Sudan University of Science & Technology

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Determination of Elements in Three Samples of Sudanese Benzene Using Laser Induced Breakdown Spectroscopy (LIBS)

تحديد العناصر المكونة لثلاث عينات من البنزين السوداني باستخدام مطيافية الانهيار الكهربي المستحث بالليزر

A thesis submitted as a partial fulfillment of the requirements for the degree of master in laser application in physics

BY:

Sofyan Sharafedin Mohamed Dawod

Supervised by:

Prof. Dr. Nafie A. AL Muslet

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بسم الله الرَّحْمَنِ الرَّحِيمِ

(وَاخْفِضْ لَهُمَا جَنَاحَ الذُّلِّ مِنَ الرَّحْمَةِ وَقُلْ رَبِّ ارْحَمْهُمَا كَمَا رَبَّيَانِي صَغِيرًا)

صدق اللَّهُ العظيم

الإسراء 24

DEDICATION

TO MY MOTHER TO MY FATHER

TO MY BROTHER

TO MY SISTERS

TO MY DISTINGUISHED COLLEAGUES

TO MY GREAT TEACHERS

TO YOU

Sofyan

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Praise be to Allah first and foremost, after thanking Allah for inspiring me to accomplish this work, I would like to express my faithful indebtedness to Prof. Dr. Nafie A. AL Muslet for his supervision this work, encouragement, guidance, advice, and patience.

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Abstract

The objective of this work was the utilization of laser induced breakdown spectroscopy (LIBS) technique in investigation of elements in three different types of Sudanese benzene. Q-switched –Nd: YAG Laser with 10 ns pulse duration, 100 mj energy per pulse, 2 Hz repetition rate was focused on the sample to achieve high power density leads to very high temperature in the focal volume and then undergo a number of reactions resulting in formation of a plasma for the sample with discrete emission lines which represent fingerprints of the atoms and ions constitute the sample. A spectrometer connected to PC was used to collect and record the emission spectra of the plasma. The recorded spectra were processed by subtracting the dark current, pumping flash lamp spectra and background radiation. The elements were identified from the emitted lines after referring to the atomic spectral database. A comparison was done between the sample contents. The results showed that there are elements found in all three samples with different amounts while there are elements that not found in all three types of benzene.

From the results obtained in this research one can conclude that: The laser induced breakdown spectroscopy (LIBS) technique is very accurate that the essential atoms forming the samples of benzene (Hydrogen and Carbon) appeared with a great amounts while other elements that were not essential as (Pb , Be , Zr , Ni, Hg, Ti, Sc, La, Zn, Tm, Y, Eu, Kr, Gd, Cl, Ge, Hf, Mo, Xe, V, Mo, Ne, He, Fe, O, W, F and Nd), appeared with a little amounts relative to the essential atoms. (C, H, Fe, Ti, W, O and S) atoms were found in the three samples with different amounts.

Also it has a good ability to detect almost all the elements and ions in the benzene samples, LIBS can be used as diagnostic technique for investigation of elements in liquid samples.

المستخلص

هدف هذا البحث هو استخدام تقنية مطيافية الانهيار الكهربائي المستحث بالليزر لاستكشاف العناصر الكيميائية المكونة لثلاث عينات من البنزين السوداني . أستخدم ليزر النديميوم- ياق ذو التشغيل المفتاحي النبضي بزمن نبضة مقداره 10 نانو ثانية وبطاقة نبضة مقدارها 100 مللي جول و بتردد مقداره 2 هيرتز. سلطت حزمة من الليزر علي العينة للحصول علي كثافة قدرة عالية أدت الي ارتفاع في درجات حرارة الجزيئات عند بؤرة الحزمة عندها تحصل علي عدة تفاعلات أدت الي تكون بلازما من العينة ذات خطوط انبعاث طيفية مميزة تعد بمثابة بصمة تعرف بها الذرات والأيونات المكونة للعينة. أستخدم جهاز مطياف موصل بجهاز الحاسب الالي لرصد وتسجيل أطياف الانبعاثات لبلازما العينة. تمت معالجة النتائج بطرح تيار الظلام والخلفية الاشعاعية . تم تحديد العناصر المكونة لكل عينة بواسطة الخطوط الطيفية المنبعثة وذلك بعد الرجوع الي قاعدة بيانات الاطياف الذرية للذرات والايونات. تمت المقارنة بين محتويات كل عينة. أوضحت النتائج أن هناك بعض المكونات موجودة في كل العينات الثلاث بكميات متفاوتة في حين أن هنالك مكونات لا توجد في كل العينات.

من النتائج التي تم الحصول عليها في هذا البحث يمكن أن نستنتج: أن تقنية الانهيار الكهربي المستحث بالليزر (LIBS) تقنية دقيقة للغاية وأن الذرات الاساسية المكونة للبنزين (الهيدروجين والكربون) ظهرت بكميات كبيرة في حين أن غيرها من العناصر غير الاساسية (الهيليوم، الاكسجين، الرصاص، الكلور، الكريبتون، الزينون، الزنك، النيتروجين، الفلور، الجرمانيوم، البيريليوم، السكانديوم، التيتانيوم، اللانتانيوم، الغاليوم، الزركونيوم، النيكل, الزئبق، اليوروبيوم، الفاناديوم، الاتريوم، التوليوم، الغادولينيوم، النيوديميوم، الهافنيوم، الموليبديوم، النيون، التنغستن، السليكون، الكبريت و الحديد) ظهرت بكميات قليلة نسبيا مقارنة مع الذرات الأساسية. أيضا تم الحصول ذرات (الكربون, الهايدروجين, التنغستن, الحديد, الاوكسجين والكبريت) في العينات الثلاث بكميات مختلفة. كما أن هذه التقنية لديها قدرة جيدة للكشف عن جميع العناصر والأيونات في عينات البنزين.

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CHAPTER ONE

Introduction and Basic Concepts

CHAPTER ONE

Introduction and Basic Concepts

1.1. Introduction:

Many scientific, military, medical and commercial laser applications have been developed since the invention of the laser in 1958. The coherency, high monochromaticity, and ability to reach extremely high powers are all properties which allow for these specialized applications [1].

Most types of laser are an inherently pure source of light; they emit near-monochromatic light with a very well defined range of wavelengths. By careful design of the laser components, the purity of the laser light (measured as the "linewidth") can be improved more than the purity of any other light source. This makes the laser a very useful source for spectroscopy. The high intensity of light that can be achieved in a small, well collimated beam can also be used to induce a nonlinear optical effect in a sample, which makes techniques such as Raman spectroscopy possible. Other spectroscopic techniques based on lasers can be used to make extremely sensitive detectors of various molecules, able to measure molecular concentrations in the parts-per-10^{12} (ppt) level. Due to the high power densities achievable by lasers, beam-induced atomic emission is possible: this technique is termed Laser induced breakdown spectroscopy [2].

From 1960 onwards, the increasing availability of intense, monochromatic laser sources provided a tremendous impetus to a wide range of spectroscopic investigations. The most immediately obvious application of early, essentially non-tunable, lasers was to all types of Raman spectroscopy in the gas, liquid or solid phase. Laser radiation is very much more intense, and the line width much smaller, than that from, for example, a mercury arc, which was commonly used as a Raman source before 1960. As a result, weaker Raman scattering can now be observed and higher resolution is obtainable.

For branches of spectroscopy other than Raman spectroscopy most laser sources may appear to have a great disadvantage, that of non-tunability. In regions of the spectrum, particularly the infrared where tunable lasers are not readily available, ways have been devised for tuning, that is, shifting, the atomic or molecular energy levels concerned until the transition being studied moves into coincidence with the laser radiation. This may be achieved by applying an electric field to the sample, and the technique is called laser Stark spectroscopy. The corresponding technique using a magnetic field is that of laser magnetic resonance (or laser Zeeman) spectroscopy [3].

A useful way of changing the wavelength of some lasers, for example the CO_2 infrared laser, is to use Isotopically substituted material in which the wavelengths of laser transitions are appreciably altered.

In regions of the spectrum where a tunable laser is available it may be possible to use it to obtain an absorption spectrum. This technique can be used with a diode laser to produce an infrared absorption spectrum. When electronic transitions are being studied, greater sensitivity is usually achieved by monitoring secondary processes which follow, and are directly related to, the absorption which has occurred. Such processes include fluorescence, dissociation, or predissociation, and, following the absorption of one or more additional photons, ionization. The spectrum resulting from monitoring these processes usually resembles the absorption spectrum very closely.

It may be apparent that, when lasers are used as spectroscopic sources, we can no longer think in terms of generally applicable experimental methods. A wide variety of ingenious techniques have been devised using laser sources [3].

1.2. Absorption and Emission of Radiation:

Atoms and molecules can exist only in certain energy states. The state of lowest energy is called the ground state; all other states have more energy than the ground state and are called excited states. Each excited state, of which there are many, has a fixed amount of energy over and above that of the ground state. Under ordinary conditions, almost all atoms and molecules are in their ground states when an atom contains the lowest amount of energy that is available to it, the atom is said to be in its "atomic ground state." If the atom contains additional energy over and above its ground state, it is said to be in an "excited atomic state"[4].

Three types of processes are possible for a two-level atomic system. Absorption, Stimulated emission, and spontaneous emission and the competition between them define the criteria for laser action.

1.2.1. Absorption:

Absorption occurs when a photon strikes an atom with just exactly the proper energy to induce an electronic transition between two energy states. This process reduces the lower level population and increases the upper level population [5]. Absorption of a photon will occur only when the quantum energy of the photon precisely matches the energy gap between the initial and final states; an electron jumps up to a higher energy level, this incoming photon excites the atomic system from a lower energy state into a higher energy state as shown in figure (1.1).

This indicates that the atoms absorb the incident energy at certain frequencies. In the interaction of radiation with matter, if there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, then the matter will be transparent to that radiation[6].

$$dN_1 = -B_{12}\rho(\nu_o)N_1 dt \qquad (1-1)$$

Where N_1 is population of atoms in ground state, N_2 population of atoms in excited state B_{12} is the Einstein coefficient of absorption and $\rho(\nu_o)$ is the spectral energy density of radiation at frequencies around ν_o. Absorption is only possible in the presence of a field; the absorption is a stimulated process.

