Sudan University of Science and Technology
College of Graduate Studies

Detection of Pollutants in used Plastic Bottles using Laser Induced Breakdown Spectroscopy

الكشف عن الملوثات في قارورات بلاستيكية مستعملة باستخدام مطيافية الانهيار الكهربي المستحث بالليزر

A thesis submitted for the fulfillment of the requirements for the degree of Doctor of Philosophy in Laser Applications in physics

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الآيــة

بسم الله الرحمن الرحيم

(اللَّهُ نُورُ السَّمَاوَاتِ وَالْأَرْضِ مَثَلُ نُورِهِ كَمِشْكَاةٍ فِيهَا مِصْبَاحٌ الْمِصْبَاحُ فِي زُجَاجَةٍ الزُّجَاجَةُ كَأَنَّهَا كَوْكَبٌ دُرِّيٌّ يُوقَدُ مِنْ شَجَرَةٍ مُبَارَكَةٍ زَيْتُونَةٍ لَا شَرْقِيَّةٍ وَلَا غَرْبِيَّةٍ يَكَادُ زَيْتُهَا يُضِيءُ وَلَوْ لَمْ تَمْسَسْهُ نَارٌ نُورٌ عَلَى نُورٍ يَهْدِي اللَّهُ لِنُورِهِ مَنْ يَشَاءُ وَيَضْرِبُ اللَّهُ الْأَمْثَالَ لِلنَّاسِ وَاللَّهُ بِكُلِّ شَيْءٍ عَلِيمٌ)

سورة النور- الآية (35)

Dedication

To

My parents

My husband

My brothers and sisters

My friends and colleagues

Acknowledgement

Primarily I would like to thank God for being able to complete this project with success. My greatest thanks are to my parents who bestowed ability and strength in me to complete this work. I wish to express my deep gratitude and sincere thanks to Supervisor Dr. Mubarak Elmahal Ahmed who guided me to the successful competition of this project. I take this opportunity to express my deep sense of gratitude to his invaluable guidance, ongoing encouragement, enormous motivation, which has sustained my efforts at all the stages of project development. Also I need to thank Co Supervisor Dr. Ali Abdel-Rahman Saeed Marouf for his help and support throughout the entire time we've worked together. I can't forget to offer my deep and sincere gratitude to Prof Nafie A. Almuslet, supervisor who started this research with me and he has taught me the methodology to carry out the research and to present the research works as clearly as possible. I am extremely grateful for what he has offered me. I am grateful to all the staff of the Institute of laser in Sudan University of Science and Technology for their support and help all the time. I would like to express my sincere thanks to classmates who helped me to carry out this project successfully and for their valuable advice and support which I have received all the time. I am also very thankful to my brother Mohamed Eltaybe for his help, inspiration, and moral support.

Abstract

This study was conducted to analyze the components of the plastic materials used in water and drug bottles by using laser induced breakdown spectroscopy (LIBS). Bottle samples were collected from some factories in Sudan, the samples were collected pre- and post-used. Samples were irradiated by Nd: YAG laser at 266 nm, repetition rate 2Hz, with pulse energy of 80mJ. The recorded spectra of the samples were analyzed using National Institute Standard and Technology (NIST) and Origin Lab Pro 9 data analysis software. The results showed all elements present in plastic water bottles and bottles caps, which are Mn, Ca, Cl, Mg, N, Pm, O, F, Fe, K, Er, Mo, Eu, and S. All these elements are normal and this is useful for recycling only one times. All elements present in plastic drug bottles were detected, they are Cd, Ra, Ac, W, V, Na, Pm, Ca, Cl, K, Ar, Nd, Tc, Sc, Pb, Pa, Li and Ce. This group of plastic bottles are not useful for recycling. This study reveals that the Laser induced breakdown spectroscopy (LIBS) is useful technique for analyses the water and drug plastic containers and this technique led to accurate determination of different elements present in plastic.

In the future can be used LIBS system as a portable system for online analysis of many types of other plastic wastes.

المستخلص

أجريت هذه الدراسة لتحليل مكونات المواد البلاستيكية المستخدمة في قارورات المياه والأدوية باستخدام مطيافية الانهيار الكهربي المستحث بالليزر (LIBS). تم جمع العينات من بعض المصانع بالسودان ، قبل الاستخدام وبعده. تم تشعيعها بواسطة ليزر Nd: YAG طوله الموجي 266 نانومتر، معدل التكرار 2 هرتز، مع طاقة نبضيه تبلغ 80 مللي جول. تم تحليل الأطياف المسجلة للعينات باستخدام قاعدة بيانات الأطياف الذرية الصادرة عن المعهد الوطني للمواصفات والتقانة (NIST) وبرنامج تحليل البيانات Origin Lab Pro 9. أظهرت النتائج أن جميع العناصر الموجودة في قارورات المياه البلاستيكية وأغطيتها هي : Mn و Ca و Cl و Mg و N و Pm و O و F و Fe و K و Er و Mo و Eu و S. كل هذه العناصر طبيعية. وهذا مفيد لإعادة التدوير مرة واحدة فقط. تم الكشف عن جميع العناصر الموجودة في قارورات الأدوية البلاستيكية وهي: Cd و Ra و Ac و W و V و Na و Pm و Ca و Cl و K و Ar و Nd و Tc و Sc و Pb و Pa و Li و Ce. هذه المجموعة ليست مفيدة لإعادة التدوير. تكشف هذه الدراسة أن مطيافية الانهيار الكهربي المستحث بالليزر (LIBS) هي تقنية مفيدة لتحليل حاويات الماء والأدوية البلاستيكية وقد أدت هذه التقنية إلى التحديد الدقيق للعناصر المختلفة الموجودة في البلاستيك. في المستقبل يمكن استخدام نظام LIBS كنظام محمول لتحليل العديد من أنواع النفايات البلاستيكية الأخرى عبر الإنترنت.

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Chapter One

Laser Spectroscopy, Basic Concepts

CHAPTER ONE

LASER SPECTROSCOPY (BASIC CONCEPTS)

1.1. Introduction

Since the early 1800s, scientists realized that elements emitted specific colors of light. As atomic theory developed, spectroscopists learned that those colors, wavelengths or frequencies were a unique signature for each atom and ion. Hence spectra became fingerprints of the emitting atomic species. This is the basis for spectroscopy analysis using atoms. Early sources of spectra were the sun, flames and gas discharges, such as the old Geissler tube. These were plasma sources, with varying degrees of ionization depending on the source conditions (Cremer and Radziemski, 2013). As soon as the 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 showed the potential for spectrochemical analysis (Radziemski, 2002). Spectroscopy is the use of electromagnetic radiation to study the structure of matter. There are various spectroscopic methods including Laser-induced breakdown spectroscopy (LIBS), the (LIBS) has been developed as a new effective chemical detection spectroscopic technique (Liu, et al, 2019). Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy (AES) method which uses a laser-generated plasma as a source for hot vaporization, atomization, and excitation. The plasma is produced by intense optical radiation (Miziolek, Palleschi and Schechter, 2006). A LIBS measurement is carried out by forming a laser plasma on the sample and then collecting and spectrally analyzing the plasma light. Qualitative and quantitative analyses are carried out by monitoring emission line positions and intensities (Liu, et al, 2019). LIBS has evolved as a flexible elemental analysis tool that attracted tremendous attention due to some of its features including rapid elemental analysis, non-preparation of samples, simultaneous detection of a number of elements (high and low Z), low detection limits (micro / nano gram levels), micron size / thickness detection capability, and in situ / remote analysis possibility (Cremers and Radziemski, 2006, Pandhija, et al, 2010). All these features together made it a promising technique for the identification and classification of the samples in widespread applications such as explosive detection, space exploration, cultural heritage, medical diagnosis, industrial applications and other (Junjuri and Gundawar, 2019). The industrial development in the plastic manufacturing sector during the first half of the 20th century led to fulfill the needs of an increasing world population from plastic products they are common use in our daily lives (Saquing, et al, 2010).

The growing and continuous use of plastic products is one of the reasons in many countries for the generation of large amounts of residue (Aguirre, et al, 2013). Currently, the worldwide consumption per year is over 380 million metric tons (Junjuri, et al, 2019). Around 50 percent of the use is for disposable products such as packaging materials, water bottles, medical equipment and disposable consumer items, etc.(Geyer, et al, 2017, Alabi, et al, 2019). A great number of packaging materials are made from polymers, such as bottles and boxes. For the manufacture of packaging materials, additives such as plasticizers, antioxidants, antistatic agents and lubricants may be used. The worst consequence of plastic production is the environmental degradation (Siddiqui, Gondal and Nasr, 2009). Recycling is a solution to this problem and the first step is the identification and classification of the polymers and determination of different elements present in it (Anzano, Bello and Lasheras, 2014). So we need proper instrumentation to analyses plastics. LIBS provides a unique advantage and rapid technique for plastic materials characterization.

In this research, spectroscopic analysis was performed using Laser Induced Breakdown Spectroscopy (LIBS) for plastic materials (polymers) samples of water and drug containers, and the LIBS technique led to the determination of the various elements present in it.

1.2. The Study Objectives

- To use Laser Induced Breakdown Spectroscopy to characterize the hazardous and other inorganic trace element constituents in pre-and post-used of plastics products as water and drug containers.
- Determine the types of contaminants found in these wastes to the importance of this information to the environment, public health and recycle as well as that it will be possible to improve the capabilities of this technique for application to various samples of environmental significance.

1.3. The Thesis Structure

This thesis consists of four chapters. The introduction, and basic concepts of laser spectroscopy and the objectives of this research work are described in the first chapter. Chapter two covered the Laser Induced Breakdown Spectroscopy, principles, capabilities, and literature review. Chapter three describes the experimental portion, including the preparation of samples, equipment and instruments, the setup of experiments and the procedure. In chapter four the results, discussion, conclusions, and recommendations are presented.

1.4. Fundamentals of Lasers

The acronym LASER means: Light Amplification by Stimulated Emission of Radiation. It developed to laser device for generation of coherent electromagnetic waves by stimulated emission of radiation (Renk, 2012). Albert Einstein had already postulated the stimulated emission in 1917, describing it as one of three processes for how light interacts with matter in order to explain Planck's (radiation) law and quantum hypothesis. However, it wasn’t until 1960 that Theodore H. Maiman exploited this process for the first realization of coherent light. The light sources used by then, the sun, light bulbs or gas discharge lamps, emit light in all directions and at various frequencies, whereas the laser produces a highly-collimated beam with narrow spectral line width. The undirected radiation from conventional sources of light results from the spontaneous random emission of the excited atoms. By contrast, the stimulated emission process produces identical photons of equal energy and phase, and travels in the same direction (Eichler, et al, 2018). The high intensity and spectral monochromaticty of lasers have opened a new class of spectroscopic techniques which allow investigation of the structure of atoms and molecules in much more detail. Stimulated by the variety of new experimental possibilities that lasers give to spectroscopists, very lively research activities have developed in this field (Demtröder, 2014).

1.4.1. Interaction of Electromagnetic Radiation with Matter

Planck discovered a theoretical explanation of black body radiation spectral distribution. This radiation, which is emitted, e.g., from a small hole in the walls of a hohlraum (the blackbody) kept at a temperature T. Its spectral distribution and the peak of the emission intensity are only a function of the blackbody temperature (Eichhorn, 2014). In Planck's derivation of this spectrum he assumed that electromagnetic radiation cannot be emitted or absorbed continuously, but only in fixed amounts of energy, the quanta, with a corresponding energy of

$$E = hv = \frac{hc}{\lambda} \text{ ------------------- } (1.1)$$

these quanta are the photons of the electromagnetic field that can be described by their frequency υ or their wavelength λ , and h : Plank's constant (6.626 x 10^{-34} J·S), c :speed of light (3 x 10^{8} m/s) (Eichhorn, 2014).

There three fundamental phenomena that occur when an electromagnetic wave interacts with a material, namely the processes of spontaneous and stimulated emission, and the process of absorption, (Träger, 2012) shown in Figure (1.1).

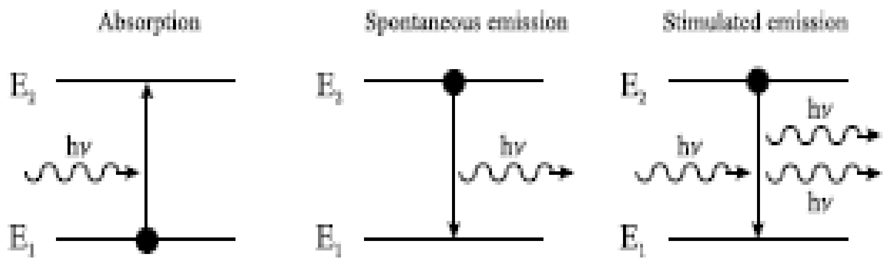


Figure (1.1): Interactions between a two-level system and a photon according to Einstein (Eichhorn, 2014).

•**The absorption**: The absorption of a photon of energy hν =E2−E1, causing a transition from level |1⟩to level |2⟩.

•**The spontaneous emission**, in which the system emits a photon of energy hν by returning from level |2⟩ to level |1⟩. This is called spontaneous emission as the moment of emission (i.e. the phase φ of the radiation), the polarization $\vec{\epsilon}$ and the propagation direction, i.e. the direction of the wave vector *k*, is random. Thus the spontaneous emission causes incoherent radiation and is responsible for the fluorescence of excited media (Eichhorn, 2014).

•**The stimulated emission**, in which an incoming photon induces a resonant transition from the excited level |2⟩ to level |1⟩, emitting a second photon of energy hν. As photons are Bosons, i.e. they are allowed to be in the same quantum mechanical state, and as stimulated emission is a resonant process, both photons are identical in all their properties. This effect, therefore, allows the amplification of light, the fundamental process of any laser.

The fundamental process that allows us to realize a laser is the stimulated emission process occurring in excited quantum-mechanical systems, giving rise to the possibility of photon amplification (Svelto and Hanna, 2010) this process assumed by Einstein in 1917.

Einstein assumed that an ensemble of N =N1 +N2 nondegenerate two-level systems with an energy difference ΔE = hν = E2−E1 is in thermal equilibrium with its environment kept at a temperature T. The absorption of the radiation then causes a transition rate from level |1⟩ to level |2⟩

$$(\frac{dN_2}{dt})_{abs} = -\left(\frac{dN_1}{dt}\right)_{abs} = B_{12}u(v,T)N_1\text{------------- (1.2)}$$

that is proportional to the (unknown) radiation energy density u (ν,T) and the number of absorbers N1 with a proportionality constant B12. The stimulated emission of the radiation causes a transition from level |2⟩ to level |1⟩ with the rate.

$$(\frac{dN_2}{dt})_{stim} = -\left(\frac{dN_1}{dt}\right)_{stim} = -B_{21}u(v,T)N_2\text{----------- (1.3)}$$

which is also proportional to the radiation density u (ν, T) and the number of emitters N2 with a proportionality constant B21. The spontaneous emission is only proportional to the number of the possible emitters N2 and causes a rate

$$(\frac{dN_2}{dt})_{spont} = -\left(\frac{dN_1}{dt}\right)_{spont} = -A_{21}N_2\text{--------------- (1.4)}$$

The proportionality constants B12, B21 and A21 are called Einstein coefficients (Eichhorn, 2014).

1.4.2. Principles of Laser

Lasers are based on the stimulated emission of light in an active material which has been pre-excited by a pump mechanism. The stimulated emission can be carried out in laser oscillators which are always the primary source of laser light. In addition, this light can be amplified via stimulated emission in light amplifiers as shown in Figure 1.2 where a master oscillator is combined with, e.g. two amplifiers in a MOPA (Master Oscillator Power Amplifier) setup. In combination with these amplifier and/or other nonlinear converter systems the light can be modified regarding almost all parameters such as, e.g., for shorter or longer pulses, different wavelengths, polarization or geometry (Menzel, 2013).

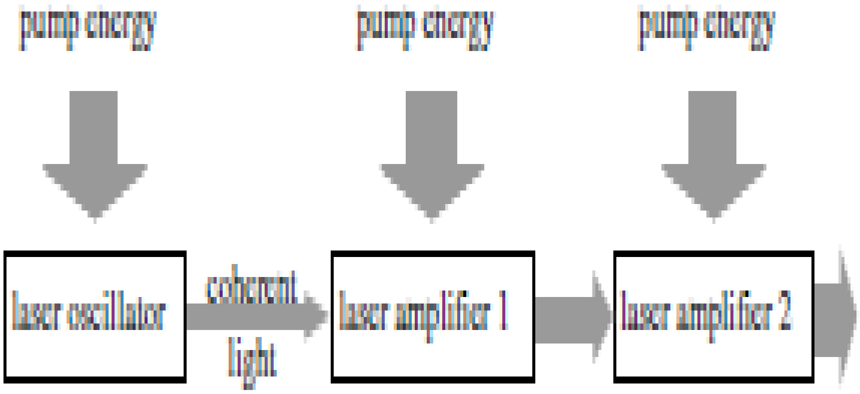


Figure (1.2): Laser setup consisting of a laser oscillator (master oscillator) and two amplifiers (MOPA scheme) (Menzel, 2013).

1.4.3. Basic Elements of Laser

A laser consists of at least three components shown as the Figure (1.3)

1. Active medium or gain medium, which determines the wavelength of the laser produced. It may be solid (crystals, glasses, semiconductors), liquid (organic dyes or solvents), or gas (e.g. argon, carbon dioxide). The lasing medium present often determines the name of the type of laser.

2. **A ‘**pump’ or excitation source, which supplies the necessary energy. There are many different types of pumps, including optical (flash lamp, continuous arc lamp, light from another laser), electrical or chemical.

3. An optical resonator, which contains the lasing medium with two parallel mirrors on either side, thus causing the photons to pass repeatedly back and forth between the two. One of the mirrors is partially transparent, allowing some of the photons to exit the device to form the laser beam. This is termed the ‘output coupler’ (Haley and Pratt, 2017).

The laser beam is usually the fractional part of light trapped in the cavity that escapes from one of the two mirrors (the *output coupler*) (Träger, 2012).

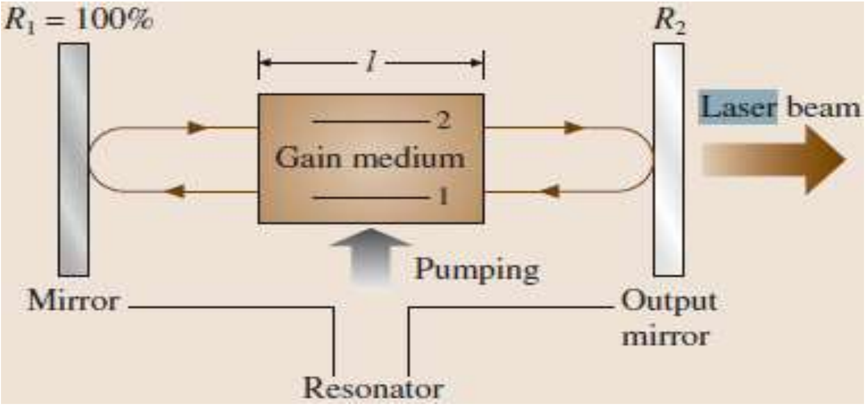


Figure (1.3): Schematic of a laser oscillator (Träger, 2012).

1.4.4 . Types of Lasers

Lasers have been classified on the basis of various parameters such as nature of active medium lasers are classified as: (Solid-state lasers, Semiconductor lasers and Gas lasers), Based on pumping mechanism lasers are classified as: (Optically pumped lasers, Gas dynamic lasers and Electrically pumped lasers), Based on nature of laser output in terms of power/energy level, lasers are classified as: (Pulsed lasers ,CW lasers), Based on operational mode, lasers are classified as: (Q-switched laser, Mode-locked lasers, Cavity- dumped lasers). Based on output wavelength, lasers are classified as: (Ultraviolet (UV) lasers, Visible lasers and Infrared (IR) lasers) (Träger, 2012, Maini, 2018). The most important way of classification of lasers seems to be on the basis of nature of lasing medium. On this basis, solid-state lasers, semiconductor lasers and gas lasers are the three major categories. In addition, there are a large number of other varieties of lasers that do not fit into any of the previously mentioned broad categories. These include dye lasers, Excimer lasers, metal vapour lasers, free electron lasers, X-ray lasers and so on (Träger, 2012).

