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Detection of heavy metal elements by using advanced optical techniques

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Abstract

The presence of heavy metals in the environment presents a significant concern, as it poses a substantial threat to both human health and food safety. Accurate measurement and identification of heavy metals in diverse sample types, encompassing water, soil, food, and biological materials, necessitate utilizing various spectroscopic techniques. In this comprehensive review, a meticulous examination of three prevalent methodologies employed for heavy metal analysis in soil is undertaken: Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Laser-Induced Breakdown Spectroscopy (LIBS), and Atomic Absorption Spectroscopy (AAS). An elaborate exposition of the operational principles underlying each method is provided, their respective strengths and limitations are delineated, and the specific contexts in which they find application are elucidated. Furthermore, recent developments and forthcoming prospects associated with each of these techniques are elucidated, underscoring the potential advantages of their combined use alongside other analytical modalities to augment precision and speed in heavy metal analysis. The analysis emphasizes that (ICP-OES), LIBS, and AAS offer distinct capabilities and restrictions within the domain of heavy metal detection. Selecting the most appropriate technique hinges on the prerequisites and situational aspects characterizing each analytical challenge. This review furnishes a holistic comprehension of these analytical methodologies, underscoring their pivotal role in addressing the pressing issue of heavy metal contamination and providing valuable insights for optimizing the selection and application of these techniques in environmental and food safety assessments.

Keywords: soil contamination, heavy metal, Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission (ICP-OES), Laser-Breakdown Spectroscopy(LIBS).

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1. Introduction

Soil is a precious natural asset that plays a significant role in our ecosystems by regulating nutrient cycling, facilitating plant growth, gas exchange, carbon storage, and waste disposal. It is composed of a mixture of eroded rocks, nutrients, living organisms, organic materials, water, and air. The solid portion of soil makes up roughly 45% of its composition, while organic matter accounts for 5%, and the remaining 50% is pore space that is evenly divided between air and water as shown in Figure 1.1 [1]. The main components of agricultural soils include mineral particles, organic matter, water, and air [2][3].

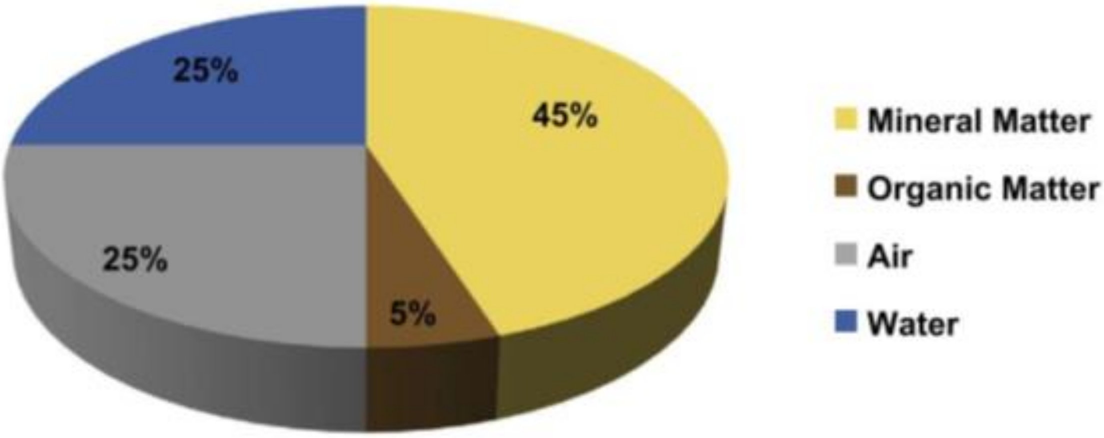

Figure 1.1. The composition of soil [1].

The mineral particles are categorized based on their size, such as sand, silt, and clay, and they are derived from the parent material. Organic matter consists of decomposed plant and animal residues, and water in agricultural soils plays a critical role in plant growth by transporting nutrients and essential elements to plant roots. Air in the soil is important for soil respiration and the exchange of gases with the atmosphere [2][3]. The soil of a particular location undergoes a series of weathering processes influenced by various factors, such as climate, biology, and geology leading to its evolution. The composition of soil can be categorized into biotic and abiotic components, with the non-living soil organisms constituting the abiotic component and the living species constituting the biotic component. Typically, the abiotic component occupies around 40-45% of the total volume of soil, while air and water account for 25% each, and living creatures constitute 5% [1], [4]. Agricultural soils are soils that are used for crop production or livestock grazing, and their specific physical, chemical, and biological properties are essential for plant growth and productivity, making them important resources for global food security [5]–[7]. The well-being of human life is directly influenced by the quality of agricultural soils. In both developed and developing nations, the unregulated release of chemicals and harmful compounds from various human activities has caused serious concerns regarding heavy metal pollution. Agricultural soils, in particular, have the potential to act as long-term storage containers for heavy metals [8]–[11]. Heavy metals accumulation, caused by continuous effluent discharge from mine tailings, coal combustion, sewage sludge, high-metal waste transportation, and fertilizer land application, can severely damage soil, which is an important environmental medium [4], [12]. The composition of soil is determined by the current rocks of the region and the climate, resulting in variations between different locations. Additionally, other factors, such as the number of plants, soil compaction, and water retention capacity, impact the soil composition of a particular area [1]. The physical and chemical properties of soil are determined by its composition, which is a combination of biotic and abiotic components. The physical and chemical characteristics of the soil are defined by the specific mixture of these components [8]. Agricultural soil serves as the primary source of crops that sustain both human and animal populations. Regrettably, human activities, which involve the release of vast quantities of man-made waste products, sludge, and other waste treatment plant outputs, are contributing to the degradation of this crucial natural resource [13]. To safeguard the fertility, productivity, and quality of soil and enhance the health of all living organisms, it is essential to implement control measures based on continuous soil pollution evaluations. Soil pollution refers to the undesired alterations in the physical, biological, and chemical features of soil that have an impact on human life, living plants and animals, industrial development, living conditions, and cultural heritage. A substance or agent that has an unfavorable effect on human health, comfort, property, or the environment is considered a pollutant [13]. Various types of pollution that can affect agricultural soils. Some of the most common types of pollution in agricultural soils include heavy metals, pesticide pollution, fertilizer pollution, and organic pollutant contamination.

Heavy metal pollution: Heavy metals such as lead, cadmium, arsenic, and mercury can accumulate in soils and pose a threat to human and environmental health [14]–[17]. Pesticide pollution: The excessive use of pesticides in agriculture can lead to their accumulation in soils, which can have adverse effects on soil quality and biodiversity [18]. Fertilizer pollution: Overuse of fertilizers can lead to nutrient imbalances in soils and nutrient runoff, which can cause water pollution and harm aquatic ecosystems [19]. Organic pollutant contamination: Agricultural activities can introduce organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) into the soil, which can be toxic and persistent [20]. Microbial pollution: Soil can become contaminated with pathogens such as bacteria, viruses, and parasites from agricultural activities, which can pose a risk to human and animal health [21], [22].