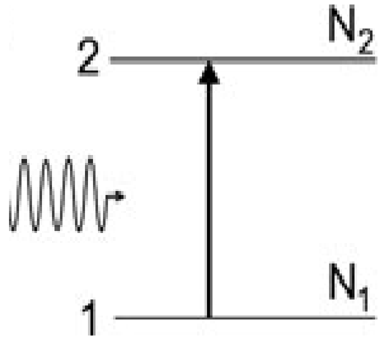

Figure (1.1) Stimulated Absorption

1.2.2. Spontaneous Emission:

Atoms don't like to stay in high energy states (this is dictated by the laws of thermodynamics), so after absorbing a photon and going to a higher energy state, they will spontaneously drop to a lower level without any outside stimulation as shown in figure (1.2). One possible result of dropping to a reduced energy state is the release of the excess energy (equaling the difference in the two energy levels) as a photon of light. Normally the average lifetime for spontaneous emissions by excited atoms before they drop to a lower energy level and emit a photon, is around 10^{-8} seconds (that is, the atom or molecule will usually take around 10^{-8} seconds before emitting the photon). Occasionally, however, there are states for which the lifetime is much longer, perhaps around 10^{-3} seconds. These states are called metastable [7].

$$dN_2 = -A_{21}N_2 dt \qquad (1-2)$$

Where A_{21} is the Einstein coefficient of spontaneous emission. The population of the upper level decays exponentially

$$N_2 = N_2(0)e^{-A_{21}t} = N_2(0)e^{-t/\tau_{sp}} \qquad (1-3)$$

N_2 (0) is the density of excited two-level atomic systems at t = 0 and τ_{sp} is the average lifetime of an excited two-level atomic system with respect to spontaneous emission (=spontaneous lifetimeτ_{sp}). We have the simple relation

$$A_{21} = 1/\tau_{sp} \qquad (1-4)$$

The Einstein coefficient A_{21} is equal to the reciprocal of the spontaneous lifetime.

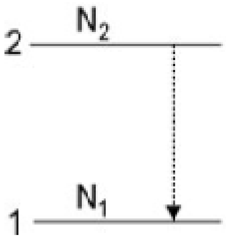

Figure (1.2) Spontaneous emission

1.2.3. Stimulated Emission:

Induced, or stimulated, emission is the inverse of the absorption process. An atom in the excited state is with an incoming photon having exactly the same energy as the transition that would spontaneously occur, the atom may be stimulated by the incoming photon to return to the lower state and simultaneously emit a photon at that same transition energy. We say that the incoming photon has stimulated the excited atom to relax to the lower state and emit a photon identical to the one stimulating it. The photon is the same in every sense: same frequency, phase, polarization and direction of propagation [7].

The laser works by the stimulated emission - one can imagine that stimulated emission can lead to more and more identical photons being released in the following way: Imagine we have an electron in an excited metastable state and it drops down to the ground state by emitting a photon. If this photon then travels through the material and meets another electron in the metastable excited state this will cause the electron to drop down to the lower energy level and another photon to be emitted. Now there are two photons of the same energy. If these photons then both move through the material and each interacts with another electron in a metastable state, this will result in them each causing an additional photon to be released, and i.e. from 2 photons we then get 4, and so on. This is how laser light is produced [5, 6].

The rate of $N_2$is:

$$dN_2 = -B_{21}\rho(\nu_o)N_2dt \qquad (1-5)$$

Where B_{21} is the Einstein coefficient of stimulated emission. The radiation created by stimulated emission has the same frequency, direction, polarization, and phase as the stimulating radiation as shown in figure (1.3).

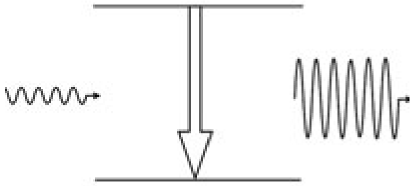

Figure (1.3) stimulated emission

1.3. Spectroscopy and Types of Interacting Materials:

1.3.1. Spectroscopy:

Spectroscopy is the study of the absorption and emission of light and other radiation by matter, as related to the dependence of these processes on the wavelength of the radiation. More recently, the definition has been expanded to include the study of the interactions between particles such as electrons, protons, and ions, as well as their interaction with other particles as a function of their collision energy. Spectroscopic analysis has been crucial in the development of the most fundamental theories in physics, including quantum mechanics, the special and general theories of relativity, and quantum electrodynamics. Spectroscopy, as applied to high-energy collisions, has been a key tool in developing scientific understanding not only of the electromagnetic force but also of the strong and weak nuclear forces [8].

Spectroscopic techniques have been applied in virtually all technical fields of science and technology. Radio-frequency spectroscopy of nuclei in a magnetic field has been employed in a medical technique called magnetic resonance imaging (MRI) to visualize the internal soft tissue of the body with unprecedented resolution. Microwave spectroscopy was used to discover the so-called three-degree blackbody radiation, the remnant of the big bang (*i.e.,* the primeval explosion) from which the universe is thought to have originated. The internal structure of the proton and neutron and the state of the early universe up to the first thousandth of a second of its existence is being unraveled with spectroscopic techniques utilizing high-energy particle accelerators. The constituents of distant stars, intergalactic molecules, and even the primordial abundance of the elements before the formation of the first stars can be determined by optical, radio, and X-ray spectroscopy. Optical spectroscopy is used routinely to identify the chemical composition of matter and to determine its physical structure.

Spectroscopic techniques are extremely sensitive. Single atoms and even different isotopes of the same atom can be detected among 10^{20} or more atoms of a different species. Trace amounts of pollutants or contaminants are often detected most effectively by spectroscopic techniques. Certain types of microwave, optical, and gamma-ray spectroscopy are capable of measuring infinitesimal frequency shifts in narrow spectroscopic lines. Frequency shifts as small as one part in 10^{15} of the frequency being measured can be observed with ultrahigh resolution laser techniques. Because of this sensitivity, the most accurate physical measurements have been frequency measurements [9, 2].

1.3.2. Types of Interacting Materials:

Spectroscopic studies are designed so that the radiant energy interacts with specific types of matter. Spectroscopy is used in physical and analytical chemistry because atoms and molecules have unique spectra. As a result, these spectra can be used to detect, identify and quantify information about the atoms and molecules [8, 10].

Atoms

Atomic spectroscopy was the first application of spectroscopy developed. Atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES) involve visible and ultraviolet light. These absorptions and emissions, often referred to as atomic spectral lines, are due to electronic transitions of outer shell electrons as they rise and fall from one electron orbit to another. Atoms also have distinct x-ray spectra that are attributable to the excitation of inner shell electrons to excited states.

Atoms of different elements have distinct spectra and therefore atomic spectroscopy allows for the identification and quantization of a sample's elemental composition. New elements were discovered by observing their emission spectra. Atomic absorption lines are observed in the solar spectrum and referred to as Fraunhofer lines after their discoverer. A comprehensive explanation of the hydrogen spectrum was an early success of quantum mechanics and explained the Lamb shift observed in the hydrogen spectrum led to the development of quantum electrodynamics [8, 10].

Modern implementations of atomic spectroscopy for studying visible and ultraviolet transitions include flame emission spectroscopy, inductively coupled plasma atomic emission spectroscopy, glow discharge spectroscopy, microwave induced plasma spectroscopy, laser spectroscopy and spark or arc emission spectroscopy. Techniques for studying x-ray spectra include X-ray spectroscopy and X-ray fluorescence (XRF).

Molecules

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states. Molecular spectra can be obtained due to electron spin states (electron paramagnetic resonance), molecular rotations, molecular vibration and electronic states. Rotations are collective motions of the atomic nuclei and typically lead to spectra in the microwave and millimeter-wave spectral regions; rotational spectroscopy and microwave spectroscopy are synonymous. Vibrations are relative motions of the atomic nuclei and are studied by both infrared and Raman spectroscopy. Electronic excitations are studied using visible and ultraviolet spectroscopy as well as fluorescence spectroscopy.

Studies in molecular spectroscopy led to the development of the first maser and contributed to the subsequent development of the laser [11].

Crystals and extended materials

The combination of atoms or molecules into crystals or other extended forms leads to the creation of additional energetic states. These states are numerous and therefore have a high density of states. This high density often makes the spectra weaker and less distinct, i.e., broader. For instance, blackbody radiation is due to the thermal motions of atoms and molecules within a material. Acoustic and mechanical responses are due to collective motions as well.

Pure crystals, though, can have distinct spectral transitions and the crystal arrangement also has an effect on the observed molecular spectra. The regular lattice structure of crystals also scatters x-rays, electrons or neutrons allowing for crystallographic studies.

Nuclei

Nuclei also have distinct energy states that are widely separated and lead to gamma ray spectra. Distinct nuclear spin states can have their energy separated by a magnetic field, and this allows for NMR spectroscopy [9].

1.4. Laser Spectroscopy:

Laser analysis based on optical detection methods is called laser spectroscopy. Spectroscopy involves stimulating a sample and then analyzing the resultant spectrum -- the range of electromagnetic radiation emitted or absorbed. Spectroscopy is so vital as an analytical tool [12].

Most spectroscopic methods are differentiated as either atomic or molecular based on whether or not they apply to atoms or molecules. Along with that distinction, they can be classified on the nature of their interaction:

1.4.1. Laser Absorption Spectroscopy:

Light transmitted through some medium (solid, liquid or gaseous) experiences attenuation due to scattering and absorption; the latter being the dominant loss contribution in many cases. Loss measurements can thus be used to deduct the concentration of a gas of interest with known absorption strength in a gas mixture. If local, in-situ values are desired, the gas sample is sucked into a gas cell and measured there. However, if a satellite measures the sunlight reflected from the earth, this also constitutes absorption spectroscopy, with the atmosphere between the earth and satellite being the gas sampled (remote sensing). The light attenuation for sufficiently small absorption is described by the Beer-Lambert-Law:

$$T = \frac{I}{I_0} = e^{-\alpha'\iota} = e^{-\sigma N} \qquad (1-6)$$

Where I is the intensity measured by the detector, $I_0$is the original intensity entering the gas cell, σ is the absorption cross section of the absorber (in cm^2 / moles) and N is the absorber's number density (in moles / cm^3). Those last two multiplied give the absorption coefficient α (α = σ · N, in 1 / cm) and L is the path length of the light-matter interaction (also sometimes called “absorption path length”) [13].

Absorption spectroscopy uses the range of the electromagnetic spectra in which a substance absorbs. This includes atomic absorption spectroscopy and various molecular techniques, such as: infrared, ultraviolet-visible and microwave spectroscopy [14].

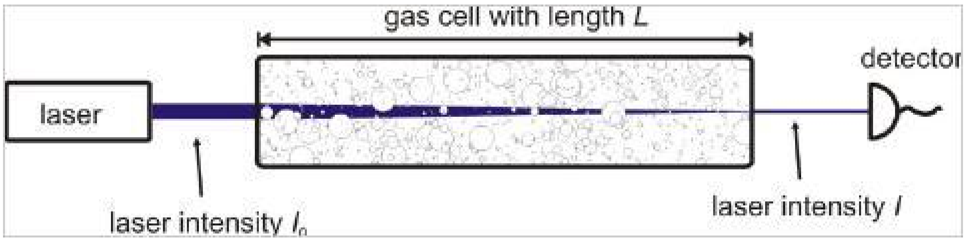

Figure (1.4) Laser Absorption Spectroscopy

1.4.2. Laser Emission Spectroscopy:

Laser Emission spectroscopy is the most common diagnostic technique used for the study of high energy levels or excited materials like hot materials and plasma characterization.

However the interpretation of the line emission spectra depends on equilibrium and modeling assumptions and relays as well on the knowledge of Stark widths and atomic rates [8, 10].

Additionally self-absorption of the lines can be an issue and result in incorrect determination of electron density values.

