

Detection of Pollutants in Soil Using Laser-Induced Breakdown Spectroscopy (LIBS)

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Conceptualization, E.J.Mahmood and M.M.Al Sultani; methodology, E.J.Mahmood; investigation, E.J.Mahmood; resources, E.J.Mahmood; data curation, E.J.Mahmood; writing—review and editing, E.J.Mahmood; visualization, E.J.Mahmood; supervision E.J.Mahmood and M.M.Al Sultani; All authors have read and agreed to the published version of the manuscript.

REVIEW

Detection of Pollutants in Soil Using Laser-induced Breakdown Spectroscopy (LIBS)

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Abstract

The tremendous development in various industrial and agricultural fields has led to an increase in pollution of soil and water bodies, which has been reflected in the quality of agricultural products and their quantity, as well as the damage that this pollution causes to human health and the growth system of other living organisms. Many soils are polluted with heavy metal elements like lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), aluminum (Al), and mercury (Hg), which makes the environmental situation more difficult. As part of this sensitive stage, monitoring and analysis have become essential to assess the risk resulting from pollution and determine current environmental trends accurately and promptly. Established on the laser's produced plasma, a novel element analysis way called laser-induced breakdown spectroscopy (LIBS) has been developed. This method involves applying laser pulses to the sample to ablate it. This process causes the material to evaporate and ionize in a hot plasma, which the spectrometer then analyzes. The concentrations of various elements of environmental importance, like copper, cadmium, calcium, barium, magnesium, chromium, manganese, titanium, phosphorus, iron, zinc, and others, are determined using this technique because it has shown to be a reliable and efficient tool. Elements are detected by their spectroscopic fingerprint. The last twenty years have witnessed the presentation of much research in this field, which has dealt with various technical and environmental aspects. In this study, provided the basic principles of LIBS for soil analysis included The formation of plasma mainly consists of heating, melting, evaporation, ionization, and excitation processes, many of these studies will be reviewed to find out the latest developments, identify differences between researchers, and discuss several aspects related to these studies. This understanding will help optimize conditions for improved signal quality and stability. Another aim is to develop effective noise decreasing methods, such as signal averaging and advanced data processing techniques, to enhance the analytical features of LIBS and ensure accurate readings. The study will also explore the pollutants detection mechanisms inherent in LIBS, and will address the challenges associated with sample preparation, striving for minimal processing to facilitate direct analysis of soil samples. By achieving these objectives, the study aims to establish LIBS as a robust and reliable tool for assessing soil health and monitoring environmental contamination. It will make it easier for readers to comprehend the state of the LIBS technique's research in soil analysis today.

Keywords: Soil pollutants, Laser-induced breakdown spectroscopy (LIBS), Heavy metals, Elemental analysis, Environmental analysis

1. Introduction

As the primary channel for exposing humans, animals, and plants to environmental toxins, soils are extremely diverse arrangements in dynamic equilibrium with other partitions. They also play a crucial role in determining the destiny of pollutants (either as a source or as a sink) in ecosystems [1]. Soil

is most impacted by heavy metal pollution among environmental partitions [2,3], namely due to managed and uncontrolled waste disposal, accidental and process spills, mining and smelting of metallic-ferous ores, and application of sewage mud to agricultural areas. Thus, the scientific community is working hard to develop analytical tools that can track the amounts of heavy metals in the soil and