Heavy metals are a type of environmental pollutant that can enter the environment through various industrial and agricultural activities such as the disposal of solid waste, application of fertilizers and pesticides, irrigation with wastewater, and the release of urban and industrial wastes and automobile exhausts [1], [4], [23]–[26]. These heavy metals are naturally occurring elements in the earth's crust and are persistent, remaining in aqueous and terrestrial environments for extended periods [12], [27]. The term "heavy metals" generally refers to a group of metals and metalloids with densities greater than or equal to 3 g/cm^3, which can have harmful biological effects and ecological consequences when present in sufficient concentrations [28]. The most important heavy metals include Ti, Va, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Ag, Cd, Sn, Sb, Te, Ba, Ce, Pt, Au, Hg, Th, Pb, Bi, and U [29]. If an element is found in higher concentrations than its natural value, it is considered a contaminant or pollutant to the environment. The contamination of urban and agricultural soils by heavy metals is a serious problem worldwide and poses a significant threat to human and animal health[26], [30]. Soil particles can bind various chemicals, making them a critical sink for contaminants from various sources [28], [31]. Heavy metals can enter the soil naturally or through human activities, and the contribution of human activities to heavy metal pollution is increasing due to the rapid population growth and expansion of industrial and agricultural processes. Anthropogenic sources of heavy metals include industrial effluents, domestic sewage, vehicle exhaust emissions, and excessive use of fertilizers, herbicides, and pesticides [32], [33]. The contamination of agricultural soils can also result in the contamination of food products, such as vegetables, fruits, grains, and legumes. Heavy metals in polluted soils can seep into groundwater reservoirs, causing further contamination and degradation. The toxicity, mobility, and bioavailability of heavy metals are influenced by soil properties and environmental conditions [31], [34]. The uptake and accumulation of heavy metals in plants and their transfer to animals through food webs can have negative impacts on human health due to the consumption of contaminated products or water. Therefore, it is crucial to assess the levels of heavy metals in agricultural soils to control pollution.

This work aims to offer a comprehensive understanding of the analytical techniques for assessing heavy metals in soil. We delve into the principles, strengths, and limitations of ICP-OES, LIBS, and AAS. We also emphasize their potential for enhancing accuracy and speed when used alongside other methods. We aim is to contribute to addressing the critical issue of heavy metal contamination in soil and its implications for human health and food safety. This work serves as a valuable resource for scientists, policymakers, and stakeholders involved in ensuring environmental and food safety.

2. Analytical Methods

Heavy metals in soils and sediments are commonly analyzed using solution-based or direct analytical techniques [34], [35]. Solution-based techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and atomic absorption spectroscopy (AAS) require aggressive acids to dissolve the samples and total extraction of elements, which can be time-consuming and hazardous [34]. Sample contamination can also be an issue during the preparation process. On the other hand, direct analytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), laser ablation inductively coupled plasma optical emission spectroscopy (LA-ICP-OES), laser-induced breakdown spectroscopy (LIBS), energy dispersive X-ray spectroscopy (EDS), and X-ray fluorescence spectroscopy (XRFS) require no or minimal sample preparation, making them less time-consuming and cost-effective. XRFS is best for analyzing major and minor elements, while LIBS and LA-ICP-MS are better for analyzing trace or low-atomic weight elements. Careful optimization of instrumental and operating conditions can help reduce interference and matrix effect problems [34].

Our study used three of these analytical techniques which are atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and laser-induced breakdown spectroscopy (LIBS).

2.1 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) is an extensively employed analytical method in various fields including chemistry, physics, and materials science. The technique measures the absorption of light at a particular wavelength to ascertain the concentrations of metals and metalloids present in a given sample. AAS is particularly beneficial for examining biological and environmental samples and is extensively utilized in forensic science [35], [36].

2.1.1 Principle of Atomic Absorption Spectroscopy

The fundamental concept behind AAS is that atoms of a particular element can absorb light at a distinct wavelength specific to that element. The sample is initially transformed into a gaseous state through atomization. Subsequently, the atoms are stimulated to higher energy levels using a light source, typically a hollow cathode lamp. As the atoms return to their original state, they emit energy in the form of light at the characteristic wavelength of the element. The quantity of absorbed light is directly proportional to the concentration of the element in the sample [35], [37].

2.1.2 Instrumentation

AAS consists of four main components: a sample introduction system, a radiation source, a monochromator, and a detector as shown in Figure 2.1. The sample introduction system is used to introduce the sample into the atomizer, which can be a flame, a graphite furnace, or a cold vapor generator. The radiation source emits light with a specific wavelength, which is absorbed by the atoms in the sample. The monochromator is used to select the wavelength of light that is absorbed by the atoms, and the detector measures the intensity of the absorbed light. The amount of light absorbed is proportional to the concentration of the element in the sample [35], [37], [38].

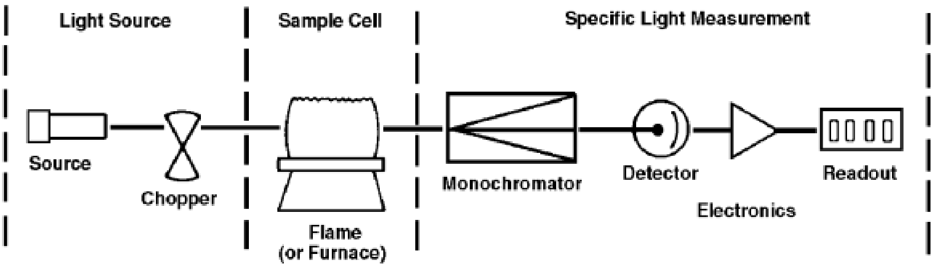

Figure 2.1. A schematic diagram of AAS system [38].

2.1.3 Advantages and Limitations

AAS offers numerous advantages over other analytical techniques, including high sensitivity, broad elemental coverage, and relatively low cost. AAS is capable of detecting trace elements at concentrations as low as parts per billion (ppb) and analyzing a wide range of elements, from lithium to uranium, in a single sample. Additionally, it is a relatively inexpensive technique, making it easily accessible to smaller laboratories. Despite its advantages, AAS has several limitations, including limited accuracy and precision, matrix effects, and interferences. Limited accuracy and precision may result from matrix effects, especially for complex matrices. Interferences can also influence the accuracy of the analysis, particularly for elements with overlapping spectral lines. Sample preparation can also be time-consuming and labor-intensive [37], [39].

2.1.4 Applications

AAS has a broad range of applications, including environmental analysis, pharmaceutical analysis, geological analysis, and metallurgical analysis. It is utilized to analyze water, soil, and air samples for the presence of contaminants, such as heavy metals, to examine drug formulations for the presence of impurities and trace elements, to analyze rocks and minerals for their elemental composition, and to analyze metals and alloys for their elemental composition and impurities [37].

2.1.5 Application of AAS in Soil

Atomic Absorption Spectroscopy (AAS) has many applications in soil analysis, as it enables the quantification of metal ions in soil samples. Here are some examples of the application of AAS in soil analysis :

Monitoring soil pollution: AAS can be used to monitor soil pollution caused by heavy metals, pesticides, and other contaminants. This information can be used to develop remediation strategies and mitigate the effects of pollution on the environment and human health [13][40][41].

Analysis of soil pH: AAS can be used to determine the pH of soil samples, which is an important parameter that affects plant growth and nutrient availability [42].