Emission spectroscopy uses the range of electromagnetic spectra in which a substance radiates (emits). The substance first must absorb energy. This energy can be from a variety of sources, which determines the name of the subsequent emission, like luminescence. Molecular luminescence techniques include Spectrofluorimetry [14].

1.4.3. Laser Scattering Spectroscopy:

Laser light scattering spectroscopy is based on the evaluation of the frequency shift of coherent light scattered by moving particles. This makes it particularly suitable for use in light guiding systems. It has been used in recent years to study the diffusive motions of macro-molecules in solution, bacterial movement. Laser light scattering spectroscopy is based on the properties of laser light: monochromaticity, coherence, and directionality [15].

Scattering spectroscopy measures the amount of light that a substance scatters at certain wavelengths, incident angles, and polarization angles. One of the most useful applications of light scattering spectroscopy is Raman spectroscopy [14].

1.4.4. Raman Spectroscopy:

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system [8]. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak in elastically scattered light from the intense Rayleigh scattered laser light. Historically, Raman spectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny-Turner (CT) monochromator, or FT (Fourier transform spectroscopy based), and CCD detectors.

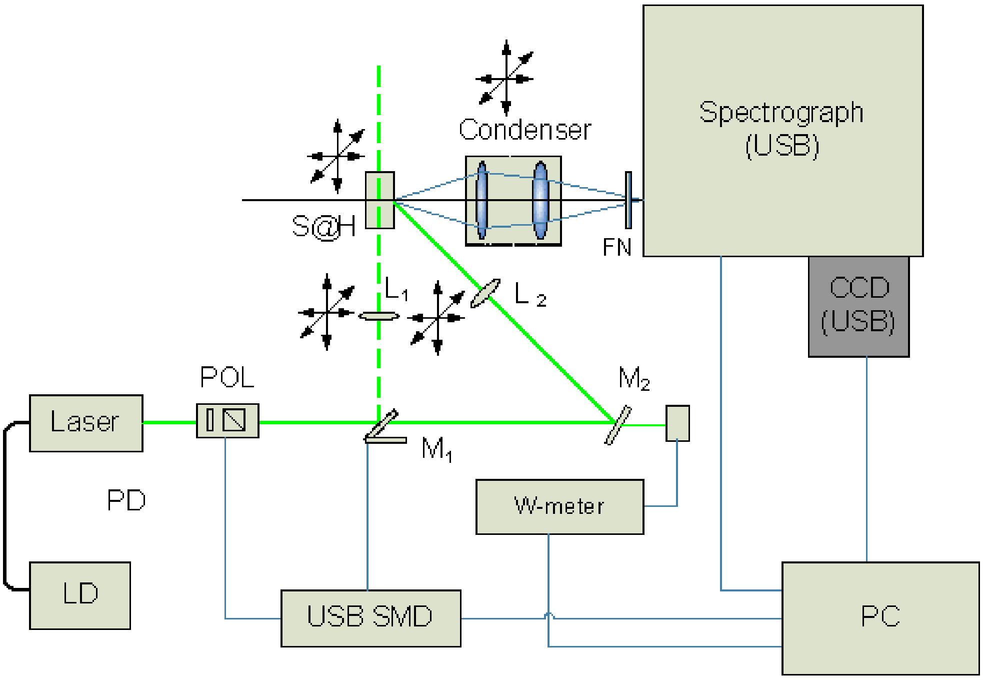

Figure (1.5) Raman Spectroscopy

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarized Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially offset Raman, and hyper Raman[8].

Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90 deg) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult than are infrared spectra [9, 10].

1.4.5. Laser Induced Fluorescence (LIF):

Laser induced fluorescence (LIF) is emitted from electronically excited levels that are populated by absorption of photons, typically in the ultraviolet and visible spectral region [16].

In this technique the laser beam is formed into a thin light sheet by a set of lenses, and this light sheet entering the observation volume. The fluorescence is captured by a collecting lens and imaged on to the detector surface; the data of the image is transferred from the camera to the control unit installed in a computer [17].

The emitted radiation is characteristic for the concentration and temperature of the regarded species as shown in Figure (1.5).

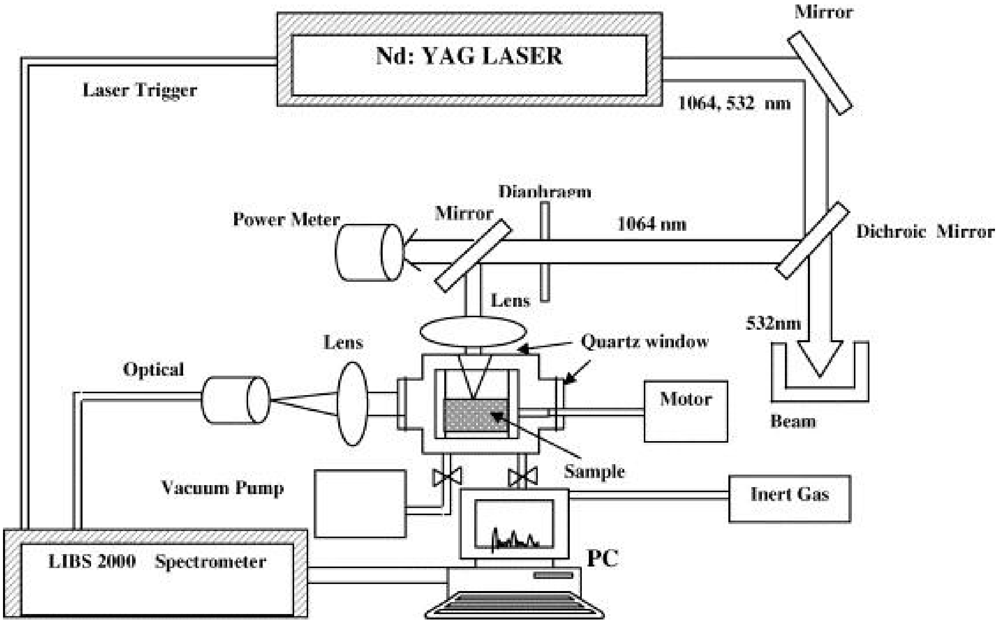

Figure (1.6) LIF Spectroscopy Setup

1.4.6. Light Detection and Ranging (LIDAR):

LIDAR was developed in the early 1960s, shortly after the invention of the laser, and combined laser’s focused imaging with radar’s ability to calculate distances by measuring the time for the signal to return. Its first applications were in meteorology, where it was used to measure clouds by the National Center for Atmospheric Research [18]. The general public became aware of the accuracy and usefulness of lidar systems in 1971 during the Apollo 15 mission, when astronauts used a laser altimeter to map the surface of the moon.

Lidar (also written LIDAR or LiDAR) is a remote sensing technology that measures distance by illuminating a target with a laser and analyzing the reflected light. The term "lidar" comes from combining the words light and radar [19].

Lidar is popularly used as a technology used to make high resolution maps, with applications in geomatics, archaeology, geography, geology, geomorphology, seismology, forestry, remote sensing, atmospheric physics,

[20] airborne laser swath mapping (ALSM), laser altimetry, and contour mapping.

Lidar uses ultraviolet, visible, or near infrared light to image objects and can be used with a wide range of targets, including non-metallic objects, rocks, rain, chemical compounds, aerosols, clouds and even single molecules [20]. A narrow laser beam can be used to map physical features with very high resolution.

Lidar has been used extensively for atmospheric research and meteorology. Downward-looking lidar instruments fitted to aircraft and satellites are used for surveying and mapping – a recent example being the U.S. Geological Survey Experimental Advanced Airborne Research Lidar [21]. In addition lidar has been identified by NASA as a key technology for enabling autonomous precision safe landing of future robotic and crewed lunar landing vehicles [22].

Wavelengths from about 10 micrometers to the UV (ca. 250 nm) are used to suit the target. Typically light is reflected via backscattering. Different types of scattering are used for different lidar applications; most common are Rayleigh scattering, Mie scattering, Raman scattering, and fluorescence. Based on different kinds of backscattering, the lidar can be accordingly called Rayleigh Lidar, Mie Lidar, Raman Lidar, Na/Fe/K Fluorescence Lidar, and so on [21]. Suitable combinations of wavelengths can allow for remote mapping of atmospheric contents by looking for wavelength-dependent changes in the intensity of the returned signal

There are several major components to a lidar system:

1. Laser — 600–1000 nm lasers are most common for non-scientific applications. They are inexpensive, but since they can be focused and easily absorbed by the eye, the maximum power is limited by the need

to make them eye-safe. Eye-safety is often a requirement for most applications. A common alternative, 1550 nm lasers, are eye-safe at much higher power levels since this wavelength is not focused by the eye, but the detector technology is less advanced and so these wavelengths are generally used at longer ranges and lower accuracies. They are also used for military applications as 1550 nm is not visible in night vision goggles, unlike the shorter 1000 nm infrared laser. Airborne topographic mapping lidars generally use 1064 nm diode pumped YAG lasers, while bathymetric systems generally use 532 nm frequency doubled diode pumped YAG lasers because 532 nm penetrates water with much less attenuation than does 1064 nm. Laser settings include the laser repetition rate (which controls the data collection speed). Pulse length is generally an attribute of the laser cavity length, the number of passes required through the gain material (YAG, YLF, etc.), and Q-switch speed. Better target resolution is achieved with shorter pulses, provided the lidar receiver detectors and electronics have sufficient bandwidth [21].

2. Scanner and optics — How fast images can be developed is also affected by the speed at which they are scanned. There are several options to scan the azimuth and elevation, including dual oscillating plane mirrors, a combination with a polygon mirror, a dual axis scanner (see Laser scanning). Optic choices affect the angular resolution and range that can be detected. A whole mirror or a beam splitter are options to collect a return signal.

3. Photodetector and receiver electronics — two main photodetector technologies are used in lidars: solid state photodetectors, such as silicon avalanche photodiodes, or photomultipliers. The sensitivity of

the receiver is another parameter that has to be balanced in a lidar design.

4. Position and navigation systems — Lidar sensors that are mounted on mobile platforms such as airplanes or satellites require instrumentation to determine the absolute position and orientation of the sensor. Such devices generally include a Global Positioning System receiver and an Inertial Measurement Unit (IMU).

