The Impact of Industrial Activities on Soil Pollution Using Laser-induced breakdown spectroscopy (LIBS)

Hawraa A. kareem[1,*], *Lazem* Hassan Aboud[1], and *Asmahan* Asaad Muhmood[2]

[1]Laser physics Department, Science College for Women, Babylon University, Babylon, Iraq
[2]Department of physics, Faculty of Science, University of Kufa, Kufa, Iraq

Abstract. The study aimed to assess the elemental composition and pollution levels in soil samples collected from various factories in different governorates of Iraq. The specific factories investigated were a cement factory in Diwaniyah governorate, a coal factory in Karbala governorate, and napo river in hilla governorate. To analyze the soil samples and identify the presence of different elements and pollutants, the researchers employed a technique called Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is a spectroscopic method that uses a laser to generate a plasma in the sample, and the emitted light from the plasma is analyzed to determine the elemental composition. The intensity of Cu, Si, Ca, Au, and Dy was found to be high, indicating their relatively higher concentration in the soil samples. On the other hand, the remaining elements exhibited medium to low-intensity levels, suggesting lower concentrations of those elements in the samples. Furthermore, when the LIBS technique was applied to study the environmental conditions around the nearby factories, the consistent presence of Ti (titanium) and Fe (iron) was observed in all the samples examined. Overall, the study provides important information about the elemental composition and pollution levels in soil samples collected from different factories in Iraq. The results highlight the presence of specific elements and their varying intensities, indicating the potential impact of these factories on the surrounding environment.

1 Introduction

Indeed, the Laser-Induced Breakdown Spectroscopy (LIBS) technique is well-suited for soil contamination analysis due to its advantages of being time-saving and cost-effective. This technique allows for rapid analysis, both in the laboratory and on-site, making it particularly useful for assessing soil contamination efficiently.LIBS can analyze substances in various forms, including solids, liquids, and gases, which further enhances its applicability to different environmental samples. This versatility enables investigators to analyze soil samples directly without the need for extensive sample preparation, thus saving time and

* Corresponding author: hwraakreem@gmail.com

resources. One of the key advantages of LIBS is its ability to provide information about both high and low concentrations of elements present in the sample. This feature is crucial when dealing with soil contamination, as it allows for the detection and quantification of trace elements that may have adverse effects on the environment or human health. Moreover, LIBS spectra not only reveal information about the concentrations of elements but also contain valuable isotopic ratios and atomic structure data. This additional information can be beneficial in identifying specific sources of contamination and understanding the chemical composition or "fingerprint" of the substances present in the soil samples. By utilizing the LIBS technique, researchers and environmental professionals can expedite the detection and monitoring of soil contamination, enabling prompt remedial actions and decontamination measures. The rapid and comprehensive analysis provided by LIBS contributes to more efficient and effective environmental management strategies [6,7]. The Nd: YAG laser, operating at a fundamental wavelength of 1064 nm, finds extensive use in the LIBS technique. This laser emits high-energy pulses that are precisely focused on the target material, resulting in vaporization, atomization, and the generation of excitation sources, leading to elevated temperatures. Consequently, a microplasma is formed on the target's surface. In essence, the process commences as the sample absorbs the energy from the pulsed laser and rapidly converts it into heat [8]. This rapid heating induces high temperatures capable of breaking molecular bonds, initiating excitation, and giving rise to unstable atoms or ions. Electrons transition from the ground state to higher energy states during this process, referred to as excitation. As a result, electrons return from their higher energy states to the ground state, releasing the acquired energy in the form of photons at distinct wavelengths. This emission of photons serves as the basis for discriminating and identifying the elements present within the sample [9]. The electronic transition gives rise to emission lines. The temperature of the plasma initially surges to 4,000 °K and can even reach 15,000°K during the early stages of plasma formation. Over time, this hot plasma gradually cools and dissipates. Eventually, both ions and electrons recombine, forming neutral atoms or even molecules, emitting light at unique wavelengths [8]. Indeed, each element on the periodic table possesses a distinct and specific arrangement of electron orbits around its nucleus [10]. In essence, these unique electron configurations set each element apart from all others. Consequently, when electrons transition between states, they emit wavelengths that are distinctive to each element. As a result, every element exhibits its own emission spectrum, which acts as a unique fingerprint, allowing for the identification of elements within a sample. Subsequently, the emitted light can be collected using fiber optics or lenses. This collected light then passes through a narrow slit, where it undergoes spectral resolution and is detected by a charge-coupled device (CCD) or an intensified charge-coupled device (ICCD) detector [11]. The collected data, in the form of digital information, is then processed and analyzed by suitable computer software. Consequently, spectrally resolved light obtained through LIBS provides valuable insights into the elemental composition of the material through spectroscopy. It's worth noting that the foundational concepts for the LIBS technique were inspired by Max Planck, who proposed that quantum theory could elucidate the characteristics of radiation emitted by heated objects [12]. The quantum theory is built on two fundamental hypotheses. The first one posits that atoms, ions, and molecules can exist only in discrete states, each characterized by a specific and quantized amount of energy. When free electrons are released during plasma formation, all molecular bonds break, resulting in continuous emission. However, this emission vanishes rapidly due to the capture of free electrons by atoms and ions. Consequently, when a species undergoes a change in its state, it either absorbs or emits an amount of energy precisely equal to the energy difference between the states of atoms, ions, and molecules. The second hypothesis postulates that the wavelength (λ) of absorbed or emitted radiation by atoms, ions, or molecules during a