1.5. Spectroscopy

Spectroscopy can be defined as the study of the interaction between electromagnetic radiation and matter. Electromagnetic radiation is characterized by its wavelength λ (the length of one wave, cm), its frequency ν (the number of vibrations per unit time, Hz), and its wave number ύ (the number of waves per unit length, cm^{-1}) (Abbas, Dardenne and Baeten, 2012, Baranska, 1987). The spectral measurements (spectrometry) are mean the measurement these interactions between the matter and the radiation, qualitatively by describe how to identify the chemical structures of these substances or quantitatively by measuring concentrations of these substances. Spectral measurement devices are called spectrometers, spectrographs, the interference pattern between matter and radiation is indicated by a spectrogram or spectrum (Demtröder, 2014). Matter is any substance that has mass and takes up space by having volume, Matter exists in various states (also known as phases). These include classical everyday phases such as solid, liquid, and gas, and other states are possible, including plasma (Penrose, 1991). Laser plasmas are shown to offer the ability to perform elemental, isotopic, molecular, quantitative, and qualitative sample analysis with sub micrometer spatial resolution, and each feature can be measured at standoff distances (Bings, Bogaerts and Broekaert, 2006).

1.6. Classifying Spectroscopy

There are multiple ways to classify types of spectroscopy. The techniques may be grouped according to the type of radiative energy (e.g., electromagnetic radiation, acoustic pressure waves, particles such as electrons), the type of material being studied (e.g., atoms, crystals, molecules, atomic nuclei), the interaction between the material and the energy (e.g., emission, absorption, elastic scattering), or by specific applications (e.g., Fourier transform spectroscopy, circular dichroism spectroscopy) (Vo-Dinh, 2006, Maini, 2018).

There are two types of spectroscopy:

(i) Molecular Spectroscopy

The molecular spectroscopy involves to the study of the electromagnetic radiation absorbed and emitted by molecules. it is technique in which we use an electromagnetic radiation with molecules in order to produce an absorption pattern (i.e. a spectrum) from which structural or compositional information can be deduced (Goodman, 1994). The results in transition between rotational and vibration energy levels in addition to electronic transitions. Absorption of a photon may excite the molecule to a higher electronic vibrational and / or rotational energy level. There are many transitions that might give rise to absorption, but only those that satisfy certain selection rules are allowed (Paisner, Radziemski and Solarz, 1987).

(ii) Atomic Spectroscopy

Atomic spectroscopy refers to the study of the electromagnetic radiation absorbed and emitted by atoms .This deals with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state (Rudzikas, 2007). Atomic spectra involve only transitions of electrons from one electronic energy level to another (Kuzmany, 2009). Therefore, atomic spectroscopy determines the type of atoms present in a given sample. There are two types of atomic spectroscopy:

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

1.6.1. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is nowadays one of the most important instrumental techniques for quantitative analysis of metals (and some few metalloids) in various types of samples and matrices. The history of atomic absorption spectrometry dates back to the discovery of dark lines in the continuous emission spectrum of the sun by Wollaston in 1802. The lines are caused by the absorption of the elements in the atmosphere of the sun. His work was taken up and further pursued by Fraunhofer in 1814 (Rosenberg and Panne, 2003). In 1860, Kirchhoff and Bunsen demonstrated that the yellow line emitted by sodium salts when introduced into a flame is identical with the so-called D-line in the emission spectrum of the sun. However, it took nearly one century before this important discovery was transferred into a viable analytical technique. In 1955, Alan Walsh published the first paper on atomic absorption spectroscopy. At the same time, and independently of Walsh, Alkemade and Wilatz published the results of their fundamental AAS experiments .But it was the vision of Walsh and his indefatigable efforts that eventually led to the general acceptance and commercialisation of AAS instrumentation in the mid-1960s. Further instrumental achievements, such as the introduction of the graphite furnace and the hydride generation technique, in the second half of the 1960s further promoted the popularity and applicability of the technique (Rosenberg and Panne, 2003, Svanberg, 2012). In absorption spectroscopy technique if a beam of light is sent into a sample, which can be a gas, liquid or solid, photons with the right energy will be absorbed. The rate of the photon absorption could be treated by using the Beer's law, the absorption can be related to the concentration of the species. If light with intensity P_0 is directed onto a cuvette the intensity decreases exponentially through the sample. The intensity P at the position X is obtained from the relation:

$$P = P_0 e^{-\mu ax} \text{ ---------------------- } (1.5)$$

Where μ_a is the absorption coefficient. μ_a describes the probability per unit distance for an absorption event to occur. More exactly, the probability for absorption in the infinitesimal distance dx is μ_a dx. The inverse of the absorption coefficient ($1/\mu_a$) is in the absence of scattering the mean free path for a photon (Jeong et al., 2007).

This method can thus be used to measure the absorption coefficient of a sample. The method is commonly used in spectrophotometers. One restriction of this method is that the sample must be homogenous and non-scattering, which often is the case in many chemical applications.

1.6.2. Atomic Emission Spectroscopy (AES)

LIBS is one method of atomic emission spectroscopy (AES). The AES is spectroscopy technique using to determine the elemental composition of a sample (solid, liquid, or gas). The analysis can range from a simple identification of the atomic constituents of the sample to a more detailed determination of relative concentrations or absolute masses. Basic steps in AES are: Atomization/vaporization of the sample to produce free atomic species (neutrals and ions), excitation of the atoms, detection of the emitted light, calibration of the intensity to concentration or mass relationship, determination of concentrations, masses, or other information. Examination of the emitted light provides the analysis because each element has a unique emission spectrum useful to “fingerprint” the species. Extensive compilations of emission lines exist (Payling and Larkins, 2001). The position of the emission line(s) identifies the element(s) and, when properly calibrated, the intensity of the line(s) permits quantification. The specific procedures and instrumentation used in each step of AES are determined by the characteristics of the sample and by the type of analysis (i.e. identification vs. quantification). It should be noted that because the first step in AES is atomization/vaporization, AES methods are generally not suitable to determine the nature of compounds in a sample. In specific cases, however, information can be obtained about molecular origins. The beginnings of AES can be traced back to the experiments of Bunsen and Kirchhoff (c. 1860) in which atomization and excitation were provided by a simple flame (Miziolek, Palleschi and Schechter, 2006). Following this, more robust and controllable methods of excitation were developed by using electrical current to interrogate the sample. Some of the more well-known methods of vaporization and excitation include electrode arcs and sparks, the ICP, the direct coupled plasma (DCP), the microwave-induced plasma (MIP), and hollow cathode lamps (Ottaway, 1980). These traditional sources typically require significant laboratory support facilities and some form of sample preparation prior to performing the actual analysis. In special cases, novel sampling methods have been developed for some of these sources for specific applications. Examples are an air-operated ICP providing direct analysis of particles contained in air and the introduction of particles collected on a filter into the hollow electrode of a conventional spark discharge. For various reasons, these methods saw very limited use. LIBS is an extension of the vaporization/excitation scheme to optical frequencies (Cremers and Radziemski, 2013).

1.7. The use of Lasers in Spectroscopy

The discovery of lasers revolutionized the spectroscopy given the opportunity to the experimentalist a monochromatic light source, powerful, directive and sometimes tunable. These properties enable the laser source to be an instrument that is not comparable with others used in spectroscopy (Loureiro, and Amorim, 2016). Laser spectroscopy comprises those measurement methods employing the specific properties of atoms or molecules and their interaction with laser radiation such as:

1.7.1. Laser Infrared Spectroscopy

Infrared spectroscopy is a spectroscopic technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining which fraction of the incident radiation is absorbed at a particular energy (Khoshhesab, 2012). The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. The dipole moment of such a molecule changes as the bond expands and contracts. The IR spectroscopy theory utilizes the concept that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling (Stuart, 2004). The electromagnetic infrared spectrum is typically divided into three regions; the near-, mid- and far- infrared, named for their connection to the visible spectrum. The near-IR higher-energy, approximately 14000–4000 cm−1 (0.7–2.5 μm wavelength) can excite overtone or combination modes of molecular vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) is generally used to study the fundamental vibrations and associated rotational–vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm) has low energy and may be used for rotational spectroscopy and low frequency vibrations. The region from 2–130 cm^{-1}, bordering the microwave region, is considered the terahertz region and may probe intermolecular vibrations (Zeitler, et al, 2007). The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties. NIR spectroscopy is the most commonly used method for polymer identification, which determines the molecular structures of polymers by recording the reflected or transmitted radiation (Yu et.al, 2014). While it is beneficial with high precision and speed of detection, black polymers are difficult to detect and the signal is vulnerable to sample surface impurities (Junjuri, 2019).

1.7.2. Fourier-transform Infrared Spectroscopy (FTIR)

IR spectroscopy has seen fairly limited application in both the qualitative and the quantitative analysis of matter, largely owing to experimental limitations. The development of Fourier transform infrared (FTIR) spectroscopy during the past two decades has revitalised the field of IR spectroscopy (Subramanian and Rodriguez, 2009). This is due not only to the superior performance of FTIR spectrometers by comparison to that of the dispersive IR spectrometers that they have virtually replaced, but also to a number of other factors. First, the development of FTIR spectrometers has been paralleled by advances in sample handling techniques. Second, the dedicated computer that is an integral component of all FTIR systems has been extensively exploited in the development of sophisticated data handling and data analysis routines. As a result of these developments, FTIR spectroscopy has the potential to become an important tool for the quantitative analysis of matter (Ismail, et al, 1997). Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time (Griffiths and De Haseth, 2007). The term Fourier-transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum (Griffiths and De Haseth, 2007). For other uses of this kind of technique an alternate method for acquiring spectra is the "dispersive" or "scanning monochromator" method. In this approach, the sample is irradiated sequentially with various single wavelengths. The dispersive method is more common in UV-Vis spectroscopy, but is less practical in the infrared than the FTIR method. One reason that FTIR is favored is called "Fellgett's advantage" or the "multiplex advantage": The information at all frequencies is collected simultaneously, improving both speed and signal-to-noise ratio. Another is called "Jacquinot's Throughput Advantage": A dispersive measurement requires detecting much lower light levels than an FTIR measurement (Connes and Connes, 1966). There are other advantages, as well as some disadvantages, but virtually all modern infrared spectrometers are FTIR instruments.

1.7.3. Laser Raman Spectroscopy

During the last decade Raman spectroscopy has matured to become one of the most powerful techniques in analytical science due to its molecular sensitivity, its ease of implementation. When light is scattered from a molecule or crystal, most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is termed the Raman Effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. If the scattering is elastic, the process is called Rayleigh scattering. If it’s not elastic, the process is called Raman scattering see Figure (1.4) (Herzberg, 1991). Thus the 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 (Cordero, et al, 2018).

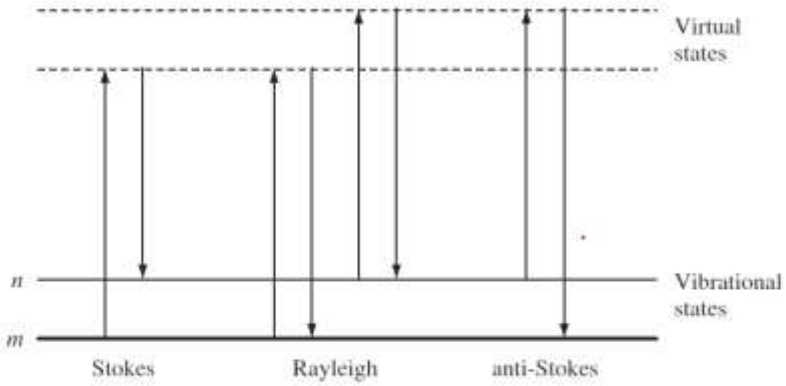


Figure (1.4): Diagram of the Rayleigh and Raman scattering processes (Smith and Dent, 2005)

The phenomenon of inelastic scattering of light was first postulated by Smekal in 1923 and first observed experimentally in 1928 by Raman and Krishnan (Smith and Dent, 2005). Since then, the phenomenon has been referred to as Raman spectroscopy. In the original experiment sunlight was focused by a telescope onto a sample which was either a purified liquid or a dust-free vapor. A second lens was placed by the sample to collect the scattered radiation. A system of optical filters was used to show the existence of scattered radiation with an altered frequency from the incident light – the basic characteristic of Raman spectroscopy (Smith and Dent, 2005). The use of Raman spectroscopy originating in physics and chemistry has spread and now includes a variety of applications in biology and medicine revealing the molecular signature of diseases and individual bacteria, ultrafast spectroscopy to unravel the sub-picosecond dynamics of structural rearrangements during chemical reaction and has reached for the stars – with the upcoming implementation of Raman spectrometers in the Mars missions of ESA and NASA .Furthermore, latest developments have merged the chemical sensitivity and specificity of Raman scattering with the high spatial resolution of confocal microscopy yielding chemical images of a sample (Dietzek, et al, 2010). For many years Raman spectroscopy has been a powerful tool for the investigation of molecular vibrations and rotations. In the pre-laser era, however, its main drawback was a lack of sufficiently intense radiation sources. 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. The research activities in laser Raman spectroscopy have recently shown an impressive expansion and a vast literature on this field is available (Demtröder, 2008).

1.7.4. Laser Induced Breakdown Spectroscopy (LIBS)

The last decade has seen major progress in Laser Induced Breakdown Spectroscopy. It is an atomic emission spectroscopy technique that can analyze solids, liquids and gasses and can quickly produce results with very little damage to the sample (Konidala, Kamala and Korallam, 2016) the use of laser-induced spark emission for elemental analysis of materials originated from the pioneering work of D. A. Kremers and L. J. Radziensky at Los Alamos National Laboratory (USA) in the early 1980s, about 20 years after the invention of the laser. Since then, LIBS has developed into a major analytical tool capable of providing real-time measurements of constituents in almost any kind of material (Musazzi and Perini, 2014).

Laser induced breakdown spectroscopy (LIBS) is based on the interaction between a laser pulse and the material. The material analyzed is vaporized, atomized, and ionized by the laser pulse. This leads to the creation of a plasma plume. At the end of the pulse, the plasma cools down and emits radiation dependent on the nature of the sample. The radiation emitted by the plasma can be collected and sent to a spectrometer for the identification of the elements present in the material (Grégoire, et al, 2011). Because of its unique features, like the absence of sample preparation, the ability to perform real-time, and in situ analysis as well as the quasi nondestructive and micro-analysis character of the measurements, the number of LIBS applications has dramatically increased in the last years (Musazzi and Perini, 2014).

Chapter Two

Laser Induced Breakdown Spectroscopy, Principles and Applications

CHAPTER TWO

LASER INDUCED BREAKDOWN SPECTROSCOPY, PRINCIPLES AND APPLICATION

2.1. Introduction

Laser-induced phenomenon of breakdown were observed in 1960, just after the laser invention. Laser induced breakdown spectroscopy (LIBS), also called laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LSS) is often named. Have developed rapidly as analytical methods over the past two decades (Cremers and Radziemski, 2013). The LIBS is a technique for atomic emission spectroscopy that uses highly intense laser pulses to induce optical sample excitation (Kearton and Mattley, 2008). The interaction between focused laser pulses and the sample creates plasma composed of ionized matter. Plasma light emissions can provide “spectral signatures” of chemical composition of many different types of materials in solid, liquid, or gas state (Anabitarte, Cobo and Lopez, 2012). The relative simplicity in instrumentation, ease of use, the ability to analyze remotely without contact, and ability to detect a wide range of elements has made LIBS a common option for the qualitative and quantitative analysis of materials such as plastics (polymers) (Gondal, and Siddiqui, 2007). It could be considered LIBS as a "put & play" technique suitable for a wide range of applications Considerable progress has been made during the last few years on very different and versatile applications of LIBS, including remote material assessment in nuclear power stations, geological analysis in space exploration, diagnostics of archaeological objects, metal diffusion in solar cells, and so forth. Today, LIBS is considered as an attractive and effective technique when a fast and whole chemical analysis at the atomic level is required (Anabitarte, Cobo and Lopez, 2012). In recent years, LIBS technique has been widely used in various areas, this growth in the applications of LIBS emerges in parallel with the technological developments in instrumentation (Ateş, 2010).

2.2. LIBS Principles

Laser induced breakdown spectroscopy (LIBS) is essentially an emission spectroscopy technique where atoms and ions are primarily formed in their excited states as a result of interaction between a tightly focused laser beam and the material sample. The interaction between matter and high-density photons generates a plasma plume, which evolves with time and may eventually acquire thermodynamic equilibrium (Thakur and Singh, 2007). In principle, LIBS can analyses any matter regardless of its physical state, be it solid, liquid or gas. Because, all the elements can emit light of characteristic frequencies, when they excited at sufficient high temperatures (Konidala, Kamala and Koralla, 2016). The technique relies on the use of a pulsed laser source (with energy per pulse ranging from tens to hundreds of mJ and pulse durations typically smaller than 10 ns) and a measuring chain for the analysis of the plasma emitted spectrum (Musazzi and Perini, 2014). In detail, the laser pulses are focused down to a target (solid, liquid as well as gas samples have so far been analyzed) so as to generate a high temperature plasma that vaporizes a small amount of material. A portion of the light emitted by the excited atomic and ionic species in the plasma is then collected and spectrally analyzed to determine the sample elemental composition. Quantitative LIBS analysis can also be performed when the assumptions of local thermal equilibrium (LTE) and optically thin plasma are satisfied (Musazzi and Perini, 2014). LIBS has rapidly developed into a major analytical technology with the capability of detecting all chemical elements in a sample, of real- time response, and of close-contact or stand-off analysis of targets (Thakur and Singh, 2007).

2.3. Definition of a Plasma

The word plasma is used to describe a wide variety of macroscopically neutral substances containing many interacting free electrons and ionized atoms or molecules, which exhibit collective behavior due to the long-range coulomb forces. Not all media containing charged particles, however, can be classified as plasmas. For a collection of interacting charged and neutral particles to exhibit plasma behavior it must satisfy certain conditions, or criteria, for plasma existence (Bittencourt, 2013). The word plasma comes from the Greek and means something molded. It was applied for the first time by Tonks and Langmuir, in 1929, to describe the inner region, remote from the boundaries, of a glowing ionized gas produced by electric discharge in a tube, the ionized gas as a whole remaining electrically neutral (Jaroszynski, Bingham and Cairns, 2009). Plasma is one of the four essential states of matter. The basic distinction among solids, liquids, and gases lies in the difference between the strength of the bonds that hold their constituent particles together. These binding forces are relatively strong in a solid, weak in a liquid, and essentially almost absent in the gaseous state. Whether a given substance is found in one of these states depends on the random kinetic energy (thermal energy) of its atoms or molecules, i.e., on its temperature. The equilibrium between this particle thermal energy and the inter-particle binding forces determines the state. By heating a solid or liquid substance, the atoms or molecules acquire more thermal kinetic energy until they are able to overcome the binding potential energy (Cairns, 2012). This leads to phase transitions, which occur at a constant temperature for a given pressure. The amount of energy required for the phase transition is called the latent heat. If sufficient energy is provided, a molecular gas will gradually dissociate into an atomic gas as a result of collisions between those particles whose thermal kinetic energy exceeds the molecular binding energy. At sufficiently elevated temperatures an increasing fraction of the atoms will possess enough kinetic energy to overcome, by collisions, the binding energy of the outermost orbital electrons, and an ionized gas or plasma results. However, this transition from a gas to a plasma is not a phase transition in the thermodynamic sense, since it occurs gradually with increasing temperature (Bittencourt, 2013).