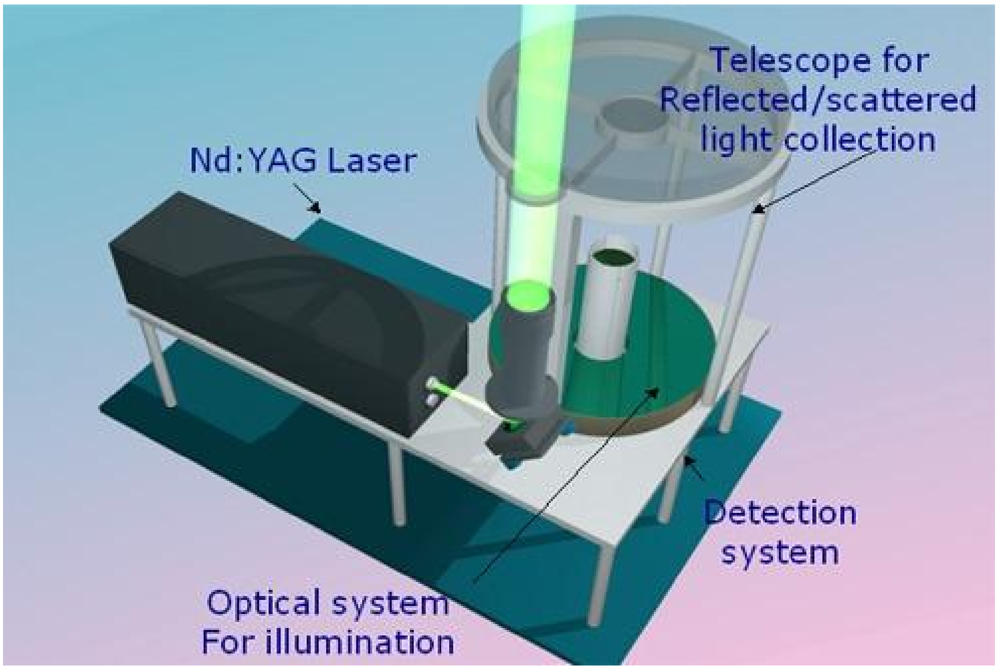

Figure (1.7) Light Detection and Ranging (LIDAR)

1.5. Laser-Induced Breakdown Spectroscopy (LIBS):

The Laser-Induced Breakdown Spectroscopy (LIBS) technique is based upon the analysis of the atomic emission lines generated close to the surface sample. The emission is observed once a laser pulse is focussed on the surface, where the very high field intensity initiates an avalanche ionisation of the sample elements, giving rise to the so-called breakdown effect. Spectral and time-resolved analyses of this emission are suitable to identify atomic species originally present at the sample surface.

Laser-induced breakdown spectroscopy, or LIBS, has been advancing significantly over the last decade. It can analyze solids, liquids and gases and can return results rapidly, with very little damage to the sample. Not only that, it can do its work from a distance, unlike some analytical tools that require samples being brought to a lab. For example, LIBS is being used to detect surface contaminants in a few nuclear reactors around the world. The laser in these systems is located several meters from the reactor surface and yet is still able to function effectively. These systems keep most of the instrumentation behind shielding material, with only a mirror and a lens (which is used to steer and focus the laser beam respectively) exposed to the nuclear radiation [23].

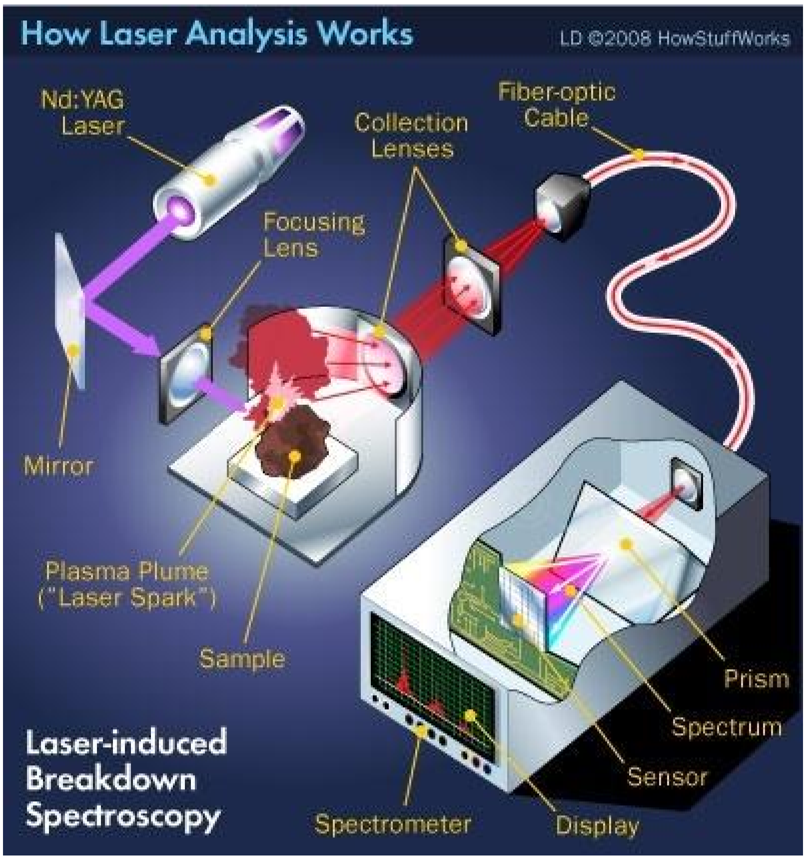

Figure (1.8) The Set-up for Laser-Induced Breakdown Spectroscopy

1.5.1. How LIBS Works:

Generally, LIBS systems use a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser at its fundamental wavelength of 1,064 nanometers, but many different lasers have been used. The laser doesn't blast the sample with a nonstop beam. Instead, it shoots pulses, with each pulse lasting about 5 to 20 nanoseconds.

The laser light passes through a lens, which focuses the energy onto the sample. Some systems work on the laboratory bench and accommodate small samples, maybe a few centimeters thick, placed inside a chamber. Other systems can be carried to a remote site and used to analyze larger objects. In either case, the more tightly focused the laser, the less energy is required to break down the sample. In fact, the laser pulses in LIBS typically carry energies of only 10 to 100 millijoules. As the particles are removed from the sample surface, they are ionized to form a small plume of plasma, what chemists call a "laser spark."

As the plasma plume expands, constituent atoms in the ionized gas become excited. Over just a few microseconds, the excited atoms began to relax, resulting in characteristic spectral emissions. The emitted light travels through a series of collecting lenses, which focus the light and deliver it to a fiber-optic system. The fiber-optic system carries the light to a spectrometer in order to be analyzed [24].

1.5.2. LIBS Advantages:

LIBS has several benefits. Because the sample requires no special preparation, the process is relatively simple and inexpensive. Not only that, LIBS can be used to determine the elemental composition of any sample, unlike certain techniques that are great at analyzing solids, but not liquids and gases. Even very hard materials are fair game because the lasers carry so much energy. But one of the greatest benefits of LIBS is its ability to provide information without destroying the sample. The laser removes less than a milligram of material, which is practically invisible [25].

1.5.3. LIBS Set-Up Components:

The main devices involved in a LIBS analysis are shown in Figure (1.9). A high-energy pulsed laser (usually in the nanosecond range) is directed at the sample [26]. This light energy vaporizes the sample and induces the plasma.

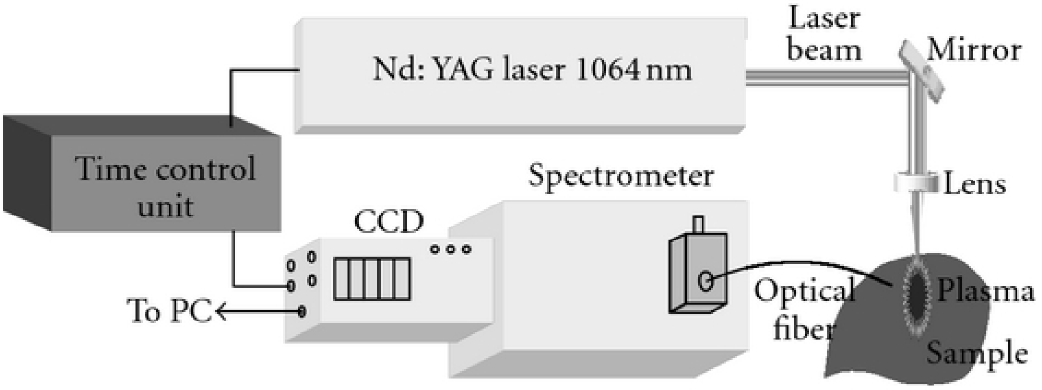

Figure (1.9) Typical LIBS Set-up

The spectrometer is in charge of diffracting the light collected, with a more or less complex optical system, in order to obtain the spectral signature. Then, the light is detected by using devices such as a photomultiplier tube (PMT), a photodiode array (PDA), or a charge-coupled device (CCD) [26, 28]. Finally, the acquired spectrum is processed by a computer for further analysis. LIBS set-ups need an accurate time control to avoid some plasma life stages and to improve the spectral signature. The choice of the laser combined with the set spectrometer-detector and time control, adapted to environmental conditions, can determine the success or failure of the experiment [26, 27, 28].

1.5.3.1. Laser Configurations for LIBS:

The main device of LIBS is the laser. It generates the energy to induce the plasma and mainly determines the plasma features. The main parameters related to the laser are the pulse time, the energy per pulse, the wavelength, and the number of pulses per burst [29]. Obviously, each application works better with a combination of these parameters. Nanosecond-pulsed lasers are the most common for LIBS. Therefore, the most of this section is related to this kind of laser.

The laser wavelength influence on LIBS can be explained from two points of view; the laser-material interaction (energy absorption) and the plasma development and properties (plasma-material interaction). When photon energy is higher than bond energy, photon ionization occurs and nonthermal effects are more important. For this reason, the plasma behavior depends on wavelength in nanosecond LIBS set-ups. In the same way, the optical penetration is shorter for UV lasers, providing higher laser energy per volume unit of material. In general, the shorter laser wavelength, the higher ablation rate and the lower elemental fractionation [30].

The plasma ignition and its properties depend of wavelength. The plasma initiation with nanosecond lasers is provoked by two processes; the first one is inverse Bremsstrahlung by which free electrons gain energy from the laser during collisions among atoms and ions. The second one is photoionization of excited species and excitation of ground atoms with high energies. Laser coupling is better with shorter wavelengths, but at the same time the threshold for plasma formation is higher. This is because inverse Bremsstrahlung is more favorable for IR wavelengths [31]. In contrast, for short wavelengths (between 266 and 157 nm) the photoionization mechanism is more important. For this reason, the shorter the wavelength in this range, the lower the flounce necessary (energy per unit area) to initiate ablation [32].

In addition, when inverse Bremsstrahlung occurs, part of the nanosecond laser beam reheats the plasma. This increases the plasma lifetime and intensity but also increases the background at the same time. Longer wavelengths increase inverse Bremsstrahlung plasma shielding, but reduce the ablation rate and increase elemental fractionation (elemental fractionation is the redistribution of elements between solid and liquid phases which modifies plasma emission) [33].

The most common laser used in LIBS is pulsed Nd:YAG . This kind of laser provides a compact, reliable, and easy way to produce plasmas in LIBS experiments. The fundamental mode of this laser is at 1064 nm and the pulse width is between 6 and 15ns. This laser can provide harmonics at 532, 355, and 266 nm, which are less powerful and have shorter time pulses (between 4 and 8 nm) [26, 28]. The fundamental and the first harmonic are the most common wavelengths used in LIBS. This harmonics can be useful to work with different wavelengths in the same environmental conditions, because a lot of Nd:YAG lasers can produce all of them. Other kinds of lasers can be used in LIBS, such as CO2 or excimer lasers to work in far IR or UV ranges, respectively. Lasers based on fiber or dye technology can reduce the pulse width if the user is attempting to work with picosecond or femtosecond pulses.

