

**A STUDY TO ASSESS PHYSICAL AND MECHANICAL
PROPERTIES OF NATURAL AND STABILIZED SOILS
USING LASER-INDUCED BREAKDOWN SPECTROSCOPY**

BY

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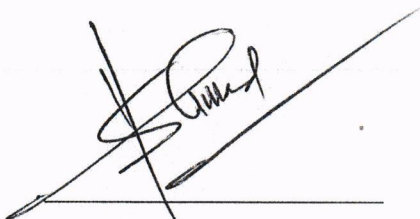
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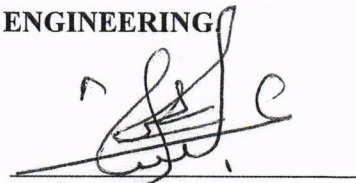
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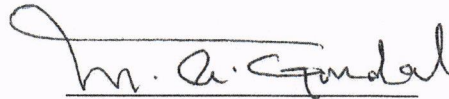
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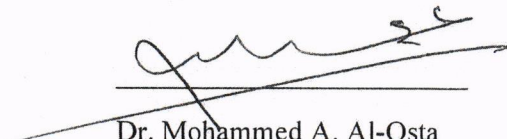
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Dedicated to my beloved family for their love, support, and encouragement.

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LIST OF ABBREVIATIONS

LIBS	:	Laser Induced Breakdown Spectroscopy
UCS	:	Unconfined Compressive Strength
ANN	:	Artificial Neural Networks
SVM	:	Support Vector Machine
SNR	:	Signal-to-Noise Ratio
CCD	:	Charged coupled devices
ICCD	:	Intensified Charged coupled devices
SEM	:	Scanning Electron Microscope
ESEM	:	Environmental Scanning Electron Microscope
XRD	:	X-Ray Diffraction
ERT	:	Electrical Resistivity Tomography
GPR	:	Ground Penetration Radar
GPR (Regression)	:	Gaussian Process Regression
PLS/PLSR	:	Partial Least Squares Regression
LASSO	:	Least Absolute Shrinkage and Selection Operator
RMSEV	:	Root Mean Square Error
NIST	:	National Institute of Standards and Technology

ABSTRACT

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Since soil parameters are decisive for designing any civil engineering structure, both standardized laboratory and in-situ tests were developed. However, some of these tests are costly, time-consuming, or difficult to perform. Therefore, tests based on empirical models have been developed to assess these soil parameters. This study is investigating the possibility of using Laser-Induced Breakdown Spectroscopy (LIBS) to estimate the physical and mechanical properties of soils. LIBS is a remarkable elemental detection and quantification technique that has been used in various fields including science, medicine, engineering, and industries. The approach of the study was to investigate the dominant chemical elements of different soils using LIBS, while utilizing the intensities of these elements to be correlated with the results of a standardized soil test. Based on the obtained results through linear regression, it was found that the performance of universal correlations for all soils is not reliable due to the large variation from one soil to another. In fact, it was noticed that another peak analysis is needed when any soil is mixed with any other foreign material. Nonetheless, this review and experimental program showed that LIBS applications can be extended to both mechanical and physical characteristics of soils using empirical correlations and standardized soil specimens.

ملخص الرسالة

الاسم الكامل: أسامة عاطف عثمان طه النجار

عنوان الرسالة: دراسة استخدام القياس الطيفي للتكسير المستحث بالليزر لتقييم الخصائص الفيزيائية والميكانيكية للتربة