Assessment of soil nutrient status: AAS can be used to quantify the concentrations of essential nutrients in soils, such as calcium, magnesium, and potassium. This information can be used to optimize soil fertility and crop productivity and AAS facilitates the analysis of the elemental composition of soil amendments such as compost, manure, biosolids, and fertilizers. It ensures the quality, safety, and suitability of soil additives for agricultural use [43] AAS is employed to analyze essential nutrients and trace elements in soil, including phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), and boron (B). It helps in evaluating soil fertility and nutrient management practices[44].

Determination of heavy metal concentrations in soils: AAS is widely used to determine the concentrations of heavy metals in soil samples, such as lead, copper, and zinc, which can have harmful effects on the environment and human health [23], [45], [46].

Many studies have been conducted on analyzing heavy metals in agricultural soils using the AAS analytical technique, from old to advanced.

In 2003, flame and graphite furnace atomic absorption spectrometry was used by Mustafa Tuzen in determining heavy metals in soil, mushroom, and plant samples collected from Tokat, Turkey. The study implemented that heavy metal levels in the soil samples taken from the roadside were higher than those of soil samples near the plants [46].

In 2005 Mico et al. collected soil samples from the surface layers of 54 agricultural fields growing vegetable crops in the Alicante province, which is a typical region in the Mediterranean area of Europe. The study was conducted to determine the content of heavy metals in agricultural soils of the testing area. The study used multivariate analysis, including atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS) to identify the sources of the heavy metals and to analyze the relationships between the heavy metal content and soil properties. The results showed that the heavy metal levels in the soils were similar to those reported in other parts of the Mediterranean region, except for Cu and Pb in some samples [12].

In 2006, Radwan et al. survey was carried out with the aim of to assess the levels of lead, cadmium, copper, and zinc in various fruits and vegetables sold in Egyptian markets. Atomic absorption spectrometry was used to estimate and evaluate the levels of these metals. This survey showed that the average concentrations detected ranged from 0.01 to 0.87, 0.01 to 0.15, 0.83 to 18.3, and 1.36 to 20.9 mg/kg for Pb, Cd, Cu, and Zn, respectively. The highest mean Pb, Cd, Cu, and Zn levels were detected in strawberries, cucumbers, dates and spinach [47].

In 2009, El-Taher research was centered on using neutron activation analysis and atomic absorption spectrometry to measure the elemental concentration in phosphate ores of two Egyptian phosphate rock mines. According to the objective of this analysis is to determine the levels of radioactive elements such as U and Th, as well as stable environmental pollutants like Cr and Zn in the phosphate raw material. The study identified that it is deemed crucial in evaluating potential radiological hazards to human health, considering that these materials may be employed as building material or as phosphatic fertilizers and animal feed ingredients [48].

In 2011, Khairy et al. study aimed to investigate the concentrations of various metals, namely Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, V, and Zn, present in road dust particles at seven different sites in the Delta region. The findings indicate that the samples were significantly contaminated with Cd, Pb, Sn, and Zn, and moderately contaminated with As, Se, Ba, and Cu, in comparison to the average crustal background metal concentrations [49].

In 2014, Abdel-Aal et al. conducted a study to determine the concentrations of heavy metals in soil samples collected from different depths in the Southeastern Soil of the Nile Delta, Egypt. Flame atomic absorption spectroscopy was employed to investigate the presence of Cd, Cu, Ni, and Pb in soil and irrigating water at varying depths of up to 100 cm. The results of the study revealed that surface samples taken at depths of up to 100 cm suggest the likelihood of heavy metal mobilization leading to the contamination of groundwater and/or drainage water in the affected areas and the conceivable contamination of the groundwater and/or drainage water results in additional spoilage of soil in other areas due to infiltration and diffusion, instigating extensive degradation of agricultural land in the Nile delta [50].

In 2014, Barbes et al. studied the accumulation of heavy metals in the leaves and bark of Populus nigra L. from either the atmosphere or the soil. The heavy metals, including Cu, Ni, Zn, Pb, and Cd, concentrations were determined by atomic absorption spectrometry (AAS) from two polluted areas in leaf, and bark. The relationship between the concentration of the metal in leaves, bark, and soil were determined by applying the regression analysis and the values of the determined coefficient have been studied. The study found that the bark of poplar can be considered a passive monitor of atmospheric pollution with the metals Ni, Pb, and Cd [51].

In 2015, Elnazer et al. a 34 soil samples were collected along the Alexandria-Marsa Matruh highway in Egypt to evaluate the contamination of roadside soils with Pb, Cd, and Zn. These samples were then analyzed using atomic absorption. The results demonstrated that The assessment of contamination with these metals was carried out by applying various indices and the significant impact that vehicular and agricultural activities have on the contents of Pb and Cd in the soil [52].

In 2019, El-Naggar et al. using the Flame atomic absorption spectroscopy (FAAS), the researchers assessed the concentration of five heavy metals (Cu, Zn, Cd, Pb, and Fe) in agricultural soil and plant samples taken from four cities in Egypt, including Kafr El-Zayat. They discovered a considerable fluctuation in heavy metal concentrations depending on location and season. Cd and Fe concentrations were found to be higher than the maximum acceptable concentration (MAC), but Cu, Pb, and Zn concentrations were lower [53].

In 2020 , Azzazy et al. conducted this research examine and contrast plants flourishing in industrial and residential areas of Sadat City, Egypt, as bioindicators and biomarkers of industrial pollution. The study concluded that the leaf extracts of plants growing in industrial areas exhibited notably higher levels of flavonoids and phenolic compounds compared to those in residential zones ($P < 0.05$). Furthermore, metal accumulation in leaves was significantly higher in the industrial zone than in the residential zone, with iron, lead, zinc, nickel, and manganese present at significantly higher levels in plants than those growing in the residential zone ($P < 0.05$) [54].

In 2023 Rasha et al. the study evaluated how industrial wastewater disposal affected the environment in the El-Khadrawiya agricultural drain in Menoufia Governorate, Egypt. It also examined the impact on the quality of water, soil, and plants in the area around the drain, which was mainly near the industrial zone. The study found that the water samples contained heavy metals that exceeded the WHO limits and posed carcinogenic risks to the population. The soil samples showed varying degrees of contamination by heavy metals, with Pb and Cr being the most problematic. The plant samples showed a high accumulation of heavy metals that could affect their growth and quality. The study suggested the need for environmental monitoring and remediation of the polluted area [55].

2.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

2.2.1 Basic Principle of (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used to determine the elemental composition of samples. The technique is based on the principle of inductively coupled plasma, which is generated by a high-frequency electromagnetic field applied to a gas, usually argon. The plasma produces excited atomic and ionic species that emit light at characteristic wavelengths. The emitted light is then analyzed using a spectrometer to determine the elemental composition of the sample. The emitted light intensity is proportional to the concentration of the element in the sample [35], [56].

2.2.2 Instrumentation

ICP-OES consists of three main components: a sample introduction system, an ICP source, and a spectrometer as shown in Figure 2.2. The sample introduction system is used to introduce the sample into the ICP source, which is usually a torch powered by a radiofrequency generator. The RF generator produces a magnetic field that creates a plasma by ionizing the argon gas flowing through the torch. Once the sample is introduced into the plasma, it is vaporized and ionized, producing excited atomic and ionic species that emit light at characteristic wavelengths. The emitted light is then passed through a spectrometer, which separates the wavelengths of the emitted light and measures their intensity [56].

