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Review

Application and Research Progress of Laser-Induced Breakdown Spectroscopy in Agricultural Product Inspection

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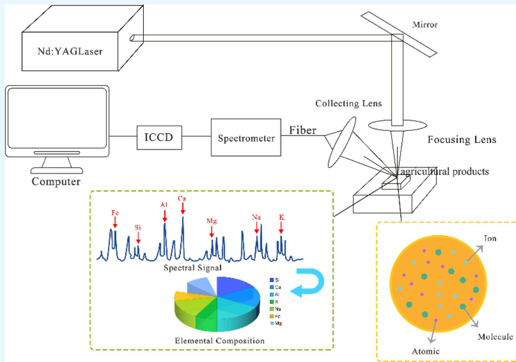
ABSTRACT: The quality and safety of agricultural products are of paramount importance in ensuring the health of the food supply chain. Additionally, the composition and trace elements in agricultural products significantly influence their quality and nutritional value. Therefore, the need for rapid and accurate analysis techniques for agricultural product composition is particularly crucial. In the current landscape of evolving compositional analysis technologies, Laser-Induced Breakdown Spectroscopy (LIBS) technology is emerging as a promising analytical tool with broad applications in agricultural product testing. Its characteristics of being rapid, real-time, and capable of simultaneous detection of multiple elements provide an efficient and reliable means for assessing the quality, monitoring safety, and tracing the origin of agricultural products. This technology is expected to play a significant role in controlling and managing the agricultural industry chain and can offer consumers safer and healthier agricultural products. This paper provides an overview of the research status and recent developments of LIBS technology in agricultural product testing applications in recent years. Based on the current research landscape, challenges and opportunities of applying LIBS technology in fields such as agricultural product quality and safety assessment, soil analysis, assessment of crop nutrition, detection of plant diseases, and identification of agricultural product varieties have been evaluated. Moreover, recommendations for further expanding the application of LIBS technology in the agricultural sector are proposed.



1. INTRODUCTION

The detection of agricultural product composition holds critical significance in maintaining the healthy operation of the food supply chain, as variations in element composition and content are closely related to the quality, safety, and potential nutritional value of agricultural products. The presence of heavy metals and chemical substances such as pesticides in agricultural products may induce complex metabolic changes, posing significant challenges to the safety and quality of agricultural products. Research indicates that heavy metal contamination may lead to adjustments in plant metabolic pathways, thereby affecting the biosynthetic pathways and production of metabolites. For instance, lead contamination often reduces the content of polyphenolic compounds and antioxidant substances in crops, while cadmium pollution may disrupt nitrogen metabolism pathways, leading to changes in amino acid content. Additionally, pesticide residues have been shown to significantly impact the metabolomics of agricultural products. Previous studies have indicated that pesticide residues may induce an increase in antioxidant enzyme activity in agricultural products and affect the synthesis pathways of their antioxidant substances. These metabolomic changes not only directly affect the quality and nutritional value of agricultural products but may also have adverse effects on human health. Duan et al.[1] conducted experiments involving varying concentrations of salt treatment during the germination and seedling stages of alfalfa. They assessed seed germination rate, survival rate, plant height, and root length under different salt stress conditions in order to investigate the effects of salt stress on the growth of alfalfa during the germination and seedling stages. Concurrently, metabolomic analysis was employed to identify key response to salt stress during the germination and seedling stages of alfalfa. Chen et al.[2] investigated the absorption, transport, and toxic effects mechanism of carbon quantum dots (C-dots) in maize and *Arabidopsis*,[2] exploring how these nanomaterials interact with plant systems. The study confirmed that partial C-dots could be secreted from the margins and tips of maize leaves and penetrate the root epidermal cells of *Arabidopsis* seedlings, entering the roots and being transported to the aboveground parts. Additionally, it was found that C-dots could enter the maize root cap cells in large quantities, primarily distributed in

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the cytoplasm. Sun et al.[3] conducted single-strain fermentation of soybeans and found that the contents of nitrogen in amino acid form, reducing sugars, and total acids in soybean paste steadily increased with fermentation time. The times at which different detected components reached their maximum values varied but were mainly concentrated between 40 and 60 days. Furthermore, the content of crude fat showed a significant decreasing trend in the first 70 days of fermentation.

Research has revealed that certain essential bioelements play a pivotal role in agricultural products, influencing their growth, metabolism, and immune regulation functions. For instance, in plant-based agricultural products, trace elements such as zinc, copper, and iron act as indispensable cofactors in plant growth. They participate in processes like photosynthesis, nutrient absorption, and antioxidant defense. Imbalances in element content, whether excessive or deficient, can lead to abnormal agricultural product growth.

To ensure the quality and safety of agricultural products, various analytical methods have been widely employed, including infrared spectroscopy, gas chromatography−mass spectrometry (GC-MS), liquid chromatography−mass spectrometry (LC-MS), nuclear magnetic resonance (NMR), atomic absorption spectroscopy (AAS), high-performance liquid chromatography (HPLC), immunoassays, etc.,[4−7] for the purpose of compositional analysis. Infrared Spectroscopy involves measuring a sample's absorption of infrared radiation to identify and analyze organic compounds in agricultural products, such as fats and proteins. However, it exhibits a comparatively lower sensitivity to nonvolatile and high-boiling-point compounds. Gas Chromatography−Mass Spectrometry (GC-MS), which separates compounds through gas chromatography and identifies/quantifies them via mass spectrometry, making it suitable for detecting pesticide residues and food additives in agricultural products. Nevertheless, its complexity and elevated maintenance costs are considered drawbacks. Liquid Chromatography−Mass Spectrometry (LC-MS) separates compounds via liquid chromatography and identifies/quantifies them through mass spectrometry. It is commonly used for detecting drug residues in agricultural products. However, its ability to analyze volatile compounds is somewhat less robust compared to GC-MS. Nuclear Magnetic Resonance (NMR) analyzes molecular structure and composition by measuring nuclear magnetic resonance signals, suitable for identifying organic molecule structures but has reduced sensitivity to certain nonorganic substances. Atomic Absorption Spectroscopy (AAS) quantifies element concentrations in samples by measuring characteristic absorption spectra of atomic vapors. However, it cannot simultaneously detect multiple elements and necessitates changing lamps for each specific element. High-Performance Liquid Chromatography (HPLC) separates mixtures via high-pressure liquid phase and analyzes them using a detector. It is commonly employed for detecting pigments and organic acids in agricultural products. Nevertheless, the separation of some polar substances may pose challenges. Immunoassay utilizes antibody−antigen interactions for analysis. It is applicable for detecting hormones and antibiotics in agricultural products. However, its specificity in complex samples is somewhat lower.

Despite the high accuracy and sensitivity of these methods, limitations such as lengthy analysis times, cumbersome sample preparation, and the inability to provide highly precise quantitative data, as well as expensive equipment costs, still persist. Table 1 provides a comparison between LIBS and

Table 1. Comparison of LIBS with Traditional Agricultural Product Composition Detection Techniques

Methods	Detection Range	Sample Preparation	Analysis Time	Detection Limit	Limitations
Infrared Spectroscopy Analysis	Functional Groups, Molecular Structures, Certain Chemical Bonds	Not required or requires simple processing	s−min	mg/L, not suitable for trace analysis	Sensitive to moisture and hydrogen bonding, not suitable for inorganic analysis
GC-MS	Organic Compounds, Volatile Substances	Sample preparation is complex, requiring extraction or derivatization	min−h	μg/L to mg/L, suitable for trace analysis	Cannot directly analyze nonvolatile compounds, limited for nonvolatile samples
LC-MS	Organic Compounds, Polar Compounds	Sample preparation is complex, requiring extraction or derivatization	min−h	ng/L to μg/L, suitable for trace analysis	High operational skill required, longer analysis time
NMR	Nuclear Types, Molecular Structures	Nondestructive, typically no sample processing needed	min−h	μg/L to mg/L, insensitive to nonvolatile and low-concentration samples	Expensive equipment, cannot directly analyze inorganic substances
AAS	Metal Elements	Sample preparation is complex, requiring dissolution or conversion to the gas phase	s−min	μg/L to mg/L, suitable for trace metal analysis	Single-element analysis, not suitable for multielement analysis
HPLC	Organic Compounds, Polar Compounds	Sample preparation is complex, requiring extraction or derivatization	min−h	ng/L to μg/L, suitable for trace analysis	High operational skill required, longer analysis time
Immunoassay	Specific Proteins or Compounds	Sample preparation is complex, requiring specific antibody reactions	min−h	ng/L to μg/L, suitable for specific analysis	Only applicable to known target analysis, influenced by antibody selection and cross-reactivity
LIBS	Multi-Element Simultaneous Detection	Not required or requires simple processing	s−min	μg/g to mg/g, limited for trace element analysis.	Sensitive to sample surface morphology and composition, sample heterogeneity affects signal accuracy

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traditional agricultural product compositional analysis techniques. Hence, in the field of agriculture, researchers are actively exploring novel analytical technologies to enhance detection efficiency, reduce costs, expedite of the process of agricultural product compositional analysis, and ensure widespread practical application in production. The application of these new technologies will contribute to safeguarding the quality and safety of agricultural products, offering robust support to agricultural production.

