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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.

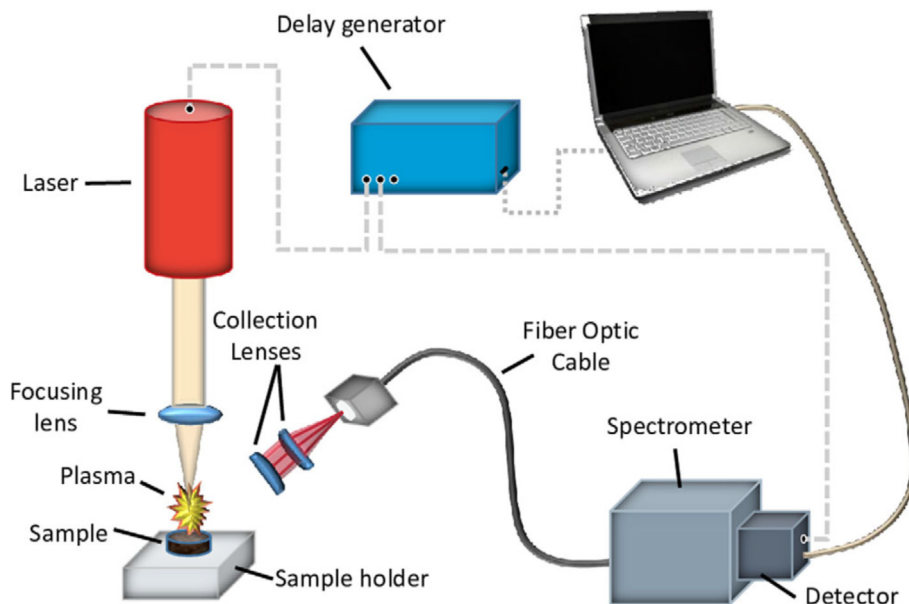


Fig. 1. A typical system setup of (LIBS), [72].

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

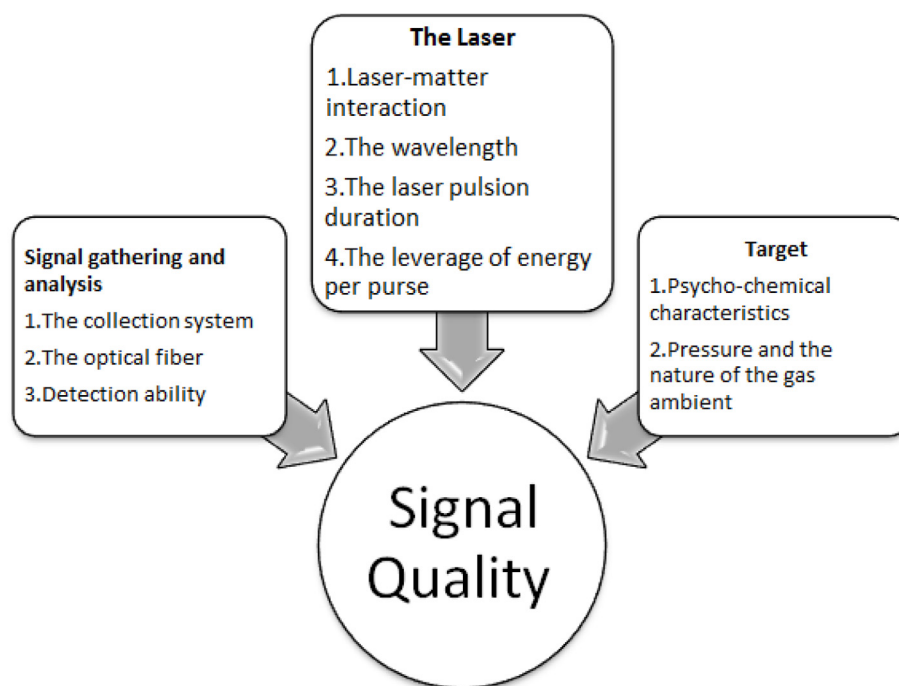


Fig. 2. Demonstrating the main parameters that affected signal quality in LIBS.

