission

- Homeland Security and the war on terror sparked interest in LIBS as an explosive detecting system, landmines, biological weapons and chemical contamination.

Michael J. Myers, John D. Myers and their team2010[11] : focused on the compact portable handheld libs system which is consist of all the equipment needed to be held by one person .this type of libs systems is very handy and useful in many environments that the normal libs systems can not work in like: mining, geology, anthropology, oil exploration, remote medical diagnostics and biological and detecting chemical weapons .the system includes safe laser gun with some safety equipment and a computer with a spectrometer as well as a head-mounted display so that the it becomes a hand free display.

Laurent Salmon 2008[14]: focused on the general technic of libs as well as the compact libs system(especially on remote analyses and on microanalyses LIBS capabilities) as well as the most important uses of libs .it highlighted as well on the CEA for the nuclear industry. The most important point on this work was that libs can work with radioactive materials by using a remote.

S. Messaoud Aberkanea 2014[26]: referred that libs can not be only be used to elemental analysis but also for surface estimating hard-ness of metallic alloys. And this method is indicated that (there is a direct proportionality between the laser induced plasma temperature and the Vickers hardness for the target surface).

T Iqbal and his team 2019[27]: they highlighted the use of two techniques which are LIBS and EDS and after collecting the results coming from each technique they compare the results.

M. Momcilovic 2019[28]: used the LIBS for making the comparison of the lead glass components to find the hardness of the glass surface. The glass surface hardness depends on ZrO_2 which increases the hardness of the lead glass. So in this study they used the LIBS to find the ratio between ionic to atomic zirconium so that by this result they can find how much there of the ZrO_2 then conclude the hardness of the glass surface.

Ming Zhu[31]: combined the LIBS and Raman filter techniques, to analyze the spectra of the mineral in air. So by combining these techniques so that Raman filter measure reveals the molecular bond of minerals and then LIBS is used to obtain the atomic emission spectrum. They could get the results about the minerals in the air.

A. F. M. Y. Haider[32]: determining the cartage of gold ornament using two methods which are LIBS and X-ray fluorescence (ED-XRF) spectrometer and showing the advantages and disadvantages of these two methods.

Minjae Cho 2019[33]: The paper is a full project of sorting the scrapes using multi techniques including. image process sensor, laser square beam and the laser 2D image sensor, LIBS process, pneumatic system, basic platform of conveyor and the starting feeder. Using this combination of techniques allows us to sort the scrap of different shapes and sizes and of course metals into basic metal containers. The main function of the sensing part is to measure the location and shape of the metals which is done by pointing the line beam laser (and of course measuring its reflection by the sensor) to know the geometric profile of the scrap like the mass and volume and centre point and then we give the feedback information to the LIBS system so that it can use less shots of laser as it needed having benefits as to reduce the time of the LIBS process secondly it gives the feedback to the pneumatic system to process. The 3D shape of the scrap parts is measured by combining the 2D laser sensor with the moving conveyor so multi 2D data leads to the 3D data. Then the LIBS process start due to the feedback we got. With controlled beam shots and centered position of the beam due to the location and the size...etc of the scrap.

Agnieszka Pawlak 2017 [34]: this paper had an interesting use of LIBS technique which is applied to paintings belonging to the collection of the Museum, so by using LIBS on these paintings and figure out the operation on the elements like Li, Ba, Ti so the origins of the pigments can be found and then using this the classification will be more easy, here in this paper the microscale LIBS used so due to this micro chemical analysis will not make any visible effect on this artworks so its so safe technique to use.

V. N. Rai[35]: focused on giving a full picture of LIBS and how to combine the LIBS set up and make the parts work together and also focused on the advantages and disadvantages of the LIBS technique as well as comparing it with other spectroscopy techniques. this study is an important base for LIBS. it tried to minimize the items and make it more sufficient in terms of sensitivity which was at least in the early beginning of using this technique the target problem

A K Pathak et al 2014 [37]: this study focused on the biomedical uses of LIBS, especially the gallstone, under the empyema and mucocele state of gallbladder, and analyze the results with the patients data base and with this results it concluded that the gallstone are most probably occur due to some oh elements like gender of the patient and also smokers and chewing tobacco or drinking alcohol. The study partly also focused on some other biomedical uses like: healthy and caries affected parts of deciduous tooth, human nail study and the analyze the results as compared with data bases to predict the weak points that causes some deceases.