Laser-Induced Breakdown Spectroscopy (LIBS) is a technique that employs laser pulses to generate high-temperature plasma on the surface of agricultural products. LIBS technology stands out as a swift, on-the-spot, minimally intrusive, cost-effective, and dependable method suitable for both qualitative and quantitative analysis of major and trace elements in solid, liquid, or gas samples. In LIBS technology, a precisely focused laser pulse is directed onto the surface of the target sample, causing the ablation of a certain amount of material and generating plasma in the process. The resulting spectrum is gathered by plotting intensity against wavelength, which is derived from light emissions produced by atomic, ionic, and molecular fragments.

The identified LIBS spectrum contains two types of information regarding the composition and content of the sample. The wavelength of the characteristic spectrum aligns with the type of element present, and the relative strength of this characteristic spectrum corresponds to the concentration of the element. Leveraging the instrumental features of LIBS allows for advanced analysis, overcoming the limitations associated with traditional chemical analytical techniques. These advantages include minimal or no sample preparation, real-time analysis, on-site field applications, and the remote detection of hazardous materials. The rapid, real-time, and nondestructive characteristics make LIBS technology an ideal choice for the analysis of agricultural product composition. By capturing and analyzing these emitted spectral signals, LIBS technology can effectively and precisely detect various elements in agricultural products, encompassing minerals, nutritional components, and potentially harmful metals.

The trace element content in agricultural products significantly influences their quality, healthiness, and market value. Building upon the current state of research, this article evaluates the challenges and opportunities that LIBS technology encounters across multiple domains, including agricultural product quality and safety inspection, soil analysis, crop nutritional assessment, plant disease detection, and agricultural product variety identification.

Furthermore, the article presents recommendations for the continued expansion of LIBS technology's application within the agricultural sector.

In chemical analysis, besides the target analyte, samples often contain other components referred to as matrix compounds. These compounds may interact with the target analyte, causing signal interference or background elevation, thus affecting the accuracy and reliability of the determination. Therefore, removing matrix compounds from samples is crucial to ensure precise analysis.

Matrix compounds can have various impacts on Laser-Induced Breakdown Spectroscopy (LIBS) analysis. First, they may generate interfering signals within the spectral range of the target element, leading to spectral overlap and cross-talk, thereby reducing the detection sensitivity and analytical accuracy of the target element. Second, the absorption or scattering of the laser beam by matrix compounds may diminish the energy available for exciting the target element, thereby affecting the intensity of its emitted spectral signal. Additionally, the presence of matrix compounds may increase the complexity of the spectral background, making it more difficult to distinguish and identify the signal of the target element, thus elevating the noise level of the analysis results. Furthermore, matrix compounds may cause drift in the spectral baseline, resulting in the displacement of the target element signal position and affecting the accuracy of quantitative analysis. Therefore, when conducting LIBS analysis, it is essential to fully consider and address the influence of matrix compounds to ensure the accuracy and reliability of the results.

To mitigate the issues caused by matrix effects, suitable methods are needed to remove matrix compounds from samples. Common removal methods include physical methods (such as solvent extraction, chromatographic separation, crystallization, etc.) and chemical methods (such as extraction, precipitation, etc.). These methods can be selected and optimized based on sample properties, matrix compound characteristics, and analysis method requirements. For example, solvent extraction separates the target analyte from the matrix by selecting appropriate solvents and dissolution conditions. Chromatographic separation utilizes differences in compound distribution between the stationary and mobile phases to achieve separation between the target analyte and matrix. Crystallization separates the target analyte from the solution by controlling the solution conditions. Extraction removes the target analyte from the sample by exploiting differences in partition coefficients between the solvent phase and water phase.

Researchers have employed various effective means and methods to minimize the influence of matrix compounds on LIBS technology in pretreated samples.[8−11] First, highly specific analysis of the sample is achieved by carefully selecting laser wavelengths to reduce spectral interference from the matrix. Second, optimization of laser pulse energy and width maximizes the excitation and ionization efficiency of the target element, thereby minimizing the influence of the matrix. Additionally, the adoption of a multielement analysis strategy, simultaneous measurement of emission spectra of multiple elements, more accurately distinguishes the signals of the target element and matrix, further reducing the influence of the matrix. Furthermore, correction methods such as the internal standard method and external calibration method have been developed and applied to correct errors caused by the matrix by introducing known concentrations of internal standard substances or using standard reference samples for calibration. Simultaneously, multiple-point measurements are conducted at various locations of the sample to assess the uniformity and variability of the matrix, ensuring the reliability and accuracy of the analysis results. Finally, reasonable processing and analysis of the obtained spectral data, including background correction, spectral fitting, and noise reduction, further reduce interference caused by the matrix, enhancing the detection sensitivity and accuracy of the target element.

In summary, by employing pretreatment methods for sample handling, followed by appropriate selection of laser wavelengths, optimization of pulse parameters, multielement analysis, development of calibration methods, multipoint measurements, and data processing, researchers have successfully overcome the influence of matrix compounds on LIBS

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technology analysis results, providing reliable solutions for sample analysis.

2. OVERVIEW OF LIBS TECHNOLOGY

2.1. Basic Principles of LIBS Technology. LIBS technology employs laser-induced breakdown effects for spectroscopic analysis. It operates by directing laser pulses onto a sample's surface to induce transient breakdown and generate plasma. Subsequently, the emitted spectral lines from the plasma are analyzed to extract information about the sample's chemical element composition. The fundamental principles of LIBS technology can be summarized as follows.

Initially, high-energy, short-pulsed laser beams are focused on the sample's surface, rapidly elevating its temperature and initiating plasma formation. This plasma zone exhibits elevated temperatures and electron densities. Within this plasma region, atoms and molecules within the sample become excited, leading to the emission of distinctive spectral lines. The wavelengths and intensities of these spectral signals correspond to the elements present in the sample and their concentrations.

Consequently, these emitted spectral signals are captured and recorded using equipment such as spectrometers. The signals are then translated into digital data, which is subsequently processed to deduce the elemental composition of the sample. Based on the recognized spectral features and intensities of elements, qualitative and quantitative analyses of sample elements can be performed. By comparing the spectral signals with data in reference databases, the types of elements present in the sample can be identified. Furthermore, the intensity of spectral signals is proportionate to the element's concentration, enabling estimation of elemental content.

The strengths of LIBS technology lie in its rapidity, real-time analysis, and nondestructive nature. It can rapidly analyze multiple elements within seconds, suitable for various sample types, encompassing solids, liquids, and gases. With no prerequisite for sample pretreatment, LIBS technology holds vast potential across domains including on-site rapid testing, biomedicine, aerospace, agricultural product inspection, and environmental monitoring.[12−16] For visual representation, refer to Figure 1[17] illustrating the principle of LIBS technology.

Despite numerous advantages of LIBS technology, it still faces significant challenges in trace element analysis. Complex interactions between intricate samples and sensors, as well as challenging operating conditions, can lead to pronounced matrix effects and insufficient detection sensitivity. To address these issues and bolster detection sensitivity, researchers are actively exploring a variety of signal enhancement methods. Techniques like spatial or magnetic confinement LIBS, nanoparticle-enhanced LIBS, double-pulse or multipulse LIBS, resonance-enhanced LIBS, and laser-induced fluorescence-assisted LIBS,[18−21] have been introduced. These approaches aim to optimize the interaction between the laser and the sample, enhance the spectral signals generated and emitted by the plasma, thereby amplifying both LIBS signal intensity and stability.