2.4. Plasma Production

A plasma can be produced by raising the temperature of a substance until a reasonably high fractional ionization is obtained. Under thermodynamic equilibrium conditions, the degree of ionization and the electron temperature are closely related. Although plasmas in local thermodynamic equilibrium are found in many places in nature, as is the case for many astrophysical plasmas, they are not very common in the laboratory (Bittencourt, 2013). Plasmas can also be generated by ionization processes that raise the degree of ionization much above its thermal equilibrium value. There are many different methods of creating plasmas in the laboratory and, depending on the method, the plasma may have a high or low density, high or low temperature, it may be steady or transient, stable or unstable, and so on. A weakly ionized plasma is one in which the ratio of electrons to other species is less than10%. At the other extreme, highly ionized plasmas may have atoms stripped of many of their electrons, resulting in very high electron to atom/ion ratios. LIBS plasmas typically fall into the category of weakly ionized plasmas (Senesi, 2014). It is photoionization processes and electrical discharge in gases that are the most common methods to create plasmas. In the photoionization process, ionization occurs by absorption of incident photons whose energy is equal to, or greater than, the ionization potential of the absorbing atom. The excess energy of the photon is transformed into kinetic energy of the electron-ion pair formed. For example, the ionization potential energy for the outermost electron of atomic oxygen is 13.6 eV, which can be supplied by radiation of wavelength smaller than about 91 nm, i.e., in the far ultraviolet. Ionization can also be produced by x-rays or gamma rays, which have much smaller wavelengths (Lynch, 1940; Bittencourt, 2013). In a gas discharge, an electric field is applied across the ionized gas, which accelerates the free electrons to energies sufficiently high to ionize other atoms by collisions. One characteristic of this process is that the applied electric field transfers energy much more efficiently to the light electrons than to the relatively heavy ions. The electron temperature in gas discharges is therefore usually higher than the ion temperature, since the transfer of thermal energy from the electrons to the heavier particles is very slow. When the ionizing source is turned off, the ionization decreases gradually because of recombination until it reaches an equilibrium value consistent with the temperature of the medium. In the laboratory the recombination usually occurs so fast that the plasma completely disappears in a small fraction of a second (Bittencourt, 2013).

2.5. Laser Induced Plasma

To produce a spark in air or a gas requires laser intensities of the order of 10^{11} Wcm^{-2}. Sparks are caused by the breakdown of the gas due to the electric field associated with the light wave. Breakdown thresholds are of the order of 10^{6} to 10^{7} Vcm^{-1}. The spark is accompanied by production of charged particles, absorption of laser light, and re-radiation of light from the spark. If the temperature of the plasma at the position of the gas breakdown becomes high enough, X-ray emission is also observed, in addition of visible and UV radiation. This phenomenon was termed laser induced breakdown in analogy with the electrical breakdown of gases (Thakur and Singh, 2007). The breakdown results from strong ionization and absorption by gases that are usually transparent to light. The breakdown is marked by a threshold irradiance below which virtually no effects are observed. The onset of the breakdown is a sudden, dramatic phenomenon occurring at an easily determined threshold. Its spatial as well as temporal profiles make interesting study (Chen, et al, 2000). The breakdown in the focal volume of the lens in which the peak laser irradiance occurs can be understood as occurring in two steps. First, the production of the initial ionization and the subsequent cascade by which the ionization grows resulting in the breakdown. Multi-photon ionization, where simultaneous absorption of many quanta by an atom produces an ion-electron pair, is considered to be a plausible mechanism for the initial ionization. An alternative possibility is multi-photon excitation of an atom to an excited state with many other excited states between it and the free electron continuum. Single photon absorption processes may rapidly ionize the atom from this excited level. A free electron in the focal volume absorbs photons and gains enough energy to ionize additional atoms by collisions. In each such ionization process, the colliding electron is replaced by two electrons with lower energy in the free electron continuum. These in turn absorb photons so that an avalanche or cascade of ionization will occur. The absorption of a photon by an electron may be visualized in two equivalent ways.

(1) It can be considered as an inverse Bremsstrahlung process in which a single light quantum is absorbed by an electron in the field of an atom or ion.

(2) Secondly it can be considered as analogous to microwave-generated breakdown, in which the electron oscillates in the electric field of the incident radiation (Thakur and Singh 2007).

2.6. Basic LIBS Apparatus

Laser-induced breakdown spectroscopy (LIBS) is a plasma-based atomic emission spectroscopy (AES) method that uses instrumentation of detection similar to that used by other AES methods. LIBS 'unique features come from using a powerful laser pulse to both "prepare" the targeted sample and then "excite" the constituent atoms to emit light. Sample preparation benefits from the target-focused laser pulse action which removes a small target mass in the form of atoms, ions, and small particles (Cremers and Radziemski, 2013). Coincident with ablation is the formation of a microplasma in the focal volume of the laser pulse that excites the resulting atoms and ions. The plasma continues this excitation after the laser pulse due to its high temperature and electron density. In addition, ablated particles are vaporized in the hot plasma and the resulting atoms excited. A typical LIBS apparatus is shown diagrammatically in Figure (2.1) along with a photo of a simple LIBS apparatus.

The main components of this system are:

1. the pulsed laser that generates the powerful optical pulses used to form the microplasma.
2. the lens that focuses the laser pulse on the target.
3. a target holder or container.
4. the light collection system (off-axis parabolic mirror, plane mirror) that collects and directs the spark light into a fiber optic that transports the light to the detection system.
5. a detection system consisting of a method to spectrally disperse the light such as the compact spectrometer/detector system shown here.
6. a computer to gate the detector, fire the laser, and store the spectrum.

The basic components of any LIBS system are similar but the component specifications are tailored to the particular application. These specifications include physical parameters such as size, weight, packaging, power, and utilities required for operation as well as technical specifications pertaining to operational performance (Cremers and Radziemski, 2006).

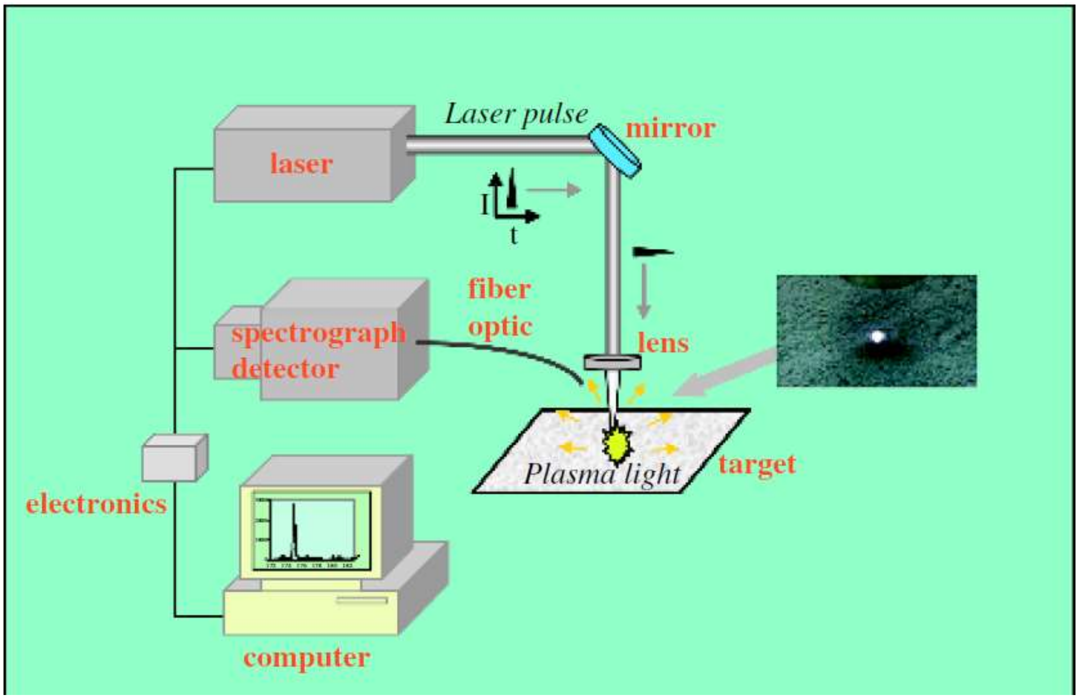


Figure (2.1): Schematic of typical experimental LIBS setup (Cremers, and Radziemski, 2006).

2.7. LIBS Applications

LIBS is useful in a wide range of fields, including those that can benefit from a rapid chemical analysis at the atomic level, without sample preparation, LIBS has been used in archeology and cultural heritage, Samples of archeological or cultural significance are often difficult to analyze. These samples cannot usually be moved or destroyed for analysis, and some chemical techniques to prepare the sample or a controlled environment in a laboratory are needed. In the first place, portable LIBS devices can be used, solving the problem when the sample cannot be moved. In the second place, LIBS does not need contact to analyze the sample, avoiding damage in valuable samples. Although LIBS ablates an amount of the sample, the crater is nearly microscopic and practically invisible to the eye (Anabitarte et al., 2012). In addition, this microscopic ablated surface improves the spatial resolution, providing accurate spatial analysis and even a depth profile analysis of the sample. The sample does not need to be prepared; hence the analysis is clean and fast. Besides, LIBS probes based on optical fibers allow the analysis of samples with difficult access. Despite these facts, LIBS is a micro destructive technique and the researcher should pay attention to experimental parameters in order to avoid critical damage in valuable samples. Many cultural heritage artifacts can be analyzed with the right LIBS set-up (Fornarini, et al, 2005). LIBS is feasible with virtually all types of materials, for instance ceramics, marble, bones, or metals, usually applying quantitative analysis. The most common analysis attempts to determine the elemental composition of the sample in order to help to date it, but it works with bones for analysis of paleodiet (Kasem, et al., 2011). LIBS has been used with delicate samples such as Roman coins or other metallic alloys like bronze, even under water. In the field of painting, it can determine the elements that compose the pigments. This analysis of pigments can help to date and authenticate frescos or paintings. Moreover, LIBS can be used, combined with other techniques, in order to sum the potential of them, such as Raman or X-ray fluorescence (XRF) (Alberghina, et al, 2011). LIBS in Biomedical Applications it used to analyze chemical compositions of biological samples such as human bones, tissues, and fluids (Liu and Zhang, 2008). LIBS can help to detect excess or deficiency of minerals in tissue, teeth, nails, or bones, as well as toxic elements. In the same way, cancer detection is possible with LIBS and it can provide a surgical device which can detect and destroy tumor cells at the same time. In addition, classification of pathogenic bacteria or virus is possible too. The analysis of samples from plants is difficult, because they need a difficult preparation of the sample based on acid digestion processes in order to obtain accurate analysis of micronutrients. LIBS can provide a fast analysis tool with easy sample preparation, for instance in micronutrient analysis of leaves (Anabitarte, et.al, 2012). LIBS has been targeting many industrial processes for many years, because it is a fast analytical tool well suited to controlling some manufacturing process. Moreover, LIBS can work at a large range of distances, allowing analysis of samples in hazardous and harsh environments. For example, remote detection of explosives has been assessed with LIBS, even at trace levels (Sarkar, et al, 2009). In the nuclear energy industry, the effects of radiation on living beings and devices are widely known. LIBS can work far away from nuclear waste or reactors, using stand-off configuration or with fiber optic probes, avoiding dangerous radiation levels. In the metallurgical industry, smelters, and final products can reach high temperatures, and LIBS can analyze the alloy compositions in production line or detect impurities in other production sectors, such as the automotive industries. LIBS can also be useful to detect toxic products like heavy metals in industrial wastes (Anabitarte, et al, 2012). These waste products should be recycled or stored, and knowing the elements in them can provide key data to reduce the environmental impact of the process. In the renewable energy field, analysis and detection of impurities in solar cells can be a useful tool to improve the manufacturing processes or to achieve high efficiency solar panels.

LIBS can work in a wide range of environmental conditions and with different atmospheres, from air to vacuum. This feature, coupled with the capability to analyze soil samples and the possibility to build a portable set-up, enables the possibility to work in the space. Recently, a spacecraft has been launched to Mars to provide spectral analysis of Mars, geological samples.

This spacecraft contains, among other things, a hybrid LIBS-Raman spectrometer (Anabitarte, et.al, 2012).

2.8. LIBS and Polymers

The plastics industry plays a significant part in each of the environmental, societal and economic dimensions of sustainable development. A great number of packaging materials such as bottles and boxes are made from polymers. Additives, such as plasticizers, antioxidants, antistatic agents and lubricants can be used to manufacture packaging materials. The worst consequence of the plastic production is the deterioration of the environment. It represents an important concern for the environment and creates a considerable waste disposal problem. Recycling is a solution of this problem and the first step is the identification and classification of the polymers (Anzano, Bello and Lasheras, 2014). The manual methods are not accurate whereas LIBS technique provides a fast and accurate classification and analysis of them. Laser-induced breakdown spectroscopy (LIBS) is mainly an elemental analysis technique which is applied several fields. LIBS can be used for qualitative and quantitative analysis of samples. However, molecular materials are almost entirely atomized when exposed to intense laser radiation sufficient for breakdown. This implies that limitations exist in application of

LIBS for identification of compounds because of the loss of molecular information in the plasma; especially organic compounds which only contain mostly carbon and hydrogen, also oxygen and nitrogen. These limitations have been solved by researchers using statistical tools as chemo metric techniques (Anzano, et al, 2014 ; Costa, et al, 2017). Among the currently available technologies for plastic identification, mid infrared (MIR), near infra-red (NIR), and Raman spectroscopy have been reported as the most reliable technologies for plastic identification. MIR spectroscopy has an excellent advantage for the identification of black plastics, but its disadvantage is that the surface of the sample needs to be relatively soft and clean. In addition, the sample must be placed in close physical contact with a high refractive index crystal; that is, remote sensing in the field is still not possible with this technique. Furthermore, it is not applicable to high-speed identification systems (Unnikrishnan, et al, 2013). NIR spectroscopy allows fast identification due to the short response time of the employed photodetectors. However, this technique is not suitable for black plastics that absorb and scatter radiation at NIR frequencies. Surface contamination may deteriorate the signal, which reduces the accuracy of the identification (Grégoire, et al, 2011). Raman spectroscopy enables near real-time plastic identification almost 100 times faster than NIR spectroscopy. However, it is sensitive to the presence of carbon-black, which can reduce the reflection in the detector. In the case of strong fluorescence, the detector becomes saturated and the peaks are difficult to discern. Due to the limitations of the above-mentioned spectroscopic methods, laser-induced breakdown spectroscopy (LIBS) has emerged as a powerful analytical technique that can be used to identify different types of plastics (Kim and Choi, 2019).

2.9. Advantages and Disadvantages of LIBS

2.9.1. Advantages

LIBS exhibits numerous appealing features that distinguish it from other elemental analysis techniques: These include

- The technique is considered essentially non-destructive or minimally destructive. Because a small amount of material is consumed during the LIBS process.
- With an average power density of less than one watt radiated onto the specimen there is almost no specimen heating surrounding the ablation site.
- Due to the nature of this technique sample preparation is typically minimised to homogenization or is often unnecessary where heterogeneity is to be investigated or where a specimen is known to be sufficiently

homogeneous, this reduces the possibility of contamination during chemical preparation steps.

- One of the major advantages of the LIBS technique is its ability to depth profile a specimen by repeatedly discharging the laser in the same position, effectively going deeper into the specimen with each shot. This can also be applied to the removal of surface contamination, where the laser is discharged a number of times prior to the analysing shot (Konidala, et al, 2016).
- LIBS is also a very rapid technique giving results within seconds, making it particularly useful for high volume analyses or on-line industrial monitoring.
- LIBS is an entirely optical technique, therefore it requires only optical access to the specimen. This is of major significance as fiber optics can be employed for remote analyses. And being an optical technique it is non-invasive, non-contact and can even be used as a stand-off analytical technique when coupled to appropriate telescopic apparatus.
- These attributes have significance for use in areas from hazardous environments to space exploration. Additionally, LIBS systems can easily be coupled to an optical microscope for micro-sampling adding a new dimension of analytical flexibility.

- With specialized optics or a mechanically positioned specimen stage the laser can be scanned over the surface of the specimen allowing spatially resolved chemical analysis and the creation of 'elemental maps'. This is very significant as chemical imaging is becoming more important in all branches of science and technology.
- Portable LIBS systems are more sensitive, faster and can detect a wider range of elements (particularly the light elements) than competing techniques such as portable x-ray fluorescence. And LIBS does not use ionizing radiation to excite the sample, which is both penetrating and potentially carcinogenic (Gottfried and De Lucia, 2010)
- A sample preparation-free measurement experience
- Extremely fast measurement time, usually a few seconds, for a single spot analysis.
- Broad elemental coverage, including lighter elements, such as H, Be, Li, C, N, O, Na, and Mg.
- Versatile sampling protocols that include fast raster of the sample surface and depth profiling.
- Thin-sample analysis without the worry of the substrate interference (Konidala, et al., 2016).

2.9.2 . Disadvantages

Like all other analytical techniques LIBS, is not without limitations.

- It is subject to variation in the laser spark and resultant plasma which often limits reproducibility.
- The accuracy of LIBS measurements is typically better than 10% and precision is often better than 5%.
- The detection limits for LIBS vary from one element to the next depending on the specimen type and the experimental apparatus used. Even so detection limits of 1 to 30 ppm by mass are not uncommon, but can range from >100 ppm to <1 ppmastics, soils, plants, soils, thin-paint coating, and electronic materials (Konidala, et al, 2016).
- Standard emission disadvantages, such as spectral interference and self-absorption.
- Complexity.

2.10. Plastics

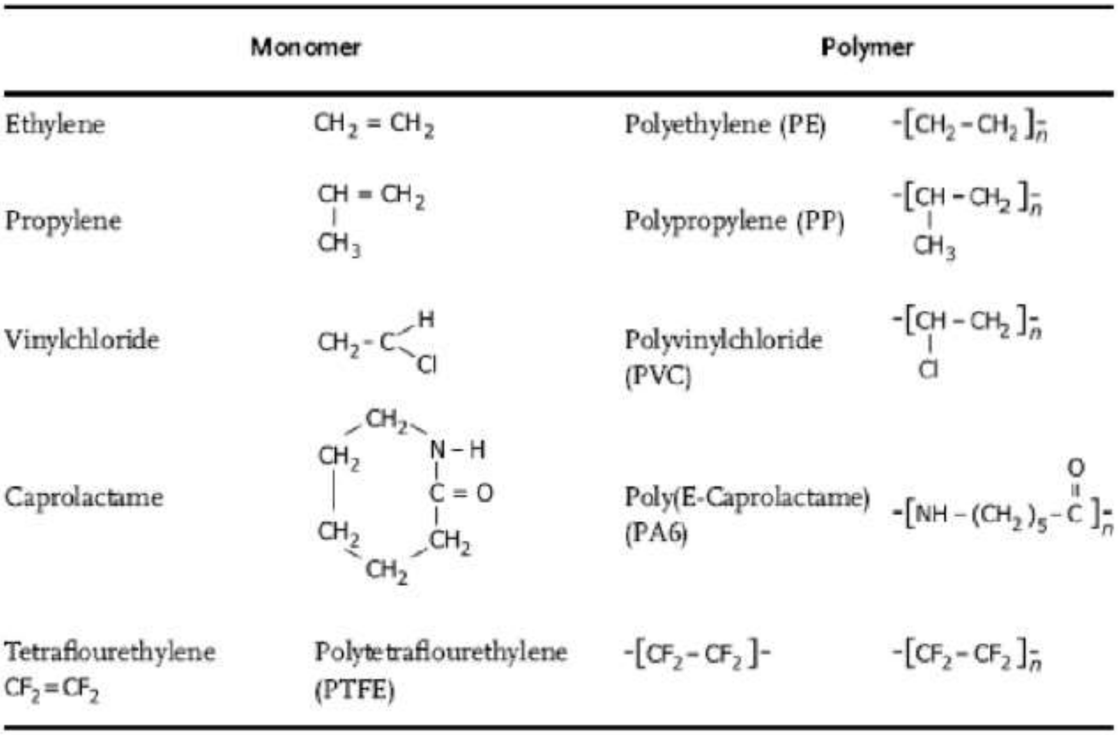
Over the last 60 years plastics production has increased significantly, where the plastic products and packaging materials are commonly used in our everyday lives (Saquing, et al, 2010), which are generally utilized in various applications such as water and drug bottles, food packaging, medical supplies, and so on (Alabi, et al, 2019; Liu, et al, 2020). Because of the many advantages of plastic materials it is soft, transparent, flexible are lightweight, plastics are cost effective, require little energy to produce, and are and biocompatible, or biodegradable and many other of properties (Proshad, et al, 2018). These characteristics have raised the demand for plastic materials that will continue to grow over the coming years (Hahladakis, et al, 2018). Plastics are typically organic polymers of high molecular mass and contain other substances such as plasticizers, antioxidants, antistatic agents, and lubricants may be used for the production of plastics materials properties (Kim and Choi, 2019). The worst consequence of the plastic production is the deterioration of the environment. This is a significant environmental issue and it generates a substantial problem of waste disposal. Recycling is a solution to this problem and the first step is to define and classify the polymers (Anzano, et al, 2014). Where recycling of plastics necessitates different treatments depending on the polymers and the additives. Moreover, several plastics have too high concentrations of some toxic additives, such as heavy metals (Saquing, et al, 2010).