https://doi.org/10.1051/e3sconf/202453701006

transition between energy states is related to the energy difference (ΔE) between those states [12].

2 The method of work

The laser-induced breakdown spectroscopy (LIBS) technique was employed to assess the elemental composition of the environment surrounding specific factories located in particular regions. This involved collecting soil samples near the areas where factory waste was disposed of and analyzing this soil to gauge the factory's impact on the local environment. The soil samples were prepared by sieving the soil through a 0.5mm mesh and then taking 5 grams of the soil, which was subsequently compressed into a soil disc using a piston. This soil disc was then subjected to testing within the LIBS system, as illustrated in the figure below. The figure outlines the components of the diagnostic system used for this purpose.

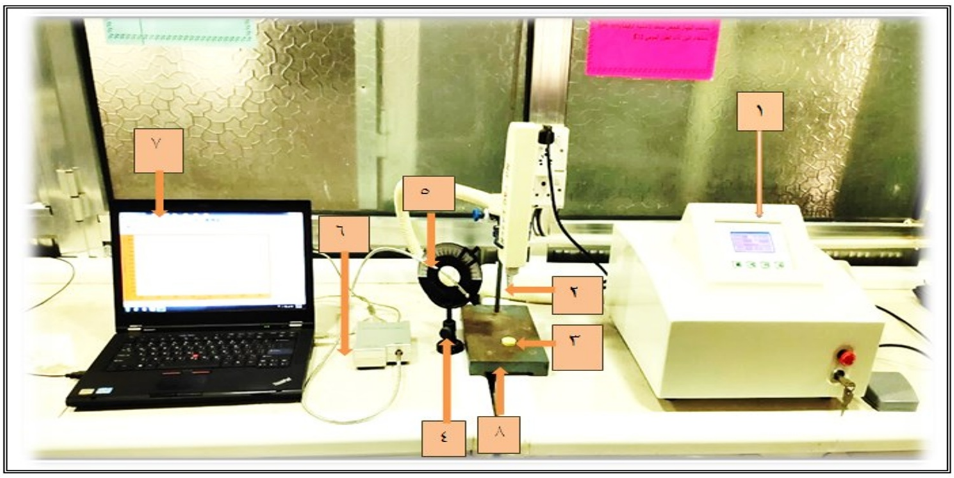

Fig. 1. The LIBS system setup.