Matrix effects and self-absorption phenomena are critical factors influencing analytical results. Since analytes are typically not single compounds, analysis detection is inevitably influenced by interference from unrelated matrices, giving rise to matrix effects. Matrix effects are primarily caused by the physical properties and chemical composition of the analytical sample, and reducing these effects can effectively enhance spectral line intensity. Factors contributing to physical matrix effects include vaporization, thermal conductivity, absorption rate, and water content, while chemical matrix effects are mainly influenced by the chemical form and stated of matrix elements. Chemical matrix effects are mainly influenced by the ionization degree the chemical form and state of matrix elements, which in turn affect the emission spectra of the analyzed elements. To minimize interference from matrix effects on analytical spectral lines, common approaches include compound separation, sample concentration dilution, and internal standard correction.

Self-absorption phenomena occur due to the presence of atoms or ions in different energy levels within a high-density plasma. Differences in energy levels result in the absorption of spectra emitted by the ground-state atoms or excited-state plasma, causing phenomena such as flattened or self-reversed (self-absorption) spectral lines. Both matrix effects and self-absorption phenomena can lead to underestimated analytical results. To avoid these issues, current practices often involve error correction through methods such as standard calibration curves, partial least-squares (PLS), discriminant analysis (DA), and principal component analysis (PCA) within the realm of chemometrics.[22−24]

2.2. Analysis Methods of LIBS Technology in Agricultural Product Inspection. In general, a positive correlation is observed between the intensities of spectral lines and the concentrations of elements. Typically, variations in plant element concentrations can be deduced directly from spectral line intensities, eliminating the need for further quantitative analysis. However, when the relative content of an element is required for analytical purposes, CF-LIBS (calibration-free LIBS) can be employed, offering the advantage of not requiring standard samples. Several other calibration methods are commonly applied for quantitative LIBS analysis of various samples, including, but not limited to, agricultural products. Researchers have integrated LIBS technology with statistical algorithms for spectral signal analysis. Techniques such as Principal Component Analysis (PCA), Support Vector Machines (SVM), Random Forest (RF), Artificial Neural Networks (ANN), Partial Least Squares (PLS), Linear Discriminant Analysis (LDA), and Decision Trees (DT),[22−25] have been employed in qualitative and quantitative analysis procedures. These algorithms facilitate the

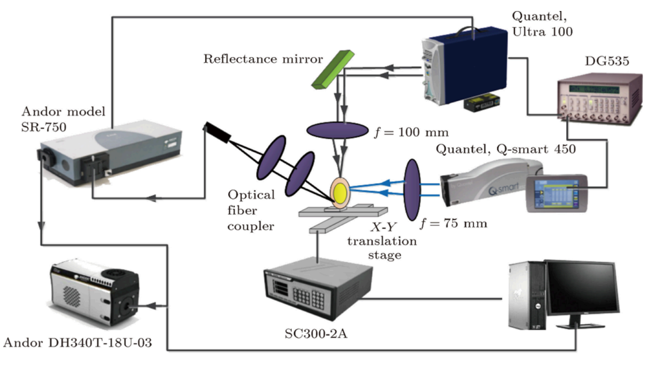

Figure 1. Schematic diagram of the experimental setup for orthogonal reheating DP-LIBS.[17] (Reprinted in part, with permission from the publisher, cited from Zheng, P. C.; Li, X. J.; Wang, J. M.; Zheng, S.; Zhao, H. D. Quantitative analysis of Cu and Pb in Coptidis by reheated double pulse laser-induced breakdown spectroscopy. *Acta Phys. Sin.* **2019**, *68* (12), 198−205. Copyright 2019 Acta Physica Sinica.)

Table 2. Literature on the Application of LIBS Technology in the Field of Agricultural Product Testing

Application Area	Sample	Elements	Sample Preparation	Analysis Methods	References
Traditional Chinese Medicine	Ginseng	C, Mg, Ca, Fe, H, N, O	Different locations	Neural Networks and Support Vector Machines	25
Traditional Chinese Medicine	Rhubarb	Pb	Powder compressed into tablets	—	26
Plants	Rhododendron Leaves	Pb	Solid−liquid−solid	—	27
Agriculture	Soil	Cu, Zn, Cr, Ni	Powder compressed into tablets	Partial Least Squares	28
Cereals	Rice	Cd	Sample preparation by tablet pressing, sample preparation by thin film	Support Vector Machines	29
Fruits	Navel Orange	Mg, Cu, Ca, Fe, CN molecule	Drying	Support Vector Machines	30
Seeds	Legumes	Ca, Mg	Powder compressed into granules	Partial Least Squares, Principal Component Regression, Multienergy Calibration, Single-point Weight Standard Addition	31
Traditional Chinese Medicine	Chrysanthemum, Juncus, Danshen, Planting Soil	K, Ca, Mg, Fe	Powder compressed into granules	Median Absolute Deviation (MAD), Segmental Feature Extraction, Wavelet Denoising	32
Plants	Lily Bulb	Cu, Pb, Zn, Al, Mg	Drying, powder compressed into granules	Partial Least Squares	33
Traditional Chinese Medicine	Turmeric	C, Na, K, Mg, Ca, Fe, Sr, Ba, Pb, Cr, CN molecule	Powder	Principal Component Analysis	34
Traditional Chinese Medicine	Cattle Gall Detoxification Tablets	As	Powder-solution	—	35
Cereals	Rice	Cd, Mg, K, Na, Si, Mn, Ca	Solid particles	Partial Least Squares	36
Plants	Moringa Leaves	Al, C, Ti, Ca, K, Fe, Na, Sr, Li, Mg	Drying, powder compressed into granules	Single-line Calibration	37
Traditional Chinese Medicine	Astragalus Root	Fe, Mg, Cu, Ca, Cr I	Drying, powder compressed into granules	Random Forest, Principal Component Analysis, RF Discriminant Model	38
Traditional Chinese Medicine	Baishao	CN molecule, Mg, Ca, K, Si, Cu	slice	conventional machine learning and deep learning	39
Plants	Tea Leaves	Fe, Mn, Cu, Zn, Ca, Mg	Picking, washing, sorting, bagging, labeling	External Standard Method, Partial Least Squares, Back-propagation Artificial Neural Network, Support Vector Machines	40
Plants	Black Tea Leaves	Mg, Mn, Na, Ca, K, Al, Cr, Zn, Cu, Ni, Pb, Fe	Powder compressed into tablets	—	41

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extraction of relevant information, dimensionality reduction, and accurate elemental analysis in samples. Table 2 provides a summary of select application literature within the agricultural product inspection field utilizing LIBS technology over the past five years.

3. APPLICATION OF LIBS TECHNOLOGY IN AGRICULTURAL PRODUCT ANALYSIS

3.1. Application and Research Progress of LIBS Technology in Agricultural Product Quality and Safety Testing. The content of trace elements in agricultural products directly affects their quality, health implications, and market value. With its high sensitivity and multielement simultaneous detection capabilities, LIBS technology has emerged as a powerful tool for assessing agricultural product quality and ensuring safety. LIBS can be employed to detect chemical components such as heavy metals, pesticide residues, and nutritional elements in agricultural products.

In the realm of rapid testing for fruits, vegetables, cereals, and other agricultural products, LIBS technology offers real-time and accurate analytical results, contributing to the assurance of product quality and safety. For instance, Zhao et al.[42] conducted in situ and in vivo three-dimensional element mapping in cornfields using a portable LIBS system. Their obtained 3D LIBS mappingdisplayed a clear pattern of pesticide residue reduction in leaf depth by moving along the axial direction in steps of 12 μm. This method demonstrated the practical application potential of LIBS technology in field environments. By combining LIBS technology with multivariate regression models, they successfully detected residues of organophosphorus pesticides. Fu et al.[43] focused on 40 naturally matured rice samples from potentially cadmium-contaminated areas. They utilized both Laser-Induced Breakdown Spectroscopy (LIBS) technology and graphite furnace atomic absorption spectroscopy to determine the reference content of Cd in rice. The results indicate that assessing the safety of rice through the analysis of LIBS spectra is promising. Zhang et al.[44] employed dual-pulse Laser-Induced Breakdown Spectroscopy (LIBS) technology for the quantitative analysis of chromium (Cr) elements in rice from five different regions (as shown in Figure 2). The results were compared with the detection results obtained using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The findings revealed that the measurement error of LIBS meets relative error standards, demonstrating the capability of LIBS for rapid quantitative analysis of elements. It proves to be an effective method for detecting the heavy metal element content in rice.