2.10.1. Structure of Plastics

The word plastic literally means "moldable." This term is widely used to denote synthetic and semi-synthetic organic polymers with a high molecular weight and consisting of different units (monomers) linked together to form long chains (Kim and Choi, 2019). The monomer units are organic carbon-based molecules. Beside carbon and hydrogen atoms as main components element like oxygen, nitrogen, sulfur, can be contained the monomer unit. The type of elements, their proportion and placing in the monomer molecule gives the basis for generating different plastics (Klein, 2012), as shown in Table (2.1).

The plastics' chemical – physical properties may be designed by varying the production processes and formulations. Indeed, by starting from the same basic resin, the final formulation may be varied by adding several types of additives (colorants, fillers, plasticizers, etc.), which then make it possible to control precisely the characteristics of the finished material. This exceptional versatility of plastics is indeed the reason for their pervasive and capillary diffusion into every field and aspect of our lives (Picollo, et al, 2014).

Table (2.1): Example of some common plastics and their monomers



Monomer		Polymer	
Ethylene	$CH_2 = CH_2$	Polyethylene (PE)	$-[CH_2-CH_2]_n^-$
Propylene	$\underset{CH_3}{\underset{\vert}{CH}} = CH_2$	Polypropylene (PP)	$-[\underset{CH_3}{\underset{\vert}{CH}}-CH_2]_n^-$
Vinylchloride	$CH_2-C\begin{smallmatrix}H\\Cl\end{smallmatrix}$	Polyvinylchloride (PVC)	$-[\underset{Cl}{\underset{\vert}{CH}}-CH_2]_n^-$
Caprolactame		Poly(E-Caprolactame) (PA6)	$-[NH-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}]_n^-$
Tetraflourethylene $CF_2=CF_2$	Polytetraflourethylene (PTFE)	$-[CF_2-CF_2]-$	$-[CF_2-CF_2]_n^-$

2.10.2. Properties and Classifications

Plastics can be classified in many ways that reflect their chemical makeup, properties, polymerization process, uses, or source:

a) Classifications based on structure: linear, branched, or cross linked polymers. Some important groups in these classifications are: the acrylics, polyesters, silicones, polyurethanes, and halogenated plastics (Negre, et al, 2016).

a) Classifications based on source: natural, synthetic, or semi-synthetic polymers.

b) Classifications based on properties: their various physical properties, such as: hardness, density, tensile strength, resistance to heat and glass transition temperature, and by their chemical properties, such as the organic chemistry of the polymer and its resistance and reaction to various chemical products and processes, such as: organic solvents, oxidation, and ionizing radiation. In particular, most plastics will melt upon heating to a few hundred degrees Celsius (Klein, 2012; Negre, et al, 2016).

c) Classifications based on polymerisation processes: chain-growth or step-growth polymers.

d) Classification based on uses: plastics, rubbers, fibers, foams, films, coatings, and adhesives.

Other classifications are based on qualities that are relevant for manufacturing or product design. Examples of such qualities and classes are: thermoplastics and thermosets, conductive polymers, biodegradable plastics and engineering plastics and other plastics with particular structures, such as elastomers.

The properties of plastics can be altered considerably by incorporation of additives and by the manufacturing process. The most important additives are fillers, colorants, flame retardants, stabilizers, plasticizers, lubricants, and blowing agents. Fillers are often added to lower cost and/or to increase the stiffness, whereas plasticizers have the opposite effect. Stabilizers are added when the plastic has to be protected against degradation by heat, UV light, and oxygen/ozone (Klein, 2012).

The most important plastics in order of demand (production volume) are polyethylene (PE), polypropylene (PP), polyvinyl chlorides (PVC), polystyrene (PS), polyethylene terephthalate (PET), and polyurethane (PUR).

2.11. Literature Review

The very first laser-induced spark emission (LISE) experiments were performed in the 1960s and involved a laser beam that generated a vapor when a solid target was irradiated and an electrical spark that subsequently excited the ablated plume (Breech and Cross 1962) hose experiments can be considered as early precursors of Laser Induced Breakdown Spectroscopy (LIBS), and since then, LIBS has demonstrated its tremendous potential as an important technique for rapid multi-element analysis (Breech and Cross 1962). During the 1970s, development continued in several countries, in several directions. For spectrochemists, direct ablation, excitation and observation of the spark on surfaces was a paramount application. On the other hand LIBS was often used by physicists for fundamental studies on breakdown in gases. Starting from the 1980s, significant achievements have been achieved in both laser and detector technology, which have made reliable and relatively inexpensive instruments available to research laboratories. This has promoted a huge development of the technique and its adaptation to the qualitative and quantitative analysis of a wide variety of solid samples (Radziemski and Loree, 1981).

The work of Anzano, et al. in 2000 at Laser- induced plasma spectroscopy for plastic identification this work was instant identification of post-consumer plastics by laser induced plasma spectrometry (LIPS). LIP spectra from plastics in a 200-800 nm spectral window were compared with reference spectral libraries stored in a computer. The libraries consisted of representative spectra from different groups of recycled plastic samples. The plasma emission spectra of polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC), low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS) were studied. Simple statistical correlation methods including linear and rank correlations were used. The probabilities of correct identification ranged from 0.8 to 1 with values close to unity for most of the polymers studied (Anzano, et al, 2000).

Gondal and Siddiquin (2007) performed various experiments for the improvement of LIBS for detection of heavy metals and other contaminants in solid samples. LIBS has shown promise as an environmental monitoring technique (Gondal and Siddiqui, 2007).

Pandhija et al in 2010, they clearly demonstrate that the combination of LIBS and CFLIBS is very useful for the study of pollutants in the environment. Their study deals with the detection and quantification of toxic heavy metals like Cd, Co, Pb, Zn, Cr, etc. in environmental samples by using the technique of laser-induced breakdown spectroscopy (LIBS) and calibration-free LIBS (CF-LIBS). A MATLABTM program has been developed based on the CF-LIBS algorithm given by earlier workers and concentrations of pollutants present in industrial area soil have been determined (Pandhija, et al, 2010).

Heavy metal contaminants in environment, especially in drinking water, are always of great concern due to their health impact. Due to the use of heavy metals as catalysts during plastic syntheses, particularly antimony.

The work of Cheng, X., et al, in 2010 at assessment of metal contaminations leaching out from recycling plastic bottles upon treatments. Methodology In this study. leaching concentrations of 16 metal elements(Al, V, Cr, Mn, Co, Ni, Cu, As, Se, Mo, Ag, Cd, Ba, Tl, Pb, Sb) were determined in 21 different types of plastic bottles from five commercial brands, which were made of recycling materials ranging from no. 1 to no. 7 (Cheng, et al, in 2010).

in 2011 Sylvain Grégoire, et al, at Laser-induced breakdown spectroscopy for polymer identification, This work was the first step of a study on in situ discrimination of organic materials by LIBS. to worked with some usual polymers families: polyethylene (PE), polypropylene (PP), polyoxymethylene, (POM), poly (vinyl chloride), polytetrafluoroethylene, polyoxyethylene (POE) and polyamide for the aliphatic ones, and poly (butylene terephthalate), acrylonitrile–butadiene–styrene, polystyrene, and polycarbonate for the aromatic ones. The fourth harmonic of a Nd: YAG laser (266 nm) in ambient air at atmospheric pressure was used. A careful analysis of the C2 Swan system (0,0) band in polymers containing no C–C (POM), few C–C (POE), or aromatic C–C linkages led us to the conclusion that the C2 signal might be native, i.e., the result of direct ablation from the sample. With use of these results, aliphatic and aromatic polymers could be differentiated. Further data treatments, such as properly chosen line ratios, principal component analysis, and partial least squares regression, were evaluated. It was shown that many polymers could be separated, including PE and PP, despite their similar chemical structures (Grégoire, et al, 2011).

Cristina Bach, et al, in 2012, they surveyed toxicological studies on PET-bottled water and chemical compounds that may be present therein. Their literature review shows that contradictory results for PET-bottled water have been reported, and differences can be explained by the wide variety of analytical methods, bioassays and exposure conditions employed (Bach, et al, 2012).

The work of Anzano, et al, in 2014 is one of the pioneering works on Laser-induced breakdown spectroscopy (LIBS) is mainly an elemental analysis technique which is applied several fields. However, molecular materials are almost entirely atomized when exposed to intense laser radiation sufficient for breakdown. This limitation has been solved by researchers using statistical tools as chemometric techniques. The authors expose one review about the identification of polymeric materials using LIBS; and particularly, the different chemometric techniques (Anzano, et al, 2014).

The work of E .Kim, WZ.Choi,2019 is one of the pioneering works on laser induced breakdown spectroscopic analysis of plastic. This study proves the analytical predictive capability of the LIBS technique for real-time analysis and identification of plastics. Due to the interference from ambient air, moisture, flame retardant additives and inorganic or organic pigments in the real fields of plastic recycling, the elements such as oxygen, nitrogen, or carbon that do not come from the polymer chain may be present. Those elements can complicate the LIBS spectra in plastics analysis. The plasma emission spectra of polypropylene (PP), acrylonitrile–butadiene–styrene (ABS), polystyrene (PS), and polyethylene terephthalate (PET), the most commonly used plastics in black household appliances, were studied. It was confirmed that the C/H spectral line intensity ratio varies depending on the type of plastics. Aliphatic and aromatic polymers were discriminated owing to the presence of delocalized C–C bonds in the aromatic fragments, revealing a correlation between the chemical structure and emission of the C2 Swan bands. Plastics containing a heteroatom could be selectively detected by monitoring the emission line characteristics of the heteroatom. Four types of plastics were successfully identified despite their similar chemical structure (Kim and Choi, 2019).

Junjuri, R., et al, in 2019 studied Identification of post-consumer plastics using laser-induced breakdown spectroscopy. In this study, they report an accurate recognition of ten different types of postconsumer plastics, including five extensively used basic plastics, by laser induced breakdown spectroscopy (LIBS). Ratio metric and correlational analysis have been performed for the classification in which C/H ratio yielded partial discrimination while an excellent correlation has been observed between the intensity of the carbon peak with carbon single bonds. Additionally, a 3D correlational approach using the emission intensities of carbon, hydrogen, oxygen and nitrogen lines successfully segregated all the plastics. Finally, they report findings from partial least squares- discriminant analysis (PLS-DA) that demonstrates classification accuracies of over 93 %. That the high classification accuracy is shown here will encourage further validation studies leading to routine application of LIBS for screening and identification of post-consumer plastics (Junjuri, et al, 2019).

Chapter Three

Materials and Methods

CHAPTER THREE

MATERILAS AND METHODS

3.1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a rapid chemical analysis technique that produces a micro-plasma on the surface of the sample using a short laser pulse (Singh and Thakur, 2007). This chapter describes the experimental portion, including the collection of samples, equipment, instruments, the setup of experiments and the procedure.

3.2. Samples Collection

The samples used in this research, were plastic materials used for water and drug containers in Sudan, both of them were collected from manufacturing factories located at Khartoum city, Sudan. The samples were collected before and after used, these plastic bottles samples were sterilized and washed with distilled water before the analysis by LIBS device to avoid any type of contamination. Also the Samples were cut for slices in size 3×3 cm^2, and thickness 2mm. The total number of samples of water bottles and water bottle caps is 9 samples, and the total number of samples of drug bottles were 9 samples. All this details are shown in table (3.1) which illustrates water bottles and water bottle caps, and it was also shown in figure (3.1), while tables (3.2) and figure (3.2) illustrates drug bottles.

Table (3.1): Water bottles and Water bottle caps

Bottle Before used	**Bottle After used**	**Bottle cap**
Sample (M11)	Sample (M21)	Sample (M31)
Sample (M12)	Sample (M22)	Sample (M32)
Sample (M13)	Sample (M23)	Sample (M33)

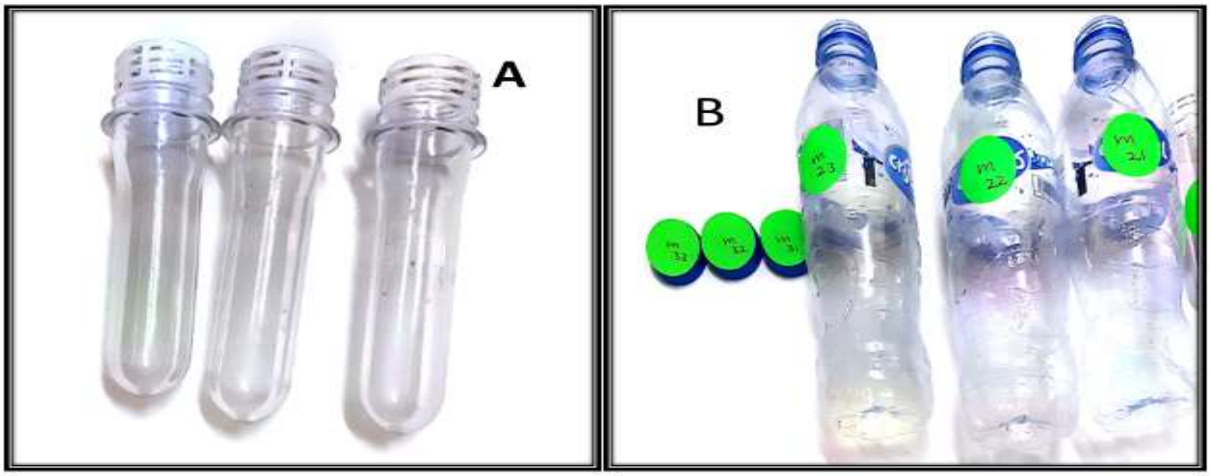


Figure (3.1): Water bottles and water bottle caps (A) Bottle before used and (B) Bottle and caps after used

Table (3.2): drug bottles

bottle at first	Bottle Before used	Bottle After used	drug in bottle
Sample (S11)	Sample (S21)	Sample (S31)	AMIBUTAMOL
Sample (S12)	Sample (S22)	Sample (S32)	AMIHISTIN
Sample (S13)	Sample (S23)	Sample (S33)	AMIDOL

Figure (3.2): Drug bottles (A) Bottle before used, (B) Bottle after used

3.3. Experimental Setup

Laboratory preparations used in this research was a RT100-B system (Applied Spectra, Inc), the RT100-B is a virtually instantaneous elemental analysis system capable of testing and processing samples in timeframes ranging from seconds to minutes. The RT100-B is a standalone machine that uses Laser Induced Breakdown Spectroscopy (LIBS) to identify unknown elements in a given sample. LIBS can be used to study and analyze plastic samples. The LIBS is a type of atomic emission spectroscopy in which an energetic laser pulse is focused onto a sample to create a luminous plasma plume. This plasma plume is the source of optical emission for identifying chemicals and their concentrations. The light from the plasma is collected via collection optics; subsequent spectral analysis of the light collected on the optical fiber yields the composition of the sample. The plasma spectrum consists of narrow spectral lines emitted from atoms, ions, molecular bands, and continuous background radiation (Figure 3.3).

A pulsed laser-beam initiates the LIBS plasma, so there is no need for any instrument to be in contact with the sample. The pulsed laser-beam can range from femtoseconds to microseconds in duration, whereas the LIBS plasma will generally exist for several microseconds (almost independent of the laser pulse duration). The intensities of the spectral lines are related to the laser energy used to create the plasma and the detection system (Peichao, et al, 2015).

With the ability to detect molecular and elemental signatures with a single laser pulse, LIBS offers unprecedented performance for chemical detection. Benefits of LIBS include: real-time data collection, analysis, display; high sensitivity; no sample preparation and no consumables; low false alarm rate; field portability; and simple operation.

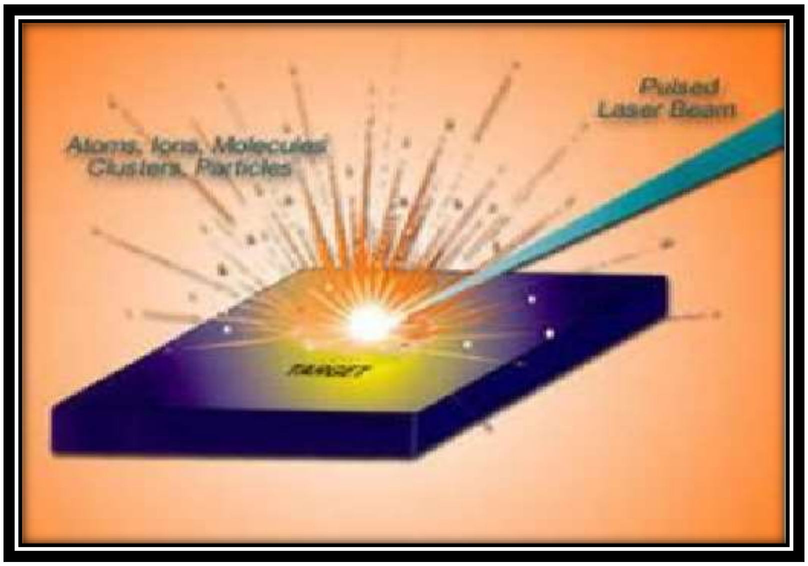


Figure (3.3): Illustration of plasma plume

The experimental setup used in this work was arranged as shown in figures (3.4) and (3.5).