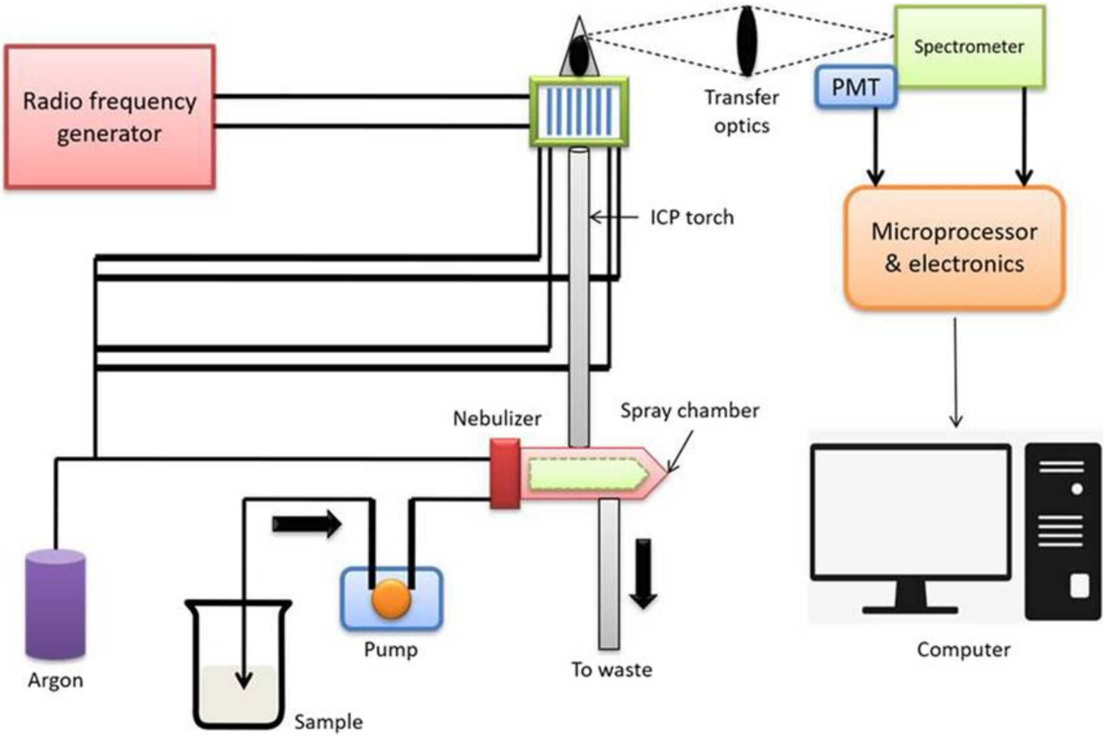

Figure 2.2. Instrumentation of ICP-OES [56].

2.2.3 Advantages & Limitations:

ICP-OES Advantages

ICP-OES has several advantages over other analytical techniques, including high sensitivity, wide elemental coverage, high accuracy and precision, and fast analysis. ICP-OES can detect trace elements at concentrations as low as parts per billion (ppb) and analyze a wide range of elements, from lithium to uranium, in a single sample. It produces highly accurate and precise results, making it suitable for quantitative analysis, and can analyze multiple elements in a single sample in a matter of minutes [57].

ICP-OES Limitations

ICP-OES also has some limitations, including high cost, matrix effects, and sample preparation. ICP-OES instrumentation can be expensive, making it difficult for smaller laboratories to afford. Matrix effects can interfere with the accuracy of the analysis, particularly for complex matrices, and sample preparation can be time-consuming and labor-intensive [57].

2.2.4 Applications

ICP-OES is used in a wide range of applications, including environmental analysis, pharmaceutical analysis, geological analysis, and metallurgical analysis. It is used to analyze water, soil, and air samples for the presence of contaminants, such as heavy metals, analyzes drug formulations for the presence of impurities and trace elements, analyze rocks and minerals for their elemental composition, and analyze metals and alloys for their elemental composition and impurities. The utilization of analytical methods are employed to determine the concentration of vital nutrients and toxic elements in food, as well as to analyze food materials. In the realm of agricultural analysis, the ICP-OES methodology serves to scrutinize a variety of samples, such as fertilizers, soils, and the toxicity of metal contamination within the soil. The ensuing sections shall elucidate a few of the noteworthy applications that have emerged within the domain of agricultural analysis [56].

Here are some common applications of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in soil analysis

Determination of Heavy Metals: ICP-OES is widely used for the quantitative analysis of heavy metals in soil samples due to its high sensitivity and multi-element capability. It enables the simultaneous determination of various elements such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), and mercury (Hg) present in soil samples [56][58][59].

Assessment of Soil Nutrients: ICP-OES can be employed to analyze essential nutrients and trace elements in soil, including phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), and boron (B)[60][61] .

Monitoring Soil Contamination: It is used to monitor soil contamination by organic and inorganic pollutants, including pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), and other chemical contaminants, providing valuable data for environmental risk assessment and remediation strategies [59].

Analysis of Soil Amendments: It is employed to analyze the elemental composition of soil amendments such as compost, manure, biosolids, and fertilizers, ensuring their quality and suitability for agricultural use [58][59] [61].

Many studies have been conducted on analyzing heavy metals in agricultural soils using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Here are many studies from old to advanced.

In 2010, Rashed Monitored contaminated toxic and heavy metals, from mine tailings through age accumulation in soil and some wild plants in Southeast Egypt. Tailings, soils, and wild plants were sampled and analyzed for toxic metals (Hg, Cd, Pb, and As) and associated heavy metals (Cr, Ag, Ni, Au, Mo, Zn, Mn, and Cu) using ICP–MS, ICP–AES, and FAAS techniques. The results reveal that Cr, Cu, Zn, Ni, Ag, Au, Mn, Hg, As, Ag, Au, and Pb in soil decreased as far away from the tailing after periodic trends as a result of input from surrounding rocks [62].

In 2014, Ali , M.F and Shakrani, S. A . In this study, the analytical performance of ICP-OES and UV-Vis spectrophotometers was compared to determine their ability to detect certain heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in soil irrigated with secondary treated wastewater. The conclusion of the study is that the quality of secondary treated wastewater and soil irrigated with it varies depending on the season, the treatment system efficiency and the soil cross-sectional area. The study also found that ICP-OES is a more reliable method than UV-Vis spectrophotometer for measuring heavy metals in soil irrigated with secondary treated wastewater. The study concluded that the quality of secondary treated wastewater and soil irrigated with it varies depending on the season, the treatment system efficiency, and the soil cross-sectional area. The study also found that ICP-OES is a more reliable method than UV-Vis spectrophotometer for measuring heavy metals in soil irrigated with secondary treated wastewater [63].

In 2015, Karima et al. carried out to determine the presence of heavy metals in sixty milk samples, each one having a distinct flavor by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The samples were found to contain many elements of heavy metals such as Al, As, Cd, and Pb but were not contaminated with Mercury (Hg). The findings results were then compared to the Maximum Permissible Limit (MPL) and the results demonstrated that the concentration of Al and Cd in all samples exceeded the MPL (100%) [64].