Here a concise description of the components in the LIBS system:

1. A short-pulsed Q-switched Nd: YAG laser source emits pulses at 1064 nm, serving as the energy source for creating the plasma plume.
2. A lens with a focal length of 10 cm is employed to precisely focus the laser beam onto the surface of the target material.
3. A target base is used to securely position the sample that is to be irradiated by the laser. The laser-to-target distance is maintained at 10 cm.
4. An objective lens system collects and directs the plasma's spectral wavelengths. These wavelengths are then transmitted via a fiber optic cable (FOC) to a spectrum analyzer for further analysis.
5. A circular fiber holder (360°) is utilized to position the fiber optic cable at the optimal angle for receiving the plasma spectrum effectively.
6. The system includes a spectrum analyzer or detection system equipped with a grating and a charge-coupled device (CCD) to disperse the emitted spectrum from the target material. This device records the spectrum in terms of intensity against wavelength, providing each element with its unique spectral signature.
7. A computer is an integral part of the setup, serving to operate the spectrum analyzer software. This software displays the data as a graph, showcasing the relationship between wavelengths and intensity. Furthermore, it stores the recorded spectra for further analysis.

8. The target is placed beneath the Nd: YAG laser handle, where it is subjected to the laser pulses for the LIBS analysis.

3 Result and discussion

3.1 Napo River

Samples of soil were collected from the banks of the Napo River in Hilla governorate, and the soil was analyzed using the Laser-Induced Breakdown Spectroscopy (LIBS) technique. The LIBS spectrum for this sample is depicted in the figure below.

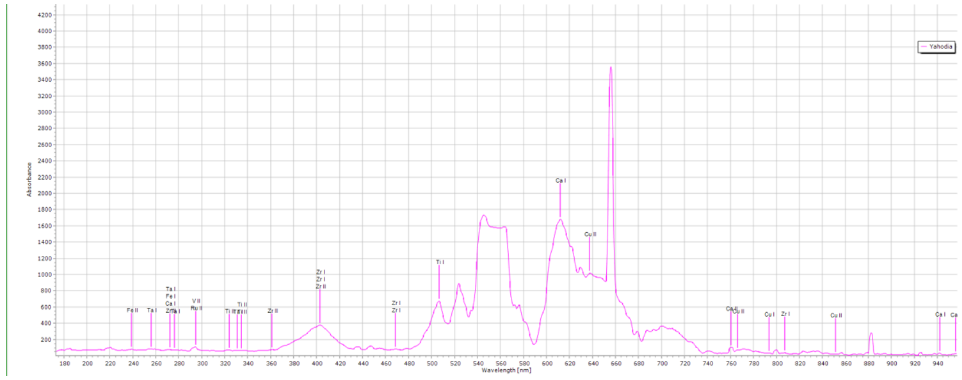

Fig. 2. The LIBS of the soil surrounding the Napo River.

Table 1. Element of the soil surrounding the Napo River.

Name	Element	Wavelength	Intensity
Carbon	c	220	100
Iron	FeII	240	75
Tantalum	TaI	255	75
Iron	FeI	275	100
Vanadium	VII,RuII	295	100
Thallium	TiII	330	50
Zirconium	ZrI	362	75
Zirconium	ZrI	405	391
Zirconium	ZrII	405	391
Zirconium	ZrI	470	80
Thallium	TiI	508	620
Dysprosium	Dy	525	900
Gold	Au	585	400
Calcium	CaI	615	1650
Silicone	Si	625	1350
Calcium	CuII	638	1000
Beryllium	Be	680	250
Carbon	C	700	388
Beryllium	Be	740	75
Calcium	CaII	760	100
Calcium	CuII	765	75
Calcium	CuI	795	50
Zirconium	ZrI	808	50
Calcium	CuII	855	25
Cesium	Cs	885	300

https://doi.org/10.1051/e3sconf/202453701006

Calcium	CaI	942	25

An analysis was conducted on a sample collected from the banks of the Nabu River in Babylon Governorate using the LIBS technique to determine the elemental composition and presence of pollutants in the soil. The results revealed the following:

The element Zirconium (Zr) exhibited four energy transitions in the spectrum, while Copper (Cu) showed three energy transitions. The elements Iron (Fe), Tantalum (Ta), Vanadium (V), Zirconium (Zr), Dysprosium (Dy), Gold (Au), Silicon (Si), Boron (B), Beryllium (Be), Calcium (Ca), Copper (Cu), and Cesium (Cs) each displayed one spectral transition in the spectrum.