The energy parameters related with laser material interaction are fluence (energy per unit area) j/cm^2… and irradiance (energy per unit area and time) w/cm^2 ablation processes (melting, sublimation, erosion, explosion, etc.) have different flounce thresholds [34]. The effect of changes in the laser energy is related to laser wavelength and pulse time. Hence, it is difficult to analyze the energy effect alone. In general, the ablated mass and the ablation rate increase with laser energy.

The first stages of LIBS-induced plasma are dominated by the continuum emission. The time gate of decay of this continuum radiation change with a wide range of experimental parameters, such as laser wavelength and pulse time, ambient pressure or sample features. Besides, these experimental parameters fixes set the time periods of atomic emission, the most interesting stage of LIBS plasmas.

Plasma evolution using an IR (Nd:YAG) and a UV (excimer) lasers has been analyzed to discover differences induced by laser wavelength [35]. The plasma continuum emission stage was around 400 ns for UV laser and several microseconds for IR laser. Laser wavelength can affect the selection of delay time (gate delay) and integration time (gate window) and these parameters are essential to optimize the signal to background ratio. The analysis of plasma evolution for Zn and Cd in sand has been analyzed in other works, with an optimal gate delay of 0.5 μs and a gate window of 1.5 μs[36].

This analysis of optimal gate delay and window can be achieved optimizing the signal to background ratio and the repeatability of this parameter. For a Nd:YAG laser at the fundamental wavelength with power density of approximately 2 $G\,w/cm^2$ the best compromise between lower relative standard deviation (R.S.D.) and higher signal-to-background ratio was found at a delay of approximately 6 μs. The integration time was fixed at 15 μs [37].

There are different points of view to optimize the gate delay and window, and the big amount of experimental parameters involved in plasma evolution makes it difficult to recommend valid values for these parameters. The selection should be determined case by case in order to achieve a compromise between high-line intensity and low background. Briefly, for Nd:YAG lasers, both times for gate delay and gate window are in the order of microseconds but this values can change if another kind of results are sought.

1.5.3.2. Spectrometers and Detectors:

The spectrometer or spectrograph is a device which diffracts the light emitted by the plasma. There are different designs, such as Littrow, Paschen-Runge, Echelle, and Czerny-Turner [38, 39]. The Czerny-Turner spectrograph is the most common device in LIBS. This spectrograph is composed of an entrance slit, two mirrors, and a diffraction grating. The light comes through the slit and reaches the first mirror which collimates the light, directing it onto the grating. Light is reflected at different angles according to its wavelength. The second mirror focuses the light on the focal plane where the detector is placed.

In recent years, the Echelle spectrograph has been used more extensively [39]. The Echelle spectrograph uses a diffraction grating placed at a high angle, producing a large dispersion in a small wavelength range in each order. As the orders are spatially mixed, a prism is used to separate them. The orders are stacked vertically on the focal plane. For that reason, Echelle devices need a two-dimensional detector. Each vertical portion of the detector contains a part of the spectra and the software composes the whole spectrum.

Different kinds of detectors are used in LIBS, depending of the application. To measure light intensity without spectral decomposition, the photomultiplier tube (PMT) or avalanche photodiode (APD) can be used. On the other hand, for one-dimensional spatial information, the researcher can combine a spectrograph and a photodiode array (PDA) or an intensified photodiode array (IPDA) for time-resolved measurements. If two-dimensional spatial information is required, the most common devices are charge coupled devices (CCD) and intensified CCD (ICCD). A CCD detector provides less background signal, although ICCD improves the signal-to-noise ratio and is better for time-resolved detection using windows of a few nanoseconds [40]. Another problem related to ICCDs is the price, which is much higher than CCDs.

1.6. Literature Review:

In 2010 Al Muslet and A. M. Salih used laser induced breakdown spectroscopy to investigate the elements in some types of Sudanese gasoline. They found that, the (LIBS) technique is so accurate that the essential atoms forming the samples of gasoline (Hydrogen and Carbon) appeared with great amounts while other elements that were not essential (like Calcium, Helium, Mercury, Potassium, Krypton, Neon, Niobium, Scandium, Silicon, Thorium, Titanium, Vandite) appeared with very little amounts.

Also Al Muslet, J. J. Lasema and S. Y Mohamed in July 2012 identified of the constituents of some Sudanese crude oil and soil using (LIBS). The emission lines of different elements were identified in the region from 230 to 950nm.

Organic compounds showed specific spectral features including sequences of the CN violet system and C_2 swan system, and H, C, N and O atomic and ionic lines. The principle for identification of organic compounds was on their spectral features and on the integrated intensity ratios of the molecular (CN, C_2) and atomic (Hα, C_2).

The main objective of that work was to demonstrate that new developments in LIBS technique are able to provide reliable qualitative and quantitative analytical evaluation of several heavy metals in soils, with special focus on the element chromium (Cr), and with reference to the concentrations measured by conventional ICP spectroscopy. The preliminary qualitative LIBS analysis of five soil samples and one sewage sludge sample has allowed the detection of a number of elements including Al, Ca, Cr, Cu, Fe, Mg, Mn, Pb, Si, Ti, V and Zn. Of these, a quantitative analysis was also possible for the elements Cr, Cu, Pb, V and Zn based on the obtained linearity of the calibration curves constructed for each heavy metal, i.e., the proportionality between the intensity of the LIBS emission peaks and the concentration of each heavy metal in the sample measured by ICP.

R. Barbini, R Fantoni and H. J.L. Vander Steven in 2000 used laser induced breakdown spectroscopy technique in quantitive analyses of soil samples. A comparison of their results with other obtained in soil samples showed that the LIBS technique is promising for on line soil analyses of various elements, without any further calibration and without sample preparation. By this technique, element concentrations were measured within reasonable errors.

1.7. The Aim of Work:

This work aimed to investigate the elements in three different samples of Sudanese benzene using laser induced breakdown spectroscopy (LIBS) technique.

CHAPTER TWO

The Experimental Part

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The Experimental Part

2.1. Introduction:

This chapter demonstrates and explains the experimental setup, materials, instruments and experimental procedure that was used during this work to identify the elements in different types of benzene.

2.2. The Experimental Setup:

The experimental setup used in this work is shown in figure (2.1) and schematically are depicted in figure (2.2).

Figure (2.1) The Experimental Setup

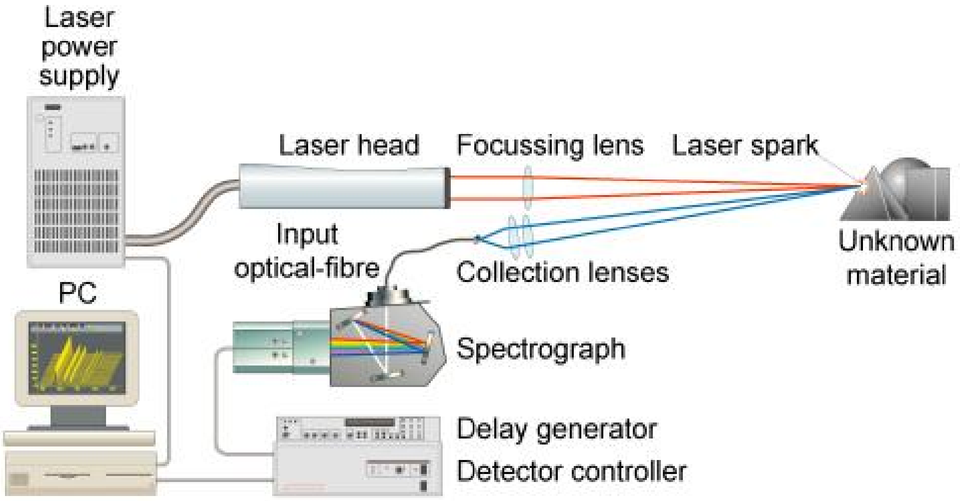


Figure (2.2) Schematic Representation of Used Setup

This setup was composed from the following equipments and tools:

2.2.1. The Laser:

Figure (2.3) shows Q-switched Nd-YAG laser was used here with two wavelengths: 1064 nm and 532 nm, this Q-switched Nd-YAG laser was used to deliver laser beam at 532nm, with 20 ns pulse duration and 2 Hz repetition rate. The pulse energy was 100 mj.

The excitation mechanism of this laser was completed through flashlamps; these flashlamps are fired to produce broadband light extending over the near UV, VIS and near IR spectral regions. A small percentage of this pumping light is absorbed by ions doped into the lasing material. Due to the electronic energy levels of the Nd ions in the laser rod, if the pumping flashlamp is sufficiently strong, a population inversion is established and a photon passing through the laser rod at the same frequency as the lasing transition will experience gain or amplification by inducing decay of some of the ions from the upper to the lower state [41]. Table (2.1) shows the Parameters of Q-switched ND: YAG Laser HS-220.

Figure (2.3) Laser Treatment Instrument »Q-switched ND: YAG Laser » Q-switched ND: YAG Laser HS-220

Table (2.1): Parameters of Q-switched Nd: YAG Laser HS-220:

Model	HS-220
Wavelength	1064 nm& 532 nm
Cooling system	Air & water cooling circulation
Spot size	(2-5) mm.
Pulse energy	1064nm (max1000mj) &532nm (max 500mj).
Pulse duration	More than 10 ns
Repetition rate	(1-5) Hz adjustable
Operation interface	6” dual color LCD
Power	400 W
Working period	Continuously working for 1~2 hours.
Power supply	100/110V, 50~60 Hz OR 230~260 V, 50~60 Hz.
Dimension	38 cm * 36 cm * 28 cm (L*W*H)

2.2.2. The Spectrometer:

To record the emission spectra, a spectrometer type was used. The Ocean Optics USB4000 Spectrometer is designed from the USB2000 Spectrometer to include an advanced detector and powerful high-speed electronics to provide both an unusually high spectral response and high optical resolution in a single package the result is a compact, flexible system, with no moving parts, that's easily integrated as an OEM component.

Figure (2.4) displays the spectrometer used in this work. It was model USB4000-UV/VIS, with dimensions (in nm scale):89.1 × 63.3 × 34.4, weigh: 190 grams. It was from ocean optics with the following specifications: a 16-bit A/D, four triggering options, a dark-level correction during temperature changes, and a 22-pin connector with eight users' programmable GPIOs. The USB4000 interfaces to computer with windows operating system. The USB4000 is responsive from 200-850nm and it can be configured with various ocean Optics Optical bench accessories, light sources and sampling optics to create application specific system for thousands of absorbance, reflection and emission applications.