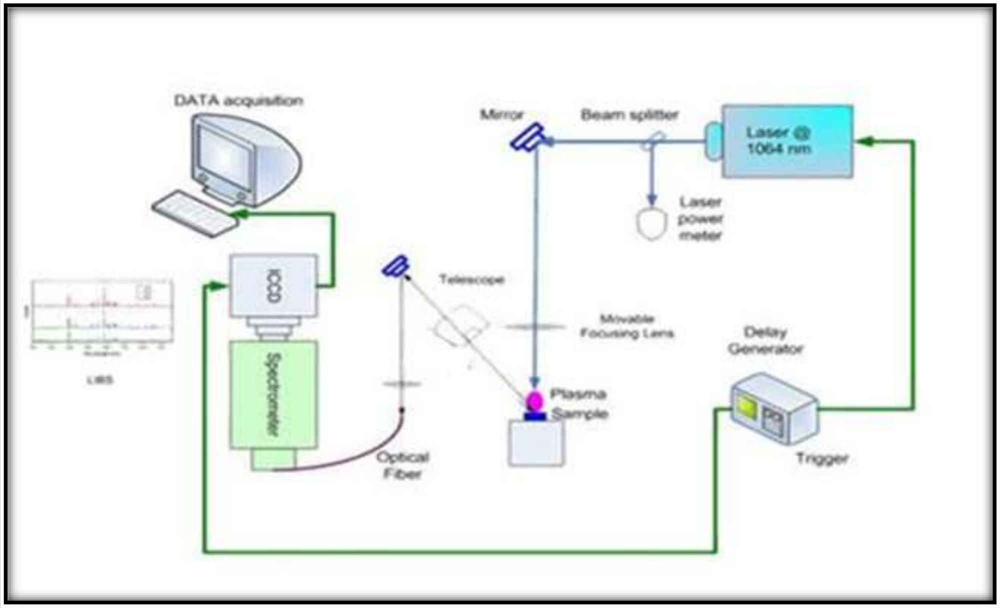


Figure (3.4): LIBS setup

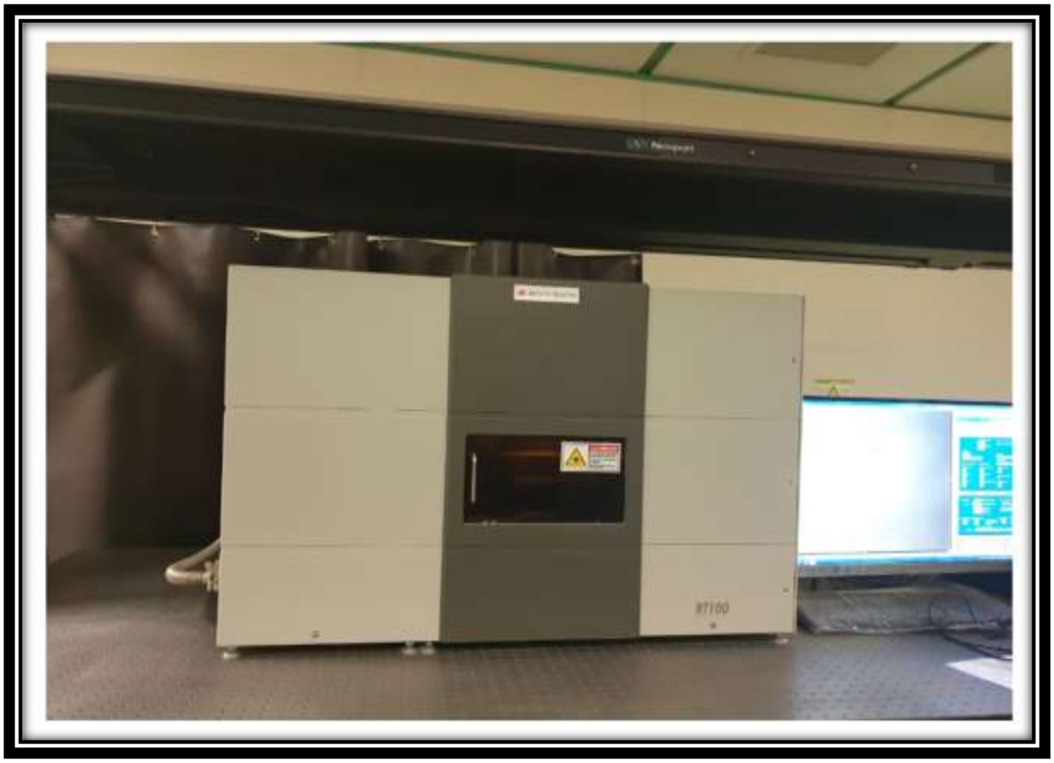


Figure (3.5): Applied Spectra's RT100 –B/LIBS instrument

The LIBS system consist of the following components:

3.3.1. The Laser

The RT100-B utilizes a neodymium-doped yttrium aluminum garnet (Nd: YAG) Laser with a wavelength 266 nm was used as a laser source. The specifications of the Nd: YAG laser that used in this work are listed in table (3.3). Where a laser was used to separate part of the target material and generate the plasma.

Table (3.3) Nd: YAG laser specifications

Component	**Specifications**
Company	APPLIED SPECTRA

Power Supply:	~230 V, 50/60 Hz
Model	RT100-B
Laser Type	Nd: YAG (266nm)
Laser wavelength	200 up to 800 nm
Weight	-
Pulse width	Controlled
Repeat frequency	2 Hz
Lead light method	-
The light spot diameter	Controlled
Power supply	Controlled
Environment temperature	21°±5°C
Relative humidity	< 60%
Cooling system	-

The laser is attached to a mounting plate. Its beam passes through a mechanical shutter and is then funneled into a microscope objective. The microscope objective focuses the laser beam into its optimum spot size.

The RT100-B comes equipped with an attenuator, which serves to control the laser energy without affecting beam quality.

3.3.2. Beam Delivering Optics

Figure (3.6) show the laser beam is delivered from the laser head through multiple laser mirrors, beam expander and final focusing objective lens to the sample surface. The mirrors used are laser line, dichroic mirrors, which only reflects the specific laser wavelength.

The objective lens used is laser line coated to protect lens from high power laser pulse damage, the incoming laser beam should be aligned to enter from the center of the lens vertically.

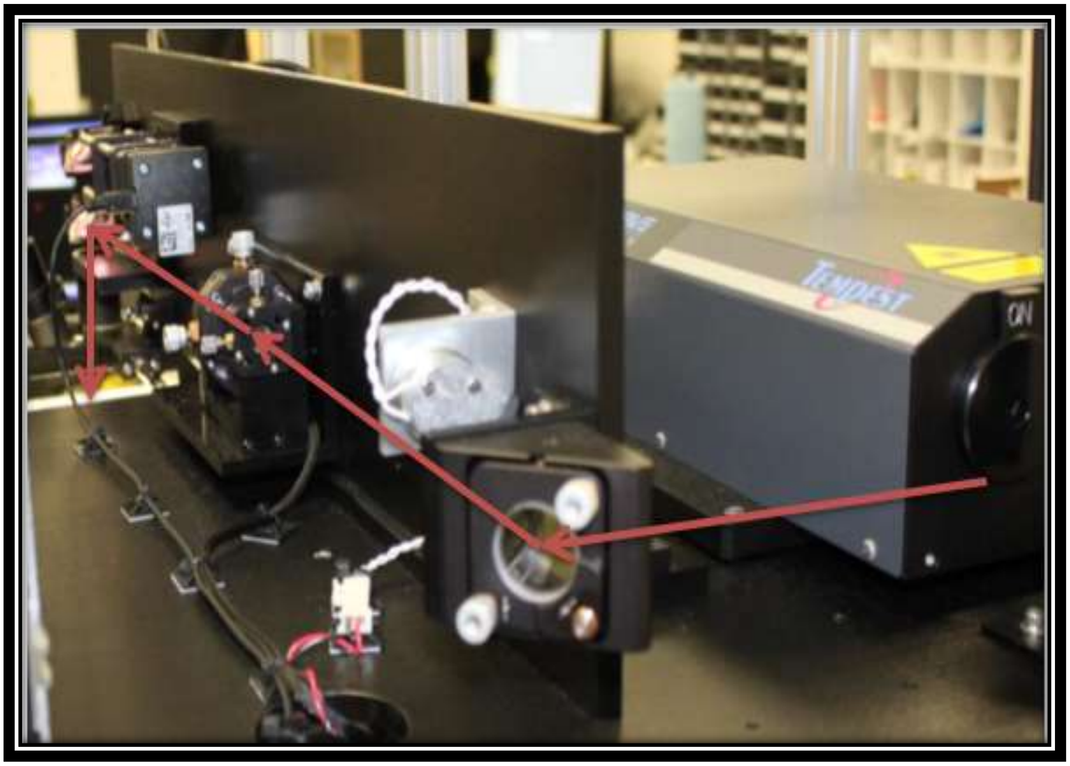


Figure (3.6): Optical Path of the Laser

3.3.3. Beam Expander

The beam expander is used to change the size and angle of the entrance laser into the final objective lens, therefore changing the final laser spot size on the sample. It is critical to ensure the incoming laser beam is aligned properly and thoroughly through the center of the beam expander lenses.

3.3.4. Spectrometer

A spectrometer is a device used to measure properties of light over a specific region of the electromagnetic spectrum. Figure (3.7) show Andor Echelle Spectrograph and DT334T ICCD used in this work.

The LIBS plasma light is collected to the spectrometer via an optical fiber. When the light enters the spectrometer, a grating disperses the light into individual wavelengths. The light is then captured on the ICCD and can be transferred into data or interpreted as a spectral graph.

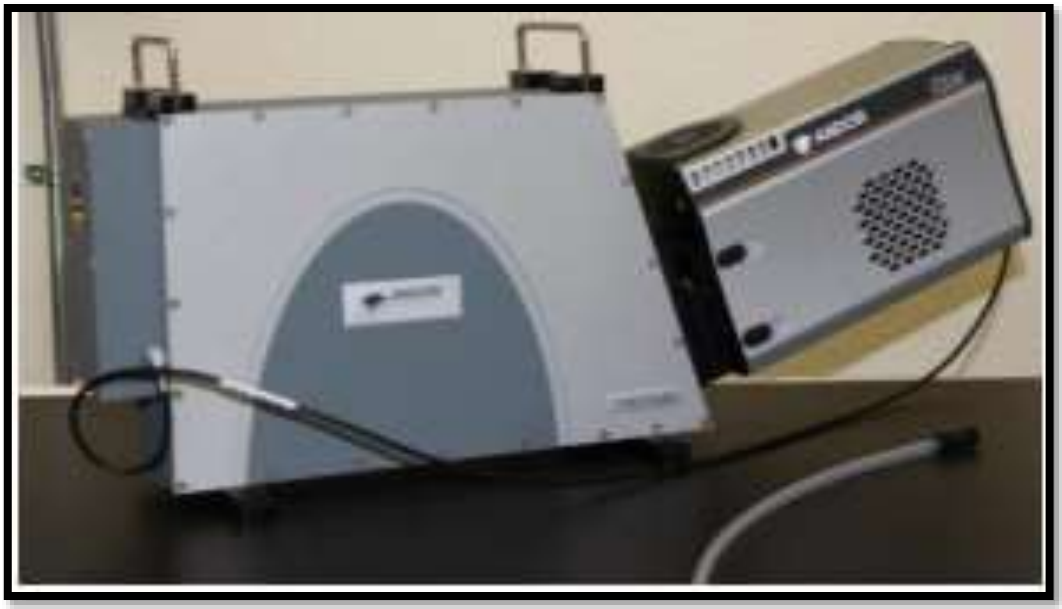


Figure (3.7): HP Echelle ICCD spectrometer unit

3.3.5. XYZ Stage

The RT100-B utilizes a heavy-duty stepper motor XYZ stage to move from sample to sample. The user can control the laser target site on the sample simply by moving the stage.

The RT100-B stage’s motion is 4”x4” XY Stages and 35mm Z Stage.

The motorized stages are controlled via an external controller box and connected to computer through RS232 communication.

3.3.6. Laser Triangulation Displacement Sensor

The laser triangulation displacement sensor (Figure 3.8) is used to determine and maintain optimum sample height. Each time, the stage moves to a new position in the recipe or calibration program, the sensor measures the height of the sample before the laser is fired. If there is a difference in height between each position, the stage will move up or down accordingly. Consequently, the distance from the laser to the sample is kept constant to ensure consistent LIBS measurements. The red laser spot also serves as a target, indicating where the sampling laser will be focused.

Figure (3.8): Laser Triangulation Displacement Sensor in the RT100-B system

3.3.7. Vacuum Sealed Chamber

The Vacuum Sealed chamber is designed to put-samples-in for LIBS analysis. It can be pressurized from 0.1 to 760 Torr. The chamber glass will need to be cleaned regularly due to particles being collected on it during analysis.

3.3.8. Vacuum Pump

The Vacuum pump, combined with a regulator will help create the vacuum needed in the Vacuum Sealed Chamber. As stated above, this Vacuum Pump can pressurize the Chamber from 0.1 to 760 Torr.

3.3.9. The Software System

The software “Axiom” was used in this work and the data analysis program USER, as shown in Figure (3.9). Axiom is a powerful software system developed by the scientists and engineers at Applied Spectra and integrated into every RT100 Series LIBS instrument. The Axiom software provides simultaneous access to the model RT100-B operation of LIBS systems. Axiom features an intuitive, user friendly interface to work through different modules from navigating different sample areas or set-up flexible laser sampling protocols. Axiom also integrates a powerful data analytics module for the efficient analysis of LIBS spectra .This software can easily manage multiple USB spectrometers – each with different acquisition parameters in multiple windows, and provides graphical and numeric representation of spectra from each spectrometer. Data analysis software allows performing the three basic spectroscopic experiments absorbance, reflectance and emission – as well as signal-processing functions such as electrical dark-signal correction, stray light correction, boxcar pixel smoothing and signal averaging.

Designed for intuitive use and flexibility, Axiom easily collects, analyzes and delivers precise and accurate LIBS spectral results. Easy to interpret icons, logical placement of action buttons, means less time setting up and more time doing chemical analysis. In less than 10 minutes, you can be collecting information about your samples! Sophisticated functions are also included to give users the flexibility to change parameters to obtain optimal results for unique samples and unique sampling conditions.

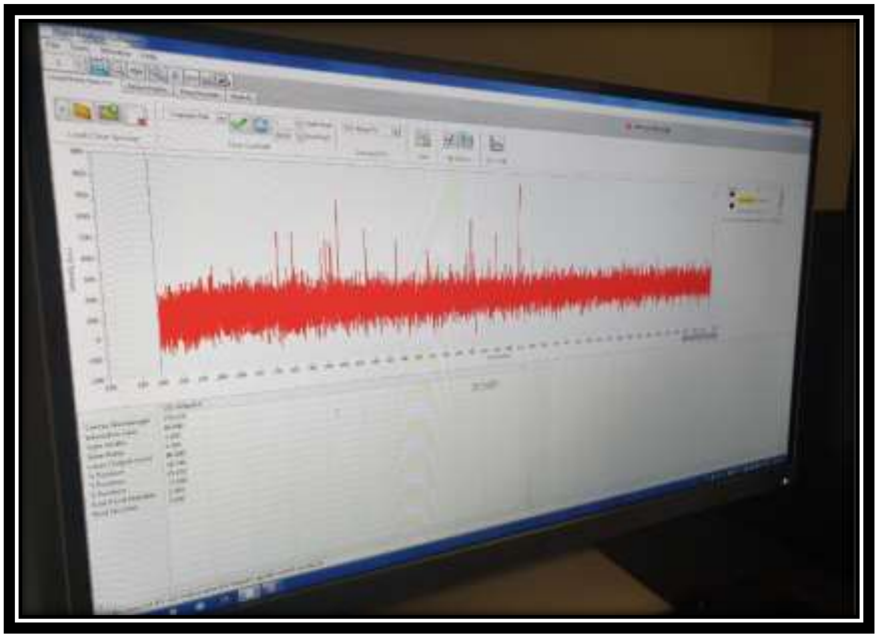


Figure (3.9): The software system

3.4. The Procedure

The experimental procedure was done as follows:

The laser energy (Applied Spectra Model RT100-B) was adjusted to obtain sufficient peak power needed to form plasma. The laser operating at 266 nm wavelength was employed as an excitation source. It can deliver maximum pulse energy of 80 m J with a pulse width of 2 ns and operates at a 2 Hz pulse repetition rate. The sample was put in the sample cell, a laser pulse was focused on the surface of the sample cell. The samples were irradiated with delay time (0.5ns), emitted light collection by a set of optical lenses and optical fiber.

Display of LIBS spectra and their subsequent analysis by the system software for both qualitative and quantitative elemental analysis. The same above procedure was done for all samples. A comparison was done between samples.

Chapter Four

Results and Discussion

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Introduction

A great number of packaging materials, such as bottles and boxes, are made of plastics (polymers). Additives such as plasticizers, antioxidants, antistatic agents, and lubricants may be used for the production of packaging materials. The worst effect of plastic production is deterioration of the environment (Anzano, et al, 2014). Recycling solves this problem and the first step is the identification and classification of the polymers and determination of different elements present in it (Siddiqui, et al, 2009). In this research, spectroscopic analyze were performed using Laser Induced Breakdown Spectroscopy (LIBS) for plastic materials samples of water and drug containers, collected from manufacturing factories located at Khartoum city, Sudan. The samples were collected before and after used, the total number of water bottles and water bottle caps is 9 samples, and so the same number of drug bottles samples.

In this chapter the results obtained are presented in tables and spectroscopic drawings. The results obtained were discussed, as well as the conclusions written and also the recommendations for future studies.

4.2. Results

4.2.1. LIBS Results of Water Bottles and Bottles Caps

Figures (4.1) to (4.9) show the LIBS emission spectra for the water bottles and bottles caps sample in the range of (100 -1100) nm recorded at delay time of 0.5ns and laser pulse energy 80mJ. Tables (4.1) to (4.9) list the analysis of the wavelengths corresponding to different elements and their intensities in the nine samples.

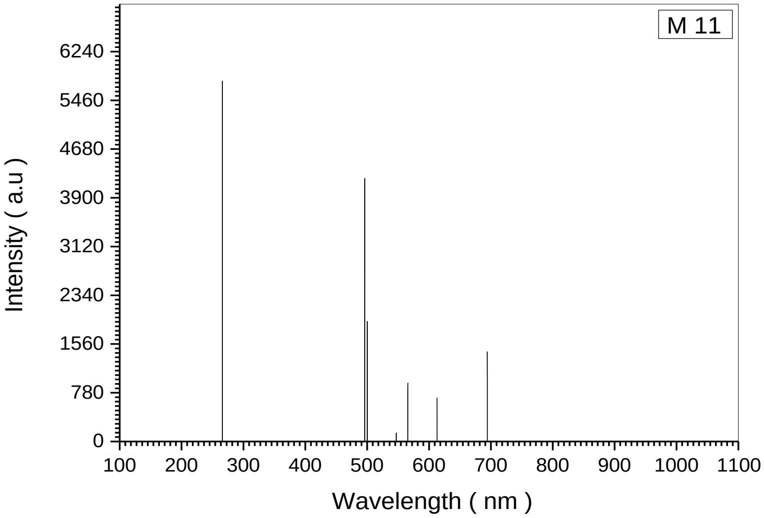


Figure (4.1): LIBS emission spectrum of sample (M11)

Table (4.1): The analyzed data of sample M11, irradiated by 80mJ.

Measured λ (nm)	Intensity (a.u)	Elements
272.121	5809	Mn II

491.773	4213	Ca I
547.361	1961	Cl II
499.547	162	S II
566.663	934	N II
612.027	713	K II
690.982	1405	F II

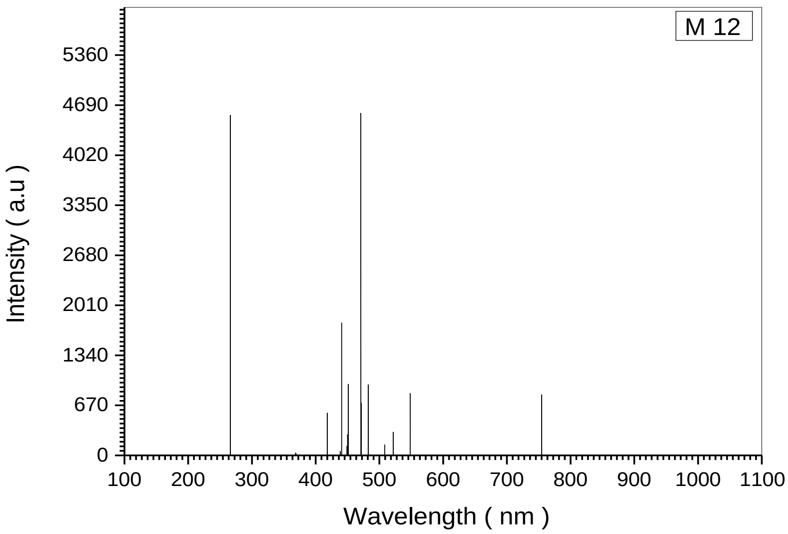


Figure (4.2): LIBS emission spectrum of sample (M12).