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نظرًا لأهمية خصائص التربة عند تصميم أي منشأ هندسي، فقد تم توحيد كل من الاختبارات المعملية والاختبارات في الموقع حسب مواصفات ومقاييس معروفة أشهرها مواصفات الجمعية الأمريكية للاختبارات والمواد (ASTM). مع ذلك، فإن بعض هذه الاختبارات مكلفة أو تستغرق وقتًا طويلاً أو يصعب تنفيذها. ولهذا، تم تطوير نماذج تجريبية باستخدام علاقات رياضية لتقدير بعض خصائص التربة دون الرجوع لهذه الاختبارات. يعزى هذا البحث لدراسة إمكانية استخدام القياس الطيفي للتكسير المستحث بالليزر (LIBS) لتقدير الخواص الفيزيائية والميكانيكية للتربة. LIBS من أحد التقنيات البارزة للكشف عن العناصر الكيميائية الموجودة في العينات التي يتم اختبارها وتقدير كميتها، حيث يتم استخدامها في مختلف المجالات بما في ذلك العلوم والطب والهندسة والصناعات. يرجع متجه هذا البحث إلى إيجاد العناصر الكيميائية الشائعة في التربة لإيجاد علاقات رياضية لربط هذه العناصر بالقيم المتحصلة من الاختبارات الموحدة باستخدام LIBS، حيث يتم استخدام شدة/كمية هذه العناصر عند إيجاد هذه العلاقات. بناءً على العلاقات التي تم الحصول عليها من خلال الانحدار الخطي، لم يتم الحصول على علاقات ذات دقة جيدة عند أخذ جميع أنواع التربة بعين الاعتبار، ويرجع ذلك إلى التباين الكبير في مكونات التربة من تربة إلى أخرى. بدلاً من ذلك، لوحظ أنه من اللازم الأخذ بعين الاعتبار كل تربة على حدة عند إيجاد هذه العلاقات، حيث هناك حاجة إلى معرفة العناصر الكيميائية الشائعة لكل تربة على حدة سواء كانت التربة طبيعية أو محسنة كيميائياً لإيجاد العلاقات اللازمة بدقة مقبولة. أخيراً، أظهرت هذه الدراسة والتجربة المعملية أن LIBS يمكن أن تستخدم لإيجاد كل من الخصائص الميكانيكية والفيزيائية للتربة بجانب التطبيقات الكيميائية المعروفة في الأدب العلمي.

CHAPTER 1

INTRODUCTION

1.1 General

For the construction of any structure, a site investigation of soil must be conducted. It consists of a visual inspection of the ground and the collection of soil samples. To benefit from this investigation, laboratory and/or in-situ tests are used to assess the collected samples. However, some of these tests are expensive, time-consuming, or sophisticated. Due to the necessity of obtaining soil parameters and overcoming the previous difficulties, empirical models are widely used in geotechnical engineering. Due to this fact, the proposed study considers using Laser-Induced Breakdown Spectroscopy (LIBS) to develop an empirical model for obtaining some of the mechanical parameters of soil.

LIBS was invented in the 60s and since then, it has been developing. This technology determines the elemental composition of materials. This is done by subjecting the material to concentrated laser pulses with high energy. Whether the material is solid, liquid, or gas, the material will transform from its state to the plasma state due to the laser's extremely high temperature. As a result, the atoms will excite and emit atomic emissions. These emissions are captured with an optical sensor called a spectrometer. The sensor is basically capturing lights with varying wavelengths and intensity. Using computer software with

algorithms calibrated with the laser setup, these wavelengths are represented as elements and their concentration is based on the intensity of these wavelengths.

LIBS has many applications in soils that are mostly related to chemical analysis of soil, such as contaminants detection, pH, and nutrient measurement. Despite its many applications with chemical analysis, LIBS has not been commonly used for the physical and mechanical analysis of soil. However, this study is considering relating the elemental composition of soil with its mechanical and physical properties. The purpose of using LIBS is because of its simplicity, and its instantaneity and can be performed in both laboratory and in-situ. On the negative side, the performance of LIBS depends on the size of the data set, correlations with standardized tests, and the accuracy of the model. Actually, any empirical model will face these challenges.