Figure (2.4) USB4000 Miniature Fiber Optic Spectrometer

The USB4000 spectrometer is distinguished by its enhanced electronics: 16-bit A/D resolution with auto nulling feature (an enhanced electrical dark-signal correction); EEPROM storage of calibration coefficients for simple spectrometer start-up; 8 programmable GGPIO signals for controlling peripheral devices; and an electronic shutter for spectrometer integration times as fast as 3.8 milliseconds, a handy feature to prevent detector saturation. In addition, the USB4000 has signal to noise of 300:1 and optical resolution (FWHM) ranging from 0.03-8.4 nm (depending on the grating and entrance aperture selection). The detector is Toshiba TCD1304AP linear CCD array detector range: (200-850) nm, with 3648 pixels of size ($8\,\mu m \times 200\ \ \mu m$) and pixel well depth about100,000 electrons with sensitivity: 130photons/count at 400 nm; 60photons/count at 600 nm. The grating of the spectrometer has 600 lines blazed at 300 nm.

The USB4000 interfaces acomputer via USB 2 Data unique to each spectrometer and is programmed into a memory chip on the USB4000; spectra suite spectroscopy operating software reads these values for easy setup and hot swapping among computers, whether they run on Linux. When connected to a computer via USB, the USB4000 draws its power from the computer. Table (2.2) shows the features of USB4000 Miniature Fiber Optic Spectrometer [42].

Table (2.2): Features of USB4000 Miniature Fiber Optic Spectrometer

Features	Details
TCD1304AP Detector	High-sensitivity detector Readout rate: 1MHz Shutter mode
Responsive	from 200 to 1100 nm, specific range and resolution depends on your grating and entrance slit choices

A wide variety of optics available	14 gratings 6 slit widths 3 detector coatings 6 optical filters
Integration times	from 10µs*to 10seconds
Onboard Pulse Generator	2 programmable strobe signals for triggering other devices Software control of nearly all pulse parameters Onboard GPIO –8user-programmable digital I/O
EEPROM storage for	Wavelength Calibration Coefficients Linearity Correction Coefficients Absolute Irradiance Calibration (optional)
power consumption	only 250 mA @ 5 VDC

The USB4000 Spectrometer Components:

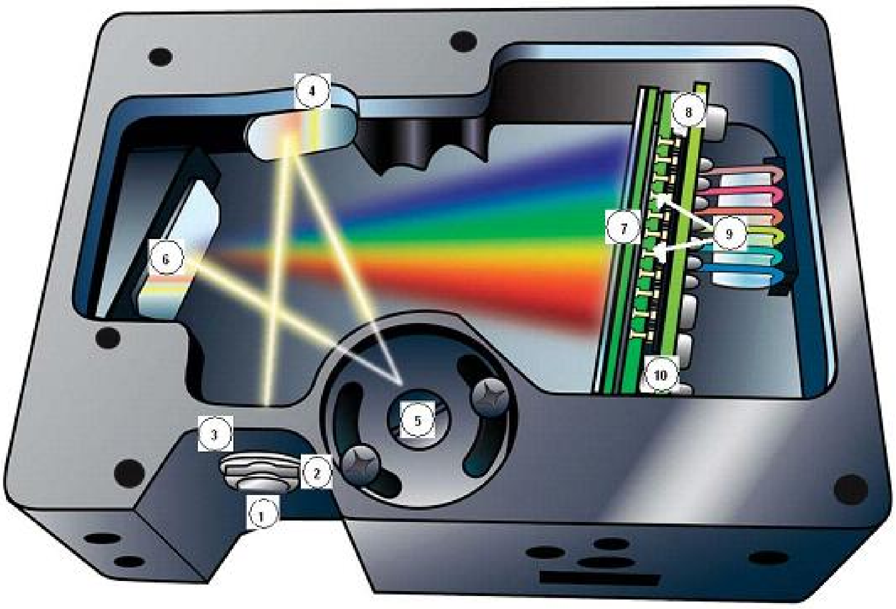


Figure (2.5): USB4000 Spectrometer with Components

Ocean Optics permanently secures all components in the USB4000 at the time of manufacture.

- SMA 905 Connector Secures: the input fiber to the spectrometer. Light from the input fiber enters the optical bench through this connector.
- SlitA dark piece of material containing a rectangular aperture, which is mounted directly behind the SMA Connector. The size of the aperture (from 5 µm to 200 µm) regulates the amount of light that enters the optical bench and controls spectral resolution.
- You can also use the USB4000 without a Slit. In this configuration, the diameter of the fiber connected to the USB4000 determines the size of the entrance aperture. Only Ocean Optics technicians can change the Slit.
- Filter Restricts optical radiation topre-determined wavelength regions. Light passes through the Filter before entering the optical bench. Both

band pass and long pass filters are available to restrict radiation to certain wavelength regions.

- Collimating Mirror Focuses light entering the optical bench towards the Grating of the spectrometer.
- Specify standard orSAG+.Light enter the spectrometer, passes through the SMA Connector, Slit, and Filter, and then reflects off the Collimating Mirror onto the Grating.
- Grating Diffract slight from the Collimating Mirror and directs the diffracted light onto the Focusing Mirror. Gratings are available in different groove densities, allowing you to specify wavelength coverage and resolution in the spectrometer.
- Focusing Mirror Receives light reflected from the Grating and focuses first-order spectra onto the detector plane.
- L4 Detector Collection Lens An optional component that attaches to the Detector to increase light-collection efficiency. It focuses light from a tall slit onto the shorter detector elements. The L4 detector collection lens should be used with large diameter slits or in applications with low light levels. It also improves efficiency by reducing the effects of stray light.
- Detector (UV or VIS) Collects the light received from the Focusing Mirror or L4 Detector Collection Lens and converts the optical signal to a digital signal. Each pixel on the detector responds to the wavelength of light that strikes it, creating a digital response. The spectrometer then transmits the digital signal to the Spectra Suite application.
- OFLV Filters: OFLV Variable Long pass Order-sorting Filters block second- and third-order light. These filters are optional.

- UV4 Detector Upgrade: The detector’s standard window is replaced with a quartz window to enhance spectrometer performance (<340 nm). This upgrade is optional [43].

2.2.3. Optical Fiber:

The optical fiber used to collect spectra was supplied by Ocean Optics. It is type UV – VIS model Qp600-2-UV-BX 600 μm diameter and two meter length silica core. Surrounding the core is a doped-fluorine silica cladding. A buffer material is then applied. A buffer coats the core and cladding, strengthens the fiber and reduces stray light even further. In most assemblies polyimide is used as the buffer; other assemblies use aluminum or acrylate. Then a jacketing is applied over the, cladding and buffer to protect the fiber and provide strain relief [44].

Precision SMA 905 connectors terminate the assembly and are precisely aligned to the spectrometer's slit to ensure concentricity of the fiber.

Finally, captive end caps protect the fiber tips against scratches and contaminants.

2.2.4. Software:

The software (Spectra Suite) used in this work was supplied from Ocean Optics and it is a completely modular, Java-based spectroscopy software platform that operates on windows, Macintosh and Linux operating systems.

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. Using Spectra Suite, one can combine data from multiple sources for applications that include upwelling /down welling measurements, dual-beam referencing and process monitoring [45].

2.3. The Materials:

The Materials used in this work as samples were three types of benzene. It was collected from different stations.

Benzene is an organic chemical compound with the molecular formula C_6H_6. Its molecule is composed of 6 carbon atoms joined in a ring, with 1 hydrogen atom attached to each carbon atom. Because its molecules contain only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.

Benzene is a natural constituent of crude oil, and is one of the most elementary petrochemicals. Benzene is an aromatic hydrocarbon and the second [*n*]-annulene ([6]-annulene), a cyclic hydrocarbon with a continuous pi bond. It is sometimes abbreviated Ph–H. Benzene is a colorless and highly flammable liquid with a sweet smell. It is mainly used as a precursor to heavy chemicals, such as ethyl benzene and cumene, which are produced on a billion kilogram scale. Because it has a high octane number, it is an important component of gasoline, composing a few percent of its mass. Most non-industrial applications have been limited by benzene's carcinogenicity as shown Figure (2.7).

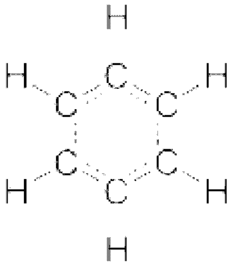


Figure (2.6) Ring Formula of Benzene

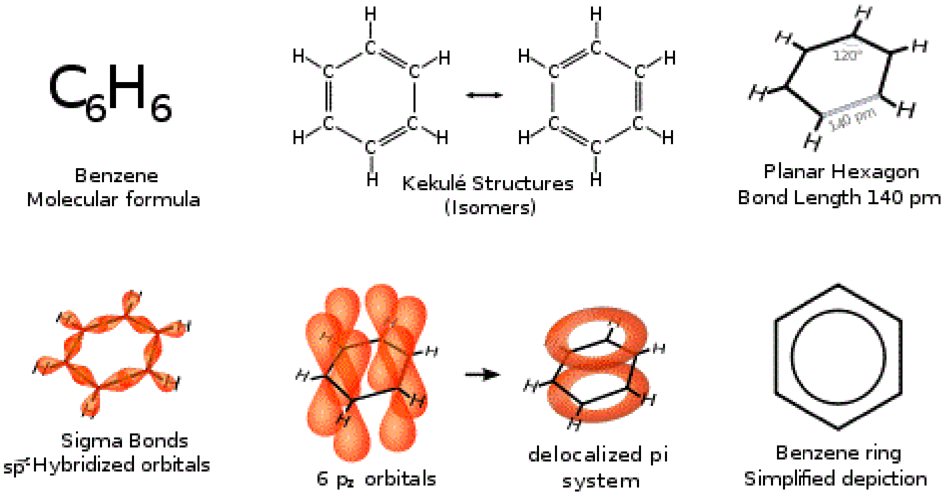
The empirical formula for benzene was long known, but it's highly polyunsaturated structure, with just one hydrogen atom for each carbon atom, was challenging to determine. Archibald Scott Couper in 1858 and Joseph Loschmidt in 1861 [46] suggested possible structures that contained multiple.

double bonds or multiple rings, but too little evidence was then available to help chemists decide on any particular structure.

In 1865, the German chemist Friedrich August Kekulé published a paper in French (for he was then teaching in Francophone Belgium) suggesting that the structure contained a six-membered ring of carbon atoms with alternating single and double bonds. The next year he published a much longer paper in German on the same subject [47, 48]. Kekulé used evidence that had accumulated in the intervening years—namely, that there always appeared to be only one isomer of any monoderivative of benzene, and that there always appeared to be exactly three isomers of every diderivative—now understood to correspond to the ortho, meta, and Para patterns of arene substitution—to argue in support of his proposed structure. Kekulé's symmetrical ring could explain these curious facts, as well as benzene's 1:1 carbon-hydrogen ratio [49].

2.3.1. Benzene Structure:

Benzene represents a special problem in that, to account for the bond lengths quantitatively, there must either be electron delocalization (MO theory) or a spin coupling of the p-orbital’s (VB theory) [50].