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ways to restrict their intake and remediate the soil [4]. An atomic analysis method called (LIBS) was created recently, to be more precise, the laser ablates the sample to create the plasma, which is subsequently created, and then the elements are determined both qualitatively and quantitatively by analyzing the spectrum signals that the plasma emits [5–9]. Among many benefits, including rapid analytical speed, easy sample pre-treatment, multi-element immediate detection, and in-situ detection capability [10], element investigation has found widespread application in a variety of fields, including industrial analysis [11], bio-medicine [12], and environmental monitoring [13,14]. Many studies on using LIBS technology for analysis and detection of pollutants in soil have been conducted throughout the last ten years. In 2007, Hussain et al. used laser-induced breakdown spectroscopy (LIBS) to determine the nutrients in the soil samples from greenhouses [15]. In 2009, the elements Cr, Al, Fe, Ca, Cu, Mg, Mn, Pb, Si, Ti, V, and Zn were detected by Senesi et al. (2009); they used the initial qualitative LIBS analysis of one sewage sludge sample and five soil samples [16]. In 2010, hazardous heavy metals, such as Cd, Co, Pb, Zn, Cr, etc., in soil samples were detected and measured by Pandhija et al. using the application of calibration-free LIBS (CF-LIBS) and laser-induced breakdown spectroscopy (LIBS) techniques [17]. In 2011, Ismael et al. conducted in situ assessments of contaminated soils using laser-induced breakdown spectroscopy (LIBS), which offers effective, immediate, semi-quantitative data on the degree of pollution [18]. In 2012 Popov et al. used (LIBS technique) to detect of Zn element in Soils [19]. In 2013, the quantities of Cr, Mn, and Fe elements in sediment samples were determined by Mekonnen et al. using (LIBS), the outcomes have been compared to those obtained using flame-atomic absorption spectroscopy (F-AAS) [20]. In 2014, the contents of Zn element in various soil types were measured by Kim et al. using laser-induced breakdown spectroscopy (LIBS); the outcomes showed that the precision and accuracy of the LIBS analysis were improved by combining the soil discarding and kriging interpolation techniques [21]. In 2015, a direct technique for measuring soil pH using (LIBS) is described by Ferreira et al. [22]. In 2016, Nicolodelli et al. used LIBS in Single Pulse (SP) and Double Pulse (DP) configurations to measure the (Ca, Mg, K, P) macronutrients, (Cu, Fe, Na, Mn, Zn) micronutrients, and contaminant (Cr) in fertilizer [23]. In 2017, the elemental composition of ambient aerosols and soils that represented less than 2.5 μm in Ny-Ålesund, Svalbard, was determined by Kim et al. using two procedures of (LIBS) [24]. In 2018, Fu

et al. increased the sensitivity of conventional LIBS and the LIBS signal in two ways and developed a unique method for measuring cadmium in soils using LIBS [25]. In 2019, Mahmood et al. employed (LIBS) and laser ablation time of flight mass spectrometry (LA-TOF-MS) to investigate soil samples obtained from Sialkot, Pakistan, which is home to leather manufacturing firms, both qualitatively and quantitatively [26]. In 2020, Sugito et al. [27] (LIBS) detected the heavy metal containment of soil contamination. In 2021, Yoon et al. [28] utilized a multivariate chemometric analysis and (LIBS) method to determine and quantify the presence of heavy metals in sediments. In 2022, Awad [29] used Inducted Coupled Plasma (ICP) and Laser Induced Breakdown Spectroscopy (LIBS) to measure and compute the concentrations of hazardous, heavy, and radioactive elements are present in Kadugli City. The objective of this review article is to present the fundamental ideas and an overview of the application of LIBS for soil physical and chemical investigation.

2. LIBS technology

In principle, LIBS can be considered as a relatively recent method of atomic emission based on AES with source of laser excitation and has proven very useful for multi-elemental investigations of a wide range of materials. This technology is a new method for determining the elements in various environmental samples, including metallurgical, metallic, and non-metallic solids, liquids, aerosols, gasses, and biological samples [30]. The standard components of a LIBS apparatus are a laser, a photosensitive system, a spectrometer, and a computer [31], Fig. 1. Samples can be subjected to both qualitative and quantitative examinations using the distinctive spectral line's wavelength and intensity [32]. The laser pulse duration for LIBS systems varies between femtoseconds (10^{-15} s) and microseconds (10^{-6} s), which impacts the produced spectra. Unlike microsecond lasers, which excite the species in the plasma with a significant amount of pulse energy, femtosecond lasers' pulses interact with the sample surface so quickly that they end earlier than the plasma develops. The most common kind of laser in the applications under evaluation were nanosecond lasers, which fall between femto and microsecond lasers. The delay generator is a key element of the LIBS setup required to synchronize the spectrometer and laser with electrical pulses ranging from nanoseconds to milliseconds. Optimizing the signal-to-noise/background ratio via fine-tuning the delay duration improves quantitative analysis.