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

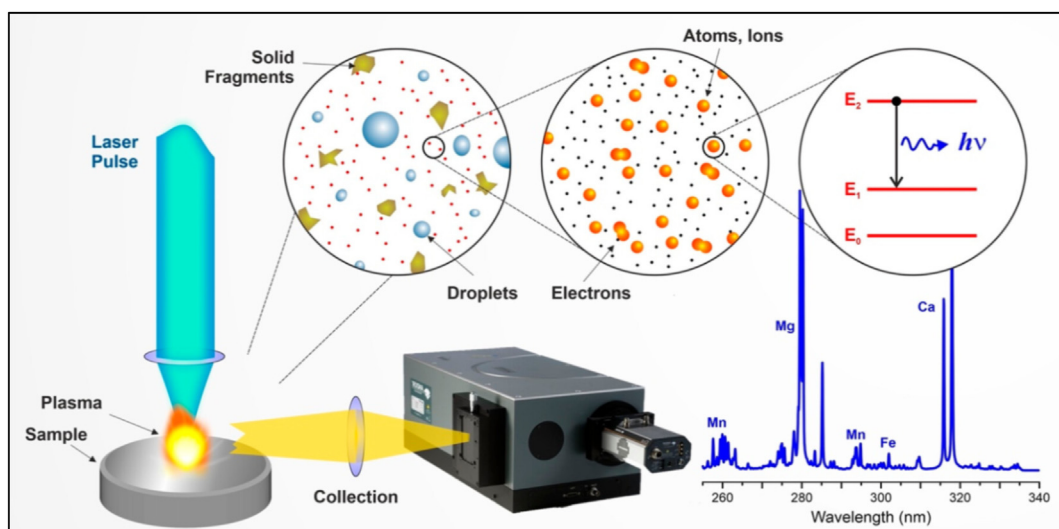


Fig. 3. The mechanism of detecting pollutants using (LIBS) technology [73].

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 μm	[79]
Urban soils	Microwave dissolution in Aqua Regia for soils <53 μm Standard Reference Material (SRM-2586) according to National Institute of Standards and Technology	[80]
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 temperature, 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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References

- [1] Dell'Aglio M, Gaudiuso R, Senesi GS, De Giacomo A, Zaccone C, Miano TM, et al. Monitoring of Cr, Cu, Pb, V and Zn in polluted soils by laser induced breakdown spectroscopy (LIBS). *J Environ Monit* 2011;13(5):1422–6.
- [2] Spectroscopic study of Cu, Mn, Cd as heavy metals in agricultural samples. In: Fayek N, Tawfik W, Khalafallah A, Hamed S, Mousa W, editors. IOP conference series: materials science and engineering. IOP Publishing; 2021.
- [3] Fayek N, Tawfik W, Khalafallah A, Hamed S, Mousa W, Fikry MJ. Evaluation of heavy metal presence in agricultural samples of *Lactuca sativa* and *Trifolium alexandrinum* using picosecond laser-induced breakdown spectroscopy and flame atomic absorption spectroscopy in banha and Giza Governorates, Egypt. *Minerals* 2023;13(10):1300.
- [4] Senesil GS, Baldassarre G, Senesi N, Radina BJ. Trace element inputs into soils by anthropogenic activities and implications for human health. *Chemosphere* 1999;39(2): 343–77.
- [5] Yu K-Q, Zhao Y-R, Liu F, He Y. Laser-induced breakdown spectroscopy coupled with multivariate chemometrics for variety discrimination of soil. *Sci Rep* 2016;6(1):27574.
- [6] Peng J, Liu F, Zhou F, Song K, Zhang C, Ye L, et al. Challenging applications for multi-element analysis by laser-induced breakdown spectroscopy in agriculture: a review. *TrAC Trends Anal Chem* 2016;85:260–72.
- [7] Fikry M, Tawfik W, Omar M. Controlling the plasma electron number density of copper metal using NIR picosecond laser-induced plasma spectroscopy. *Opt Appl* 2021;51(3).
- [8] Fikry M, Tawfik W, Omar M. Measurement of the electron temperature in a metallic copper using ultrafast laser-induced breakdown spectroscopy. *J Russ Laser Res* 2020; 41(5):484–90.
- [9] Ismail MA, Imam H, Elhassan A, Youniss WT, Harith MAJ. LIBS limit of detection and plasma parameters of some elements in two different metallic matrices. *J Anal At Spectrom* 2004;19(4):489–94.
- [10] Peng J, He Y, Ye L, Shen T, Liu F, Kong W, et al. Moisture influence reducing method for heavy metals detection in plant materials using laser-induced breakdown spectroscopy: a case study for chromium content detection in rice leaves 2017;89(14):7593–600.