In 2016, Amany F. and Mokhtar B. they made a study to determine the concentrations of seven heavy metals (Mn, Fe, Zn, Cu, Pb, Cd, and Ni) in breast milk and drinking tap water samples collected from Damietta Governorate, Egypt. The study analyzed 20 samples of breast milk and drinking tap water (10 samples each) using the Inductively Coupled Plasma-Mass Spectrometry (ICP-OES). The outcome of the investigation has determined that the levels of Manganese, Iron, Zinc, Copper, Lead, and Nickel present in drinking tap water and breast milk samples, as well as the concentration of Cd in drinking tap water, were within the safe limits of WHO regulations. However, in contrast, the concentration of Cd detected in breast milk samples was exceeding the safe limits and thus poses a substantial health hazard to infants [65].

In 2017 Vázquez et al. they study conducted with the aim of finding a simple procedure for the determination of multiple elements in vitreous humor to be used as a complementary tool in forensic science to diagnose drowning. The study compared the performance of ICP-MS and ICP-OES for the analysis of 14 elements (Li, Mn, Co, Cu, Zn, As, Se, Sr, Mo, Cd, Fe, Mg, K, and Ca) in vitreous humor samples. The result showed that ICP-MS is more suitable than ICP-OES for the multi-element analysis of vitreous humor samples due to its high sensitivity, low detection limits, and wide dynamic range [66].

In 2018 Khalifa and Gad studied the agricultural soils of Quessna District in the Southwestern Nile Delta to examine the lateral and vertical distributions of heavy metals in this area using the inductively coupled plasma-optical emission spectroscopy technique. the study reported that the concentrations of the studied metals decreased in the order of Zn > Cr > Pb > Cu > Ni > Co [67].

In 2019, Jain et al. research aimed to assess the potentially toxic elements contamination in the surface soils of the Kulsi River Basin in North East India based on the analysis of 50 soil samples collected from the basin. The results of this research were Summarized in the surface soils of the Kulsi River Basin in North East India are contaminated by potentially toxic elements, especially Co, Ni, Pb, and Zn. The study found that these elements exceeded the background levels and showed significant enrichment factors, indicating human activities as the main source of pollution. The study also evaluated the ecological risk of these elements and found that it was low at all the sampling sites [68].

In 2020 Kandil et al. Seventy samples of different fruits and vegetables were collected from the different Egyptian local markets in Giza. All collected samples were subjected to heavy metals analysis by microwave digestion and determination by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), to investigate the concentration of elements (Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Sn, and Zn). The results showed that the concentration ranges, in mg/kg, were as follows: for (Cd) < 0.02 – 0.12, < 1 – 1.5 (Cr), < 1 – 5.5 (Cu), 1.5 – 768 (Fe), < 0.05 – 0.35 (Pb), < 1 – 40.1 (Mn), < 1 – 5.6 (Ni) and < 1 – 492.9 (Zn) all analyzed samples and all detectable amount of Co, and Sn in all tested samples were found to be less than the quantifications limits toxic elements in fruits and vegetables [69].

In 2021 Yassin et al. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was applied to investigate multi-elements (Zn, Cu, Pb, and Cd) of Egyptian olive oil collected from different regions in Egypt. The data showed that the concentration ranges were 0.6486-2.4166 µg/g, 0.0092-0.6919 µg/g, 0.0185-0.1026 µg/g, and 0.0009-0.0186 µg/g for Zn, Cu, Pb and Cd, respectively. The results indicated that the highly toxic metal content did not exceed that recommended by FAO/WHO [70] .

In 2021, Mankoula et al . This study aimed to determine the concentrations of heavy metals in the agricultural soils of Kafr El-Zayat city using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).".The research analyzed 16 agricultural soil samples using LA-ICP-MS after combined acid wet digestion and reported that the concentrations of 21 elements (Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Mo, Sn, Ba, Pb, Th, and U) and compared them with the worldwide background concentrations and the Canadian soil quality guidelines. The study found that V, Cr, Co, Ni, and Cu exceeded the permissible limits and indicated moderate contamination of the soils. The study suggested that heavy metal contamination may pose a risk to human health and the environment [71].

In 2022, Alsaid et al. this study carried out with the aim of assessing the levels of Pb, As, Ni, Cr, and Cd in the sea and freshwater samples collected from five major seaport areas in Oman and one freshwater canal using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).". The study found that most of the trace metals in the water samples from Oman were within the permissible limit, except for lead, which was higher than the safe level in some samples. The study recommended that water treatment should be applied to reduce the lead concentration and prevent health risks for humans and animals. The study also concluded that the ICP-OES method is a sensitive and reliable technique for measuring trace metals in sea and freshwater samples [72].

2.3 Laser-Induced Breakdown Spectroscopy (LIBS)

2.3.1 Basic Principle of LIBS

The basic theory behind LIBS is plasma emission spectroscopy, which describes the spectral emission of a plasma produced by a laser-induced breakdown. In the case of LIBS, the sample is ablated by the high-energy laser, creating a plasma plume, which emits light. The light emitted by the plasma plume contains spectral lines, which correspond to the atomic and molecular transitions of the elements present in the sample.

The intensity of the spectral lines in the LIBS spectrum can be quantitatively related to the concentration of the elements in the sample using the Boltzmann equation:

$$I_\lambda = A_\lambda \, n_\lambda \, g_\lambda \, e^{-(-E_\lambda/kT)} \qquad [73]$$

Here, I_λ is the intensity of the spectral line, A_λ is a proportionality constant, n_λ is the number density of the emitting species, g_λ is the statistical weight of the lower energy level, E_λ is the energy difference between the upper and lower energy levels, k is the Boltzmann constant, and T is the temperature of the plasma.

The LIBS technique is highly sensitive and can detect elements at low concentrations, down to parts-per-billion levels. It is also fast and non-destructive, making it useful for a wide range of applications, including environmental monitoring, industrial process control, and forensic analysis [73], [74].

2.3.2 LIBS Instrumentation:

A typical LIBS system consists of several components, including a laser, a sample chamber, a spectrometer, and a data acquisition system as shown in Figure 2.3 [74].

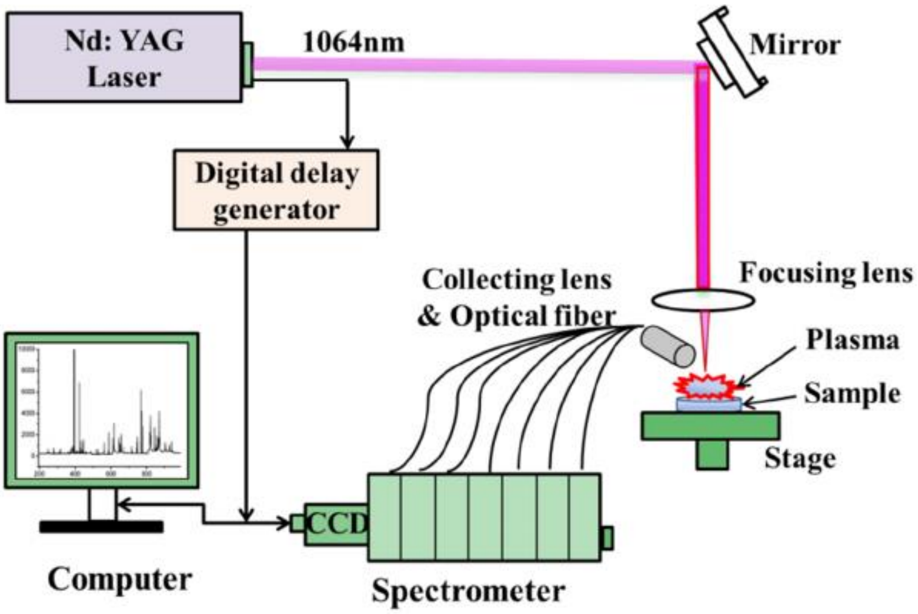

Figure 2.3. A schematic diagram of LIBS system [74].