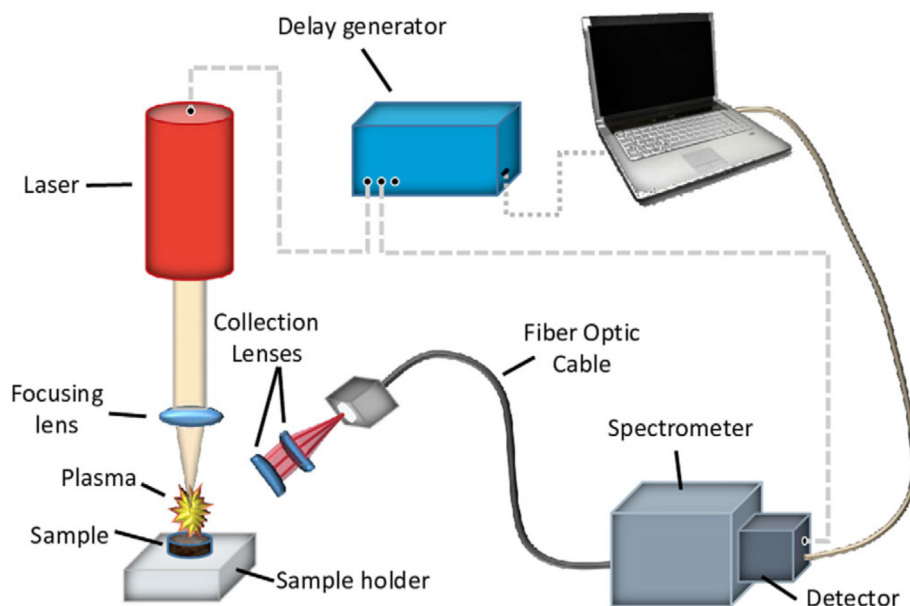


Fig. 1. A typical system setup of (LIBS), [72].

2.1. Plasma evolution

The primary processes involved in the production of plasma include heating, which follows melting, then evaporation, and finally ionization and excitation. A few micrograms of material on the sample surface to be analyzed are removed by the high-energy laser beam once it is focused on it [33]. Subsequently, the excited atoms, ions, and electrons combine to create the plasma, which can heat up to 100,000 °C instantly. The high temperature of the plasma causes it to spread outward at supersonic speed before quickly cooling down. When the plasma becomes in cool condition, background radiation decreases and excited states of atoms and ions transition to lower energy levels, releasing light at wavelengths unique to individual elements. The emission lines of the plasma are gathered and sent to an optical spectrometer either directly or via optical fibers. A spectrometer, typically consisting of an intensified range polychromator and a charge-coupled device (CCD) or strengthened charge-coupled device (ICCD) detector, is used to resolve plasma emission. Since most elemental emission lines are observable between 200 nm and 1000 nm, this is the wavelength range in which most polychromators function. The spectrometer's resolution determines the quality of a LIBS measurement by enabling the separation of successive emission lines without the need for extensive processing, particularly for spectra derived from complicated matrices like soil samples.

2.2. Noise decreasing methods

The signal intensity and stability of traditional LIBS are inadequate for identifying trace components in soil samples. Numerous environmental conditions influence the plasma's lifespan and properties, which alters the technique's performance for atomic-level chemical investigation and its spectrum emission, Fig. 2 summarize the parameters influencing the quality of signal.