In order to use LIBS to assess some of the soil parameters, standardized soil tests must be used to build the correlation first. The unconfined compression strength (UCS) test is a well-known standardized soil test that measures the compression strength needed to crush unconfined soil cylindrical specimens. Specimens are made and tested according to ASTM D2166-16 standards.

1.2 Purpose of Research

There are many chemical applications of LIBS that are presented in the literature for soil analysis. These applications are generally based on the detection of chemical elements in soils and their chemical concentration. However, the possibility of using LIBS to determine the physical and mechanical properties of soils from the detected chemical elements has not been well investigated in the literature. This research was assigned to introduce this

innovative technology to the field of geotechnical engineering to overcome the limitations of conventional soil tests. Further, this research project was powered by a decent experimental program to enrich the field of soil investigation using electromagnetic waves.

1.3 Objectives

The principal objective of this proposed study is to introduce LIBS to the field of Geotechnical Engineering as an alternative approach for soil assessment. The detailed objectives are as follows:

- 1- To provide a detailed literature review of the applications of LIBS with soils.
- 2- To introduce LIBS as an alternative approach for soil assessment.
- 3- To investigate the general performance of LIBS with the physical property of UCS in soils.

CHAPTER 2

LITERATURE REVIEW

This review focuses on the recent progress and challenges in the application of LIBS for geotechnical engineering. The research also discusses the widely employed calibration-free LIBS methods such as chemometrics, artificial neural networks (ANN), and support vector machine (SVM) for the quantification of constituent elements. The various applications of LIBS in geosciences such as in mineralogy, soil studies, rocks investigations, and fluid analysis have also been presented. Despite the robustness of LIBS in soil studies, it is hitherto challenging to investigate some soil physical parameters. In general, chemical applications such as contamination detection and nutrients are based on detecting certain elements or ions. On the other hand, physical and mechanical applications such as soil texture and soil humification degree may require the usage of a correlation between the chemical elements and the desired parameters. This work, therefore, summarizes how LIBS works with soils and its current uses in determining the physical or mechanical properties of soils and presents the possibilities of this technology in the field of Geotechnical Engineering.

2.1 Background

The laser-induced breakdown spectroscopy is an elemental detection and quantification technique that has found a variety of applications in sciences, medicine, and engineering [1–5]. Since its inception in the 60s, the technique has been widely employed in the investigation of different materials' compositions to analyze the elemental content for

various applications. The method has been applied by the food processing industries to identify heavy or radioactive elements present in the sample. This is done by subjecting the material to concentrated laser pulses with high energy [6]. The material to be investigated could be in a solid, liquid, or gaseous state. The material-laser interaction facilitates the formation of the plasma which constitutes the atomic emission signatures of the elements present. These emissions are captured with an optical sensor called a spectrometer. The sensor is basically capturing lights with varying wavelengths and intensities [7].

The LIBS operates based on the principle of matching elements to the wavelengths of their emission lines. However, since more than one electron can be excited within the same or different energy levels while forming a plasma plume, the elements would not have a unique wavelength. In fact, one element can be related to multiple wavelengths. There are multiple reasons for this phenomenon. In the early days of LIBS, the plasma plume formed from the excitation of the material was not strong enough due to the low energy of the laser. Scientists could only detect very few chemical elements using this technology, mostly metal elements. After that, many fundamental studies were conducted on laser-material interaction to expand the possibilities for assessing other elements [3–5,8–10].

These studies opened the doors for modern LIBS systems that can generate stronger emissions to be recorded with greater resolutions. This results in more possibilities for LIBS to be utilized in further applications within different environments, not only for specific laboratory conditions. Since then, LIBS has been adopted for practical underwater analysis, biomedical analysis, radioactive materials studies, geological studies, and many other fields. The literature is now rich with the theory and the fundamentals behind this

technology, resulting in an extreme advancement of the research to consider further practical applications.