In terms of intensity, Copper (Cu), Silicon (Si), Calcium (Ca), Gold (Au), and Dysprosium (Dy) exhibited high levels, while the remaining elements showed medium to low intensities. These findings provide insights into the soil composition in the vicinity of the Nabu River, with notable concentrations of elements such as Copper (Cu), Silicon (Si), Calcium (Ca), Gold (Au), and Dysprosium (Dy), and relatively lower concentrations of other elements.

Because the Nabu River passes through many popular areas in Babil Governorate, and because the soil sample used in the study was taken from a residential area, the elements that appeared in the spectrum could have resulted from materials thrown into the river, algae present in the river, or resulting from plants or... Organisms and microbes found in theNAPO river.

3.2 Coal factory

Samples of soil were collected from the banks of the coal factory in karbala governorate, and the soil was analyzed using the Laser-Induced Breakdown Spectroscopy (LIBS) technique. The LIBS spectrum for this sample is depicted in the figure below.

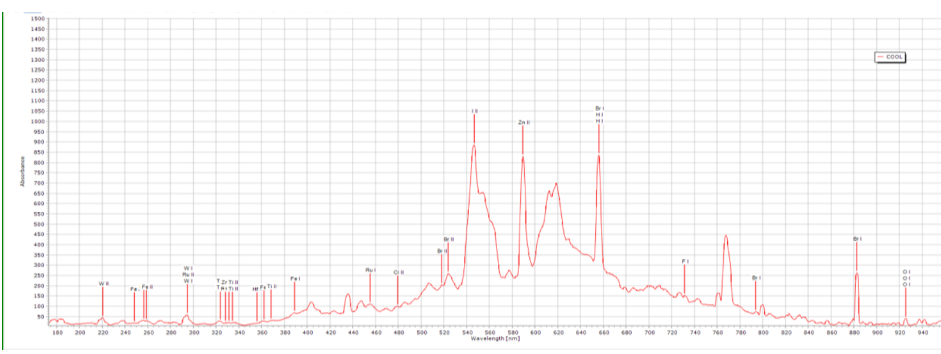

Fig. 3. The LIBS of the soil surrounding the coal factory.

Table 2. Element of the soil surrounding the coal factory

Name	Element	Wavelength	Intensity
Iron	feII	260	48
Iron	feI	250	25
Iron	feI	385	75
Hafnium	HF	385	20
Lodine	III	545	875
Oxygen	OII	925	48
Oxygen	OII	925	48
Ruthenium	RUI	458	125

Thorium	THI	368	48
Thorium	THI	325	25
Thorium	THI	328	25
Thallium	TiI	365	48
Tungsten	Wi	295	55
Zinc	ZnII	585	625
Prom	BrII	506	205
Prom	BrII	525	255

An analysis was conducted on the soil surrounding the coal factory in Karbala Governorate using LIBS technology. The results revealed the presence of two energy transitions for the elements (Br, Ti, and Fe) in the spectrum, while the elements (Th) showed three energy transitions, and the elements (Hf, Ne, O, F, Zn, I, Be, and W) showed one energy transition.

The elements that are used in making coal are (carbon, hydrogen, oxygen, nitrogen, and sulfur). In addition to these basic elements, coal may also contain other minerals such as iron, manganese, aluminum, phosphorus, and rare metals, the composition of which may vary depending on the type of coal and the geographical area in which it is made. Extracting coal from it. These elements may be present in the environment surrounding the coal factory due to the factory throwing its waste into the soil next to it. As for the other elements that were obtained in the (LIBS) results for the soil sample surrounding the coal factory, they may be the result of other factors or materials outside the factory, or it is possible that It is one of the components of this soil.