Several signal enhancement techniques were put forth to lower the limit of detection (LOD) and raise the signal-to-noise ratio (S/N) of the LIBS spectrum. Significant signal augmentation is possible with various experimental designs and settings. Magnetic Field Enhancement LIBS (MFELIBS) [34], Double-Pulse LIBS (DP-LIBS) [35], Spatial Confinement LIBS (SC-LIBS) [36], Microwave-Assisted LIBS (MA-LIBS) [37], inductively coupled plasma/optical emission spectroscopy (ICP/OES) [38], and laser ablation-spark induced breakdown spectroscopy (LA-SIBS) [39] are the primary signal augmentation techniques. From another point of view, adding a second pulse to the LIBS signal is one method to enhance its quality. In this method may use two lasers firing separate pulses or a single laser firing two successive pulses. The first pulse produces a plasma and ablates a portion of the sample surface; the second pulse re-excites the plasma to improve the signal-to-noise ratio [40]. There is a complicated relationship between the type of laser used and the LIBS's ability to identify pollutants. These aspects include

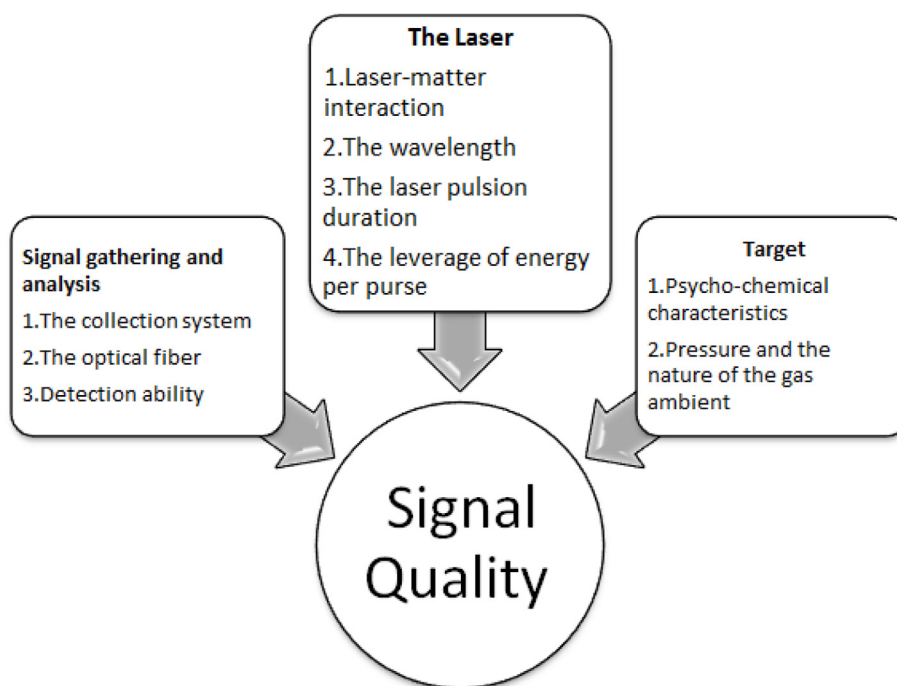


Fig. 2. Demonstrating the main parameters that affected signal quality in LIBS.

wavelength, energy, pulse duration, and sample properties. Selecting the right kind of laser can maximize the ability to identify particular contaminants, boost sensitivity, and improve analytical performance all around [41]. Organic pollution detection can be more difficult. Because femtosecond lasers can shield organic substances from heat degradation, it is possible to identify organic contaminants more accurately. Inorganics and Metals, Most laser types are generally well-detected, but UV and nanosecond lasers are frequently chosen because of how well they can excite metallic species. Commonly employed in LIBS, Nd lasers (1064 nm) are effective on metals but less so on light elements like magnesium, sodium, or lithium, which need higher energy photons. A few techniques for improving signals are

listed in Table 1, together with the pollutant detection limit for each sample.

2.3. LIBS analytical features

(LIBS) is able to measure a large number of elements, usually ranging from uranium (U) to hydrogen (H). Its limited detection is caused by lower ionization energies and possible matrix effects, especially for elements like boron (B), lithium (Li), and beryllium (Be), iron (Fe), copper (Cu), lead (Pb), and zinc (Zn) for transition metals, all of which are well-quantified. LIBS is an effective tool for detecting heavy metals, including arsenic (As), cadmium (Cd), and mercury (Hg), [41,42]. By contrasting with the Elemental Range of Instrumental

Table 1. Some techniques for improving signals in LIBS.