- [11] Canel T, Demir P, Kacar E, Oztoprak BG, Akman E, Gunes M, et al. Optimization of parameters for depth resolution of galvanized steel by LIBS technique. *Opt Laser Technol* 2013;54:257–64.
- [12] Rehse S, Salimnia H, Miziolek AJ. Laser-induced breakdown spectroscopy (LIBS): an overview of recent progress and future potential for biomedical applications. *J Med Eng Technol* 2012;36(2):77–89.
- [13] Yu X, Li Y, Gu X, Bao J, Yang H, Sun L, et al. Laser-induced breakdown spectroscopy application in environmental monitoring of water quality: a review. *Environ Monit Assess* 2014;186:8969–80.
- [14] Tawfik W, Bousiakou LG, Qindeel R, Farooq W, Alonizan NH, Fatani AJ. Trace analysis of heavy metals in groundwater samples using laser induced breakdown spectroscopy (LIBS). *Optoelectron Adv Mater* 2015;9:185–92.
- [15] Hussain T, Gondal M, Yamani Z, Baig M. Measurement of nutrients in green house soil with laser induced breakdown spectroscopy. *Environ Monit Assess* 2007;124:131–9.
- [16] Senesi G, Dell'Aglio M, Gaudioso R, De Giacomo A, Zaccone C, De Pascale O, et al. Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium. *Environ Res* 2009;109(4):413–20.
- [17] Pandhija S, Rai N, Rai AK, Thakur SN. Contaminant concentration in environmental samples using LIBS and CF-LIBS. *Appl Phys B* 2010;98:231–41.
- [18] Ismael A, Bousquet B, Michel-Le Pierres K, Travaillé G, Canioni L, Roy S. In situ semi-quantitative analysis of polluted soils by laser-induced breakdown spectroscopy (LIBS). *Appl Spectrosc* 2011;65(5):467–73.
- [19] Popov A, Kozhnov M, Labutin T, Zaytsev S, Drozdova A, Mityurev N. Rapid determination of zinc in soils by laser-induced breakdown spectroscopy. *Tech Phys Lett* 2013;39: 81–3.
- [20] Mekonnen KN, Ambushe AA, Chandravanshi BS, Abshiro MR, du Plessis A, McCrindle RI. Assessment of the concentration of Cr, Mn and Fe in sediment using laser-induced breakdown spectroscopy. *Bull Chem Soc Ethiop* 2013;27(1):1–13.
- [21] Kim K-R, Kim G, Kim J-Y, Park K, Kim K-WJ. Kriging interpolation method for laser induced breakdown spectroscopy (LIBS) analysis of Zn in various soils. *J Anal At Spectrom* 2014;29(1):76–84.
- [22] Ferreira EC, Neto JAG, Milori DM, Ferreira EJ, Anzano JM. Laser-induced breakdown spectroscopy: extending its application to soil pH measurements. *Spectrochim Acta Part B At Spectrosc* 2015;110:96–9.
- [23] Nicolodelli G, Senesi GS, de Oliveira Perazzoli IL, Marangoni BS, Benites VDM, Milori DMBP. Double pulse laser induced breakdown spectroscopy: a potential tool for the analysis of contaminants and macro/micronutrients in organic mineral fertilizers. *Sci Total Environ* 2016;565: 1116–23.
- [24] Kim G, Yoon Y-J, Kim H-A, Cho H-j, Park KJ. Elemental composition of Arctic soils and aerosols in Ny-Ålesund measured using laser-induced breakdown spectroscopy. *Spectrochim Acta Part B At Spectrosc* 2017;134:17–24.
- [25] Fu X, Li G, Tian H, Dong D. Detection of cadmium in soils using laser-induced breakdown spectroscopy combined with spatial confinement and resin enrichment. *RSC Adv* 2018; 8(69):39635–40.
- [26] Mahmood Akhtar MA, Abdul Jabbar AJ, Shaukat Mahmood SM, Umar Z, Rizwan Ahmed RA, Baig M. Analysis of soil by magnetic field assisted calibration-free laser induced breakdown spectroscopy (CF-LIBS) and laser ablation-time-of-flight mass spectrometry (LA-TOF-MS). *Anal Lett* 2019;52(14):1–17.
- [27] Detection of heavy metal containment of soil pollution due to waste of paper industry using Nd: YAG laser induced breakdown spectroscopy. In: Sugito H, Khumaeni A, Binu Q, editors. *Journal of Physics: Conference Series*. IOP Publishing; 2020.
- [28] Yoon S, Choi J, Moon S-J, Choi JH. Determination and quantification of heavy metals in sediments through laser-induced breakdown spectroscopy and partial least squares regression. *Appl Sci* 2021;11(15):7154.