Various methods were introduced to overcome some difficulties in some LIBS applications [11]. For instance, double-pulsed LIBS were developed to enhance the observed signal in sensitive materials. Two colinear or perpendicular pulsed lasers are used to increase the plasma plume's temperature to obtain a better signal. However, the improvement of the signal's intensity is not guaranteed. Hence, Femtosecond LIBS and Resonant LIBS were introduced. The former uses ultrashort pulses that do not interact with the formed plasma plume. The main advantage of the femtosecond pulses is that the ablated material will have a lower threshold and higher efficiency than longer laser pulses. The Resonant LIBS suppresses the background interaction with the laser pulses and selectively excites the material to a plasma plume [12]. This method requires previous knowledge of the material that is being excited. The majority of the methods used in current applications are either approximately quantifying the chemical elements from the measured intensity of the atomic emissions or combining LIBS with other spectroscopic techniques [13].

The birth of modern geotechnical engineering is considered when Karl Terzaghi proposed his theory of effective stress, which led to what today we call soil mechanics. This type of mechanics is somewhat new to the field of engineering, and it is used to predict the complex behavior of soils. It is worth mentioning that the theory and quantitative models used for developing the intrinsic nature and the behavior of soils are not more than an approximation. Since soil structure is too complex and its assessment parameters are not more than a realistic approximation, the principle of the factor of safety was introduced. This factor addresses the calculated risk; hence, simpler soil models were developed by

combining statistical analysis with soil mechanics [14]. These theories and methods are strongly needed to be studied and understood to obtain the safest conditions for any civil engineering structure.

There have been many massive developments in soil mechanics in form of testing techniques. Improved laboratory and in-situ tests were developed and standardized within the field. This led to an impressive advancement in the geotechnical investigation of soils. These tests are used to get quantitative measurements of soil parameters used for design and condition assessment. However, some of these tests are expensive, time-consuming, or sophisticated. Due to the necessity of obtaining soil parameters and overcoming the previous difficulties, empirical models are widely used in geotechnical engineering. Due to this fact, some researchers considered LIBS in soil assessment. However, most studies considered the chemical applications in soils, such as contamination detection, soil nutrient, and soil pH [15]. Few studies are considering the possibility of using LIBS to determine the physical and mechanical properties of soils, which are the essential parameters used in geotechnical engineering [16].

This review presents the recent progress and persistent challenges in the applications of LIBS for geotechnical engineering. It summarizes the spectral processing techniques for quantitative analysis of the constituent elements. It also highlights the important parameters to be controlled for better accuracy.

2.2 Principles of Laser-Induced Breakdown Spectroscopy

LIBS configuration consists of three major components [17–20]. The first essential component is the Q-switch laser. The main difference between this type of laser and a non-Q-switch is that the latter generates continuous laser beams like laser pointers. On the other

hand, a Q-switch laser generates a pulsed laser with a duration of fractions of a second for each pulse. This is essential for high-energy lasers to be considered non-destructive while simultaneously providing enough energy to heat the material and form a plasma plume [21]. This phenomenon is called laser ablation when a focused laser pulse is heating and exciting a very small portion of the material to form a plasma plume (Figure 1). Multiple parameters are used to describe pulsed lasers: the laser energy, the wavelength, and the delay time. Laser energy is described in two terms, fluency and irradiance. Both terms are used to relate the energy per unit area. However, irradiance is considering the factor of time as well. Each material has a different fluence threshold for the ablation processes and formation of the plasma plume. For the same material, the higher the laser energy is, the higher would be the ablation rate in general. However, the energy cannot be only used for determining the laser characteristics, and this is because the energy is dependent on the laser wavelength and pulse time and its effect cannot be studied alone. The laser wavelength is used to determine the energy absorption by the material and the plasma properties. Studies indicate that shorter wavelengths produce a higher ablation rate in general. It is worth mentioning that the plasma formation threshold is higher at shorter wavelengths ranging from 157 nm to 266 nm [22].