Techniques	Laser type	Wavelength (nm)	Pollutants	References
ICP OES	Q-switched Nd:YAG	1064	Pb	[38]
CF LIBS	Q-switched Nd:YAG	1064	Cd, Co, Pb	[17]
	Q-switched Nd:YAG	532	Zn, Cr	
SC LIBS	Nd:YAG	1064	As, Pb, Hg, Mn, V, Ba	[50]
DP LIBS	Q-switched Nd:YAG	1064	Ca, Mg, K, P	[23]
SP LIBS	Q-switched Nd:YAG	532	Cu, Fe, Na, Mn, Zn	
MFE LIBS	Nd:YAG	532	Cr	[34]
ICP LIBS	Q-switched Nd:YAG	1064	Al, Ba, V, Ti, Sr, Fe, S, Ca, Mg, Cr, K, Na	[74]
LA SIPS	Nd:YAG	1064	Hg	[75]
LA ICP MS	Excimer Laser	193	Mg, Al, Si, Ca, Mn, Ti, V, Cr, Fe, Co, Ni, Cu, Rb, Sr, U, Mo, Sn, Ba, Pb, Th	[76]
MA LIBS	Nd:YAG	1064	Cu	[37]

Neutron Activation Analysis (INAA), which can quantify more than 60 elements, ranging from sodium (Na) to uranium (U). It is quite good at finding traces of components. With a focus on heavy metals, the element range found by comparing with X-ray fluorescence (XRF) is suitable for detecting elements ranging from fluorine (F) to uranium (U). In the context of X-ray photoelectron spectroscopy (XPS), primarily focused on the surface (up to a few nanometers) and sensitive to elements in the range of lithium (Li) to uranium (U), [43–45].

Depending on the sample matrix, ambient conditions, and calibration, LIBS can achieve moderate to high accuracy. It frequently has to be carefully calibrated against established standards [46]. When comparing duplicate measurements of the same sample, LIBS often displays relative standard deviations (RSD) in the range of 5–10 %, indicating acceptable precision [47–49]. Variations in laser energy and sample heterogeneity are two examples of issues that can affect precision. The sensitivity of LIBS is comparatively high; it can identify elements at parts per million (ppm) concentrations. However, depending on the element and its spectral properties, sensitivity might vary greatly [50]. For many elements, detection limits typically range from 100 ppm to several ppm; however, with the right setups, trace elements may be found at lower quantities [51]. For many elements, the limit of detection (LOD) for LIBS can vary from 10 to 100 ppm. However, certain elements can be detected at lower levels using more sophisticated methods like double-pulse LIBS or by employing particular wavelengths. Atmospheric conditions and other environmental elements might also affect the LOD [52]. Both the well-known methods

Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma (ICP) have advantages and disadvantages when it comes to these analytical aspects. ICP and INAA perform better than LIBS when compared to one another, providing excellent accuracy and precision. Matrix effects and calibration can affect LIBS accuracy. For trace element analysis, ICP and INAA are often the better options due to their higher sensitivity and lower LODs than LIBS. Fast analytical times and little sample preparation are two major benefits of LIBS, which are important in some applications.

2.4. Pollutants detection mechanisms

The principles behind Laser-Induced Breakdown Spectroscopy (LIBS) involve the creation of a plasma followed by the analysis of the emitted light to determine the elemental composition of a sample, Fig. 3. LIBS provides a rapid and non-destructive method for elemental analysis, enabling quick identification of elements even in complex samples. Its applications range from analyzing geological samples to identifying contaminants in industrial materials, and it's often used in situations where rapid, on-site analysis is crucial. The mechanism of pollutants detection can be summarized as:

- **Laser Pulse:** A high-energy laser pulse is focused onto the sample's surface. This intense light pulse rapidly heats and vaporizes a small portion of the material, creating a high-temperature plasma.
- **Plasma Formation:** The intense energy of the laser pulse causes the material to undergo ablation, where a small portion of the sample is