Benzene
Molecular formula

Kekulé Structures
(Isomers)

Planar Hexagon
Bond Length 140 pm

Sigma Bonds
sp^2-Hybridized orbitals

6 p_z orbitals

delocalized pi
system

Benzene ring
Simplified depiction

Figure (2.7) The Various Representations of Benzene

X-ray diffraction shows that all of six carbon-carbon bonds in benzene are of the same length of 140 picometres (pm). The C–C bond lengths are greater than a double bond (135 pm) but shorter than a single bond (147 pm). This intermediate distance is consistent with electron delocalization: the electrons for C–C bonding are distributed equally between each of the six carbon atoms. Benzene has 8 hydrogen atoms fewer than the corresponding parent alkane, hexane. The molecule is planar [51]. The MO description involves the formation of three delocalized π orbital's spanning all six carbon atoms, while in VB theory the aromatic properties of benzene originate from spin coupling of all six π orbital's [52, 53]. It is likely that this stability contributes to the peculiar molecular and chemical properties known as aromaticity. To indicate the delocalized nature of the bonding, benzene is often depicted with a circle inside a hexagonal arrangement of carbon atoms [54, 55].

2.3.2. Physical Properties

The chemical formula for benzene isC_6H_6, and it has a molecular weight of 78.11 g/mol. 4) Benzene occurs as a volatile, colorless, highly flammable liquid that dissolves easily in water.

Benzene has a sweet odor with an ASTDR reported odor threshold of 1.5 ppm (5 mg/m^3).

The vapor pressure for benzene is 95.2 mm Hg at 25 °C, and it has a log octanol/water partition coefficient.

2.3.3. Benzene Purity

Provided is a reforming process for producing a high purity benzene product using a non-acidic zeolitic catalyst. The high purity benzene is extracted from a light fraction of reformate that has less than 500 ppm by weight toluene. Generally, a hydrocarbon feed is reformed in a reformer under reforming conditions in the presence of a non-acidic catalyst to produce reformate. That reformate is separated into a light fraction and a heavy fraction. The extraction unit, preferably an extractive distillation unit, is then used to separate the light fraction into an aromatic extract stream and a nonaromatic raffinate stream.

Table (2.3) Benzene Product Specification:

Parameter	Unit	Specification
Benzene Purity	Wt%	99.95 min
Appearance	-	Clear, colourless liquid, free of sediments or Haze
Colour	Pt/Co	10 max
Bromine Index	mg/100g	10 max
Solidification point	C^0	5.45 min
Distillation range 1 to 96%	C^0	
Water	-	No free water
Moisture	Wt ppm	300 max.
Acid Wash Colour	-	1 max
Toluene	Wt ppm	200 max
Non Aromatics	Wt ppm	400 max
Thiophene	Wt ppm	0.6 max
Total Sulphur	Wt ppm	1 max
Total Chlorine (as chlorides)	Wt ppm	3 max
Total Nitrogen	Wt ppm	0.8 max

Benzene specifications are based on ASTM test methods; the key tests are:

- Solidification temperature
- Relative density

- Color
- Boiling range
- Acidity and residual sulfur
- Non-aromatics content

2.4. The Experimental procedure:

The Experimental procedure was done as follows:

- The setup was arranged as shown in figure (2.1).
- The laser pulse energy ($100\,mj$) was adjusted by adjusting the flash lamp voltage in order to obtain sufficient peak power need to form plasma.
- Then the spectrometer was connected to the PC through USB cable and the program spectra suit was launched.
- The desired parameters (integration time, scans to average, and boxcar width) were set to ensure accurate data.
- The different samples of benzene get from three different stations.
- A laser pulse was fired in the cell (a plate of glass), the without sample and the LIBS spectrum was recorded and saved as background that would be subtracted when getting the sample spectrum. This procedure was so important because the flash lamp of the laser emits radiation contain UV/VIS with intensity often higher than the emission signal of the sample under testing.
- Before starting the sample acquisition, the optical fiber terminal was aligned during laser firing till maximum intensity was collected and appeared on the screen. This was done to enhance signal to noise ratio.
- After that the sample was put in the cell and a pulse from the laser was fired and the emission spectrum of the plasma was recorded.

- The sample spectrum was processed by subtracting the background.
- By referring to the atomic spectra database the atoms and ions in the sample were identified.
- The same above procedure was followed for all samples.
- A comparison was done between the samples contents.

CHAPTER THREE

Results and Discussion

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Results and Discussion

3 - 1 Introduction:

In this chapter the results of elements investigation in three types of benzene, using laser induced breakdown spectroscopy (LIBS), are presented and discussed. The emission spectra of the three samples were analyzed and discussed. Comparison between the three samples constituents was done. This chapter contains also the conclusions and the suggested work for future studies.

3 - 2 LIBS Results:

The LIBS emission spectra for the three benzene samples were collected and analyzed using the atomic spectral database (ASD). The obtained results are as follows:

3 – 2 – 1 Sample No. 1:

Figure (3-1) shows the LIBS emission spectrum of the benzene (sample No.1). Table (3-1) lists sample, the emitted wavelengths, and their relative intensities elements.

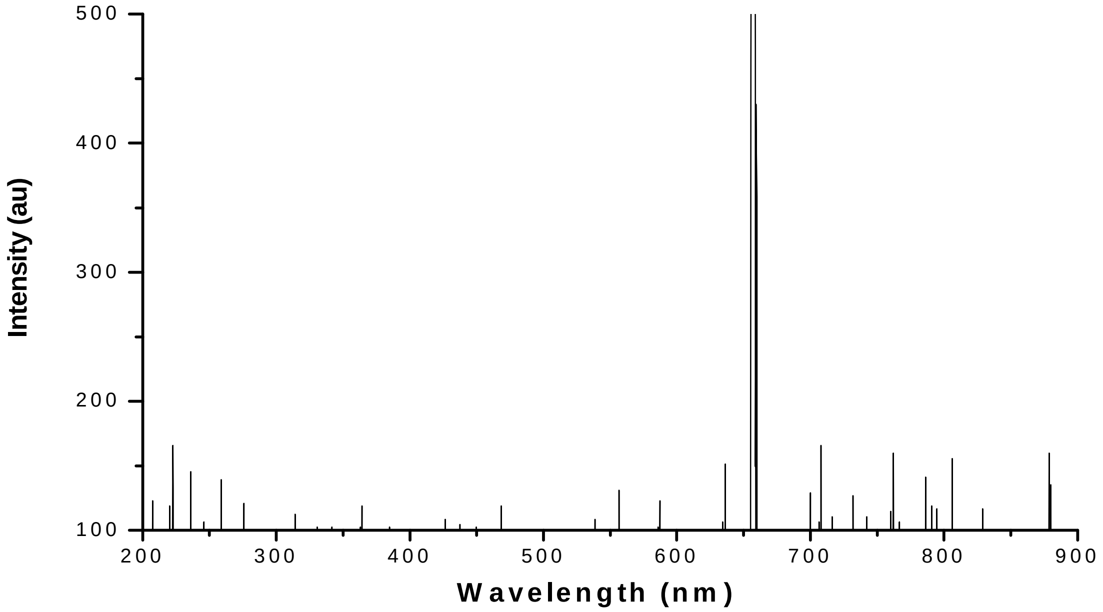

Figure (3-1): LIBS Spectrum of Benzene Sample No. 1

Table (3.1): Analysis of LIBS Emission Spectrum of Sample No 1

Wavelength (*nm)*	**Intensity (*a.u*)**	**Element**
210.39	124.719101	C IV
221.83	167.41573	C III
224.80	167.41573	W I
238.80	147.191011	Pb I
248.13	108.314607	Be I
260.48	146.516854	C II
278.56	121.797753	Co II
316.18	113.707865	C III
366.13	127.191011	H I
387.66	104.044944	C II
428.92	109.438202	Ti III
439.73	106.741573	Ti IV
471.91	120.449438	Zr I
541.84	109.662921	Kr II

559.68	133.033708	Si III
590.08	124.494382	Kr II
638.37	153.483146	Fe II
703.00	130.11236	Ni I
710.01	167.191011	C I
719.09	112.359551	Hg I
720.22	112.134831	C I
735.21	128.764045	Ti I
743.95	112.259551	Ag II
763.86	161.797753	B II
769.20	142.47191	C I
789.00	120.449438	S I
794.30	117.752809	O I
797.77	157.752809	Sc I
808.60	117.752809	La I
831.42	161.797753	H I
882.04	108.089888	O I

3 – 2 – 2 Sample No. 2:

Figure (3-2) shows the LIBS emission spectra of the benzene (sample No.2). Table (3-2) lists sample, the emitted wavelengths and their intensities.

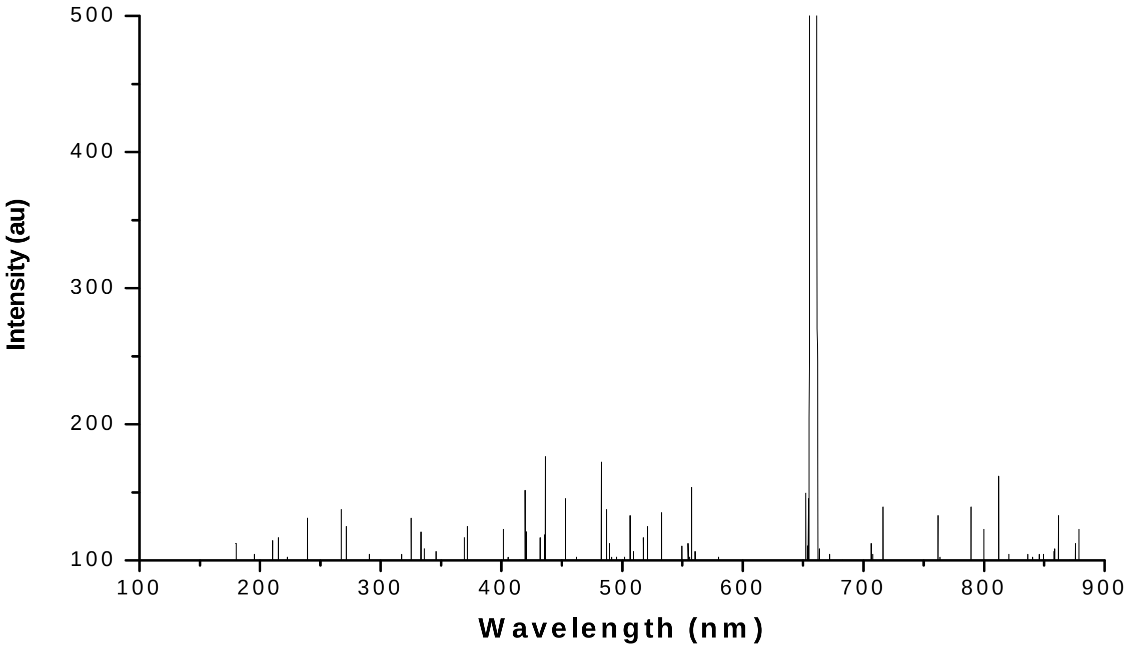

Figure (3-2): LIBS Spectrum of Benzene Sample No.2:

Table (3-2): Analysis of Emission Spectrum of Sample No 2

Wavelength (*nm*)	**Intensity (*a.u*)**	**Element**
180.94	113.707865	Mn II
195.31	106.741573	Ne III
209.69	116.404494	Zn I
215.72	117.752809	Ne IV
240.44	113.033708	C IV
266.86	138.426966	S II
271.20	124.719101	Eu III
291.59	105.393258	Fe I
318.35	105.393258	C II
326.36	131.685393	Ti II
334.72	120.674157	Xe II
346.76	106.741573	Ti I
371.50	124.719101	O III

402.25	123.370787	Tm I
420.63	152.134831	Mn II
432.67	116.404494	Fe I
437.13	176.853933	C I
453.40	145.393258	Y I
483.82	172.808989	Ti III
488.17	137.078652	Cd II
506.19	133.033708	Kr II
520.93	124.719101	Zr I
532.96	135.730337	O I
549.34	111.011236	Fe I
557.71	153.483146	Eu I
672.45	105.617978	C II
707.14	112.359551	W I
717.17	139.775281	Ti III
762.30	133.033708	Fe I
789.04	139.775281	S I
799.07	123.370787	Kr I
811.44	161.797753	La III
821.80	105.393258	Gd I
835.90	105.393258	H I
846.70	105.393258	H I
850.24	105.393258	H I
858.597	108.089888	Cl I
862.60	133.033708	W I
877.03	112.359551	Cd II
878.98	123.370787	Ge I

3 – 2 – 3 Sample No. 3:

Figure (3-3) shows the LIBS emission spectrum of the benzene (sample No.3). Table (3-3) lists sample, the emitted wavelengths, and their relative intensities elements.