CHAPTER 4

4. EXPERIMENTAL

4.1 The theory of the analysis

In this experiment we explored the spectra of a mixtures. We focus in this work on five elements including: iron, aluminum, zinc, copper and magnesium. We make a comparison between each elements spectrum pick points and our data which includes the elements and also we figure out the area under the curve for each pick point of our data so that we can tell the percentage of that specific element. When we compare the pick points of our data with the elements pick points we take in count the intensity of those pick points so that we can decide if that element exist or not exist in our data sets We experimented 3 data sets we named them AA, BB and CC .which includes the values from 186.263 to 888.604.wavelengths. The plot of the different elements spectrum is:

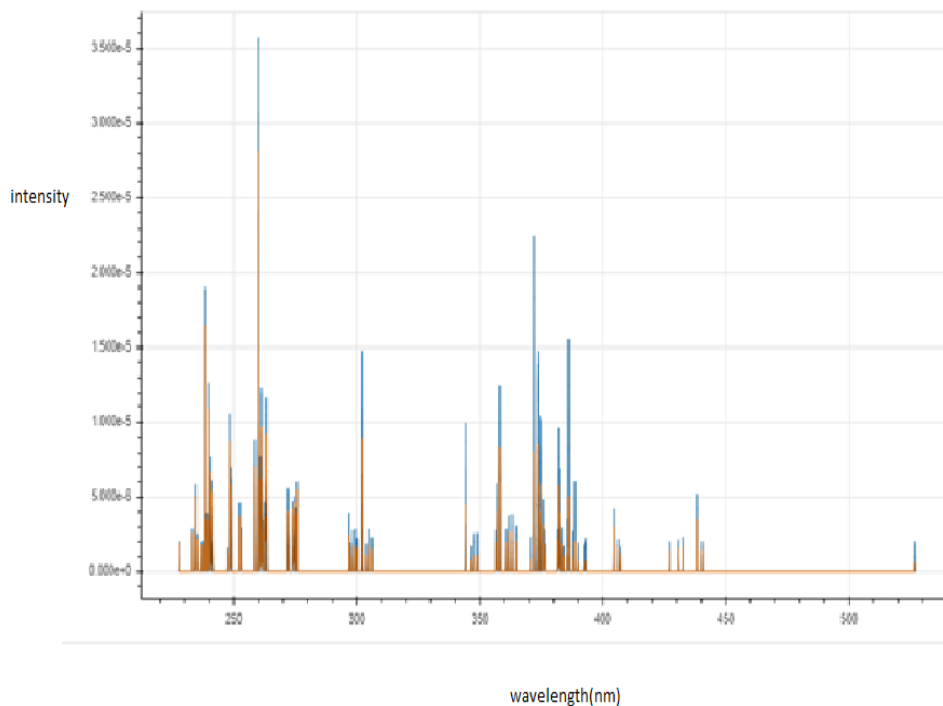


Figure 4.1 FE spectrum[36]