- **Laser**: The laser is a critical component of a LIBS system. It is used to generate a high-energy pulse that ablates a small amount of material from the sample and generates a plasma plume. The laser used in a LIBS system must have specific characteristics, such as a high repetition rate and a short pulse duration, to ensure optimal performance [73]. High-power Nd:YAG lasers at 1064 nm and 532 nm are the most common pulsed lasers used in LIBS applications [75], [76].
- **Lens and Sample Chamber:** The laser beam used in LIBS is collimated, coherent, and has a narrow diameter. However, focusing the beam using only one convex lens may not provide enough energy to cause a breakdown, or the resulting plasma volume may be too small and inconsistent. To address this issue, the beam is typically expanded and collimated to produce a larger diameter beam, which is then focused onto the sample for analysis [77].

The function of the sample chamber in LIBS is to hold the sample and create a regulated environment for analysis. It is constructed in a way that guarantees the correct placement of the sample concerning the laser beam and prevents the plasma plume generated by the laser from interfering with the analysis. Additionally, the sample chamber may feature components for regulating the temperature, pressure, and other environmental factors [77].

- **Spectrometer:** The spectrometer is used to analyze the light emitted from the plasma plume. It is typically a high-resolution device capable of detecting light in a specific wavelength range. The spectrometer separates the light into its component wavelengths, allowing for the identification and quantification of the elements present in the sample [77], [78].
- **Data Acquisition System:** The data acquisition system records the spectra obtained from the spectrometer. It typically includes software for processing and analyzing the data, allowing for the identification and quantification of the elements present in the sample. The data acquisition system may also include mechanisms for controlling the laser and the spectrometer and for automating the analysis process [77], [78].

2.3.3 Advantages & Limitations:

Advantages of a LIBS System:

Non-Destructive Analysis: One of the primary advantages of a LIBS system is that it allows for non-destructive analysis of samples. Only a small amount of material is ablated from the sample, leaving the rest of the sample intact for further analysis [79], [80].

Rapid Analysis: LIBS analysis is a fast and efficient method for elemental analysis. The analysis can be completed in seconds or even milliseconds, allowing for rapid screening of samples [79], [80].

Wide Elemental Coverage: LIBS can analyze a wide range of elements, from lithium to uranium. This makes it useful for a variety of applications, including environmental monitoring, materials science, and forensics [79], [80].

High Sensitivity: LIBS has a high sensitivity, allowing for the detection of trace amounts of elements. This makes it useful for applications such as detecting contaminants in food and monitoring trace elements in geological samples [79], [80].

Limitations of a LIBS System:

Sample Homogeneity: LIBS requires a homogeneous sample to ensure accurate and precise analysis. Samples with non-uniform compositions can lead to errors in the analysis [79], [80].

Matrix Effects: The presence of other elements in the sample can interfere with the analysis of the target element. This can lead to inaccurate results [79], [80].

Calibration: A LIBS system requires calibration to ensure accurate and precise analysis. This can be time-consuming and expensive [79], [80].

Spectral Overlap: Spectral overlap can occur when the emission lines of two or more elements overlap, making it difficult to distinguish between them. This can lead to errors in the analysis [79], [80].

2.3.4 Applications

LIBS has various applications in different fields. Here are some examples:

Environmental Analysis

LIBS is utilized for environmental analysis, such as soil analysis, water analysis, and air pollution analysis. Some examples of specific applications of LIBS in environmental analysis are the detection of contaminants and pollutants in water, such as heavy metals, nutrients, microorganisms, and organic compounds. Analysis of soil quality and fertility, such as pH, organic matter, nutrients, and trace elements. Monitoring of air quality and emission sources, such as particulate matter, greenhouse gases, and toxic meta. Characterization of waste materials and hazardous substances, such as nuclear waste, electronic waste, and explosives [81], [82].

Material Science

LIBS is employed in material science to analyze the elemental composition of different materials. Some examples of specific applications of LIBS in material science are:
Quality control and process monitoring in steel and coal industries. Sorting of waste materials for selective recycling [83]. Elemental mapping and depth profiling of materials[84]. Characterization of nanomaterials and thin films. Identification of phase transitions and crystal structures [84].

Archeology Applications

LIBS has been used in archeology to analyze the composition of ancient artifacts and to determine their origin. Some examples of specific applications of LIBS in archaeology are the identification of pigments and polychromes in painted artworks and icons. Analysis of metals and alloys in coins, weapons, jewelry, and sculptures. Characterization of ceramics and glass in pottery, vessels, beads, and mosaics. Determination of provenance and authenticity of stone artifacts and buildings [85]–[87].

Medical Applications

LIBS is utilized in medical applications for the analysis of biological tissues and fluids. Some examples of specific applications of LIBS in medical applications are diagnosis of diseases and identification of pathogens in biological samples. Detection of contaminants and pollutants in water and food. Analysis of drugs and metabolites in blood and urine. Investigation of cellular processes and interactions [88], [89].

Soil Applications

Laser-induced breakdown spectroscopy (LIBS) has many applications in soil analysis. Some of the common applications of LIBS in soil analysis are

Soil classification and identification using LIBS: LIBS has been used for the classification and identification of different types of soils based on their elemental composition.

Analysis of heavy metals and contaminants in soil: LIBS has been used for the analysis of heavy metals in soil samples. Some examples of specific applications of LIBS in soil are:

Detection of toxic metals in soils for environmental remediation [90]–[92]. Analysis of soil nutrients and fertility for agricultural management [90], [91], [93]. Characterization of soil organic matter and carbon sequestration. Identification of soil provenance and origin [90], [91]. There have been several studies conducted on the analysis of heavy metals in Egyptian soil using Laser-Induced Breakdown Spectroscopy (LIBS) and the is much research about it. The following are some of the relevant studies.

In 2008, M. Hassan et al. invested in the potential of scented geranium, Pelargonium zonal, as a phytoremediator of lead-contaminated soil and also tested the effect of EDTA as a chelator to enhance lead uptake by the plant. LIBS was used as a non-destructive technique to measure lead concentrations in soil and plant tissues. Results showed that scented geranium could accumulate lead in its shoots and that EDTA increased the availability and uptake of lead. The study suggested that scented geranium is a suitable plant for phytoremediation of lead-contaminated soil and that LIBS is a reliable tool for monitoring lead levels in soil and plant tissues reliable and efficient technique for heavy metal detection in soil samples [94].

In 2013, Farooq et al. The study has successfully used LIBS to analyze soil samples from different desert areas of Riyadh city in Saudi Arabia. The authors have found that the plasma parameters (electron temperature and density) vary with the elemental concentration and the sample matrix. They have also shown that the plasma cooling processes are slow for soil samples compared to metallic samples. The study has suggested that LIBS can be used for remote online environmental monitoring by measuring the plasma parameters for one element using an optical fiber probe [95].