Similarly, LIBS technology has achieved success in detecting trace elements in various other agricultural products. Sun et al.,[45] for instance, utilized onion as an example to successfully perform trace element detection in fresh vegetables using LIBS technology, affirming its advantages in rapid analysis. Luo et al.[46] applied LIBS technology to analyze cadmium elements in spinach, employing optimized parameters and Partial Least Squares (PLS) for quantitative analysis. Experimental results showed that the PLS method outperformed the univariate calibration model, demonstrating higher predictive performance and accuracy, with an average relative error of only 2.56%. Yao et al.[47] employed LIBS technology and the Least Squares method to detect the heavy metal Cd in fresh green leafy vegetables contaminated by Cd solutions. Liu et al.,[48] on the other hand, targeted the detection of Cu elements in rice, comparing the effects of univariate and multivariate regression

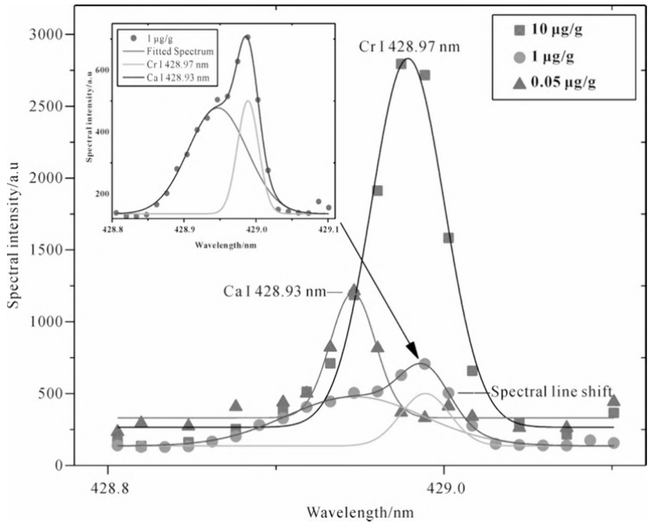

Figure 2. Spectra of Cr I 428.97 nm line rice under different Cr element concentrations.[44] (Zhang, H. Y.; Zhang, X. Q.; Zhang, W.; Qiu, R. Detection and analysis of Cr element in rice by laser induced breakdown spectroscopy. *J. At. Mol. Phys.* **2023**, *40* (04), 110−115.)

models on quantitative analysis, achieving an optimal detection limit of 5 mg/kg.

However, despite the significant progress that LIBS technology has made in the field of agricultural product quality and safety testing, it still faces a series of challenges, whose resolution is crucial for further advancing this technology. These challenges include complex matrix effects, the need for standardization, detection of low-concentration elements, sample heterogeneity, and instrument costs. To address these obstacles, scientists are persistently enhancing LIBS instruments and integrating sophisticated data analysis techniques such as multivariate statistics and machine learning to augment the precision and dependability of this technology. Additionally, establishing applicable standards, enhancing instrument performance, and focusing on the practical applicability and cost-effectiveness of the technology are also key factors driving the ongoing development of LIBS technology in agricultural product analysis.

3.2. Research Progress in Soil Detection Using LIBS Technology. Soil plays a pivotal role in modern agriculture by providing essential mineral nutrients for plant growth. However, toxic elements such as barium, cobalt, cadmium, chromium, mercury, lead, molybdenum, and antimony can potentially contaminate soil through various pathways and be absorbed by plants, posing potential adverse effects on human health. Chemicals from fertilizers, pesticides, sewage waste, solid waste, as well as industrial and traffic emissions are major sources of heavy metals and toxic elements in soil. Considering factors such as population growth, food security, hazardous chemicals, environmental degradation, and climate change, accurate measurement and control of heavy metal elements and organic pollutants in soil have become significant challenges in modern agriculture. In addressing this challenge, LIBS technology is playing an increasingly important role.

During their quantitative analysis of nickel elements in soil, Li et al.[49] found that the characteristic peak of nickel at a wavelength of 373.68 nm was influenced by the aluminum spectral line at 373.39 nm in the soil. Consequently, they conducted comparative measurements between soil spectra on pure aluminum substrates and compressed soil samples. To eliminate the interference of aluminum elements in the soil background on nickel elements, they proposed using pure aluminum as the substrate and subtracting the aluminum spectral line from the soil background.. Experimental results, as shown in Figure 3. Similarly, Liu et al.[50] employed a

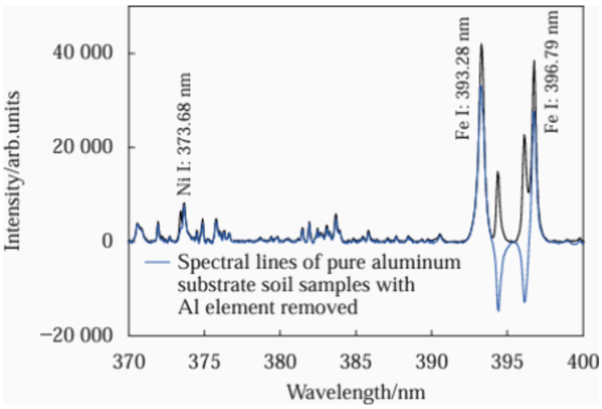

Figure 3. 370−400 nm spectrum line of pure aluminum substrate soil sample with A1 deducted.[49] (Li, H. L.; Wang, H.B.; Kang, S.S.; Fang, L. D.; Li, X. T. LIBS experimental study of eliminating the interference of Al element in soil base based on background subtraction method. *Infra. Laser Eng.* **2021**, *50* (01), 257−262.)

combination of Laser-Induced Breakdown Spectroscopy (LIBS) technology and Support Vector Machine (SVM) to study soil classification issues. Ding et al.[51] proposed a novel analysis method combining LIBS technology and Interval Partial Least Squares (IPLS) for determining the content of Cr, Cu, Ni and Zn in oil-contaminated soil samples. By segmenting the spectrum into multiple subintervals and optimizing the IPLS model, they achieved higher accuracy and faster computation speed, providing an effective approach for soil trace element content determination. Zhao et al.[52] integrated Principal Component Analysis with deep learning, successfully classifying LIBS data from tobacco-planted soil samples with varying lead contents. In accordance with the conventions of academic paper composition, it is evident that deep belief networks have displayed both robustness and superior classification performance when applied to the analysis of contaminated soil samples, surpassing the performance of support vector machines and partial least-squares discriminant analysis. This collective body of research underscores the potential of LIBS technology in the analysis of trace elements in soil, in accordance with the standards of academic paper writing.

Liu et al.[53] combined cavity confinement with traditional Laser-Induced Breakdown Spectroscopy (LIBS) technique to establish a univariate calibration model based on peak integration, as well as multivariate Principal Component Regression (PCR) and Artificial Neural Network (ANN) calibration models, for quantitative analysis of the metal Ba element in soil. The spectral intensities collected under traditional LIBS and cavity confinement LIBS (CC-LIBS) methods are compared, as shown in Figure 4. Chatterjee et al.[54] collected soil samples from both thermal emission zones and remote areas, utilizing Principal Component Analysis (PCA) to readily distinguish soil elemental spectral lines. Pan et al.[55] investigated the enhancement effect of different ratios of NaCl powder doping in soil samples on the LIBS spectra of heavy metal Cd elements. The results indicate that the addition

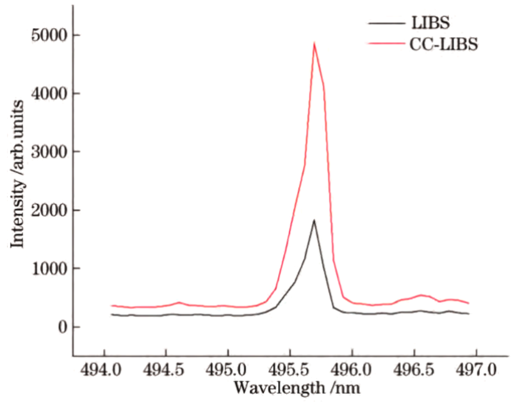

Figure 4. Comparison diagram of Ba element spectra under traditional LIBS and CC-LIBS.[53] (Reprinted, in part, with permission from the publisher, cited from Liu,Y. K.; Hao, X. J.; Yang, Y. W.; Sun, P. Analysis of Ba Content in Soil Based on Cavity Confinement LIBS Combined with Multivariate Regression. *Laser. Optoelectron. Progress* **2022**, *59* (5), 36−42. Copyright 2022 Laser & Optoelectronics Progress.)

of NaCl powder to soil samples can significantly enhance the intensity of characteristic spectral lines for Cd elements.)-Meanwhile, Liu et al.[56] utilized an externally added cavity constraint combined with Laser-Induced Breakdown Spectroscopy (LIBS) technology to obtain soil spectral data. Machine learning was employed for the analysis of heavy metal elements Ni and Ba content in the soil.