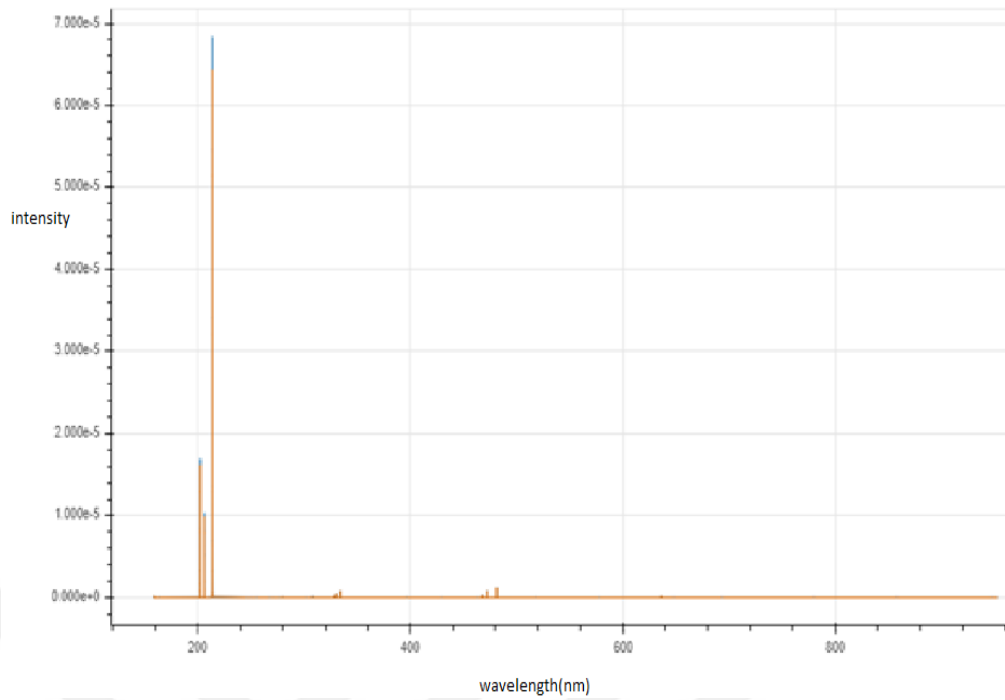


Figure 4.2 ZN Spectrum[36]

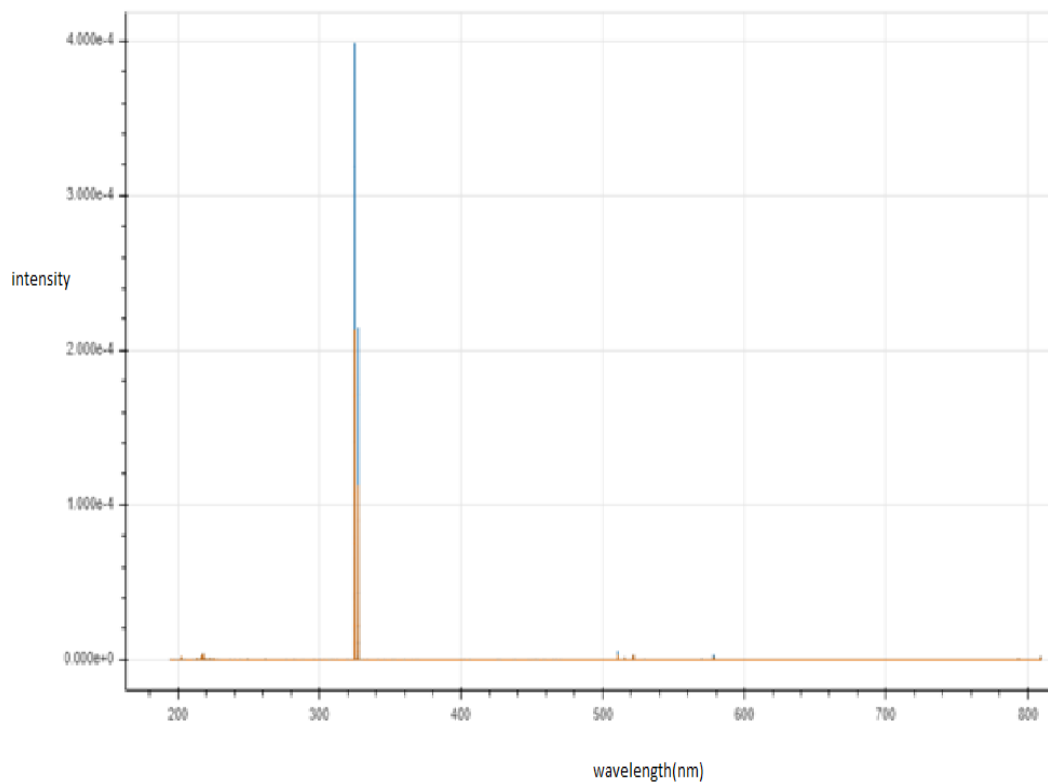


Figure 4.3 CU Spectrum[36]