In 2014, W. Tawfik et al. demonstrated a new method to improve the detection limits of LIBS for manganese in drinking water by using medium-density fiberboard (MDF) wood as a substrate. They have optimized the LIBS parameters and obtained high-sensitivity measurements. The results achieved a correlation coefficient of 0.98 and a limit of detection of 623 ppb for manganese and also estimated the plasma temperature of manganese under local thermodynamic equilibrium conditions. The study claimed that the used method was useful for nondestructive in-situ environmental monitoring and analysis of manganese in water [96].

In 2015, W. Tawfik et al. used LIBS as a technique for detecting Cr, Mn, Cu, Cd, Mg, and Fe in groundwater samples from the Haier basin near Riyadh, Saudi Arabia. The technique used wooden sticks as a substrate to absorb the liquid sample and to enable laser-solid interaction. The optimal experimental conditions for LIBS analysis are determined and the elemental composition of the samples from three different wells was compared. The results showed that the groundwater samples did not contain Cr, Cu, and Cd, but varied in the concentrations of Mn, Mg, and Fe. The study showed that LIBS is a promising technology for environmental monitoring of groundwater quality in arid regions [97].

In 2016, T. S. Salahdin et al. the study investigated the removal efficiency of heavy metals from water using charcoal filters of different depths and contact times. The study used LIBS to measure the heavy metal concentrations before and after filtration. The study found that the removal efficiency increased with contact time until reaching an equilibrium condition that depended on the type and concentration of the heavy metal. The study also found that the filter combinations with higher concentration, depth, and contact time had higher removal efficiency values [98].

In 2018, A. A. I. Khalil et al. analyzed a series of 13 coffee brands using dual-pulsed laser induced breakdown spectroscopy (DP-LIBS) and a standard analytical technique like inductively coupled plasma/optical emission spectrometry (ICP-OES) used standard matrices and calibration curves to quantify the elements of interest. The results of the study were exactly identified a micro-toxic element, such as Al, Pb, Zn, and Cr, that exists in the coffee brands. The result also showed that DP-LIBS was a sensitive and reliable technique for monitoring pollution and ensuring food safety in coffee products [99].

In 2019, El Faham et al. study was run to evaluate the feasibility of co-processing cement solid wastes from a cement plant in Egypt using LIBS and ICP-OES techniques. The study concluded that the samples had the main elements needed for clinker and cement production and had low levels of heavy metals and hazardous elements. The study suggested that LIBS and ICP-OES could be used as a fast and efficient method for deciding on the co-processing of cement solid wastes [100].

In 2020, Nasar et al. The study monitored the toxicity of antidiabetic tablet drugs. It was performed utilizing a novel method that combines CF-LIBS and LA-TOF-MS. The results indicated that metformin (C4H11N5•HCl), with hydrogen (7.3%), carbon (29.1%), nitrogen (42.4%), and chlorine (21.2%), is present in the core of the Zolid Plus 850 mg and Glucophage 1000 mg tablets, whereas the core of the GSCC tablets is primarily composed of calcium (60.7%), magnesium (24.2%), sodium (4.3%), potassium (2.5%), barium (2.4%), and silicon (5.8%) [101].

In 2020, M. Fikry et al. study was executed to investigate the effects of different wavelengths and pulse energies of a single shot picosecond Nd:YAG laser on the plasma generation and characterization of a pure copper sample using LIPS. The study concluded that the plasma electron temperature and density increased with the increase in the laser wavelength and pulse fluence due to the variations of mass-ablation rates, inverse-Bremsstrahlung, and photo-ionization. The study showed that the plasma parameters could be controlled by applying proper picosecond pulse parameters for different applications of material science spectroscopic analysis and plasma interaction dynamics [102].

In 2021 A. A. I. Khalil, et al. used short-long orthogonal double-pulse laser-induced plasma spectroscopy (SLODP-LIPS) and an inductively coupled plasma-optical emission spectrometer (ICP-OES) to analyze the micro-toxic elements in various brands of commercial ink powders (CIPs) available in Saudi Arabia. The results showed that the emission spectra of the CIPs revealed the presence of 13 elements with different intensities, some of which are harmful to human health and the environment. This study demonstrates that SLODP-LIPS is a powerful tool for the analysis of micro-toxic trace elements in solid materials, especially CIPs, which are widely used in various industries and applications [103].

In 2022, K. Elsayed. This research presented a novel method to measure phosphorus concentration in phosphogypsum waste samples using calibration-free LIBS. The plasma parameters, such as electron temperature and electron density, were determined from the emission intensity and stark broadening of P I lines under air and helium atmospheres. The results showed that the plasma parameters vary linearly with phosphorus concentration in the samples. The plasma parameters can be used as a fingerprint to identify phosphorus concentration in phosphogypsum samples without a complete analysis [104].

In 2022, O. A. Nassef and Y. E. E. D. Gamal showed the application of ns-LIBS as a technique for characterizing heavy elements in Nile River sediments. The technique used compact pellets of milled sediment samples and two values of laser pulse energy. The LIBS spectra was revealed the presence of various heavy elements that indicate the pollution sources of the Nile. The LIBS results were supported by XRD analysis. The work also proposed a mathematical-based approach for calculating the spectral line intensity using the Boltzmann plot and the plasma excitation temperature. The method was claimed to correct and balance the signal fluctuations due to matrix effect or experimental conditions [105].

3. Current study

Our group is the first to apply ICP- OES and LIBS to the analysis of agricultural soils surrounding areas of Abu Zaabal factory, Al-Khanka city. In this study, we provide the laser-induced breakdown spectroscopic (LIBS) analysis under the action of the ultrafast picosecond Nd:YAG laser and the specifications calculated from the electron temperature of plasma generated by the fundamental (1064 nm), second (532 nm), third (355 nm), and fourth (266 nm) laser harmonics.

3.1 Sample Collection and Sample Preparation

During winter 2022 six soil samples were collected from an agricultural region surrounding areas of Abu Zaabal Factory, Al-Khanka city which is located to the west of the Nile Delta in Egypt. Three soil samples were collected from one direction at different locations, the other samples were collected from opposite directions and the other samples were collected from the opposite direction at different regions as shown in Figure 3.1. To obtain representative samples, enough soil was collected at each sampling site from four sub-samples by using a shovel and an axe and by making a square of 1 m side length at a depth of 20 cm. The four sub-samples were manually mixed to form a single composite sample. The samples were manually mixed to form a single composite sample. Use clean plastic zip-lock bags to place the sample in it and transport it to the laboratory. Under the sun samples were left to dry for about four days and cleaned manually by removing plant residues and any strange objects ground using a mortar and pestle and finally sieved using meshes of different sizes to obtain powders of small particle sizes. The powdered soil samples were prepared for ICP-OES and AAS analysis by using the wet digestion method which take place by using 1 gram of powered soil which is weighed and digested using nitric acid and hydrochloric acid, then filtered into a standard 50 ml flask. Then we supplement with double-distilled water to reach 50 ml, and then measure for the elements to be estimated Standards solution 1000 µg/ml of four trace elements (Cadmium (Cd), Nickel (Ni), Zinc (Zn), and Iron (Fe)) were procured from ScharlauChemie, Spain. Nitric acid and Hydrochloric acid AR grade were produced from Merck Specialist Chemical Limited. All glassware used were “A” grade and calibrated. Calibrated micropipette with range 100µl to 1000µl was used. Whatman filter paper no. 41 was used for filtration [106][107]. The LIBS technique requires a solid sample with a flat and smooth surface to generate a stable and reproducible laser-induced plasma [108]. The obtained homogenized powders were prepared for analysis by Ps-LIPS technique by pressing 1gm of powders into pellets of 1 cm diameter and about 3 to 4 mm thickness using a hydraulic at a pressure of 5 Ton.