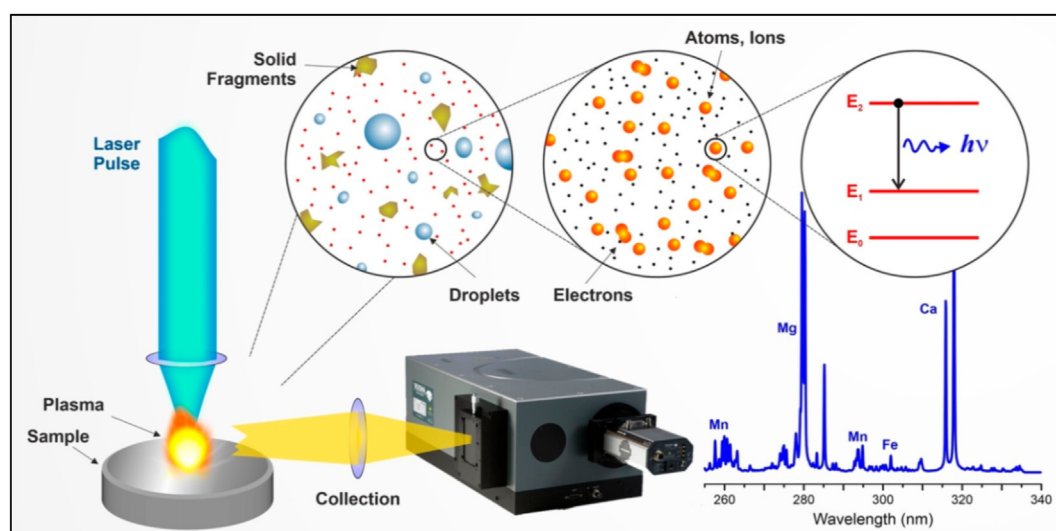


Fig. 3. The mechanism of detecting pollutants using (LIBS) technology [73].

transformed into a plasma a hot, ionized gas consisting of free electrons and ions.

- **Emission of Light:** When the plasma is formed, it emits light due to the recombination and relaxation of the ions and electrons. This light contains spectral information about the elements present in the sample.
- **Spectral Analysis:** The emitted light is collected and directed to a spectrometer. The spectrometer disperses the light into its constituent wavelengths (like a rainbow), separating it according to the different energies associated with various elements.
- **Elemental Identification:** By analyzing the wavelengths and intensities of the emitted light (spectral lines), the presence and concentration of elements within the sample can be determined. Each element emits characteristic wavelengths of light when transitioning between energy levels, allowing for identification.

Quantitative Analysis: The intensity of the emitted light at specific wavelengths correlates with the concentration of elements in the sample. Calibration curves or known standards are often used to quantify the elements present.

3. Sample preparation

Soil detection necessitates a basic sample processing procedure. Eliminating contaminants, drying, grinding, sieving, pressing into tablets, and completing LIBS measurements are typical steps in the laboratory detection process [53]. Pelletizing, grinding, and sieving are further helpful in minimizing the matrix impact and enhancing spectral quality [54]. Also, the water content significantly influences the LIBS spectral signal strength. Even under identical circumstances, there may be differences in the spectra of two successive LIBS observations of the same soil sample [55]. The analyst can normalize each spectrum or average many shots (like 100) to compensate for this problem. Powdered soil samples that have been homogenized mechanically or manually using a mortar and pestle can also be used for the LIBS analysis [56]. As a result, although the preparation takes longer per sample, the final spectra differ less than those produced for intact materials. To reduce surface roughness, pelletized soil samples that have been ground and homogenized can also be used [57]. Since it is challenging to locate certified reference materials (CRM) with a comparable matrix in soil samples, these samples are made by combining a finely powdered soil sample with the metal (in the form of