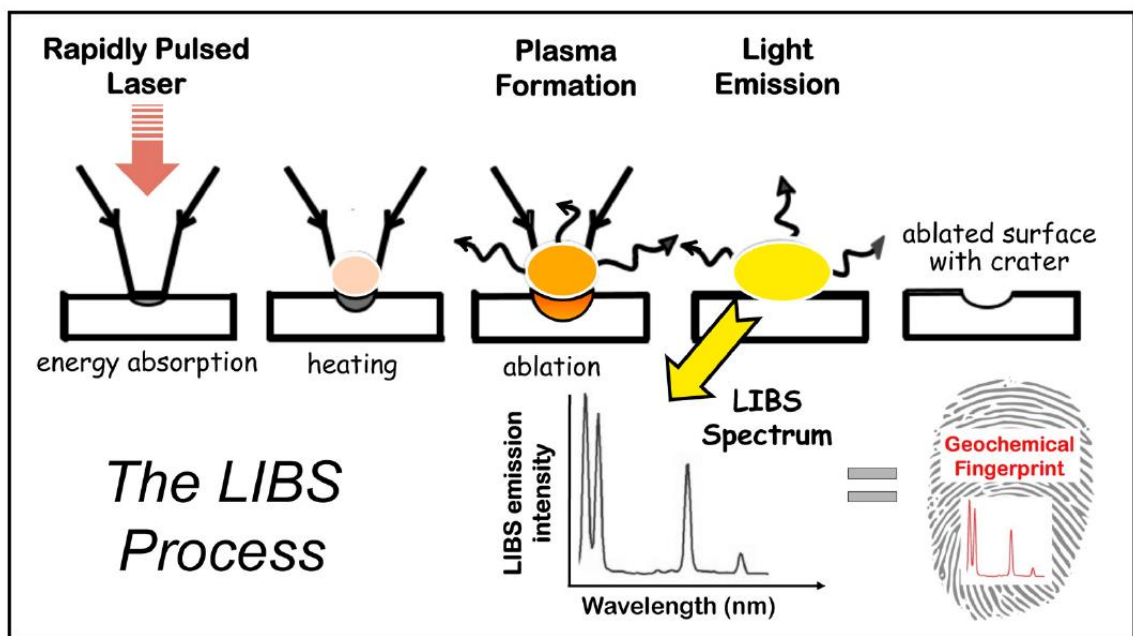


Figure 1 A schematic diagram showing the multi-step process that takes place when the laser irradiation strikes the sample surface. Adapted from [94].

On the contrary, the ablation initiation rate is lower at longer wavelengths and elemental fractionation is higher. It is not desirable to have elemental fractionation since the elemental phase change between solid and liquid modifies the emissions from the plasma plume [23]. The delay time or the required pulse duration is the time needed to ablate and form a plasma plume [24]. This parameter is heavily dependent on the laser's wavelength, ambient pressure, and sample features. The delay time shall be optimized for each material by experimentation; however, it has been reported in the literature that laser pulse duration from 50 to 200 ns results in a rapid increase of the plasma size [25].

The other major component is the optical fibers. This essential device is used to acquire light from plasma emissions. For this device to perform well, the laser pulses must be focused with a single or a set of lenses to increase the irradiance of the plasma [26]. Hence,

fiber optics can catch more light. In summary, the principle behind this device is measuring the variations in the periodic refractive index, among other factors, due to the light transmitting through the glass or plastic fiber. The most prevalent optical fibers are fabricated by fused silica, in other words, fibers with glass cores. The diameter of these fibers may vary between 50 μm and 1 mm. Furthermore, this device can collect data other than capturing the emitted lights from the formed plasma. Shockwaves in induced laser plasma can also be detected using fiber optics instead of classical microphones. This type of wave is generated due to the sudden change in the material phases when ablated by the laser, resulting from a small but strong explosion that can be detected based on optical fiber devices such as Fiber Bragg Grating. Sometimes, fiber optics may catch unwanted emissions due to the ablation of the surrounding gas in addition to the material in concern. Depending on the study's type and sensitivity, the ablated material might be placed in a vacuumed chamber of a typical LIBS system (Figure 2) to eliminate the ambient gas's effect and enhance the fiber optics light acquisition [27].