- [29] Awad ARM. Analysis of toxic elements, heavy and radioactive in Kadugli soil using spectroscopic techniques. *Sudan University of Science & Technology*; 2022.
- [30] Gupta S, Pandotra P, Gupta A, Dhar J, Sharma G, Ram G, et al. Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of *Zingiber officinale* collected from different locations of North Western Himalayas by Atomic Absorption Spectroscopy. *Food Chem Toxicol* 2010;48(10):2966–71.
- [31] Zhang Y, Zhang T, Li H. Application of laser-induced breakdown spectroscopy (LIBS) in environmental monitoring. *Spectrochim Acta Part B At Spectrosc* 2021;181:106218.
- [32] Villas-Boas PR, Romano RA, de Menezes Franco MA, Ferreira EC, Ferreira EJ, Crestana S, et al. Laser-induced breakdown spectroscopy to determine soil texture: a fast analytical technique. *Geoderma* 2016;263:195–202.
- [33] Fortes FJ, Moros J, Lucena P, Cabalin LM, Laserna JJ. Laser-induced breakdown spectroscopy. *Anal Chem* 2013;85(2): 640–69.
- [34] Akhtar M, Jabbar A, Mehmood S, Ahmed N, Ahmed R, Baig M. Magnetic field enhanced detection of heavy metals in soil using laser induced breakdown spectroscopy. *Spectrochim Acta Part B At Spectrosc* 2018;148:143–51.
- [35] Guo L, Zhang B, He X, Li C, Zhou Y, Wu T, et al. Optimally enhanced optical emission in laser-induced breakdown spectroscopy by combining spatial confinement and dual-pulse irradiation. *Opt Express* 2012;20(2):1436–43.
- [36] Zakuskin AS, Popov AM, Zorov NB, Labutin TA. Confinement of laser plasma by shock waves for increasing signal intensity in spectrochemical determination of trace elements in ores. *Tech Phys Lett* 2018;44:73–6.
- [37] Liu Y, Bousquet B, Baudalet M, Richardson M. Improvement of the sensitivity for the measurement of copper concentrations in soil by microwave-assisted laser-induced breakdown spectroscopy. *Spectrochim Acta Part B At Spectrosc* 2012;73: 89–92.
- [38] Rehan I, Gondal M, Rehan K. Determination of lead content in drilling fueled soil using laser induced spectral analysis and its cross validation using ICP/OES method. *Talanta* 2018; 182:443–9.
- [39] Li KeXue LK, Zhou WeiDong ZW, Shen QinMei SQ, Ren Zhijun RZ, Peng BaoJin PB. Laser ablation assisted spark induced breakdown spectroscopy on soil samples. *J Anal At Spectrom* 2010;25(9):1475–81.
- [40] Cremers DA, Radziemski LJ. *Handbook of laser-induced breakdown spectroscopy*. John Wiley & Sons; 2013.
- [41] Khan Z, Ullah MH, Rahman B, Talukder AI, Wahadoszamen M, Abedin K, et al. Laser-induced breakdown spectroscopy (LIBS) for trace element detection: a review. *J Spectrosc* 2022;2022(1):3887038.
- [42] Thakur SN, Singh JPJL-IBS. *Fundamentals of LIBS and recent developments*. 2020. p. 3–22.
- [43] Jean-Noëla MK, Arthurb KT, Jean-Marc B. LIBS technology and its application: overview of the different research areas. *J Environ Sci Public Health* 2020;4(3):134–49.
- [44] Pathak AK, Kumar R, Singh VK, Agrawal R, Rai S, Rai AK. Assessment of LIBS for spectrochemical analysis: a review. *Appl Spectrosc Rev* 2012;47(1):14–40.
- [45] Khater MA. Trace detection of light elements by laser-induced breakdown spectroscopy (LIBS): applications to non-conducting materials. *Opt Spectrosc* 2013;115:574–90.
- [46] Xu X, Du C, Ma F, Shen Y, Zhou J. Fast and simultaneous determination of soil properties using laser-induced breakdown spectroscopy (LIBS): a case study of typical farmland soils in China. *Earth-Sci Rev* 2019;3(4):66.
- [47] Sun C, Tian Y, Gao L, Niu Y, Zhang T, Li H, et al. Machine learning allows calibration models to predict trace element concentration in soils with generalized LIBS spectra. *Sci Rep* 2019;9(1):11363.