Table (4.2): The analyzed data of sample M12, irradiated by 80mJ.

Measured λ (nm)	**Intensity (a.u)**	**Elements**
268.824	4620	Mn I

422.672	637	Ca I
442.541	1814	Ca I
457.110	975	Mg I
476.864	4606	Cl I
480.328	940	N II
507.829	153	Cl II
521.155	311	Sc I
547.362	845	S II
755.223	817	F I

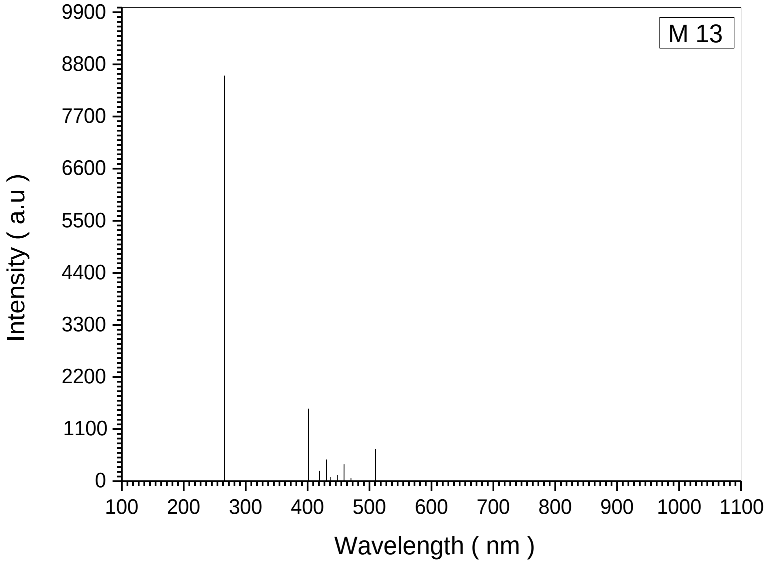


Figure (4.3): LIBS emission spectrum of sample (M13).

Table (4.3): The analyzed data of sample M13, irradiated by 80mJ.

Measured λ (nm)	Intensity (a.u)	Elements
268.824	8516	Mn I
422.672	1551	F I
402.473	278	Ca I
430.771	517	Ca I
457.133	374	Mg I
507.829	711	Cl II

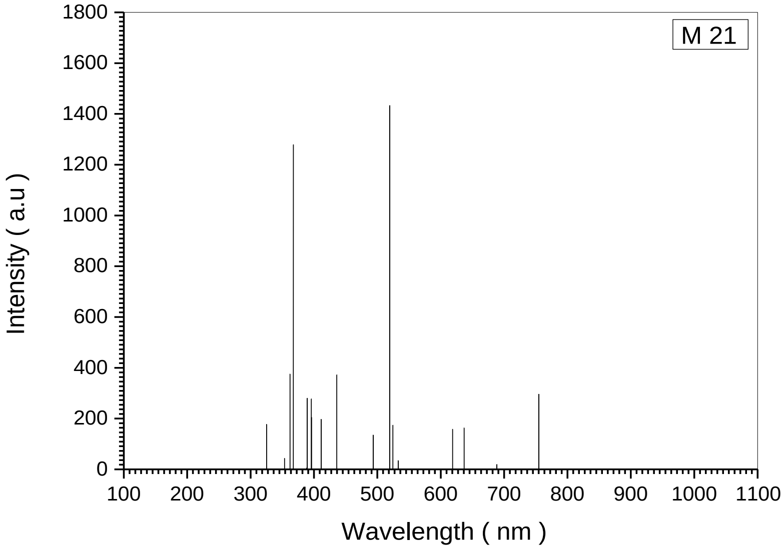


Figure (4.4): LIBS emission spectrum of sample (M21).

Table (4.4): The analyzed data of sample M21, irradiated by 80mJ.

Measured λ (nm)	Intensity (a.u)	Elements
325.295	186	Mn I
370.633	368	Ca II
373.690	1301	Ca II
413.247	203	Cl II
396.877	275	Ca II
435.119	74	Mg I
496.392	147	N I
518.808	1447	Ca II
524.616	1456	Pm II
615.818	186	O II
634.851	170	F I
755.224	301	F I

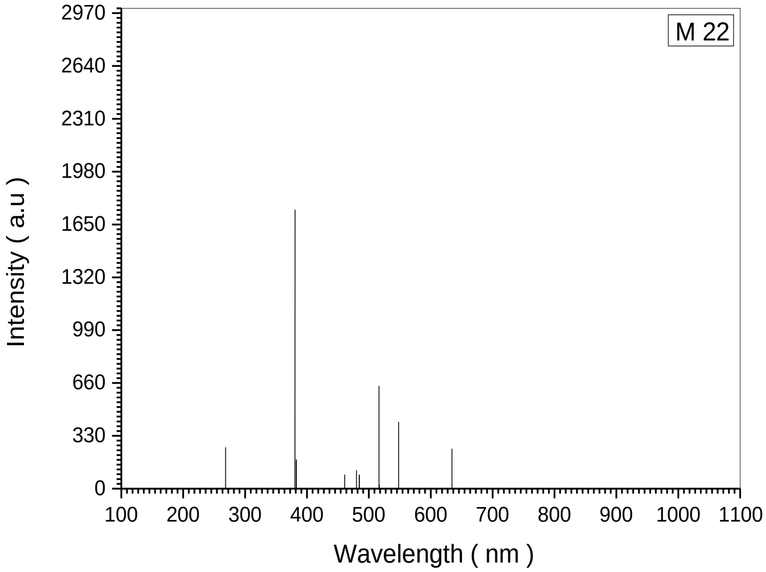


Figure (4.5): LIBS emission spectrum of sample (M22).

Table (4.5): The analyzed data of sample M22, irradiated by 80mJ.

Measured λ (nm)	**Intensity (a.u)**	**Elements**
268.921	286	Fe I
373.670	1745	Ca II
460.845	82	K II
480.327	124	N II
487.885	95	Ca I
518.363	640	Mg I

545.702	424	Cl II
634.851	250	F I

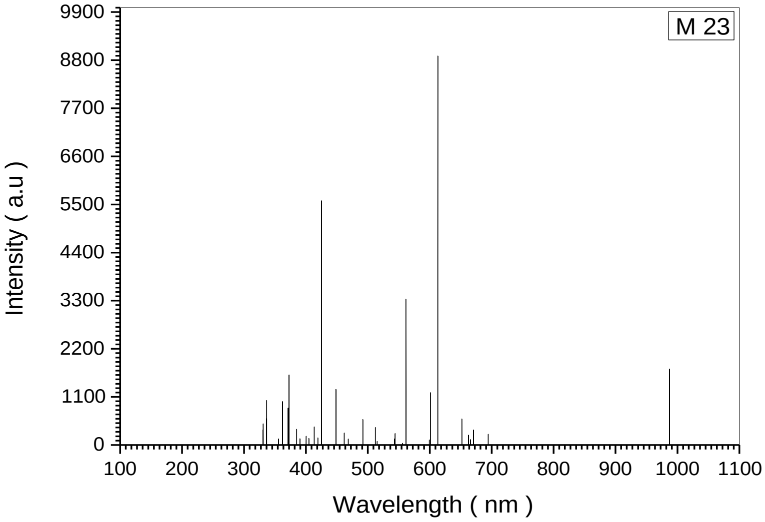


Figure (4.6): LIBS emission spectrum of sample (M23).

Table (4.6): The analyzed data of sample M23, irradiated by 80mJ.

Measured λ (nm)	**Intensity (a.u)**	**Elements**
331.235	518	Er II
336.827	1083	Mo I
361.848	1024	K II
370.601	1648	Ca II
424.179	5683	N II

444.779	1264	F II
491.772	591	Cl II
511.226	398	K I
571.121	330	Mg I
600.973	1144	Eu I
612.024	8876	K II
654.595	582	Mg II
989.062	1744	Ca II

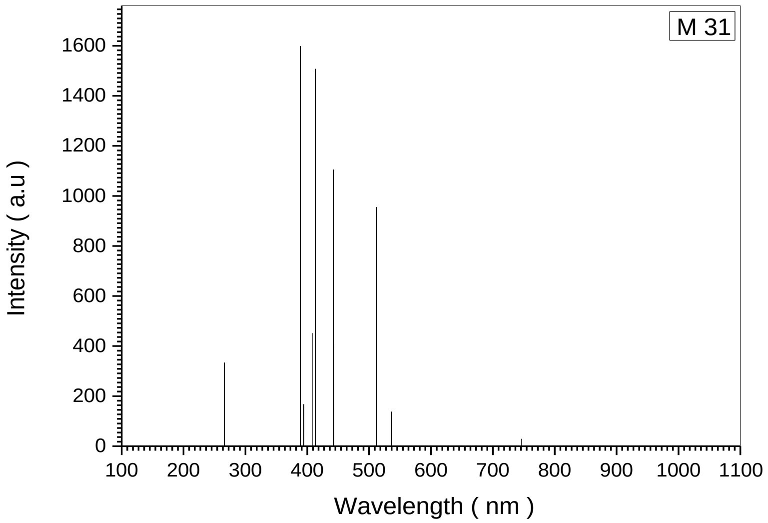


Figure (4.7): LIBS emission spectrum of sample (M31).

Table (4.7): The analyzed data of sample M31, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
268.921	329	Mo I
386.097	1603	Cl II
393.347	157	Ca II
404.176	444	N II
410.386	1502	F II
448.113	1108	Mg II
511.228	963	K II
539.212	146	Cl II

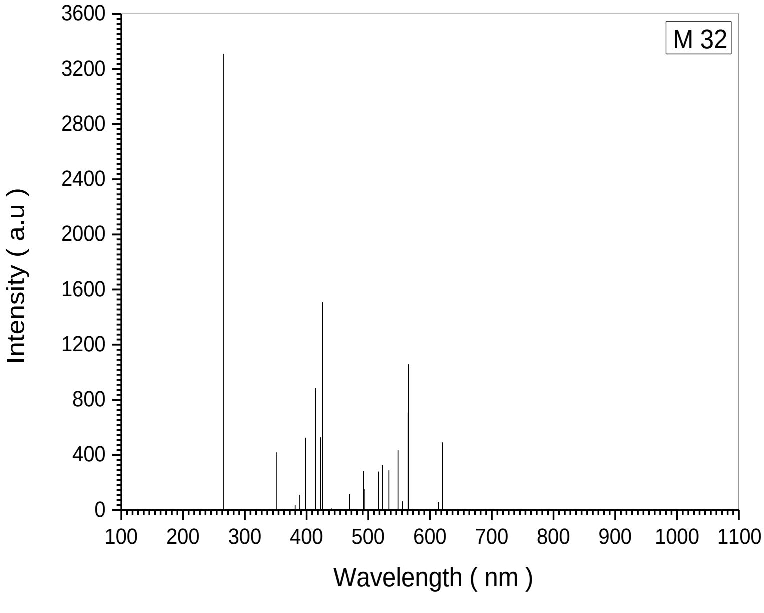


Figure (4.8): LIBS emission spectrum of sample (M32).

Table (4.8): The analyzed data of sample M32, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
268.977	3310	Fe I
353.073	455	K II
393.364	110	Ca II
398.848	520	Ca II
413.249	908	Cl II
424.133	520	N II
424.623	1225	F II
457.109	120	Mg I
533.969	316	K I
545.702	430	Cl II
563.997	1018	S II
623.964	522	F I

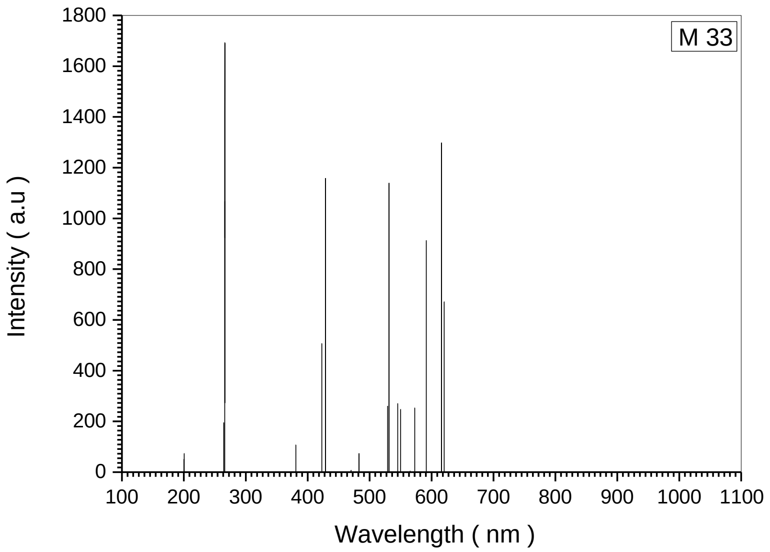


Figure (4.9): LIBS emission spectrum of sample (M33).

Table (4.9): The analyzed data of sample M33, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
199.719	88	Mn I
268.921	1705	Fe I
373.674	130	Ca II
424.183	502	N I
424623	1157	F II
481.947	82	Cl II
532.328	1168	K I
545.702	262	Cl II

547.362	250	S II
571.037	268	N I
593.175	917	N II
615.423	1307	Na I
623.965	676	F I

9 of plastic water bottle samples divided into three gropes; first one (M11,M12 and M13) the second (M21,M22 and M23) and the last one (M31,M32 and M33) were sampled using the LIBS technique to assess the presence and amounts of certain elements in this case (Mn, Ca, Cl, Mg, N, Pm, O, F, Fe, K, Er, Mo, Eu, Na, and S) . We found little difference in the spectra lines between the different samples, which would be expected, because they are different between the groups (M11, M12and M13) was the bottle before used and (M21, M22and M23) was the bottles after used and at last (M31, M32 and M33) was bottle caps, for that caused the charred surfaces simply were to add or remove some elements. Figures (4.1), (4.2) and (4.3) show the spectra lines of (M11, M12 andM13) samples that was water container. The spectra for all these samples represents in the ranged (200 - 1150) wavelengths by nanometers. In figure (4.1) for sample M11 shows 7 peaks, as tabling in table (4.1) and they were analyzed to their corresponding

elements (Mn II, Ca I, Cl II, S II, N II, K II, and F II). But for sample M12 shows 8 peaks, as tabling in table (4.2) and they were analyzed to their corresponding elements (Mn I, Ca I, Mg I, Cl I, N II, Sc I, S II, and F I) only Ca I has two peaks. At last sample in first group M13 at figure (4.3) shows 6 peaks, as tabling in table (4.3) and they were analyzed to their corresponding elements (Mn I, F I, Ca I, Mg I, and Cl II) only Ca I was two peaks. The second group was (M21, M22 and M23) are showing the chemical compounds spectra for all this samples in figures (4.4), (4.5) and (4.6). The spectra for all this samples represents in the ranged (200-1150) wavelengths by nanometers. In figure (4.4) for sample M21 shows 12 peaks, as tabling in table (4.4) and they were analyzed to their corresponding elements (Mn I, Ca II, Cl II, Mg I, N I, Pm II, O II and F I) but many elements have two or more peaks because of the different chemical compounds and states of existence these elements can attain (Ca II and F I) as showing figure (4.4).But for sample M22 shows 8 peaks, as tabling in table (4.5) and they were analyzed to their corresponding elements (Fe I, Ca II, K II, N II, Mg I, Cl I, and F I) but (Ca II) elements have two peaks as showing figure (4.5). At last sample in the second group M23 shows 13 peaks, as tabling in table (4.6) and they were analyzed to their corresponding elements (Er II, Mo I, K II, Ca II, N II, F II, Cl II, Mg I, and Eu I) but (K II, Mg I and Ca II) elements have two peaks as showing figure

(4.6). For the last groups (M31, M32 and M33) are showing the chemical compounds spectra for all this samples in figures (4.7), (4.8) and (4.9). The spectra for all this samples represents in the ranged (200 - 1150) wavelengths by nanometers. In figure (4.7) for sample M31 shows 7 peaks, as tabling in table (4.7) and they were analyzed to their corresponding elements (Mo I, Ca II, Cl II, N II, F II, Mg II, and K II) but only Cl II was two peaks. But for sample M32 shows 12 peaks, as tabling in table (4.8) and they were analyzed to their corresponding elements (Fe I, K I, Ca II, Cl II, N II, F II, Mg I, and S II) but only (Cl II, Ca II, K I and F I) was two peaks as showing figure (4.8). At last sample in the third group M33 at figure (4.9) shows 13 peaks, as tabling in table (4.9) and they were analyzed to their corresponding elements (Mn I, Fe I, Ca II, N I, F I, Cl II, K I, S II, and Na I) but only (Cl II, and F I) was two peaks and N II three peaks.

4.2.2. LIBS Results of Drug Bottles

Figures (4.10) to (4.18) show the LIBS emission spectra for the drug bottles samples after irradiation with 80mJ pulse energy. Tables (4.10) to (4.18) lists the analysis of the wavelengths corresponding to different elements and their intensities in the nine samples.

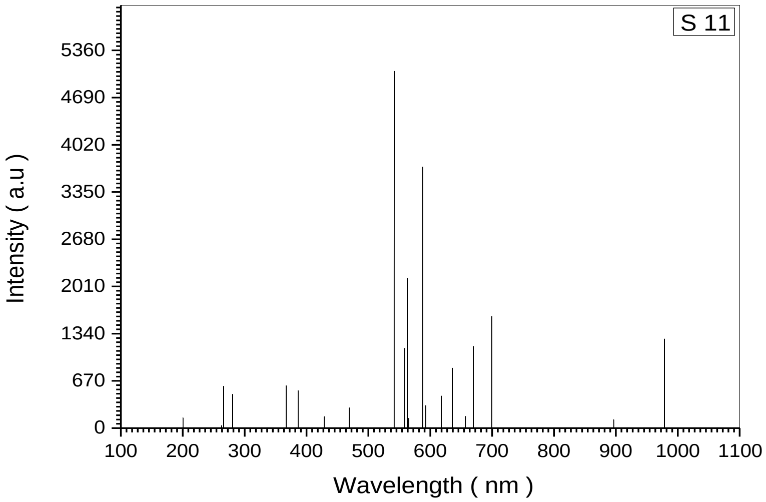


Figure (4.10): LIBS emission spectrum of sample (S11).

Table (4.10): The analyzed data of sample S11, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
200.145	1169	Os I
265.415	1609	Pt I
280.108	1507	Pb I
367.357	1645	Nb II
386.824	1574	Tc I
429.461	1306	W I

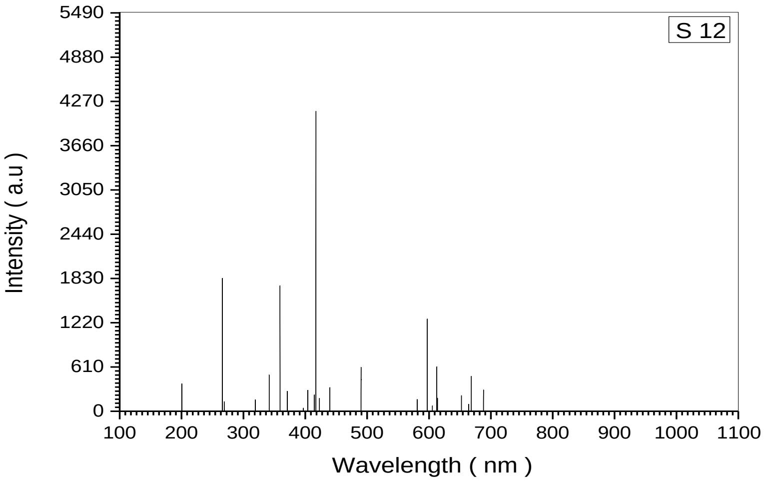


Figure (4.11): LIBS emission spectrum of sample (S12).