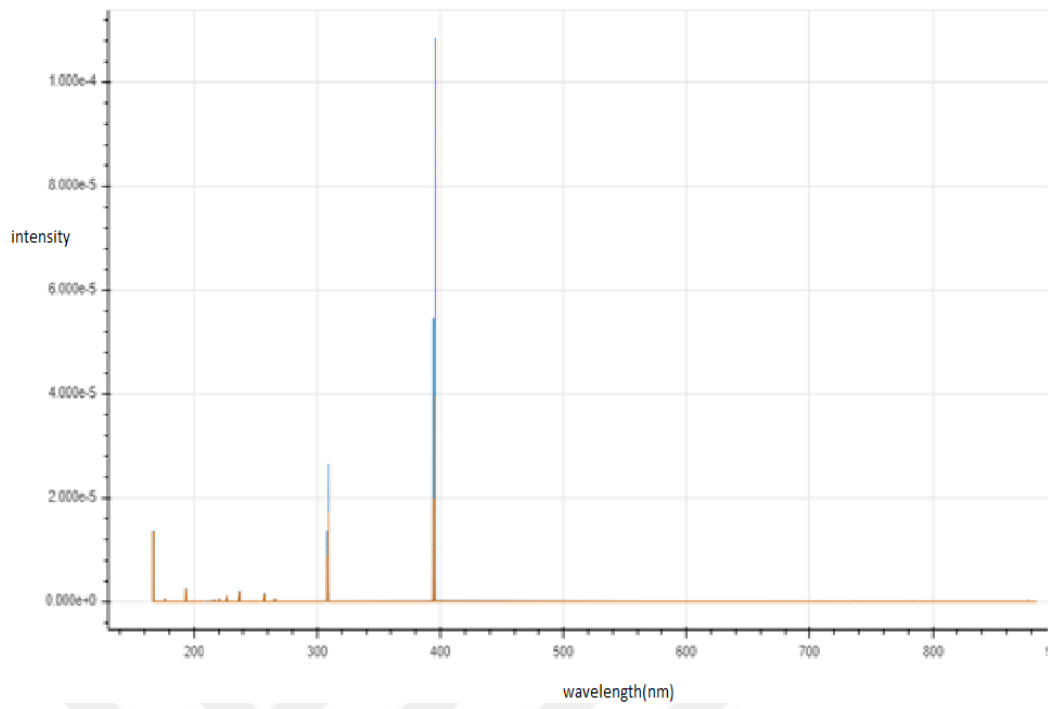


Figure 4.4 AL spectrum[36]

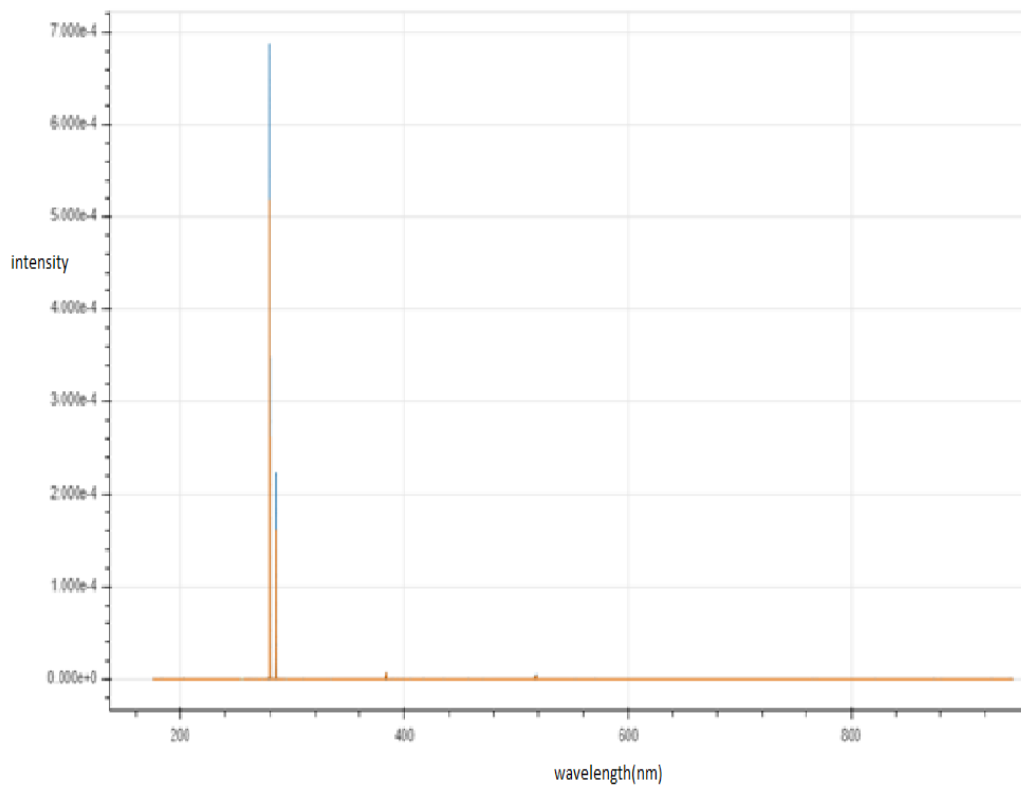


Figure 4.5 MG spectrum[36]