3.3 Diwaniyah Cement factory

Samples of soil were collected from the banks of the Cement factory in Diwaniyah governorate, and the soil was analyzed using the Laser-Induced Breakdown Spectroscopy (LIBS) technique. The LIBS spectrum for this sample is depicted in the figure below.

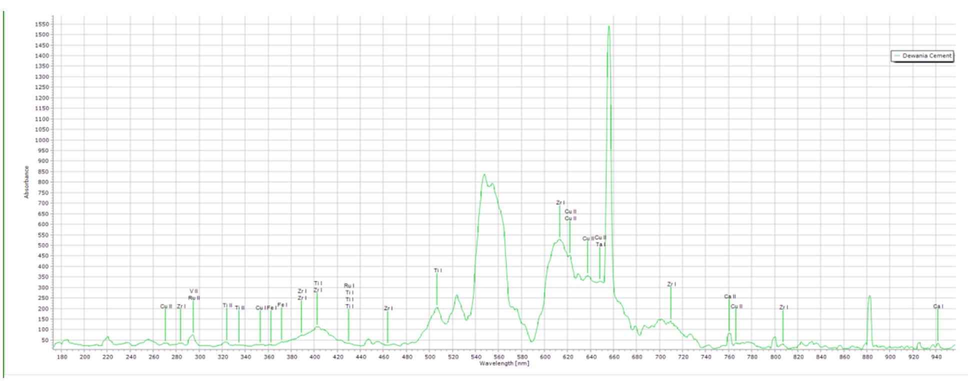

Fig. 4. The LIBS of the soil surrounding the cement plant.

Table 3. Element of the soil surrounding the cement plant.

Name	Element	Wavelength	Intensity
Carbon	C	220	60
Silver	Ag	238	75
Nitrogen	N	258	50
Copper	CUII	270	45
Zirconium	ZrI	285	45
Ruthinum	RuII	395	75

Thallium	TiII	325	45
Thallium	TiII	338	25
Copper	CUI	355	25
Iron	FeI	362	25
Iron	FeI	372	45
Zirconium	Zrl	390	75
Zirconium	ZrI	408	110
Thallium	TiI	430	45
Manganese	Mn	445	60
Zirconium	ZrI	465	25
Manganese	Mn	470	25
Manganese	Mn	475	45
Thallium	TiI	510	200
Nicel	Ni	525	255
Molybdenum	Mo	535	153
Tungsten	W	589	125
Tungsten	W	588	175
Zirconium	ZrI	615	555
Copper	CuII	625	500
Copper	CuII	638	330
Tantalum	TaI	650	325
Copper	CUII	650	325
Tungsten	W	658	1550
Beryllium	Be	680	125
Nitrogen	N	688	125
Titanium	Ti	700	150
Zirconium	ZrI	710	180
strontium	Sr	745	25
calcium	CaII	760	85
Copper	CuII	765	45
Zirconium	Zrl	808	25
Krypton	Kr	825	45
Manganese	Mn	838	40
Manganese	Mn	845	25
Neon	Ne	858	38
Neon	Ne	868	25
Nitrogen	N	880	40
lanthanum	La	890	30
calcium	CaI	943	30

Analysis of the soil near the cement factory in Diwaniyah Governorate using LIBS showed the following results:

The element (Zr) was abundant in the local environment, and seven energy transitions for this element appeared in the spectrum. The elements (Cu and Mn) were also prevalent, each showing five energy transitions in the spectrum. It has been observed that the elements (N, Ti, and W) have three energy transitions in the spectrum. The elements (Ti, Ne, and Fe) had two energy transitions. Various other elements were detected, including (C, Ru, Mo, La, Be, Ag, Ni, Sr, Kr, Cr, Ta, Ca, and Cd) for which only one energy transition appeared in the spectrum. It is worth noting that the element density (W) was exceptionally high. The element (Cu) also showed high intensity. However, the intensity of the remaining items was relatively low.