- [48] Guo G, Niu G, Shi Q, Lin Q, Tian D, Duan Y. Multi-element quantitative analysis of soils by laser induced breakdown spectroscopy (LIBS) coupled with univariate and multivariate regression methods. *Anal Methods* 2019;11(23):3006–13.
- [49] Jantzi SC, Almirall JR. Elemental analysis of soils using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) with multivariate discrimination: tape mounting as an alternative to pellets for small forensic transfer specimens. *Appl Spectrosc* 2014;68(9):963–74.
- [50] Popov AM, Colao F, Fantoni RJ. Spatial confinement of laser-induced plasma to enhance LIBS sensitivity for trace elements determination in soils. *At Spectrom* 2010;25(6):837–48.
- [51] Zhou R, Tang Z, Liu K, Zhang W, Liu K, Li X, et al. High sensitivity analysis of soil by laser-induced breakdown spectroscopy with Ag nanoparticles. *Opt Laser Technol* 2022;155:108386.
- [52] Villas-Boas PR, Franco MA, Martin-Neto L, Gollany HT, Milori DM. Applications of laser-induced breakdown spectroscopy for soil characterization, part II: review of elemental analysis and soil classification. *Eur J Soil Sci* 2020;71(5):805–18.
- [53] Kim G, Kwak J, Kim K-R, Lee H, Kim K-W, Yang H, et al. Rapid detection of soils contaminated with heavy metals and oils by laser induced breakdown spectroscopy (LIBS). *J Hazard Mater* 2013;263:754–60.
- [54] Lal B, Zheng H, Yueh F-Y, Singh JP. Parametric study of pellets for elemental analysis with laser-induced breakdown spectroscopy. *Appl Opt* 2004;43(13):2792–7.
- [55] Brickleyer RS, Brown DJ, Barefield JE, Clegg SM. Intact soil core total, inorganic, and organic carbon measurement using laser-induced breakdown spectroscopy. *Soil Sci Soc Am J* 2011;75(3):1006–18.
- [56] Brickleyer RS, Brown DJ, Turk PJ, Clegg S. Comparing vis–NIRS, LIBS, and combined vis–NIRS-LIBS for intact soil core soil carbon measurement. *Soil Sci Soc Am J* 2018;82(6):1482–96.
- [57] Brickleyer RS, Brown DJ, Turk PJ, Clegg SM. Improved intact soil-core carbon determination applying regression shrinkage and variable selection techniques to complete spectrum laser-induced breakdown spectroscopy (LIBS). *Appl Spectrosc* 2013;67(10):1185–99.
- [58] Beal SA, Mossell AM, Clausen JL. Matrix and target particle-size effects on LIBS analysis of soils. 2020.
- [59] Pouzar M, Kratochvíl T, Kaski S, Kaiser J, Knotek P, Čapek L, et al. Effect of particle size distribution in laser-induced breakdown spectroscopy analysis of mesoporous V–SiO₂ catalysts. *J Anal At Spectrom* 2011;26(11):2281–8.
- [60] Asgill ME, Hahn DW. Particle size limits for quantitative aerosol analysis using laser-induced breakdown spectroscopy: temporal considerations. *Spectrochim Acta Part B At Spectrosc* 2009;64(10):1153–8.
- [61] McIntyre TJP. Phytoremediation of heavy metals from soils. 2003. p. 97–123.