The use of LIBS technology for soil analysis presents several difficulties and challenges. First, the complexity of soil samples is a significant issue as they contain various chemical components such as organic matter, minerals, microorganisms, and moisture. This complexity makes it challenging to detect specific elements or compounds in soil due to the presence of numerous interfering signals. Second, soil samples exhibit strong light absorption and scattering properties, which can limit the propagation of laser energy and the acquisition of spectral signals. This can reduce the sensitivity and detection limits of LIBS technology, especially for deep-soil analysis, which becomes more challenging. Additionally, sample preparation is a challenge as it requires complex procedures like drying, grinding, and thorough mixing, and inadequate sample preparation can result in inaccurate analysis results. Variations in atmospheric conditions, including humidity, temperature, and air pressure, can also impact LIBS technology as it is sensitive to atmospheric conditions. Establishing accurate soil analysis methods requires suitable standard samples and calibration curves, but the availability and applicability of standard samples may be limited for different types and geographical locations of soil. Lastly, processing the spectral data generated by LIBS involves complex data processing and analysis to extract useful information from the intricate spectra, necessitating specialized data science skills and software tools. Despite these challenges, LIBS technology still holds potential in soil analysis, especially in real-time or on-site analysis. Continued research and technological advancements can help overcome these challenges and enhance the application value of LIBS technology in soil testing. Future developments encompass improving instrument sensitivity and resolution to more accurately detect elements and compounds even at low concentrations. The application of multielement analysis is poised to expand, facilitating a

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comprehensive understanding of soil sample composition. Optimizing data processing and analysis algorithms will heighten the precision of elemental quantification. Real-time monitoring and on-site applications will contribute to practical implementations in soil monitoring and its related domains.

Additionally, refining sample preparation methods and standardizing analysis procedures will be pivotal for future progress, ensuring data comparability and reliability. The synergic utilization of diverse analytical techniques could further amplify data richness and credibility.

3.3. Research Progress in Crop Nutritional Assessment. The robust nutritional status of crops plays a pivotal role in agricultural production, and LIBS technology has emerged as a potent tool for rapidly evaluating these nutritional conditions. By monitoring the elemental composition within plant leaves, LIBS provides precise recommendations for nutritional management in agriculture. Additionally, it facilitates elemental distribution imaging of agricultural products, thereby offering valuable insights for refining cultivation and processing procedures.

Within the realm of plant science, the application of ultrafast lasers, such as femtosecond lasers (fs-LIBS), for three-dimensional depth profiling and imaging of plant tissues is advancing rapidly. Carvalho et al.[57] harnessed an fs-LIBS system to quantitatively assess nutritional elements in pressed leaves from 31 economically significant crops. This encompassed macroelements like calcium, magnesium, phosphorus, as well as trace elements such as copper, iron, manganese, and zinc. Notably, these investigations spanned diverse plant samples, each with distinct matrices. On a similar note, Kunz et al.[58] leveraged fs-LIBS technology to analyze elemental content in plants cultivated under standard environmental conditions, encompassing barley grass, wheat, soybean, bell pepper, among others. Their findings underscored the substantial potential of fs-LIBS in gauging elemental content within plant tissues and achieving imaging capabilities.

In summation, the integration of LIBS technology in assessing crop nutrition has yielded robust outcomes. The employment of fs-LIBS for deep tissue analysis and imaging is proving to be a promising avenue in the realm of plant science. This technique not only furnishes accurate insights into the nutritional elements present in crops but also contributes to the optimization of cultivation practices and the enhancement of product quality.

Ding Qiping et al.[59] collected comprehensive LIBS full-spectrum data spanning the wavelength range of 200 to 900 nm for leaves of both Huanglongbing-affected and healthy navel oranges. After preprocessing the spectral data, they employed the PCA method to extract the first three principal components. These components were then fed into various training classification models. The outcomes of this classification endeavor demonstrated that the combination of the PCA method with the MLP classification model yielded the most accurate results for distinguishing between Huanglongbing-affected and healthy navel orange leaves. The model achieved an impressive accuracy of 99.43% on the training set and 98.48% on the prediction set.

Jiang Bo et al.[60] delved into the feasibility of utilizing LIBS technology to swiftly detect the distribution of sodium (Na) elements in sweet sorghum. They also explored the unique distribution characteristics of $Na+$ within sweet sorghum plants subjected to varying salt stress conditions. Their study provided valuable insights into the advantageous traits of hybrid sweet sorghum in ameliorating saline-alkali soil.

Wang Haiping et al.[61] devised a novel quantitative analysis method for metal elements in sorghum roots. They achieved this by combining Laser-Induced Breakdown Spectroscopy (LIBS) with the Variable-Dimension Particle Swarm Optimization and Combination Moving Window (VDPSO-CMW) wavelength selection algorithm. This innovative approach notably improved the accuracy of quantifying elements such as Na and Fe, resulting in enhanced RMSECV and RMSEP values. The findings underscored that LIBS, when coupled with suitable chemometric algorithm processing, holds the potential to achieve precise determination of metal elements in sorghum roots. Ercioglu et al.[62] effectively harnessed LIBS technology to discern various spice plants based on their chemical compositions. By integrating LIBS with Principal Component Analysis (PCA), they achieved rapid and accurate differentiation of culinary herbs, such as laurel, basil, black pepper, lavender, and ginger. This holds immense significance for the spice plant industry, as it paves the way for developing standardized quality control measures for raw materials. Zivkovic et al.[63] highlighted the utility of LIBS in detecting diverse elements in peppermint tea samples, spanning aluminum, calcium, copper, manganese, barium, potassium, and strontium. Their successful application of the calibration curve method demonstrated precise determination of manganese and barium concentrations, with regression coefficients (R2) surpassing 0.95.

Not only in the realm of plant science, but LIBS technology also demonstrates substantial potential in medicinal plant research. Andrade et al.[64] applied LIBS and ICP-OES to the measurement of essential and toxic metals in some medicinal herbs. The elements detected and quantified were Ca, Co, Cu, Cd, Cr, Fe, Mg, Mn, Na, Ni, Pb, and Zn. The analyzed samples were all herbs belonging to a particular species and constituted different morphological plant parts. The morphological differences were correlated with different characteristic distributions in the 2D score plots acquired using PCA. The authors reported a strong correlation between LIBS and ICP-OES results, particularly with respect to the Ca, K, and Mg content. Table 3 compiles reference literature employing LIBS technology to detect plant minerals, particularly within the contexts of medicinal significance and plant science background.

LIBS technology demonstrates potential advantages in assessing crop nutrition, but it also presents a series of issues and challenges. First, there is complexity in sample preparation due to significant variations in chemical composition across different parts of crops, demanding meticulous sample preparation methods for accuracy. Moreover, this complexity in sample preparation also results in increased analytical complexity and time costs. Second, plant samples from agricultural fields exhibit a high degree of heterogeneity, influenced by factors such as soil, climate, and growth conditions, which can lead to unstable and inconsistent analysis results. Furthermore, different growth stages of plants may cause variations in nutrient content and distribution, necessitating analyses at different time points, thereby adding to the complexity of the assessment. LIBS technology is typically more suited for analyzing metallic elements, while crop nutrition assessment requires the analysis of nonmetallic elements such as nitrogen, phosphorus, potassium, and others. This aspect can potentially introduce higher technical

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Table 3. Utilizing LIBS for the Analysis of Mineral Elements in Different Plant Varieties, Including Medicinal Herbs

Plant species	Elements	References
Salvia miltiorrhiza	Al, Ca, Mg, Ti, Sc, Fe	65
radish, duckweed	Y, Yb, Er	66
Rosa rugosa Thunb., Rosa sp. *Rosa chinensis* Jacq.	C, H, O, N, Mg, Ca, Na, K, CN	67
Taraxacum officinale, Hyoscyamus niger, Ajuga bracteosa, Elaeagnus angustifolia, *Camellia sinensis*, Berberis lyceum	Ca, K, Mg	68
rhododendron leaves	Pb	69
soybean and sugar caneleaf	Ca, Mg, Mn, P	70
pea seedlings(Embryonic axis, germ, root segment, Middle, cotyl)	C, Mg, Fe, Na, K, Ni, Cu, Cr, Ca, Pb	71
rice stems	Cd	72
Lactuca sativa and Trifolium alexandrinum	Zn, Mn, Cu, Ni, Cd, Pb, Cr	73
Tall fescue (Festuca arundinacea)	Fe, Ca, Pb, Mg, Cd, Zn, Mn	74

difficulties and complexity. In addition, establishing accurate LIBS analysis methods requires the availability of appropriate standard samples and calibration curves. However, obtaining suitable standard samples for crop analysis can be challenging due to variations in soil and climatic conditions across different regions. Moreover, the spectral data generated by LIBS demands intricate data processing and analysis, necessitating specialized data science skills and software tools. Lastly, the practical application of LIBS technology in agricultural field environments may encounter a range of challenges, including difficulties in accessing plants, environmental condition changes, and external interferences. These challenges highlight the need for further research and development to harness the full potential of LIBS technology for crop nutrition assessment.