Table (4.11): The analyzed data of sample S12, irradiated by 80mJ

Measured λ (nm)	**Intensity (a.u)**	**Elements**
200.145	381	Os I
265.945	1836	Pt I
269.567	160	W I
319.329	182	Fe I
342.490	554	Gd II
358.946	1783	Nb I
404.551	316	V I
417.117	4142	W I

422.673	201	Ca I
440.512	351	Na I
490.003	600	Er II
585.745	209	Ca I
596.607	1313	Eu II
612.027	580	K I
651.421	235	Na II
667.583	460	Ne I
687.211	316	Xe I

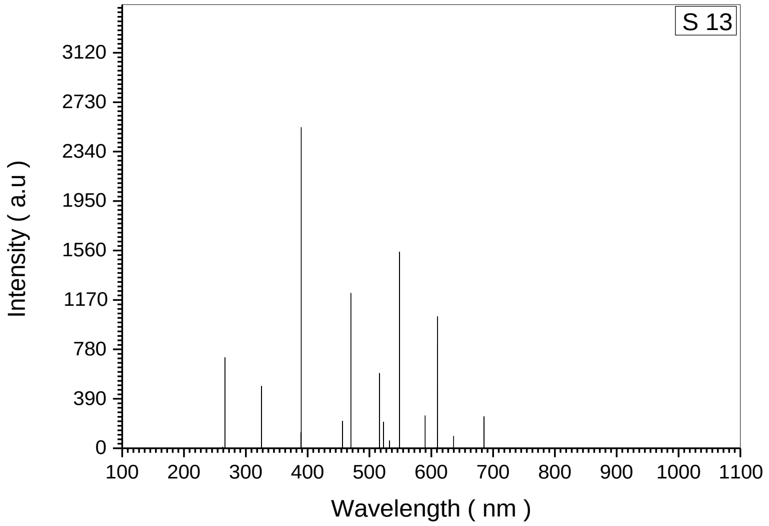


Figure (4.12): LIBS emission spectrum of sample (S13).

Table (4.12): The analyzed data of sample S13, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
265.954	730	Pt I
324.520	478	Pu I
390.291	2541	Cr I
456.236	225	Ce II
470.241	1216	Tb II
518.885	596	Ca I
522.011	201	Pr II
548.511	1548	Li II
589.593	243	Na I
601.815	1034	Eu I
635.472	116	Cd II
685.603	277	F I

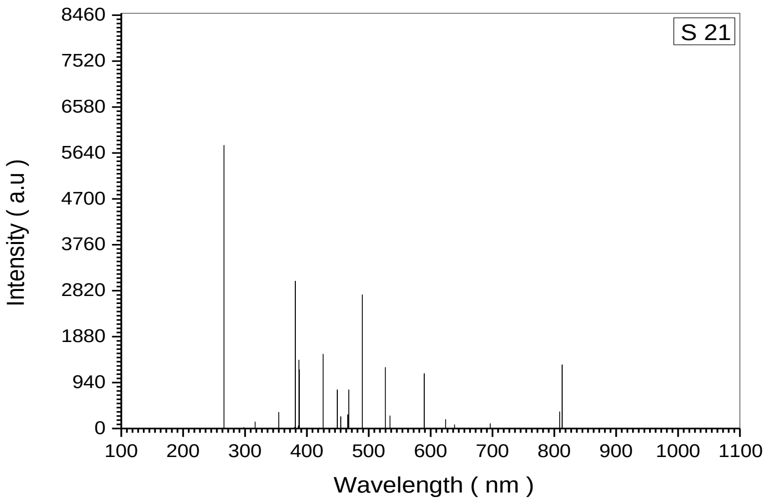


Figure (4.13): LIBS emission spectrum of sample (S21).

Table (4.13): The analyzed data of sample S21, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
265.945	5866	Pt I
354.818	383	Ni I
386.492	3062	Ra II
425.936	1512	Ar I
449.087	856	Na II
464.237	774	K II
490.007	2756	Er II
526.556	1304	Ca I
534.294	331	K I

589.592	1162	Na I
807.962	363	K I
813.296	1304	Kr I

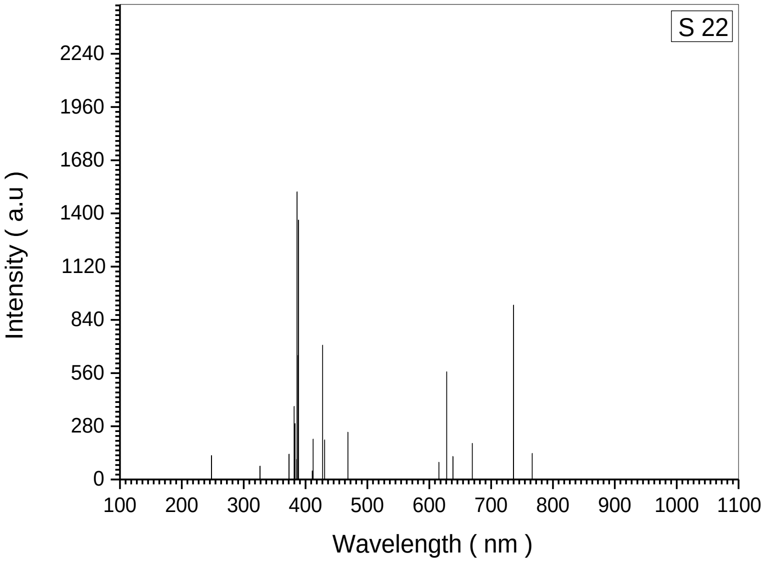


Figure (4.14): LIBS emission spectrum of sample (S22).

Table (4.14): The analyzed data of sample S22, irradiated by 80mJ

Measured λ (nm)	**Intensity (a.u)**	**Elements**
248.144	143	W I
326.478	71	Er II
372.538	131	Bk I
381.442	336	Ra II

386.824	1472	Tc I
411.762	215	Pa I
426.340	697	K II
430.774	209	Ca I
468.580	263	He II
616.217	95	Ca I
628.606	564	Pm I
637.528	113	Xe II
669.602	198	Al I
737.022	937	Eu II
769.897	145	K I

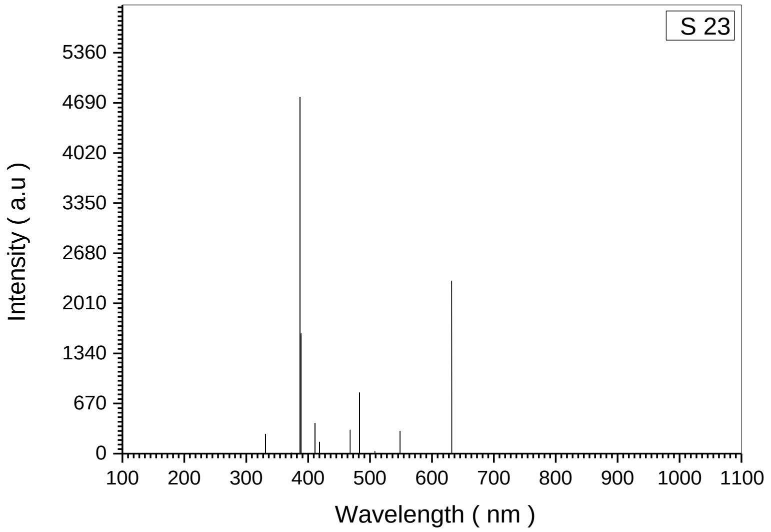


Figure (4.15): LIBS emission spectrum of sample (S23).

Table (4.15): The analyzed data of sample S23, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
331.639	242	Er II
386.824	4774	Tc I
411.762	458	Pa I
418.624	198	K II
468.581	328	He II
482.923	834	K I
598.614	344	Pr I
630.729	2307	K I

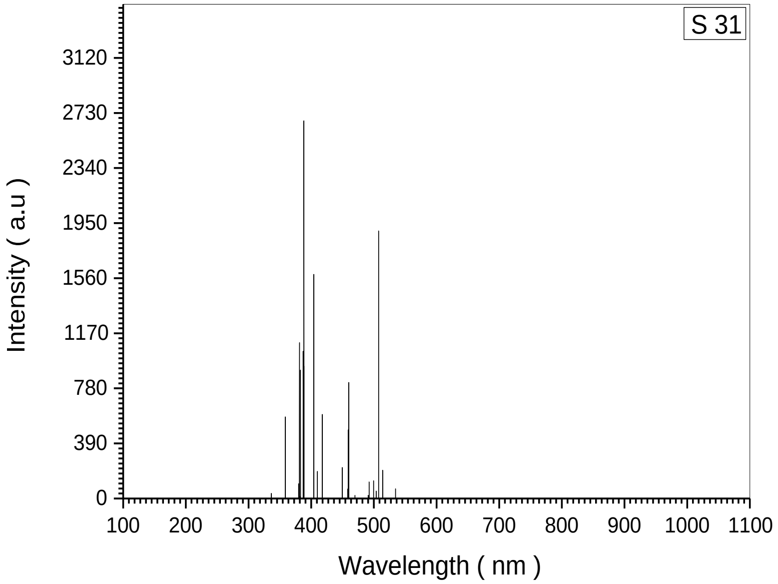


Figure (4.16): LIBS emission spectrum of sample (S31).

Table (4.16): The analyzed data of sample S31, irradiated by 80mJ.

Measured λ (nm)	Intensity (a.u)	Elements
358.496	604	Cd II
381.442	1143	Ra II
388.556	2677	Ac I
404.559	1598	W I
409.978	167	V I
417.117	588	W I
449.087	217	Na II
459.755	815	Pm I
487.817	133	Ca I
499.547	125	Cl I
514.883	225	Na I
533.969	65	K I

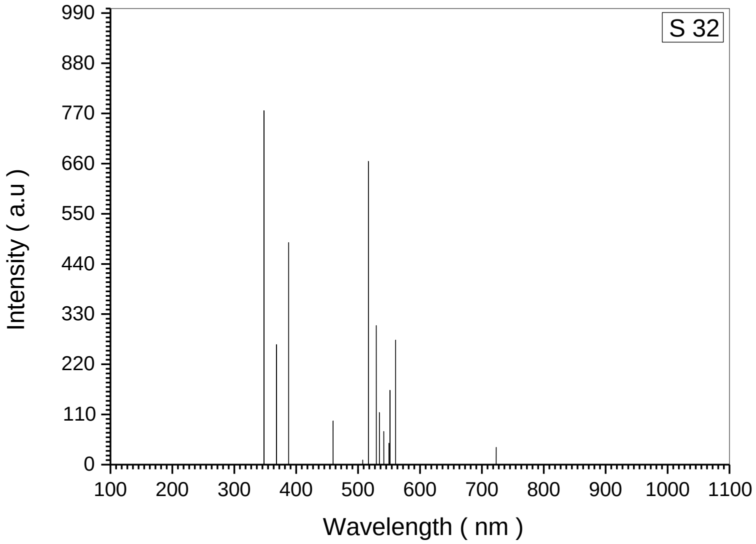


Figure (4.17): LIBS emission spectrum of sample (S32).

Table (4.17): The analyzed data of sample S32, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
347.675	779	Ar II
367.354	269	Nd II
388.556	486	Ac I
459.755	98	Pm I
518.885	666	Ca I
528.507	308	Tc I
539.212	117	Cl II
541.455	72	Na II

552.052	156	Sc I
560.885	274	Pb I
722.713	45	Pa I

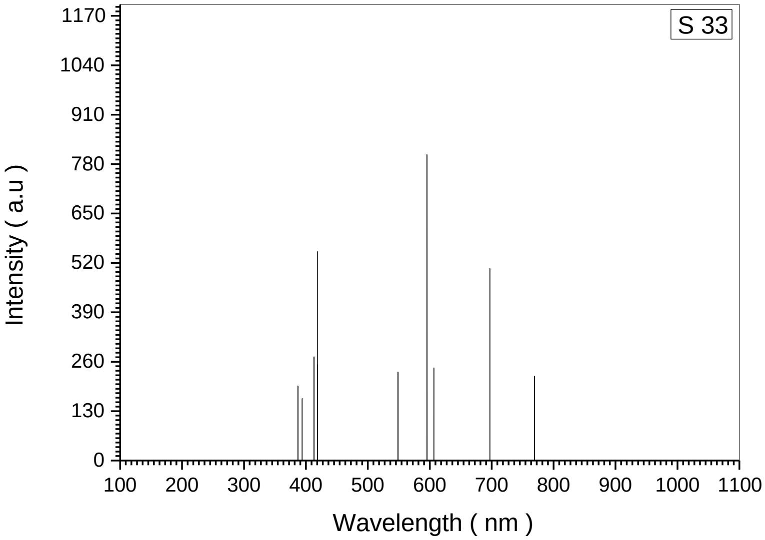


Figure (4.18): LIBS emission spectrum of sample (S33).

Table (4.18): The analyzed data of sample S33, irradiated by 80mJ

Measured λ (nm)	**Intensity (a.u)**	**Elements**
386.824	198	Tc I
393.888	172	Nd II
413.448	271	V I
418.624	554	K II

548.511	230	Li II
594.649	808	Pm II
607.201	245	Ce I
696.418	502	K I
767.242	224	Cl I

All of the plastic drug bottles samples divided into three groups. The first group (S11,S12 and S13) that drug bottles at first (Before preparation), the second (S21,S22 and S23) , and the last one consists of (S31,S32and S33) were sampled using the LIBS technique to assess the presence and amounts of certain elements in this case (Cd, Ra, Ac, W, V, Na, Pm, Ca, Cl, K, Ar, Nd, Tc, Sc, Pb, Pa, Li and Ce). Difference in the spectral lines between the different samples, which would be expected, because there are different between the groups (S11, S12 and S13) were before preparation (S21, S22and S23) were the bottles before used and at last (S31, S32 and S33) were the bottles after used. That caused the charred surfaces simply were to add or remove some elements. Figures (4.10), (4.11) and (4.12) show the spectra lines of (S11, S12 and S13) samples. The spectra for all these samples represented in the range (200 - 1150) wavelengths by nanometers. In figure (4.10) for sample S11 shows 6 peaks, as tabling in table (4.10) and they were analyzed to their corresponding elements (Os I, Pt I, Pb I, Nb II, Tc I and W I). Figure (4.11) for sample S12 shows 17 peaks, as tabling in table (4.11) and they were analyzed to their corresponding elements (Os I, Pt I, W I, Fe I, Gd II, Nb I, V I, Ca I, Na I, Er II, Eu II, K I, Ne I and Xe I). Whereas, many elements have two peaks because of the different chemical compounds and states of existence these elements can attain (W I, Ca II and Na II). At last samples in first group S13 at Figure (4.12) shows 12 peaks, as tabling in table (4.12) and analyzed to their corresponding elements (Pt I, Pu I, Cr I, Ce II, Tb II, Ca I, Pr II, Li II, Na I, Eu I, Cd II and F I). The second group was (S21, S22 and S23) are showing the chemical compounds spectra for all of these samples in figures (4.13), (4.14) and (4.15). The spectra for all this samples represented in the range (200 - 1150) wavelengths by nanometers. Figure (4.13) for sample S21 shows 12 peaks, as tabling in table (4.13) and analyzed to their corresponding elements (Pt I, Ni I, Ar I, Ra II, Na II, K I, Er II, Ca I and Kr I) but (K I and Na II) elements have two peaks as showing figure (4.13). Whereas. Figure (4.14) sample S22 shows 15 peaks, as tabling in table (4.14) and they were analyzed to their corresponding elements (W I, Er II, Bk I, Ra II, Tc I, Pa I, K II, Ca I, He II, Pm I, Xe II, Al I and Eu II) but (Ca I and K I) elements have two peaks as shown in figure (4.14). The last sample in the second group S23 at figure (4.15) shows 8 peaks, as tabling in table

(4.15) and analyzed to their corresponding elements (Er II, Tc I, Pa I, K II, He II and Pr I) but (K I) element have three peaks. The chemical compound spectra of the last group (S31, S32 and S33) are shown in figures (4.16), (4.17) and (4.18). The spectra for all of these samples represents in the range (200 - 1150) wavelengths by nanometers. Figure (4.16) for sample S31 shows 12 peaks, as tabling in table (4.16) and analyzed to their corresponding elements (Cd II, Ra II, Ac I, V I, Pm I, Ca I, Cl I, and K I) but both (Na II and W I) shows two peaks. Whereas, figure (4.17) for sample S32 shows 11 peaks, as tabling in table (4.17) and analyzed to their corresponding elements (Ar II, Nd II, Ac I, Pm I, Ca I, Tc I, Cl II, Na II, Sc I, Pb I and Pa I). The last sample in the third group S33 at Figure (4.18) shows 9 peaks, as tabling in table (4.18) and analyzed to their corresponding elements (Tc I, Nd II, V I, K I, Li II, Pm II, Ce I and Cl I) but only (K I) shows two peaks.

Discussion

The detection limit of plastic materials samples of water and drug containers was detecting the elements present in the sample.

For all samples the detection limit is (200 – 1150 nm) according to detector sensitivity it was out ranged of the main element's that made for water containers polyethylene terephthalate (PET) (C and H) element in the ranged before 200 nm for this response these two elements were not found on the results.

For LIBS spectrum of the first group (M11, M12and M13), for water bottle before use, the most sensitive lines (finger print wavelength) for identification of elements were found by using NIST database the elements (Mn II, Ca I, Cl II, S II, N II, K II, and F II), For M 11sample, (Mn I, Ca I, Mg I, Cl I, N II, Sc I, S II and F I), for M 12 sample and (Mn I, F I, Ca I, Cl II and Mg I), for M13 sample. Most of these elements are in agreement with the results of previous studies published in scientific literature (Bach, et al, 2012, Waheed, et al, 2012), except for the elements (Cl II, FII) that were first observed. This group are useful for recycling only once time.

For LIBS spectrum of second group (M21, M22and M23), water bottles after use are (Mn I, Ca II, Cl II, Mg I, N I, Pm II, O II and F I) for M21, (Fe I, Ca II, K II, N II, Mg I, Cl I, and F I) for M 22 and (Er II, Mo I, K II, Ca II, N II, F II Cl II, Mg I and Eu I) for M23 and also all elements are agree with the results of previous studies (Cheng, et al, 2010, Waheed, et al, 2012, Junjuri, et al, 2019), except (Cl II, F II) the spectra showed lines corresponding to elements that have not been observed by other techniques, such as Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption

Spectroscopy (AAS) (Waheed, et al.2012), this elements group was normal and useful for recycling only once time.

At the bottle cap for the last group of water petals (M31, M32 and M33) the finger print wavelength are (Mo I, Ca II, Cl II, N II, F II, Mg II, and K II) for M31 sample, (Fe I, K II, Ca II, Cl II, N II, F II, Mg I and S II) for M32 sample and (Mn I, Fe I, Ca II, N I, F II, Cl II, K I, S II and Na I) for M33 sample, and also all elements were normal . Although there are a heavy metals, but it usually found at trace levels, such as Fe and Mo.

The LIBS spectra showed that the elements of (S11, S21and S31) samples that drug bottles (AMIBUTAMOL DRUG) are (Os I, Pt I, Pb I, Nb II, Tc I and W I) for sample S 11 (bottle at first Bottle), (Pt I, Ni I, Ra II, Ar I, Na II, K II, Er II, Ca I and Kr I) for sample S21 (Before used Bottle) and (Cd II, Ra II, Ac I, W I,V I, Na II, Pm I, Ca I, Cl I and K I) for sample S31 (After used). Some elements in sample S31 were not found in in sample S11 and sample S21 like (Cd II, Ac I, V I, Pm I and C l I,). This group is bad recycling samples.