4.2 AA dataset

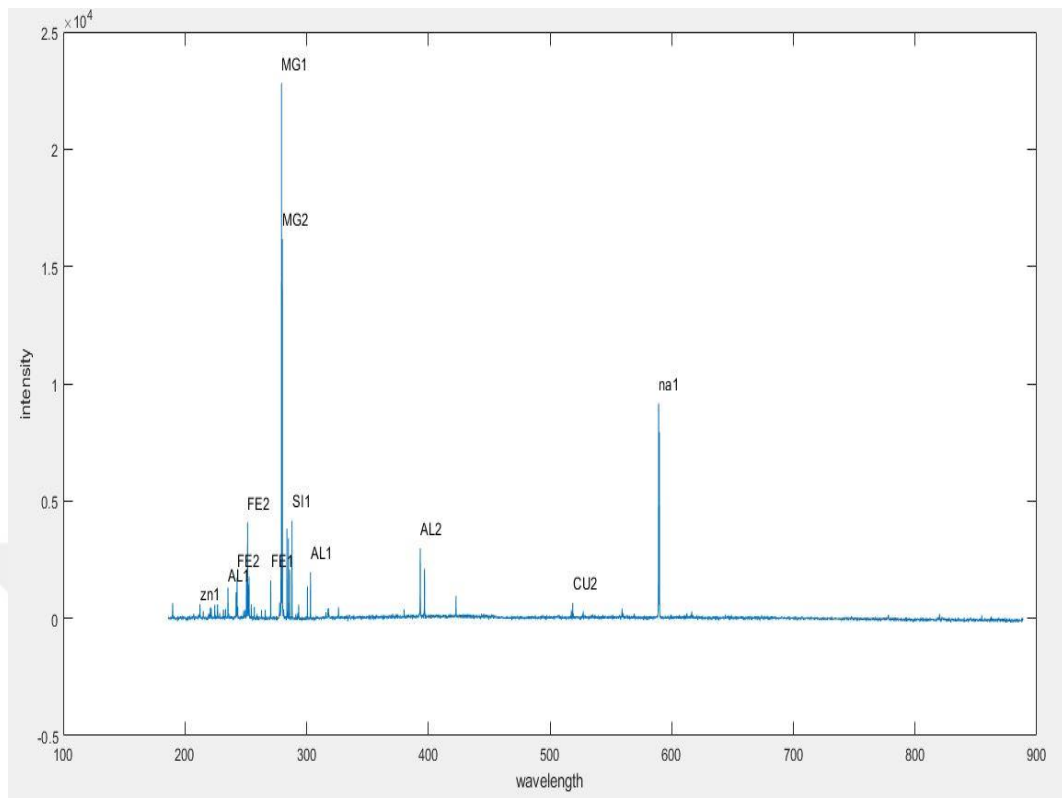


Figure 4.6 aa.data set

$$wwzn1 = 4.2484e+03$$

$$wwAL1 = 4.7081e+03$$

$$wwFE2 = 4.8570e+03$$

$$wwfe2second = 5.0301e+03$$

$$wwFE1 = 5.4106e+03$$

$$wwmg1 = 5.5876e+03$$

$$wwMG2 = 5.6017e+03$$

$$wwSi1 = 5.7595e+03$$

$$wwAL1second = 6.0645e+03$$

$$wwal2 = 7.8672e+03$$

$$wwcu2 = 1.0373e+04$$

wwna1 = 1.1786e+04

4.3 bb data

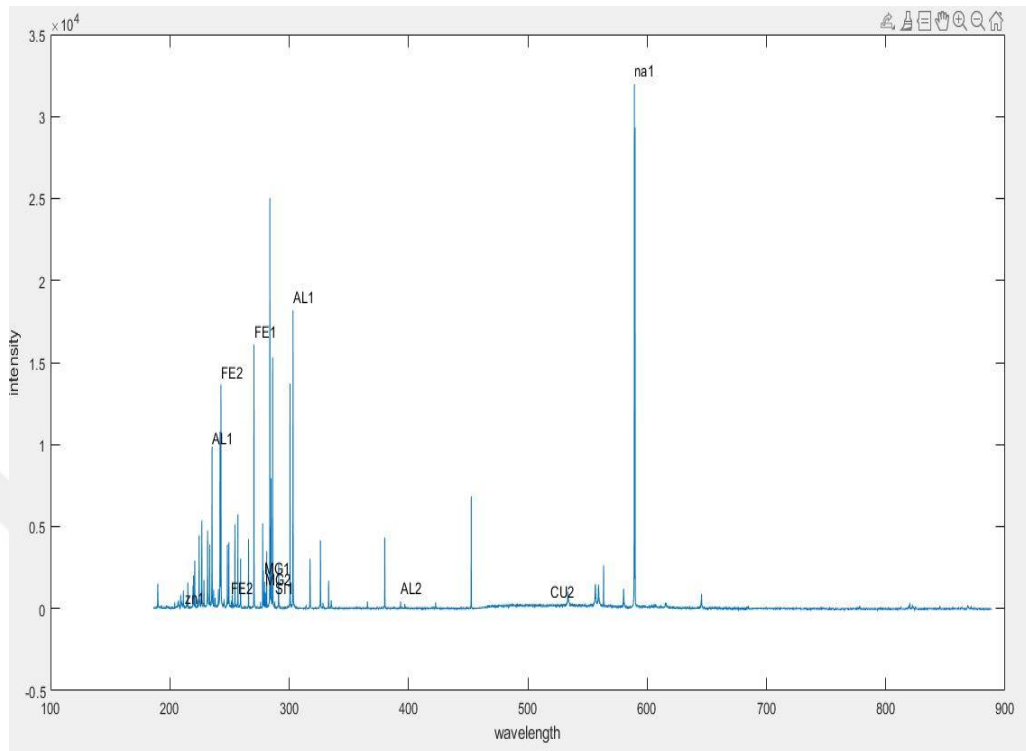


Figure 4.7 bb result

wwzn1 = 4.2484e+03

wwAL1 = 4.7081e+03

wwFE2 = 4.8570e+03

wwfe2second = 5.0301e+03

wwFE1 = 5.4106e+03

wwmg1 = 5.5876e+03

wwMG2 = 5.6017e+03

wwSi1 = 5.7595e+03

wwAL1second = 6.0645e+03

wwal2 = 7.8672e+03

wwcu2 = 1.0373e+04

wwna1 = 1.1786e+04

4.4 CC data

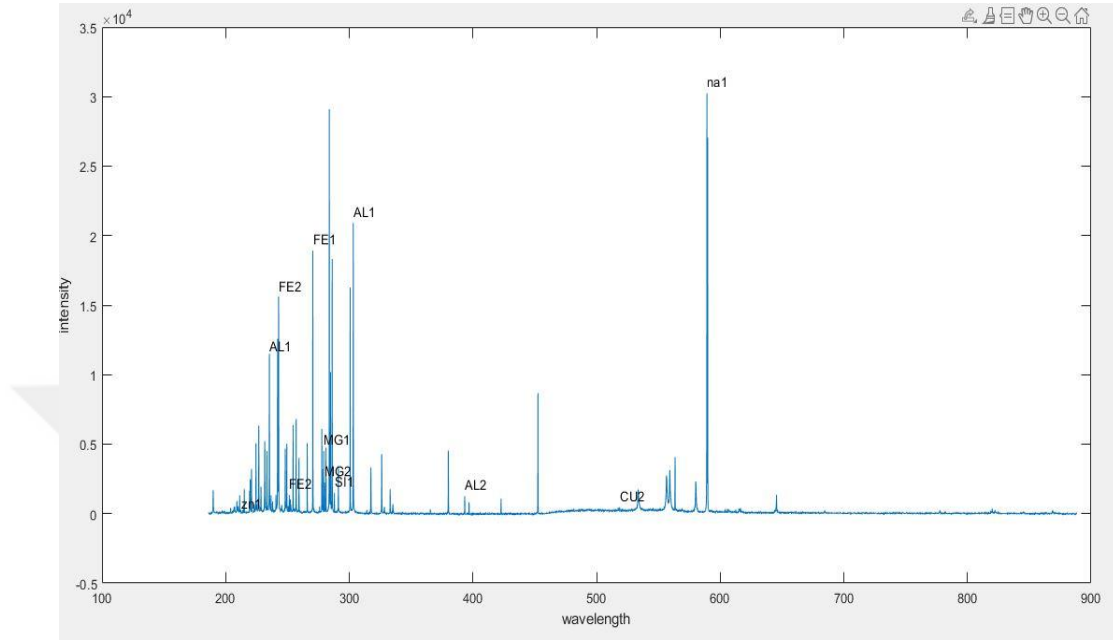


Figure 4.8 cc results

wwzn1 = 4.2484e+03

wwAL1 = 4.7081e+03

wwFE2 = 4.8570e+03

wwfe2second = 5.0301e+03

wwFE1 = 5.4106e+03

wwmg1 = 5.5876e+03

wwMG2 = 5.6017e+03

wwSi1 = 5.7595e+03

wwAL1second = 6.0645e+03

wwal2 = 7.8672e+03

wwcu2 = 1.0373e+04

wwna1 =1.1786e+04

The area under the curve was founded by taking integration from both sides of each pick point (since we have same pick points with different picks and different slopes). As well as we found the SNR as well as we cut the background noise in our samples we applied this method for the BB data set and we got the results through the formula
noise = response signal(actual signal) – signal with no noise
rawratio = signal /abs(noise)
snr = 10*log10(rawratio)