Future trends in this field are likely to encompass the following areas: First, the multielement analysis capability of LIBS is set to positively impact crop nutrient status assessment. This technology has the potential to simultaneously detect various key elements like nitrogen, phosphorus, and potassium, offering comprehensive nutrient insights. Second, the advancement toward real-time monitoring is expected to lead to more precise agricultural management. This approach allows for continuous tracking of changes in nutrient demands within fields, facilitating optimized fertilization strategies and boosting crop yield and quality. Furthermore, the adaptability of LIBS technology across diverse crop types and growing environments is a notable concern. It should maintain accurate and dependable performance across various agricultural contexts. Standardizing data processing and analysis will enhance result comparability and credibility, fostering collaboration and knowledge exchange among various research initiatives. Lastly, the integration of LIBS with other agricultural technologies, such as remote sensing and geographic information systems, holds the potential to broaden the scope of crop nutritional assessment. This integration could further advance the goals of sustainable agricultural development and resource management.

3.4. Advancements in Plant Disease Detection. Minerals play an indispensable role across virtually all plant species. Whether found in fruits, vegetables, medicinal herbs, grasses, or shrubs, these minerals are pivotal for driving plant growth, tissue development, and functional operations, thereby sustaining regular metabolic processes. Given the typically minute concentrations of trace nutrients within plants, robust technological methods are imperative to detect these subtle nutrient levels. Plants assimilate these essential minerals either through organic materials or inorganic fertilizers drawn from the soil.

Unique mineral nutritional requirements exist for each plant species, with appropriate mineral levels necessary for optimal functioning varying accordingly. However, an overabundance of specific minerals can impede plant growth and potentially trigger a range of diseases, ultimately culminating in diminished crop yields. In-depth comprehension of mineral distribution and movement throughout different plant parts is essential for unraveling their functions and metabolic pathways. The insights derived from plant metabolic pathways offer not only a deeper grasp of plant physiological processes but also carry substantial significance for fields like agricultural crop research and genetic exploration.

LIBS technology plays a significant role in plant science, especially in mineral analysis. Researchers harness LIBS technology to conduct high-resolution mapping analysis of trace elements within plants. Khan et al.[75] conducted a study on Taraxacum officinale, Hyoscyamus niger, Ajuga bracteosa, Elaeagnus angustifolia, *Camellia sinensis*, and Berberis lyceum using LIBS technology in combination with chemometric methods. In the experiments, silicon (Si), aluminum (Al), iron (Fe), copper (Cu), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), manganese (Mn), phosphorus (P), and vanadium(V) were found in all medicinal plant samples with molecular forms containing carbon and nitrogen. They detected Ca, Mg, Si, and P as the major components in all plant samples, along with V, Fe, Mn, Al, and Ti as essential medicinal metals, and other trace elements such as Si, Sr, and Al. This technique demonstrates its capability not only for rapid, sensitive, and quantitative analysis of trace elements in herbal and plant samples but also for the rapid classification of herbal medicines.

Researchers like Krajcarova[76] employed DP-LIBS technology to explore fir plant stems. By comparing fluorescence microscopy and LIBS imaging, and directly correlating fluorescence intensity with ICP-MS data, they revealed the distribution and absorption mechanisms of elements within the samples. Additionally, they utilized LIBS technology to investigate copper absorption, transport, and toxicity in broad beans. In a 7-day experiment involving the treatment of broad bean roots with 10 mM $CuSO_4$, they unveiled that even at low concentrations, copper exerts a toxic effect on plants.

When plants lack essential mineral nutrients, a range of disease symptoms emerges, including yellowing leaves, root nodules, seed coat disorders, and morphological distortions. However, many diseases often escape notice as their symptoms appear underground, remaining hidden from view on the plant's surface. These early stage imperfections and diseases are termed latent defects, and their diagnosis necessitates the application of advanced analytical methods. Tang et al.[71] used peas as a hydroponic plant model and employed a Laser-Induced Breakdown Spectroscopy (LIBS) device for in situ elemental imaging analysis of pea plants. They analyzed the differential distribution of heavy metals Ni, Cu, Cr, and Pb within the plant body and investigated the absorption pathways of these four heavy metals. The results showed

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that the elemental imaging device could effectively analyze the presence of major matrix elements such as C, Mg, Fe, Ca, Na, and K in the plant body. After heavy metal stress, there was a significant accumulation of heavy metals within pea plants, and different heavy metals exhibited distinct distribution trends within the plants. Nickel ions were predominantly present in the hypocotyl and embryonic shoot, contrasting with the distribution of copper ions, which were heavily absorbed and enriched in the primary root structures. Chromium, a heavy metal, accumulated significantly in the middle part of pea roots and in the embryonic shoot and hypocotyl, while lead was largely enriched in the hypocotyl and embryonic shoot, with the least content in the root tip (as shown in Figures 5 and 6).

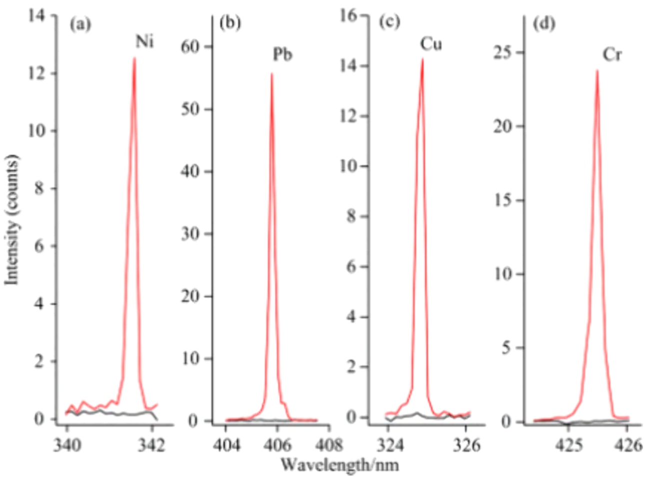

Figure 5. Direct LIBS analysis results of heavy metals in *Pisum sativum* Linn. The red line is the plant after heavy metal stress. The black line is the plant without heavy metal stress. (a) Ni; (b) Pb; (c) Cu; (d) Cr.[71] (Tang, Q.; Zhong, M. J.; Yin, P. K. Analysis of elements under heavy metals stress based on laser-induced breakdown spectrum. *Spectrosc. Spect. Anal.* **2023**, *43*, 1485−1488.).

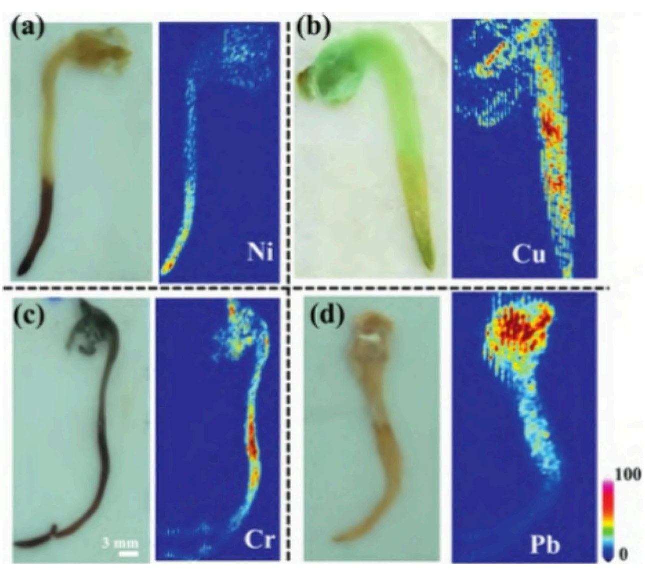

Figure 6. Element distribution imaging of *Pisum sativum* Linn under different heavy metal stresses. (a)Ni, (b) Cu, (c) Cr, (d) Pb.[71] (Tang, Q.; Zhong, M. J.; Yin, P. K. Analysis of elements under heavy metals stress based on laser-induced breakdown spectrum. *Spectrosc. Spect. Anal.* **2023**, *43*, 1485−1488.)