- [62] Singh R, Gautam N, Mishra A, Gupta RJ. Heavy metals and living systems: an overview. *Indian J Pharmacol* 2011;43(3):246.
- [63] Labutin TA, Zaytsev SM, Popov AM, Zorov NBJ. A novel approach to sensitivity evaluation of laser-induced breakdown spectroscopy for rare earth elements determination. *J Anal At Spectrom* 2016;31(11):2223–6.
- [64] Akhtar M, Jabbar A, Mahmood S, Umar ZA, Ahmed R, Aslam Baig M. Analysis of soil by magnetic field assisted calibration-free laser induced breakdown spectroscopy (CF-LIBS) and laser ablation–time-of-flight mass spectrometry (LA-TOF-MS). *Anal Lett* 2019;52(14):2312–28.
- [65] Mukhono P, Angeyo K, Dehayem-Kamadjeu A, Kaduki K. Laser induced breakdown spectroscopy and characterization of environmental matrices utilizing multivariate chemometrics. *Spectrochim Acta Part B At Spectrosc* 2013;87:81–5.
- [66] Morra M, Hall M, Freeborn L. Carbon and nitrogen analysis of soil fractions using near-infrared reflectance spectroscopy. *Soil Sci Soc Am J* 1991;55(1):288–91.
- [67] Hossen MA, Diwakar PK, Ragi S. Total nitrogen estimation in agricultural soils via aerial multispectral imaging and LIBS. *Sci Rep* 2021;11(1):12693.
- [68] Martin MZ, Wullschlegler SD, Garten CT, Palumbo AV. Laser-induced breakdown spectroscopy for the environmental determination of total carbon and nitrogen in soils. *Appl Opt* 2003;42(12):2072–7.
- [69] Kuo S, Sparks DJSSoA, Madison WI. Methods of soil analysis. Part 3: Chemical methods. 1996. p. 894–5.
- [70] Dixon JSSSAJMW. Kaolin and Serpentine group minerals. In: Dixon JB, Weed SB, editors. *Minerals in soil environments*; 1989. p. 551–634.
- [71] Rühlmann M, Büchele D, Ostermann M, Bald I, Schmid T. Challenges in the quantification of nutrients in soils using laser-induced breakdown spectroscopy—A case study with calcium. *Spectrochim Acta Part B At Spectrosc* 2018;146:115–21.
- [72] Villas-Boas PR, Franco MA, Martin-Neto L, Gollany HT, Milori DM. Applications of laser-induced breakdown spectroscopy for soil analysis, part I: review of fundamentals and chemical and physical properties. *Eur J Soil Sci* 2020;71(5):789–804.
- [73] Fabre CJ. Advances in Laser-Induced Breakdown Spectroscopy analysis for geology: a critical review. *Spectrochim Acta Part B At Spectrosc* 2020;166:105799.
- [74] Hussain T, Gondal M. Monitoring and assessment of toxic metals in Gulf War oil spill contaminated soil using laser-induced breakdown spectroscopy. *Environ Monit Assess* 2008;136:391–9.
- [75] Srungaram PK, Ayyalasomayajula KK, Yu-Yueh F, Singh JP. Comparison of laser induced breakdown spectroscopy and spark induced breakdown spectroscopy for determination of mercury in soils. *Spectrochim Acta Part B At Spectrosc* 2013;87:108–13.