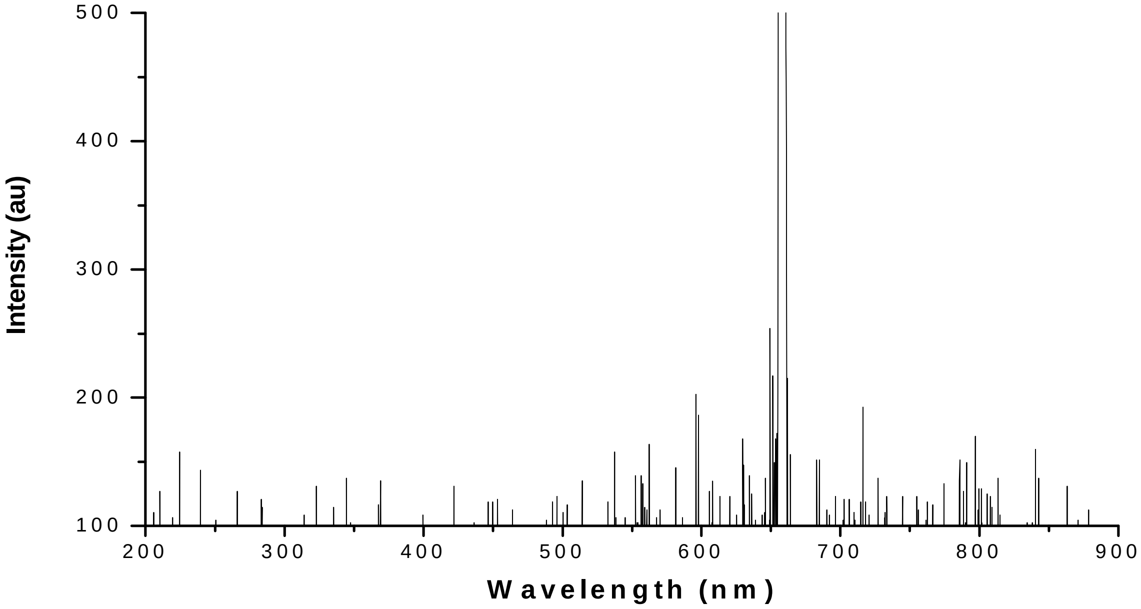

Figure (3.3): LIBS Spectrum of Benzene Sample No.3:

Table (3.3): Analysis of Emission Spectrum of Sample No.3:

Wavelength (*nm*)	**Intensity (*a.u*)**	**Element**
206.89	111.011236	C VI
210.39	127.415730	C VI
224.22	106.741573	Fe II
224.73	157.752809	W III
240.82	144.044944	Ar II
251.64	105.393258	Fe II
265.97	127.415730	Si II
283.82	120.674157	Fe II

314.24	108.314607	Tm I
323.31	131.460674	S III
335.89	115.05618	Hf I
344.66	137.078652	Hg I
369.71	135.730337	H I
400.24	108.314607	Ti I
423.32	131.685393	O I
446.75	119.101124	Ce II
450.73	119.101124	S I
454.06	120.449438	Fe I
464.89	112.359551	Ne II
493.20	119.101124	C I
497.06	123.370787	W I
500.60	111.011236	Si I
505.21	116.404494	C I
514.92	135.730337	Fe II
532.77	119.101124	N II
538.03	157.752809	C I
545.34	106.741573	Gd I
552.65	139.775281	Mo I
557.92	139.775281	Xe I
563.19	164.494382	W I
570.53	112.359551	Ti I
583.07	145.168538	V I
586.60	106.741573	W I
597.42	203.146067	Hf I
607.95	135.730337	Mo I
613.50	123.370787	V I

620.55	1230370787	C III
631.36	168.539326	Ne I
634.85	139.775281	F I
685.18	159.101124	Fe II
690.42	112.359551	Kr I
697.44	123.370787	Ti II
703.00	120.674157	Ni I
706.51	120.674157	He I
717.33	193.258427	W I
727.87	137.078652	Si III
733.45	123.370787	Nd I
746.00	123.370787	Ti III
754.78	123.370787	Fe I
763.83	119.101124	Ti I
767.40	116.404494	Hg I
774.68	132.808989	Kr I
787.35	152.134831	O III
792.52	149.438202	Fe II
797.83	170.11236	Ti II
813.90	137.078652	Fe II
841.33	160.449438	H I
864.26	131.685393	Eu I
871.26	105.393258	Co II
880.38	112.359551	Ar II

The spectra of the samples show that atoms (C and H) that form the benzene appeared with different amounts for each sample, There were also common relatively large amounts of other elements including (Fe, Ti, W, S and O) found in all three samples with different amounts as showed in table (3.4). The Iron was found with so little amount in sample 1 while samples 2 and 3 contained larger amounts of Fe, also Tungsten was found in large amounts in sample 3 while it appeared with very little amounts in samples 2 and 3. Titanium was found with a large amount in sample 3 whereas it appeared with large amount in sample 1 and with a very little amount in sample 2. The oxygen and Sulphur were found with nearly equal amounts in all the three samples.

The appearance of Oxygen is due to that the experiments were done in the atmosphere which is rich with Oxygen.

Also the appearance of Tungsten is due to tiny function of the background of laser lamp intensity that was not stored due to the change in its intensity.

Carbon and Hydrogen atoms were found also with different amounts in each sample, as benzene is hydrogen compound with chemical formulas typically between C_6H_6 and $C_{12}H_{26}$with average compound C_8H_{18}, it is clear that there is limited ratio of hydrogen to carbon.

These ratios determine the octane rating which is the measure of resistance of petroleum to engine knocking that damage it quite quickly.

Also there were relatively small amounts of neutral atoms which are not common for the three samples including (Pb , Be , Zr , Ni, Hg, Ti, Sc, La, Zn, Tm, Y, Eu, Kr, Gd, Cl, Ge, Hf, Mo, Xe, V, Mo, Ne, He and Nd). This depicts that the crude oil which the sample obtained from were brought from various fields and different refinery techniques were used to get benzene, it's also may be due to the added compounds in order to enhance the benzene quality.

Table (3.4) Comparison between the elements in the three samples:

Element	**Sample No.1 Intensity (a.u)**	**Sample No.2 Intensity (a.u)**	**Sample No.3 Intensity (a.u)**
C	421.744	176.853	395.258
H	288.988	316.179	296.179
Fe	153.483	465.846	383.595
Ti	128.764	106.741	339.775
Hg	112.359	0	253.483
Kr	0	123.370	245.168
Eu	0	153.483	131.685
Nd	0	0	123.370
Ni	130.112	0	120.674
He	0	0	120.674
W	167.415	133.033	394.606
Ne	0	0	168.539
Hf	0	0	318.202
Mo	0	0	275.505
V	0	0	268.539
Xe	0	0	139.775
Gd	0	105.393	106.741
Si	0	0	111.011
S	120.449	139.775	119.101
O	108.089	135.730	131.685
Tm	0	123.370	108.314
Ge	0	123.370	0
Cl	0	108.089	0
Zr	120.449	124.719	0
Y	0	145.393	0

Zn	0	116.404	0
Sc	157.752	0	0
La	117.752	0	0
Pb	147.191	0	0
Be	108.314	0	0
F	0	0	139.775

Beside neutral atoms, ions of different amounts and ionization stages also were found as shown in table (3.5). All these ions may not present in the samples originally, where some of these ions are produced due to the ionization of neutral atoms by the laser irradiance.

Table (3.5) Comparison between ions in the three samples:

Ion	**Sample No.1 Intensity (a.u)**	**Sample No.2 Intensity (a.u)**	**Sample No.3 Intensity (a.u)**
C IV	124.719	113.033	238.426
C III	281.123	0	123.370
Co II	121.797	0	105.393
C II	250.561	211.011	0
Ti III	109.438	312.584	123.370
Ti IV	106.741	0	0
Kr II	234.157	133.033	0
Si III	133.033	0	137.078
Ne IV	0	117.752	0
Fe II	0	0	659.325
Ag II	112.259	0	0
B II	161.797	0	0
Mn II	0	265.842	0
Ne III	0	106.741	0

S II	0	138.426	0
Eu III	0	124.719	0
Ti II	0	131.685	293.483
Xe II	0	120.674	0
O III	0	124.719	152.134
Cd II	0	249.438	0
La III	0	161.797	0
W III	0	0	157.752
Ar II	0	0	256.404
Si II	0	0	127.415
S III	0	0	131.460
Ce II	0	0	119.101
Ne II	0	0	112.359
N II	0	0	119.101

3.3. Conclusions:

From the results obtained in this research one can conclude that:

1. The laser induced breakdown spectroscopy (LIBS) technique is very accurate. The essential atoms forming the samples of benzene (Hydrogen and Carbon) appeared with great amounts while other elements such as (Pb , Be , Zr , Ni, Hg, Ti, Sc, La, Zn, Tm, Y, Eu, Kr, Gd, Cl, Ge, Hf, Mo, Xe, V, Mo, Ne, He and Nd) were appeared with little amounts relative to the essential atoms.
2. The emission lines of different elements were identified in the region from 180 nm to 900 nm.
3. (C, H. Fe, Ti, W, O and S) atoms were found in the three samples with different amounts.
4. LIBS is capable to detect almost all the elements and ions in the benzene samples.
5. LIBS can be used as diagnostic technique for investigation of elements in liquid samples.

3.4. Future work:

From the results, the followings can be suggested as future work:

- LIBS method can be considered in the future for analysis of many classes of organic compounds.
- Diode pulse lasers can be used to overcome the laser flash lamp background.
- Study the percentage of the heavy elements in the benzene.
- Study the effect of the addition of chemical improvements on the Sudanese benzene.

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