Singh et al.[77] investigated the accumulation of lithium (Li) and its diffusion in plant leaves using Laser-Induced Breakdown Spectroscopy (LIBS). The research findings indicate that the diffusion of Li in plant leaves occurs through their veins, specifically the vascular bundles. Furthermore, the concentration of Li decreases as one moves away from the exposed areas to lithium chloride (LiCl). These studies furnish valuable insights into comprehending element content within plants and its impact on plant health. Furthermore, LIBS technology exhibits promise in the early diagnosis of plant diseases. Researchers have harnessed LIBS technology to analyze plant leaves and detect various diseases, including Huanglongbing (HLB).

Ranulfi et al.[78] employed LIBS technology for citrus leaf analysis to identify the presence of Huanglongbing. Through the establishment of models, they successfully differentiated healthy leaves, HLB-symptomatic leaves, and asymptomatic HLB leaves. Ouyang et al.[79] employed Laser-Induced Breakdown Spectroscopy (LIBS) in conjunction with chemometrics for the qualitative detection of Huanglongbing (HLB) in citrus leaves. Experimental results indicate that the LIBS signal intensities of nutritional elements P(II), Mn(I), Si(I), and Fe(I) are directly related to the health status of citrus leaves. Specifically, the characteristic spectral intensities of P(II), Mn(I), Si(I), and Fe(I) exhibit a sequential decrease in citrus leaves categorized as healthy, moderately infected with HLB, and severely infected with HLB. Zhang et al.[80] rapidly discriminated between healthy and Huanglongbing states in Gan-Nan oranges' juice using LIBS technology. Leveraging Principal Component Analysis and neural network models applied to juice LIBS spectra, they achieved a prompt assessment of the juice's health status and whether it was influenced by Huanglongbing.

Furthermore, researchers have achieved promising results in a range of studies concerning citrus and tobacco leaves. Rao et al.[81] conducted a study with the aim of distinguishing between healthy citrus plants and those infected with Huanglongbing (HLB) using LIBS technology. In their research, they preprocessed LIBS spectra of citrus fruit peel using smoothing and multiplicative scatter correction (MSC). Subsequently, they employed Random Forest (RF) based on Continuous Wavelet Transform (CWT) and Principal Component Analysis (PCA) to effectively differentiate between HLB-infected and healthy samples. Results demonstrated average accuracy rates exceeding 96% for both the training and validation sets. This study highlights the potential of combining LIBS technology with chemometrics for a rapid, cost-effective, and robust differentiation of HLB-infected and healthy citrus plants. Ponce et al.[82] utilized LIBS technology in conjunction with Principal Component Analysis (PCA) to classify different citrus varieties. By integrating a multipulse laser system with a microscope, they acquired LIBS spectra from citrus flavedo, encompassing emission lines of elements like calcium (Ca), sodium (Na), nitrogen (N), hydrogen (H), and iron (Fe), along with emission lines of molecules CN and C2. Applying PCA analysis to the LIBS data revealed a high accuracy (approximately 90%) in distinguishing healthy samples from those infected with HLB. This study further substantiated the potential of combining LIBS technology and chemometrics for diagnosing citrus diseases, offering rapidity, cost-effectiveness, and a considerable degree of efficacy. Peng et al.[83] concentrated on classifying tobacco leaves afflicted by Tobacco Mosaic Virus (TMV). Their research unveiled that

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the moisture content of fresh leaves significantly impacted analysis stability, leading to suboptimal classification outcomes. To enhance the situation, they established a PLS-DA model using LIBS spectral data from fresh and dried granulated leaf samples, achieving positive classification outcomes. Concurrently, they employed the Support Vector Machine (SVM) method, which, despite yielding results opposite to the PLS-DA method, helped mitigate the adverse influence of moisture content on classification accuracy, ultimately improving the precision of classification.

These research examples illustrate the significant potential of LIBS technology in the field of early diagnosis of plant diseases. It can not only be employed to differentiate between various health and infection states of plants but also for classifying different plant varieties. This provides a rapid, cost-effective, and efficient tool for disease monitoring and management.

LIBS technology holds immense potential in the detection of plant diseases, but it also comes with a series of challenges. First, the complexity of plant tissue samples is a significant hurdle, as different parts of the samples contain various organic and inorganic components. This complexity introduces multiple interfering factors into the analysis process, increasing its complexity. Second, plant tissues exhibit a relatively high level of light absorption and scattering, which can potentially lower the sensitivity of LIBS technology, especially in the detection of deep-seated tissues or damaged areas. Optical signal attenuation can lead to inaccurate analysis results. Moreover, the establishment of accurate LIBS analysis methods requires appropriate standard samples and calibration curves. However, obtaining suitable standard samples for plant disease detection can be challenging, as the types and severity of diseases may vary by region and season. Additionally, sample preparation can be relatively complex, and real-time analysis is crucial for certain applications such as plant disease monitoring in fields or greenhouses. Despite these challenges, LIBS technology still holds tremendous promise, and by overcoming these issues, accurate, reliable, and practical plant disease detection results can be achieved. Future research and technological advancements are expected to enhance the application value of LIBS technology in the field of plant protection. Future developments could encompass the establishment of comprehensive spectral databases, amalgamation of LIBS technology with other spectroscopic techniques, realization of real-time monitoring, and incorporation of machine learning and artificial intelligence. Furthermore, the utilization of mobile devices will facilitate convenient on-site applications of LIBS for rapid field detection, aiding farmers in promptly identifying and managing plant disease problems. Simultaneously, the establishment of standardized detection methods and procedures to ensure result comparability and credibility will play a pivotal role in propelling the wide-ranging utilization of LIBS technology in the realm of plant science.

3.5. Research Progress in Agricultural Product Variety Identification. With the growing complexity of agricultural supply chains and consumers' escalating demands for food safety and quality, the accurate differentiation of agricultural product varieties and the traceability of their origins have gained paramount importance. In this context, LIBS technology emerges as a rapid, nondestructive elemental analysis technique, and its remarkable applications in the agricultural product sector are evidenced by the studies presented in Table 4. By scrutinizing the spectral characteristics of samples, LIBS technology facilitates precise differentiation among diverse agricultural product varieties and their respective origins. This capability provides robust support for both agricultural production and effective market management.

Table 4. Relevant Literature on the Application of LIBS Technology in Agricultural Product Variety Identification and Origin Tracing

Samples	Elements	Model	References
Tea	Mg, Fe, Ca, C	DA, RBF, MLP	84
Panax ginseng	Ca	RF-SVM, RF-BPNN	85
Wine	Mn, C, N, Al, Ba, Rb, Fe, Na, B, O, Si, Li, K, P, Ti, Mg, Cu, Zn, Ca, Si, Pb, H	PCA, RF	86
raw sugar cane	K, Ca, Na, O, Mg, H, C, N	PCA	87
coffee blends	C, CN, C_2, N, O	LDA	88
Rice	K, O, C−N, C, H, Ca, Al, Mn, Mg, Na, Si, C−C, N	RF, PCA, PLS-DA, DT, LDA, SVM	89
Ginkgo biloba leaves	Fe, Mg, Ca, Al, CN, H, K, N, O	PCA, LDA, SVM	90
Epimedium	Si, K, Mn, Ca, C, N, Mg, H, Fe	KNN, PCA, LDA, SVM, RF	91
Rhizoma Dioscoreae	C, O, H, Mg, Ca, Al, Na, K, C−N	MSC-IGA-SVM, KNN	92
Astragalus mongholicus	K, O, Ti, S, Al, Mg, Ca, P, Cu, Fe, H, Rb, Mn, Si, Cl, Na	CNN-CBAM, LDA, SVM	93
Rice	C, Mg, Cu, CN, Ca, Na, H, N, K, O	PCA, SVMR, PLSR	94

Tea, as a vital agricultural product, exhibits significant compositional differences among different varieties and origins. In the study by Wang et al.,[95] a randomized forest algorithm (RF) optimized with parameters combined with LIBS technology achieved high accuracy in classifying Guizhou green tea. This classification success extended to achieving 100% accuracy across various provinces' green teas. Furthermore, Yao et al.[96] employed an improved adaptive mutation probability genetic algorithm (IGA) coupled with LIBS spectra for classification, yielding favorable outcomes. Additionally, Tao et al.[97] introduced the sparrow search optimization support vector machine (SSA-SVM) algorithm, successfully enabling tea classification and presenting a novel approach to tea variety identification. Quality and origin are closely intertwined in wine, rendering precise grape variety identification and geographic traceability highly significant. Tian et al.[98] quantitatively detected Fe and Ti elements in wine using LIBS technology, and accurately classified wines from distinct regions with 100% accuracy. Olive oil, another extensively studied agricultural product, demonstrates a strong link between quality and geographical factors. The Stelios Couist team pioneered the application of machine learning-assisted LIBS technology for olive oil classification, yielding highly accurate classification outcomes.[99,100] Furthermore, in citrus breeding, Magalhaes et al.[101] effectively employed LIBS technology to distinguish different citrus varieties, introducing a novel research avenue for citrus breeding.