- [76] Shaheen ME, Tawfik W, Mankoula AF, Gagnon JE, Fryer BJ, El-Mekawy F, et al. Determination of heavy metal content and pollution indices in the agricultural soils using laser ablation inductively coupled plasma mass spectrometry. *Environ Sci Pollut Res* 2021;28:36039–52.
- [77] Suyanto H, Lie TJ, Kurniawan KH, Kagawa K, Tjia MO. Practical soil analysis by laser induced breakdown spectroscopy employing subtarget supported micro mesh as a powder sample holder. *Spectrochim Acta Part B At Spectrosc* 2017;137:59–63.
- [78] Hussein NA, Hameed MA. Design and constructions laser-induced breakdown spectroscopy system to determine the fertility of north Iraqi soil. *Iraqi J Sci* 2018;16(38):56–65.
- [79] Essington ME, Melnichenko GV, Stewart MA, Hull RA. Soil metals analysis using laser-induced breakdown spectroscopy (LIBS). *Soil Sci Soc Am J* 2009;73(5):1469–78.
- [80] Yang N, Eash NS, Lee J, Martin MZ, Zhang Y-S, Walker FR, et al. Multivariate analysis of laser-induced breakdown spectroscopy spectra of soil samples. *Soil Sci* 2010;175(9):447–52.
- [81] Nicolodelli G, Marangoni BS, Cabral JS, Villas-Boas PR, Senesi GS, Dos Santos CH, et al. Quantification of total carbon in soil using laser-induced breakdown spectroscopy: a method to correct interference lines. *Appl Opt* 2014;53(10):2170–6.
- [82] Hassan M, Sighicelli M, Lai A, Colao F, Ahmed AH, Fantoni R, et al. Studying the enhanced phytoremediation of lead contaminated soils via laser induced breakdown spectroscopy. *Spectrochim Acta Part B At Spectrosc* 2008;63(10):1225–9.
- [83] Erler A, Riebe D, Beitz T, Löhmannsröben H-G, Gebbers R. Soil nutrient detection for precision agriculture using handheld laser-induced breakdown spectroscopy (LIBS) and multivariate regression methods (PLSR, Lasso and GPR). *Sensors* 2020;20(2):418.
- [84] Radziemski L, Cremers DA, Benelli K, Khoo C, Harris RD. Use of the vacuum ultraviolet spectral region for laser-induced breakdown spectroscopy-based Martian geology and exploration. *Spectrochim Acta Part B At Spectrosc* 2005;60(2):237–48.

- [85] Diaz D, Hahn DW, Molina A. Evaluation of laser-induced breakdown spectroscopy (LIBS) as a measurement technique for evaluation of total elemental concentration in soils. *Appl Spectrosc* 2012;66(1):99–106.
- [86] Popov AM, Labutin TA, Zaytsev SM, Seliverstova IV, Zorov NB, Kal'ko IA, et al. Determination of Ag, Cu, Mo and Pb in soils and ores by laser-induced breakdown spectrometry. *J Anal At Spectrom* 2014;29(10):1925–33.
- [87] Multari RA, Foster LE, Cremers DA, Ferris MJ. Effect of sampling geometry on elemental emissions in laser-induced breakdown spectroscopy. *Appl Spectrosc* 1996;50(12):1483–99.
- [88] Harris RD, Cremers DA, Ebinger MH, Bluhm BK. Determination of nitrogen in sand using laser-induced breakdown spectroscopy. *Appl Spectrosc* 2004;58(7):770–5.