powder or aqueous standard solution). The calibration curve is very highly sensitive to the homogeneity of the CRM produced in the aforementioned approach due to the small size of the focused laser spot and the little mass (microgram) of the sample vaporized by the laser spark [17]. Researchers suggested using metal mesh sample holders, adsorption plates, and other supports to put samples, or using phase conversion to enrich components in soil samples in order to prevent dirt splashing and remove the complicated tableting procedure. Because smaller particles have a higher surface area to volume ratio, they can absorb laser energy more effectively and facilitate the production of more efficient plasma. Larger particles can impact the temporal resolution of the measurements because they require more energy to reach the necessary temperatures for efficient ablation; smaller particles can improve the detection limits for trace elements because they allow for more material to be vaporized and analyzed in a single shot, which may improve the detection of low-concentration elements; inconsistent particle sizes can cause measurement variability, which reduces precision; and a homogeneous sample with controlled particle size is likely to produce more replicable results. More strong spectrum signals may result from this. Bigger particles could result in less interaction with the laser or partial ablation, which could affect the quality of the signal or produce inconsistent findings. Smaller particles, on the other hand, typically provide more consistent signal quality and homogeneous laser contact. Reduced matrix effects could result from a more uniform distribution of elements caused by smaller particles. While larger or irregularly shaped particles can introduce noise and result in less accurate data, smaller particles may give clearer signals [58–60]. Table 2 lists some sample preparation ways.

4. Heavy metal elements

Any species of metal that appears in an undesirable location or in a concentration or form that has a negative impression on the environment or people might be classified as a “contaminant”. The main inorganic contaminants found in soil are heavy metals. Metals and metalloids comprise lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminum (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U) [61]. Most of them can enter the human body through the food chain and cause

Table 2. Different ways of soil sample preparation.

Soil source	Soil sample preparation way	Reference
Standard soils	The Cu sub-target supported micro mesh	[77]
Field soils	Slurry state using cation exchange resin	[25]
Occupational Exposure Limits (OEL) soils	Pellets of 2 mm thick and 12 mm in diameter	[19]
Field soils	Pellets of 20 mm in diameter	[78]
Watershed sediment soils	Freeze-dried for soils > 53 μ m	[79]
Urban soils	Microwave dissolution in Aqua Regia for soils <53 μ m	[80]
	Standard Reference Material (SRM-2586) according to National Institute of Standards and Technology	
Brazilian forests soils	Pellets using a press of 5 tons for 30 s.	[81]
Agricultural soils in Nile Delta, Egypt	Pellets of 3 mm thick and 10 mm in diameter using a press of 15 tons.	[76]
Agricultural soils	Tablets of 5 mm thick and 12 mm in diameter	[82]
Italian undisturbed silty loam, sandy clay loam, and clay loam soil	Pellets of 3 mm thick	[1]
Oil spill contaminated soil	Pellets of 10 mm thick and 20 mm in diameter using a press of 3 tons for 30 min.	[74]

major health risks when concentrations are exceeded. Therefore, one of the main strategies to improve food security is to accurately identify and effectively regulate the amount of heavy metals in soil [62]. One challenging aspect of LIBS is choosing element characteristic spectral lines. Saturation prevents the very strong emission line from reflecting changes in concentration. The chosen spectral lines of the targeted element should not overlap with lines from other elements since sensitivity drops as the emission line becomes weaker [63]. The magnetic field-assisted LIBS is useful when identifying heavy elements and their residues in soil and environmental samples. In addition to improving the number density, plasma temperate, and emission intensity, the application of LIBS in conjunction with a magnetic field allowed for the detection of many new emission lines that would not have been possible without it. In both the presence and absence of a magnetic field, the quantitative analysis utilizing CF-LIBS revealed excellent agreement for the principal elements by LA-TOF-MS within a 10 % error range [64]. For the quantitative measurement of Cr, Cu, Pb, V, and Zn in soil, there was excellent agreement between the findings obtained using the calibration curve technique and the ICP-OES. Conversely, compared to the group that employed SP-LIBS (355 nm) in conjunction with the calibration curve approach (18 mg/kg), the LOD of zinc (55 mg/kg) was greater [19]. Rehan et al. [38] employed the integrated intensity ratio approach and the standard calibration curve method to determine the lead concentration in drilling-fuelled soil. The test findings agreed with the ICP-OES measurements, Pb has a LOD of 130 mg/L. The PLS approach has benefits over conventional linear calibration methods in that it

can fully utilize the spectral line information for soil samples that exhibit significant spectral line interference and complicated matrices. Traditional PLS frequently builds the model using the entire spectrum as an input variable, which requires more computation and yields worse prediction results. Those with the highest correlation can be effectively chosen using variable selection [65].