LIBS technology has demonstrated remarkable applications in the identification of various agricultural product varieties and the traceability of their origins beyond just the fields of tea and wine. In the domain of ham origin identification, Guo et al.[102] combined laser-induced breakdown spectroscopy (LIBS) with machine learning algorithms to identify the origin of ham

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samples. The research team collected spectral data from 16 ham samples and applied algorithms such as KNN, SVM, and DNN for classification, while also incorporating PCA dimensionality reduction to enhance model efficiency. Experimental results indicated that PCA dimensionality reduction accelerated the modeling speed of KNN and SVM, with the PCA-augmented SVM algorithm achieving the highest classification accuracy. The DNN algorithm outperformed the rest, attaining an 85.56% classification accuracy, surpassing the performance of KNN and SVM.

Rao et al.[103] conducted research on the identification of Navel oranges' origins. They collected plasma plume evolution morphology images and LIBS spectra of Navel oranges from various provinces and cities (as shown in Figures 7 and 8), and assessed the feasibility of origin identification using a qualitative analysis approach. Furthermore, they utilized techniques such as Principal Component Analysis (PCA) and Multilayer Perceptron Neural Networks in conjunction with data preprocessing. This allowed successful identification of Navel orange origins in a wide geographic range, including seven provinces and cities, as well as smaller areas like Nankang in Ganzhou, Jiangxi. The total accuracy of training and prediction sets both exceeded 95%.

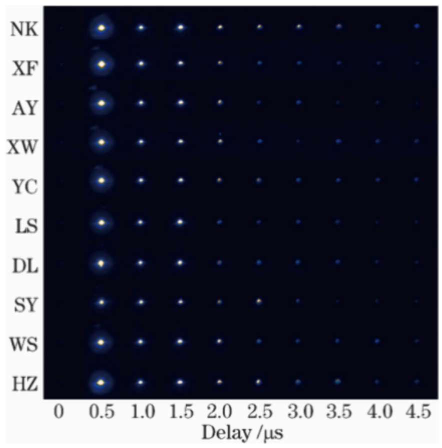

Figure 7. Morphological images of plasma plume of navel orange in 10 origins.[103] (Reprinted, in part, with permission from the publisher, cited from Rao, G. F.; Huang, L.; Liu, M. H. Identification of navel orange origin based on laser-induced breakdown spectrum. *Laser. Optoelectron. Progress* **2018**, *55*, 440−445. Copyright 2018 Laser & Optoelectronics Progress).

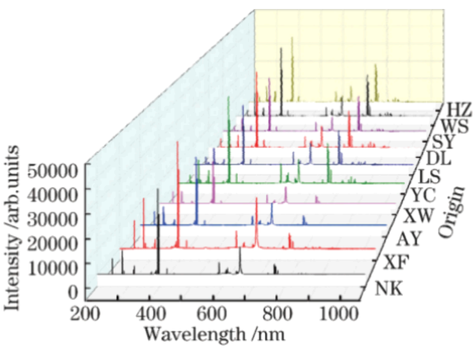

Figure 8. LIBS spectra of navel orange in 10 origins at a wavelength of 200−1100 nm.[103] (Reprinted, in part, with permission from the publisher, cited from Rao, G. F.; Huang, L.; Liu, M. H. Identification of navel orange origin based on laser-induced breakdown spectrum. *Laser. Optoelectron. Progress* **2018**, *55*, 440−445. Copyright 2018 Laser & Optoelectronics Progress).

Hou et al.,[104] on the other hand, applied LIBS technology to the identification of rice seeds. They collected spectra from rice seeds of ten different regions and extracted characteristic spectra of elements such as K, Si, Mg, Ca, and Na. By employing a Backpropagation neural network (BPNN) algorithm, they established identification models for rice seeds using full spectra, segmented spectra, and characteristic spectra. Through spectral identification before and after preprocessing, they achieved over 96% high accuracy.

Considering these instances, it is evident that LIBS technology holds vast potential for the identification of agricultural product varieties and origin tracing. Whether in the fields of resin herbal medicine, ham origins, Navel oranges, or rice seeds, LIBS provides reliable technical support for agricultural production and market management.

LIBS technology has made significant progress in the field of agricultural product variety identification. Future development trends include establishing comprehensive spectral databases that encompass a wide range of agricultural product varieties, enhancing model accuracy and identification reliability. Multiparameter fusion is another crucial direction, involving the integration of LIBS with other spectroscopic techniques or analytical methods, particularly useful for identifying complex components in agricultural products. The application of machine learning and data mining techniques will efficiently handle extensive spectral data, improving the precision of variety identification. Employing LIBS technology in portable devices allows rapid on-field identification of agricultural product varieties, providing immediate assistance to farmers and producers, ensuring product quality. Furthermore, combining variety labeling and traceability helps consumers understand product origins and variety information, enhancing market transparency and food safety. Establishing standardized identification methods and processes will ensure result consistency and credibility, promoting widespread application of the technology in agricultural product variety identification.

The application of LIBS technology in the identification of crop varieties is accompanied by a series of challenges and difficulties. First, the diversity of agricultural products is a crucial issue, as different plant species, parts, or growth environments can lead to significant variations among samples, increasing the complexity of identification. Consequently, LIBS technology needs to adapt its analysis approach according to different types of agricultural products. Second, agricultural products exhibit significant differences in chemical composition, including organic compounds, inorganic substances, and moisture content. These variations may affect the signal characteristics of LIBS technology, making it challenging to establish a universal identification method. Third, handling the vast spectral data generated by LIBS requires complex data processing and analysis to extract key features related to the variety information. Additionally, real-time capabilities are essential for certain applications, prompting the need for improvements in analysis speed and real-time performance. Furthermore, the establishment of accurate variety identification methods necessitates suitable standard samples and calibration curves. However, obtaining standardized samples applicable to various agricultural products may pose some challenges. Finally, the application of LIBS technology in actual agricultural fields or market environments may face challenges related to equipment portability, environmental factors, and

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operational simplicity. Despite these challenges, by overcoming these issues, LIBS technology holds the potential to achieve accurate, efficient, and reliable crop variety identification results. Future research and technological advancements are expected to enhance the application value of LIBS technology in the field of agriculture.

In the future, the development of LIBS technology in agricultural product variety identification will focus on building spectral databases, multiparameter fusion, machine learning, portable device applications, variety labeling and traceability, and the promotion of standardized methods. These directions will offer more reliable support for agricultural production and market management.

4. SUMMARY AND OUTLOOK

In the realm of agricultural product quality and safety testing, despite some advancements, LIBS technology still faces a range of challenges compared to its widespread applications in other fields.

In soil analysis, the complexity and diversity of soil types demand that LIBS technology address variations in sample matrices to ensure accurate elemental analysis. Furthermore, in the assessment of crop nutrition, the low-concentration element analysis capability of LIBS needs further enhancement to meet the demands of trace element analysis. Simultaneously, improvements are needed in the rapid detection of large volumes of samples to align with the requirements of agricultural production. In the domain of plant disease detection, LIBS technology encounters challenges in the identification and detection of different pathogens, particularly in cases of mixed infections and complex scenarios. To enhance the accuracy of LIBS, the establishment of more extensive sample libraries and advancements in data processing and analysis methods are essential to differentiate various diseases. Additionally, in the identification of agricultural product varieties, considerations must be made for the differences between different plant species and how to leverage LIBS technology for the swift and precise differentiation of various agricultural product varieties.

In summary, the application of LIBS technology in agriculture faces challenges such as sample complexity, low-concentration element analysis, data processing speed, and the detection of diverse samples. For the future, interdisciplinary research efforts must continue to elevate the stability, accuracy, and user-friendliness of LIBS technology to meet the practical requirements of agricultural product quality and safety testing. This will provide a more effective analytical toolset for agricultural production.

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Notes

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