Cement is a building material used to stabilize and bind other materials in construction and civil engineering. Cement consists of a mixture of several main elements, namely (calcium, silica, alumina, iron). These main elements interact with each other in the presence of water to form cement hydrate compounds, which give cement its bonding and hardening properties upon drying and hardening. Some additional materials are also added, such as gypsum, to regulate the hardening process and improve the final cement properties. These materials may be present in the environment surrounding the cement factory, as the appearance of these elements in the soil sample surrounding the factory is due to factory waste. As for the other elements that appeared in The spectrum of the sample may result from factors and materials outside the factory, or these elements may be present among the soil components.

4 Conclusion

The utilization of the LIBS technique proved to be effective in determining the elemental composition and pollution status of soil samples from (the cement factory in Diwaniyah governorate, the coal factory in Karbala governorate and napo river in babil governorate). The study identified the repeated occurrence of Zr and Cu, along with the presence of several other elements in the soil. The high intensity of Cull, Si, Ca, Au, and Die suggests their potential contribution to the pollution levels in the area. Moreover, the consistent presence of Ti and Fe in all samples indicates a likely influence from nearby industrial activities. These findings provide valuable insights for further environmental monitoring and remediation efforts in the region to mitigate potential risks associated with soil pollution.

References

1. M. Kompitsas, F. Roubani-Kalantzopoulou, I. Bassiotis, A. Diamantopoulou, A. Giannoudakos, *Laser Induced Plasma Spectroscopy (Libs) As an Efficient Method for Elemental Analysis of Environmental Samples* (University of Athens, 2000).
2. D. Díaz, D.W. Hahn, and A. Molina, Applied Spectroscopy, **66(1)**, 99-106 (2012).
3. R.L. Vander Wal, T.M. Ticich, J.R. West, and P.A. Householder, Trace Metal Detection by Laser-Induced Breakdown Spectroscopy, Louisiana, 71134 (1999).
4. A. Williams and S. Phongikaroon, *Laser-Induced Breakdown Spectroscopy (LIBS) Measurement of Uranium in Molten Salt*., (Virginia, VA 23284, USA, 2018).
5. Z.A. Saleh, *Laser-Induced Breakdown Spectroscopy (LIBS): An Innovative Tool for Elemental Analysis of Soils*., (Mustansiriyah University, 2016).
6. D.A. Cremers, A. Beddingfield, R. Smithwick, Rosemarie, C. Chinni, C.R. Jones, B. Beardsley, and L. Karch, *Monitoring Uranium, Hydrogen, and Lithium and Their Isotopes Using a Compact Laser-Induced Breakdown Spectroscopy (LIBS) Probe and High-Resolution Spectrometer* (Arizona (B.B.), Virginia, 2011).
7. D. Alamelu, A. Sarkar, S.K. Aggarwal, *Laser-induced breakdown spectroscopy for simultaneous determination of Sm, Eu, and Gd in aqueous solution*, (Mumbai 400085, India, 2008).
8. El-Deftar, Moteaa Mohamed Anwar, *Evaluation of Laser-Induced Breakdown Spectroscopy (LIBS) for the Elemental Profiling of Forensic Evidence,* Theses, Diss. University of Canberra, 9-41 (2014).
9. Ismael H. Jasim, *Design and Constructions Laser Induced Plasma System to Determine Calcium Rate in Bones,* Thesis, M.Sc., University of Wasit, 10-16 (2015).
10. Norman E. Schmidt, and Scott R. Goode, Applied Spectroscopy, **56**, 370-374 (2002).
11. P. Singh, Jagdish, and Surya Narayan Thakur, *Laser-induced breakdown spectroscopy*, (Book, Elsevier, 2007).

12. J. Goujon, A. Giakoumaki, V. Piñon, O. Musset, D. Anglos, E. Georgiou, J.P. Boquillon, Spectrochimica Acta Part B: Atomic Spectroscopy, **63**, 1091-1096 (2008).