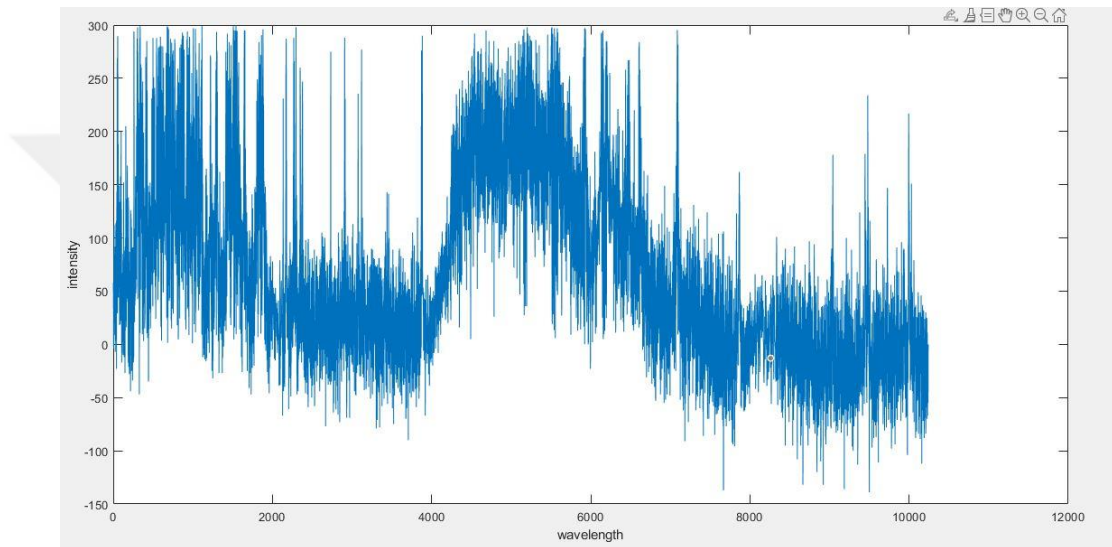


Figure 4.9 noise for BB data set

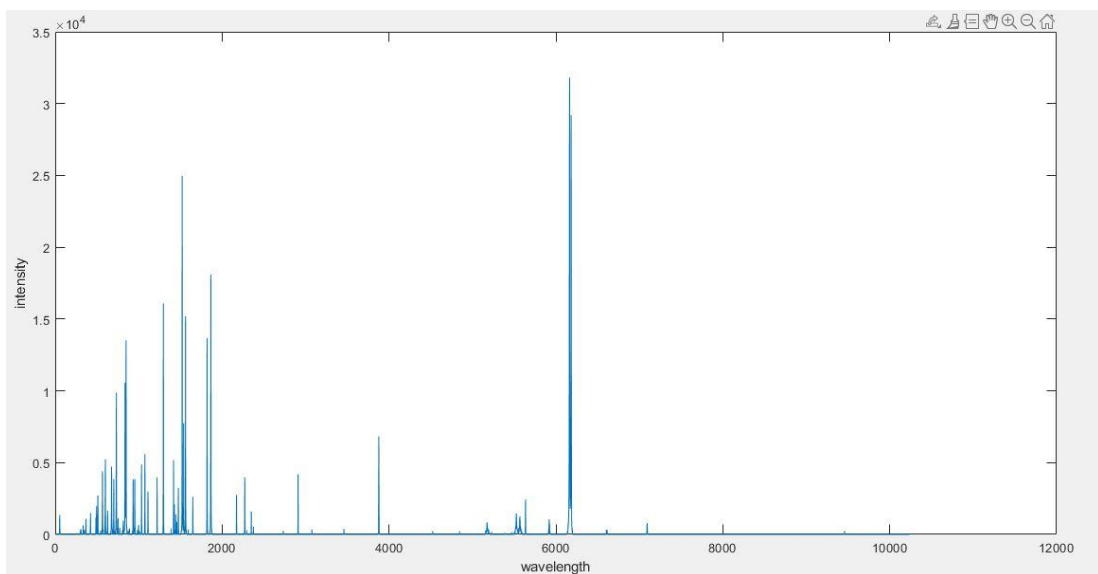


Figure 4.10 BB data set signal after eliminating the noise

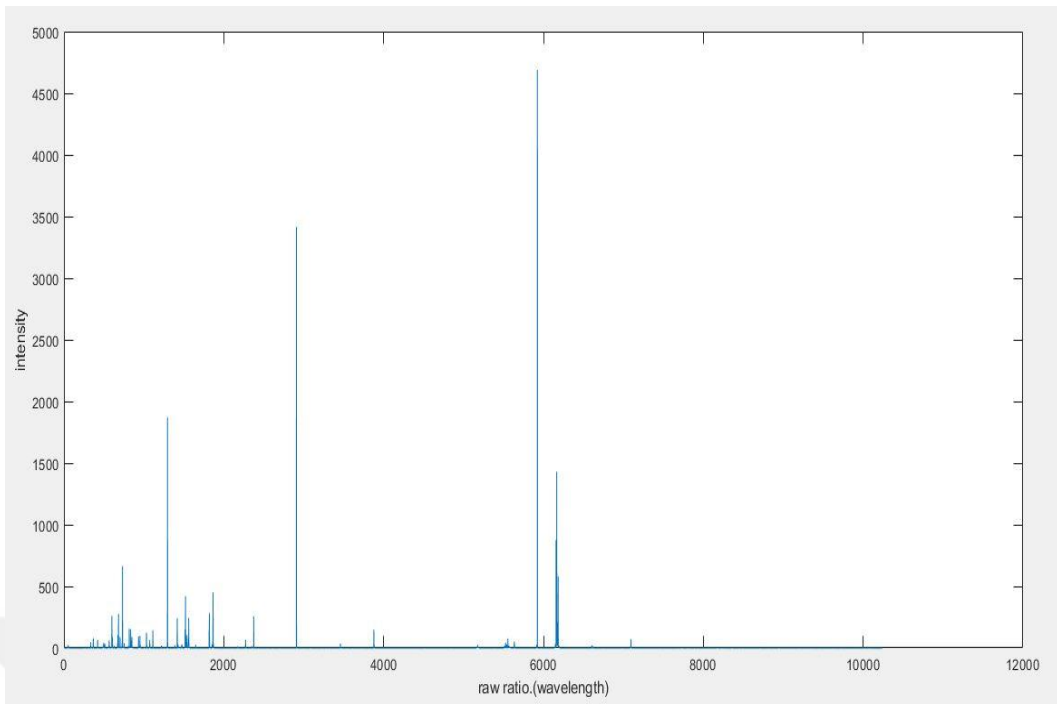


Figure 4.11 Raw ratio of BB data set

CHAPTER 5

5. CONCLUSION AND TUTURE WORKS

5.1 Conclusions

LIBS technique has rapidly developed during last years. By using advanced lasers combined with detecting systems and advanced data analysis techniques many groups could improve LIBS measurement of different samples, the large number of LIBS studies refers to the adaptability of LIBS as a new promising technique which will be used in huge range of applications. The availability of high-resolution spectrometers, gated cameras with significant gain factor, and ready-to-go data analysis software buttress the opportunity of the commercial use of LIBS for in situ and online elemental analysis. In our work we discuss the results we got from the setup, we compared the results with the Nist data base, we analyze the pick points of each data base and then finding the area under the curves to figure out the percentage of each element. This analyzing method can be applied on elements mixtures.

5.2 Future works

LIBS have found many areas to explore including scientific, industrial, biomedical, security, environment and food industry. Possible directions can be summarized as: Ambient air particle analysis, Continuous emission monitor, Detection of toxic elements in water, Soil analysis, Slurry sample analysis, Powder sample composition, Radioactive analysis, Molten material, Military applications, Space exploration, Phytoremediation analysis, Food safety, Nanoparticle-enhanced LIBS (NELIBS) and LIBS imaging.

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