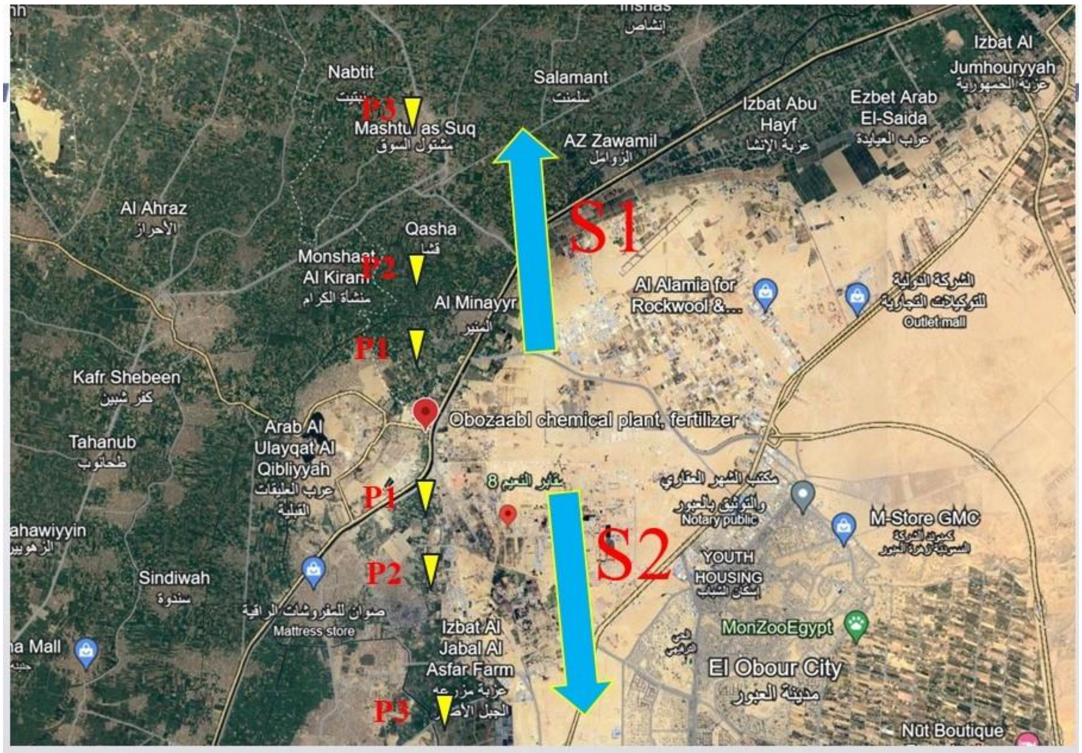

Figure 3.1. The sample collected studied sites.

3.2 Results

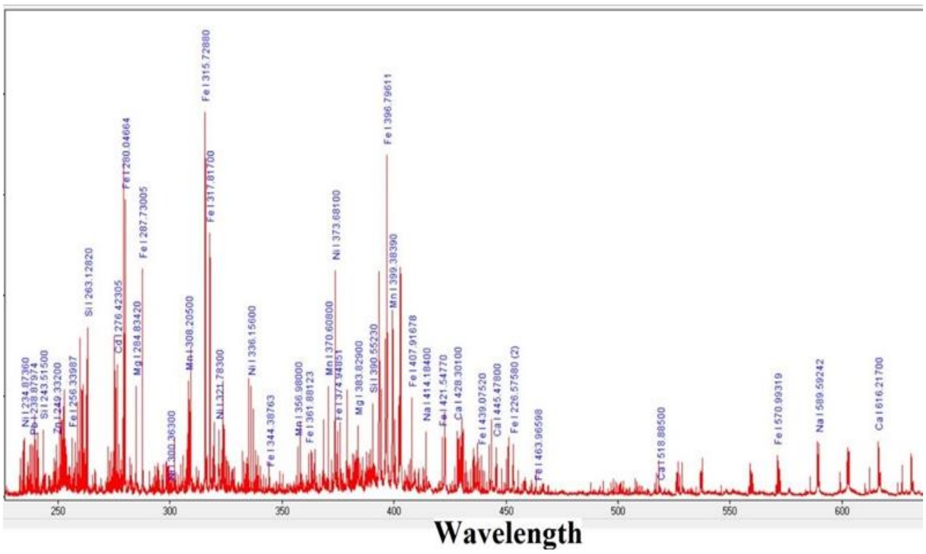

Fig 3.2 Illustrate LIBS emission spectra of the wavelength of the elements in the studied soil sample.

The qualitative analysis of the soil samples was conducted through the examination of optical spectra, obtained using the Laser-Induced Breakdown Spectroscopy (LIBS) method. This technique involved the application of a single laser shot from a Near-Infrared (NIR) picosecond Nd:YAG pulsed laser, characterized by a pulse duration of 170 picoseconds and a pulse energy of 100 millijoules. The detection was carried out with a gate time of 2 microseconds and a delay of 1000 nanoseconds. Figure 3.2 showcases the high-resolution LIBS emission spectra, capturing the wavelengths of various elements. Among these elements, trace elements such as Lead (Pb), Manganese (Mn), Iron (Fe), Nickel (Ni), and Zinc (Zn) were identified, alongside other significant elements including Calcium (Ca), Magnesium (Mg), Sodium (Na), and Silicon (Si). These findings exemplify the comprehensive results derived from our study, illustrating the LIBS technique's efficacy in detecting a wide spectrum of elements within soil samples.

4. Conclusion

In conclusion, our group is pioneering the application of ICP-OES and LIBS in the analysis of agricultural soils surrounding the areas of Abu Zaabal Factory in Al-Khanka city, Egypt. The presence of heavy metals in this region poses a significant threat to human health and food safety, necessitating precise measurement and identification methods. This comprehensive review has examined three prevalent methodologies for heavy metal analysis in soil: inductively coupled plasma (ICP), laser-induced breakdown spectroscopy (LIBS), and atomic absorption spectroscopy (AAS). Each of these techniques has its unique strengths and limitations, making them suitable for different analytical challenges. Additionally, recent developments and future prospects for these techniques have been discussed, highlighting the potential advantages of their combined use with other analytical methods to enhance the precision and speed of heavy metal analysis. The choice of the most appropriate technique should be based on the specific requirements and context of the analysis. This review underscores the pivotal role of ICP, LIBS, and AAS in addressing the pressing issue of heavy metal contamination in the Abu Zaabal Factory vicinity and provides valuable insights for optimizing their selection and application in environmental and food safety assessments.

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