For LIBS spectra (finger print wavelength) for (AMIHISTIN DRUG) are (Os I, Pt I, W I, Fe I, Gd II, Nb I, V I, Ca I, Na I, Er II, Eu II, K I, Ne I and Xe I) for S 12 sample (bottle at first), (W I, Er II, Bk I, Ra II, Tc I, Pa I, K II, Ca I, He II, Pm I, Xe II, Al I and Eu II) for S 22 sample (Before used Bottle) and element (Ar II, Nd II, Ac I, Pm I, Ca I, Tc I, Cl II, Na II, Sc I, Pb I and Pa I) for S32 sample (After used). There are some strange elements like (Ar II, Nd I I, Ac I, Sc I, Pa and Pb I) some of these elements are agree with the results of previous studies (Cheng, et al, 2010, Koyuncu and Alwazeer, 2019) also all elements for above samples of this group is bad recycling samples.

At the last group (AMIDOL DRUG) the finger print elements of LIBS spectra are (Pt I, Pu I, Cr I, Ce II, Tb II, Ca I, Pr II, Li II, Na I, Eu I, Cd II and F I) for sample S13 (bottle at first Bottle) , (Er II, Tc I, Pa I, K II, He II and Pr I) for sample S23 (Before used Bottle) and (Tc I, Nd II, V I, K II, Li II, Pm II, Ce I and Cl I) for S33 sample (After used). There are some strange elements like (Tc I, Nd I, V I, Li II, Pm , and Ce I). For above elements this group is bad recycling samples also.

4.3. Conclusions

From the obtained results one can conclude that:

1. Laser induced breakdown spectroscopy (LIBS) is useful technique for analyses the plastics water and drug containers samples and this technique led to accurate determination of different elements. The pulse energy irradiated to the samples at 80mJ were suitable to detect high amounts of elements.

2. All elements present in plastic water bottles were detected using laser induced breakdown spectroscopy RT-100B, the elements that detected are (Mn, Ca, Cl, Mg, N, Pm, O, F, Fe, K, Er, Mo, Eu) present in plastic water bottles samples were estimated and results achieved are in good agree and all these elements are normal and these groups are useful for recycling only once time.
3. All elements present in plastic drug bottles were detected using laser induced breakdown spectroscopy. The elements that detected are (Cd, Ra, Ac, W, V, Na, Pm, Ca, Cl, K, Ar, Nd, Tc, Sc, Pb, Pa, Li and Ce).
4. Element that present in plastic drug bottle samples were estimated and results achieved are in good agree and all of these elements were normal and this group is not useful for recycling.
5. The sensitive lines for the above-mentioned heavy elements were identified using standard data published by NIST for the elemental analysis in different plastic and drug bottles samples.
6. This study reveals that the plastics drug bottles samples collected from manufacturing factories located at Khartoum city, Sudan. They could cause a lot of problems in recycling, it is not recommended recycling this samples.

4.5 Recommendations

The followings can be suggested as future work:

1. Double pulse lasers can be used to enhance the detected signal.
2. The LIBS system can be used as a portable system for on line analysis of plastic (water and drug) bottles from factories located at Khartoum city, Sudan. Investigations should be made to reduce the size and the initial cost of the instrumentation.
3. LIBS system can be used in the future to analysis of many types of other type plastic wastes.

References:

Abbas, O., Dardenne, P., & Baeten, V., 2012. Near-infrared, mid-infrared, and Raman spectroscopy. *Chemical analysis of food: Techniques and applications*, *3*, 59-91.

Aguirre, M.Á., Hidalgo, M., Canals, A., Nóbrega, J.A. and Pereira-Filho, E.R., 2013. Analysis of waste electrical and electronic equipment (WEEE) using laser induced breakdown spectroscopy (LIBS) and multivariate analysis. Talanta, 117, pp.419-424.

Alabi, O.A., Ologbonjaye, K.I., Awosolu, O. and Alalade, O.E., 2019. Publicand environmental health effects of plastic wastes disposal: a Review. *J Toxicol Risk Assess*, *5*, p.021.

Alberghina, M.F., Barraco, R., Brai, M., Schillaci, T. and Tranchina, L., 2011. Comparison of LIBS and μ-XRF measurements on bronze alloys for monitoring plasma effects. In *Journal of Physics:Conference Series* (Vol. 275, No. 1, p. 012017). IOP Publishing.

Anabitarte, F., Cobo, A. and Lopez-Higuera, J.M., 2012. Laser-induced breakdown spectroscopy: fundamentals, applications, and challenges. *ISRN spectroscopy*, *2012*.

Anzano, J.M., Bello-Gálvez, C. and Lasheras, R.J., 2014. Identification of Polymers by Means of LIBS. In *Laser-Induced Breakdown Spectroscopy* (pp. 421-438). Springer, Berlin, Heidelberg.

Anzano, J.M., Gornushkin, I.B., Smith, B.W. and Winefordner, J.D., 2000. Laser-induced plasma spectroscopy for plastic identification. *Polymer engineering & science*, *40*(11), pp.2423-2429.

Ateş Arıca, D., 2010. *Laser Induced Breakdown Spectroscopic analysis of metal aerosols generated by pneumatic nebuliztion of aqueous solutions* (Master's thesis, İzmir Institute of Technology).

Bach, C., Dauchy, X., Chagnon, M.C. and Etienne, S., 2012. Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: a source of controversy reviewed. *Water research*, *46*(3), pp.571-583.

Baranska, H., 1987. An introduction to Raman scattering. *Laser Raman Spectrometry: Analytical Applications (Eds: H. Baranska, A. Labudzinska and J. Terpinski)*, pp.9-31.

Bings, N.H., Bogaerts, A. and Broekaert, J.A., 2006. Atomic spectroscopy. *Analytical chemistry*, *78*(12), pp.3917-3946.

Bittencourt, J.A., 2013. *Fundamentals of plasma physics*. Springer Science & Business Media.

Breech, F. and Cross, L., 1962. Optical microemission stimulated by a ruby maser. Appl. Spectrosc, 16(59), p.1.

Cairns, R.A. ed., 2012. *Plasma physics*. Springer Science & Business Media.

Chen, Y.L., Lewis, J.W.L. and Parigger, C., 2000. Spatial and temporal profiles of pulsed laser-induced air plasma emissions. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *67*(2), pp.91-103.

Cheng, X., Shi, H., Adams, C.D. and Ma, Y., 2010. Assessment of metal contaminations leaching out from recycling plastic bottles upon treatments. Environmental Science and Pollution Research, 17(7), pp.1323-1330.

Connes, J. and Connes, P., 1966. Near-infrared planetary spectra by Fourier spectroscopy. I. Instruments and results. *JOSA*, *56*(7), pp.896-910.

Cordero, E., Latka, I., Matthäus, C., Schie, I.W. and Popp, J., 2018. In-vivo Raman spectroscopy: from basics to applications. *Journal of biomedical optics*, *23*(7), p.071210.

Costa, V.C., Aquino, F.W.B., Paranhos, C.M. and Pereira-Filho, E.R., 2017. Identification and classification of polymer e-waste using laser-induced breakdown spectroscopy (LIBS) and chemometric tools. *Polymer Testing*, *59*, pp.390-395.

Cremers, D. A., & Radziemski, L. J., 2006. Basics of the LIBS Plasma. Handbook of laser-induced breakdown spectroscopy, 23-52.

Cremers, D.A. and Radziemski, L.J., 2013. *Handbook of laser-induced breakdown spectroscopy*. John Wiley & Sons.

Demtröder, W. 2008, Laser Spectroscopy: Vol. 2 Experimental Techniques, 4th edn, Springer Berlin Heidelberg, Berlin, Heidelberg.

Demtröder, W., 2014. Laser spectroscopy 1: basic principles. Springer.

Dietzek, B., Cialla, D., Schmitt, M. and Popp, J., 2010. Introduction to the fundamentals of Raman spectroscopy. In *Confocal Raman Microscopy* (pp. 21-40). Springer, Cham.

Eichhorn, M., 2014. Laser physics: from principles to practical work in the lab. Springer Science & Business Media.

Eichler, H.J., Eichler, J. and Lux, O., 2018. Lasers: basics, advances and applications (Vol. 220). Springer.

Fornarini, L., Colao, F., Fantoni, R., Lazic, V. and Spizzicchino, V., 2005. Calibration analysis of bronze samples by nanosecond laser induced breakdown spectroscopy: a theoretical and experimental approach. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *60*(7-8), pp.1186-1201.

Geyer, R., Jambeck, J.R. and Law, K.L., 2017. Production, use, and fate of all plastics ever made. Science advances, 3(7), p.e1700782.

Gondal, M.A. and Siddiqui, M.N., 2007. Identification of different kinds of plastics using laser-induced breakdown spectroscopy for waste management. *Journal of Environmental Science and Health Part A*, *42*(13), pp.1989-1997.

Goodman, B. A., 1994. Molecular spectroscopy: introduction and general principles. In *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods* pp. 1-10, Springer, Dordrecht.

Gottfried, J.L. and De Lucia Jr, F.C., 2010. *Laser-induced breakdown spectroscopy: capabilities and applications*. ARMY RESEARCH LAB ABERDEEN PROVING GROUND MD WEAPONS AND MATERIALS RESEARCH DIRECTORATE.

Grégoire, S., Boudinet, M., Pelascini, F., Surma, F., Detalle, V. and Holl, Y., 2011. Laser-induced breakdown spectroscopy for polymer identification. *Analytical and bioanalytical chemistry*, *400*(10), pp.3331-3340.

Griffiths, P.R. and De Haseth, J.A., 2007. *Fourier transform infrared spectrometry* (Vol. 171). John Wiley & Sons.

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E. and Purnell, P., 2018. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of hazardous materials*, *344*, pp.179199.

Haley, D. and Pratt, O., 2017. Basic principles of lasers. Anaesthesia & Intensive Care Medicine, 18(12), pp.648-650.

Herzberg, G, 1991, Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules, Krieger Publishing.

Ismail, A.A., van de Voort, F.R. and Sedman, J., 1997. Fourier transform infrared spectroscopy: principles and applications. In Techniques and instrumentation in analytical chemistry (Vol. 18, pp. 93-139). Elsevier.

Jaroszynski, D.A., Bingham, R.A. and Cairns, R.A. eds., 2009. *Laser plasmainteractions*. CRC Press.

Jeong, S.H., Kim, K.K., Jeong, S.J., An, K.H., Lee, S.H. and Lee, Y.H., 2007. Optical absorption spectroscopy for determining carbon nanotube concentration in solution. *Synthetic Metals*, *157*(13-15), pp.570-574.

Junjuri, R. and Gundawar, M.K., 2019. Femtosecond laser-induced breakdown spectroscopy studies for the identification of plastics. Journal of Analytical Atomic Spectrometry, 34(8), pp.1683-1692.

Junjuri, R., Zhang, C., Barman, I. and Gundawar, M.K., 2019. Identification of post-consumer plastics using laser-induced breakdown spectroscopy. *Polymer Testing*, *76*, pp.101-108.

Kasem, M.A., Russo, R.E. and Harith, M.A., 2011. Influence of biological degradation and environmental effects on the interpretation of archeological bone samples with laser-induced breakdown spectroscopy. *Journal of Analytical Atomic Spectrometry*, *26*(9), pp.1733-1739.

Kearton, B. and Mattley, Y., 2008. Sparking new applications. *Nature photonics*, *2*(9), pp.537-540.

Khoshhesab, Z.M., 2012. Reflectance IR spectroscopy. *Infrared spectroscopy—materials science, engineering and technology*, *11*, pp.233-244.

Kim, E. and Choi, W.Z., 2019. Real-time identification of plastics by types using laser-induced breakdown spectroscopy. *Journal of Material Cycles and Waste Management*, *21*(1), pp.176-180.

Klein, R., 2012. *Laser welding of plastics: Materials, processes and industrial applications*. John Wiley & Sons.

Konidala, S.K., Kamala, G. and Koralla, S., 2016. Laser induced breakdown spectroscopy. *Research Journal of Pharmacy and Technology*, *9*(1), pp.91-100.

Koyuncu, M. and Alwazeer, D., 2019. Determination of trace elements, heavy metals, and antimony in polyethylene terephthalate–bottled local raw cow milk of Iğdır region in Turkey. *Environmental Monitoring and Assessment*, *191*(11), p.666.

Kuzmany, H., 2009. *Solid-state spectroscopy: an introduction*. Springer Science & Business Media.

Liu, K., Tian, D., Li, C., Li, Y., Yang, G. and Ding, Y., 2019. A review of laser-induced breakdown spectroscopy for plastic analysis. TrAC Trends in Analytical Chemistry, 110, pp.327-334.

Liu, K., Tian, D., Yue, X. and Yang, G., 2020. A software system for rapid analysis of plastics using laser-induced breakdown spectroscopy. Journal of Instrumentation, 15(04), p.T04002.

Liu, X.Y. and Zhang, W.J., 2008. Recent developments in biomedicine fields for laser induced breakdown spectroscopy. *Journal of Biomedical Science and Engineering*, *1*(3), p.147.

Loureiro, J., & Amorim, J. , 2016. Laser Spectroscopy. In *Kinetics and Spectroscopy of Low Temperature Plasmas* , pp. 383-412. Springer, Cham.

Lynch, W.A., 1940. Fundamental Processes of Electrical Discharge in Gases. *Thought: Fordham University Quarterly*, *15*(2), pp.375-376.

Maini, A.K., 2018. *Handbook of defence electronics and optronics: fundamentals, technologies and systems*. John Wiley & Sons.

Menzel, R., 2013. Photonics: linear and nonlinear interactions of laser light and matter. Springer Science & Business Media.

Miziolek, A.W., Palleschi, V. and Schechter, I. eds., 2006. Laser induced breakdown spectroscopy. Cambridge university press.

Musazzi, S. and Perini, U., 2014. Laser-induced breakdown spectroscopy. *Springer Series in Optical Sciences*, *182*.

Negre, E., Motto-Ros, V., Pelascini, F. and Yu, J., 2016. Classification of plastic materials by imaging laser-induced ablation plumes. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *122*, pp.132-141.

Ottaway, J.M., 1980. T. Torok, j. mika and e. gegus, Emission Spectrochemical Analysis: Akademiai kiado, budapest, and adam hilger, bristol, 1978, 692 pp. price£ 31.50.

Paisner, J. A., Radziemski, L. J., & Solarz, R. W. (Eds.)., 1987. *Laser Spectroscopy and Its Applications*. Marcel Dekker, Incorporated.

Pandhija, S., Rai, N.K., Rai, A.K. and Thakur, S.N., 2010. Contaminant concentration in environmental samples using LIBS and CF LIBS. *Applied Physics B*, *98*(1), pp.231-241.

Payling, R. and Larkins, P., 2001. *Optical emission lines of the elements*. John Wiley & Sons.

Peichao, Z.H.E.N.G., Minjie, S.H.I., Jinmei, W.A.N.G. and Hongdi, L., 2015. The spectral emission characteristics of laser induced plasma on tea samples. *Plasma Science and Technology*, *17*(8), p.664.

Penrose, R., 1991. The mass of the classical vacuum. *The Philosophy of Vacuum. Clarendon*. Oxford University Press. p. 21. ISBN 978-0-19 824449-3.

Picollo, M., Bartolozzi, G., Cucci, C., Galeotti, M., Marchiafava, V. and Pizzo, B., 2014. Comparative study of Fourier transform infrared spectroscopy in transmission, attenuated total reflection, and total reflection modes for the analysis of plastics in the cultural heritage field. *Applied spectroscopy*, *68*(4), pp.389-396.

Proshad, R., Kormoker, T., Islam, M.S., Haque, M.A., Rahman, M.M. and Mithu, M.M.R., 2018. Toxic effects of plastic on human health and environment: A consequences of health risk assessment in Bangladesh. International Journal of Health, 6(1), pp.1-5.

Radziemski, L.J. and Loree, T.R., 1981. Laser-induced breakdown spectroscopy: time-resolved spectrochemical applications. *Plasma Chemistry and Plasma Processing*, *1*(3), pp.281-293

Radziemski, L.J., 2002. From LASER to LIBS, the path of technology development. Spectrochimica Acta Part B: Atomic Spectroscopy, 57(7), pp.1109-1113.

Renk, K.F., 2012. Basics of laser physics. Berlin: Springer Berlin Heidelberg.

Rosenberg, E. and Panne, U., 2003. Atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES). *Handbook of Spectroscopy*, pp.421-496.

Rudzikas, Z., 2007. *Theoretical atomic spectroscopy* (Vol. 7). Cambridge University Press.

Saquing, J.M., Saquing, C.D., Knappe, D.R. and Barlaz, M.A., 2010. Impact of plastics on fate and transport of organic contaminants in landfills. Environmental science & technology, 44(16), pp.6396 6402.

Sarkar, A., Telmore, V., M. Alamelu, D. and Aggarwal, S. K., 2009 “Laser induced breakdown spectroscopic quantification of platinum groupmetals in simulated high level nuclear waste,” Journal of Analytical Atomic Spectrometry, vol. 24, No. 11, pp.1545–1550.

Senesi, G.S., 2014. Laser-Induced Breakdown Spectroscopy (LIBS) applied to terrestrial and extraterrestrial analogue geomaterials with emphasis to minerals and rocks. *Earth-Science Reviews*, *139*, pp.231-267.

Siddiqui, M.N., Gondal, M.A. and Nasr, M.M., 2009. Determination of trace metals using laser induced breakdown spectroscopy in insoluble organic materials obtained from pyrolysis of plastics waste. *Bulletin of environmental contamination and toxicology*, *83*(1), pp.141-145.

Singh, J.P. and Thakur, S.N. eds., 2007. *Laser-induced breakdown spectroscopy*. Elsevier.

Smith, E. and Dent, G., (2005), Introduction, basic theory and principles. Modern Raman spectroscopy-A practical approach: pp.1-21.

Stuart, B. H. , 2004. Infrared spectroscopy: Fundamentals and applications, 1. Aufl. ed. Hoboken: Wiley.

Subramanian, A. and Rodriguez-Saona, L., 2009. Fourier transform infrared (FTIR) spectroscopy. Infrared spectroscopy for food quality analysis and control, pp.145-178.

Svanberg, S., 2012. *Atomic and molecular spectroscopy: basic aspects and practical applications* (Vol. 6). Springer Science & Business Media.

Svelto, O. and Hanna, D.C., 2010. Principles of lasers (Vol. 1). New York: Springer.

Thakur, S.N. and Singh, J.P., 2007. Fundamentals of laser induced breakdown spectroscopy. In *Laser-induced breakdownspectroscopy* (pp. 3-21). Elsevier.

Träger, F. ed., 2012. Springer handbook of lasers and optics. Springer Science & Business Media.

Unnikrishnan, V.K., Choudhari, K.S., Kulkarni, S.D., Nayak, R., Kartha, V.B. and Santhosh, C., 2013. Analytical predictive capabilities of laser induced breakdown spectroscopy (LIBS) with principal component analysis (PCA) for plastic classification. *Rsc Advances*, *3*(48), pp.25872-25880.

Vo-Dinh, T. ed., 2006. *Handbook of spectroscopy*. John Wiley & Sons. Waheed, S., Rahman, S., Husnain, S. and Siddique, N., 2012. Hazardous and other element characterization of new and used domestic plastic food containers using INAA and AAS. *Journal of Radioanalytical and Nuclear Chemistry*, *292*(3), pp.937-945.

Yu, Y., Guo, L.B., Hao, Z.Q., Li, X.Y., Shen, M., Zeng, Q.D., Li, K.H., Zeng, X.Y., Lu, Y.F. and Ren, Z., 2014. Accuracy improvement on polymer identification using laser-induced breakdown spectroscopy with adjusting spectral weightings. *Optics Express*, *22*(4), pp.3895-3901.

Zeitler, J.A., Taday, P.F., Newnham, D.A., Pepper, M., Gordon, K.C. and Rades, T., 2007. Terahertz pulsed spectroscopy and imaging in the pharmaceutical setting-a review. *Journal of Pharmacy and Pharmacology*, *59*(2), pp.209-223.