5. Nutrient elements

Macro and micronutrients in soil are the fundamental resources needed to maintain the surface ecology. Meanwhile, the amount of nutritional components in the soil might indicate its fertility and is regarded as a crucial indicator for assessing crop productivity [66]. The direct correlation between the element concentration and the spectral line's intensity may deteriorate due to the self-absorption effect. As a result, determining the element content quantitatively from the spectral line's strength becomes challenging. The N, P, K, S, Ca macronutrients, as well as Mg are the hardest to measure using LIBS, followed by S. Because ambient N₂ contributes to plasma generation, soil nitrogen (N) cannot be identified in atmospheric air using LIBS, making it impossible to quantify the fraction of soil N [67]. In order to prevent ambient (N) influence and involvement in plasma generation, Martin et al. [68], suggested concentrating the small energy pulse (energy of 23 mJ) at 266 nm well below the sample's surface. Because Phosphorus (P), boron (B), chlorine (Cl), and Sulphur (S) are non-metals, are prevalent in mineral soils, and have weak emission lines, LIBS may not be sensitive enough to identify them unless the LIBS signal is amplified. While S is present in mineral soils in the

Table 3. Some LOD and emission lines of soil nutrients.

Nutrients	LOD (g/Kg)	Emission lines (nm)	References
Aluminum (Al)	6.45	220.8	[83]
Boron (B)	1.0	255.14	[84]
Calcium (Ca)	89	317.9	[85]
Chlorine (Cl)	75	133.6	[84]
Copper (Cu)	0.6	324.75	[86]
Iron (Fe)	10	274.6	[85]
Magnesium (Mg)	4	280.27	[85]
Manganese (Mn)	7	380.67	[87]
Molybdenum (Mo)	0.3	313.26	[86]
Nitrogen (N)	8.0	742.36	[88]
Phosphorus (P)	0.251	178.3	[85]
Potassium (K)	46	404.7	[85]
Sulphur (S)	1.1	180.7	[69]
Zinc (Zn)	18	213.86	[19]

range of 0.02–0.6 g/kg [69], the range of phosphorus concentrations is 0.2–5 g/kg [70]. Macronutrients with strong and observable lines of emission, even at low concentrations, like K, Ca, and Mg, are also easier to create calibration models for than other macronutrients. The micronutrients copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), and molybdenum (Mo) are also shown to have intense lines. Nutrient analysis with LIBS and calibration curves can only measure an element's total concentration; it is cannot determine the element's bioavailable concentration for uptake by microorganisms or plants. Creating multivariate models to assess available nutrients while taking into account the relationship between their emission lines and those of other components is one way to solve the problem. There were few studies that could be located, and the bulk of them only examined a small number of samples with somewhat different matrices. It's still quite difficult to lower the LOD for several minerals, particularly P and S. More controlled atmospheric investigations are required since the N quantification is still unresolved [71]. The primary findings and factors to be considered when measuring macro and micronutrients are reviewed, along with the LOD and emission lines that are typically employed and discovered in the literature, Table 3.

6. Conclusions and future recommendations

The use of LIBS technology in environmental monitoring might become quite common. In environmental monitoring, LIBS technology will become more and more common as scholarly research advances and real monitoring systems are created. As a method of analysis, LIBS can identify materials in a variety of mediums, including soil, water, and air aerosols. Moreover, it has the benefits of quick, easy

sample preparation and multiple element detection at once. While many elements using LIBS measurements currently have LODs that are below environmental protection norms or have even met them, much research is still focused on finding ways to lower the detection limits further. Furthermore, the majority of these test findings were acquired in a laboratory setting, whereas environmental monitoring necessitates quick measurement ideally in real time. Before the LIBS methodology can rival existing analytical methods for metal analysis, such ICP and AAS, a number of theoretical and experimental issues must be resolved. These include the proper regulation of plasma temperature, matrix effects, laser-sample and laser-plasma interactions, and plasma plume behavior brought on by laser ablation.

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