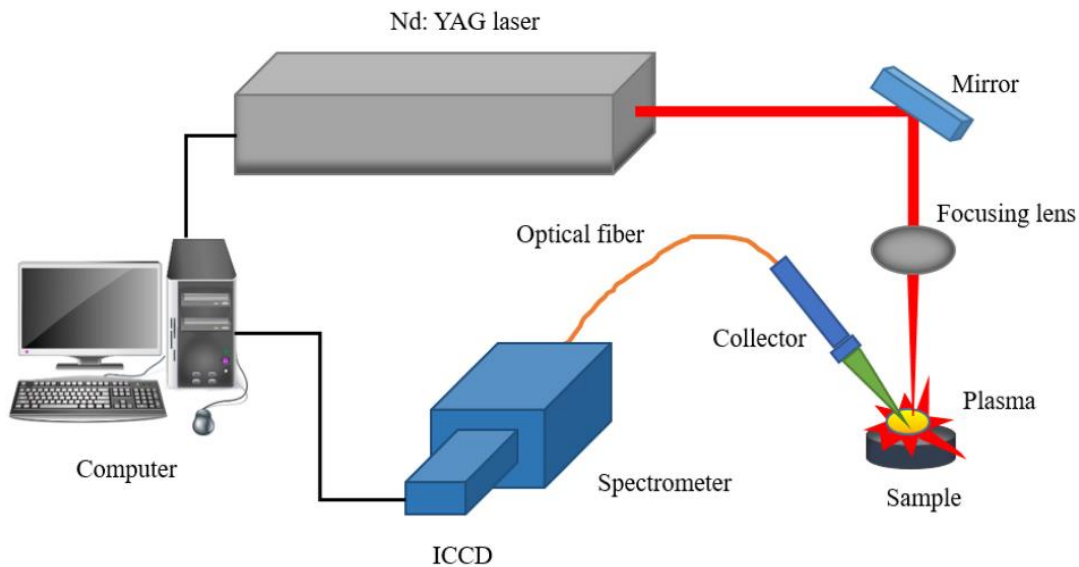


Figure 2 A schematic diagram for a typical single-pulsed LIBS system. Adapted from [182].

After capturing the lights by the fiber optics, they will be directed to the last typical component of any LIBS setup, which is the spectrometer. This device diffracts the collected light using gratings and sometimes prisms into its constituent wavelengths and detects their corresponding intensities. Nowadays, most spectrometers have a compact design, allowing LIBS setups to be transportable if a portable computer were attached (Figure 3) [28–30]. Computers are used as control units to present and store the collected data from spectrometers. Spectrometers have multiple configurations, and each one of them is used for different applications. The most used spectrograph in LIBS setups is Czerny-Turner's design. It consists of an entrance slit that directs the light source to a single or set of collimating mirrors [31]. The mirror will direct the collected light to the diffraction grating, which is placed at a certain angle. Then, the grating will diffract the light into distinct wavelengths with different angles. A focusing mirror will then be used to divert the separated wavelengths toward a detector. The detector choice depends on whether one or two-dimensional spatial information is required and the desired signal-to-noise ratio (SNR). Charged coupled devices (CCD) are commonly used since they are cheaper than other detectors and provide two-dimensional spatial information [7]. However, this detector provides weaker peaks or signals and a higher spectral baseline or noise. This results to lower SNR values compared to more expensive detectors. This device contains pixels sensitive to lights. When a photon hit one of these pixels, an electrical charge is generated and detected by a set of electronics [32].



Figure 3 A portable hand-held LIBS device. Reprinted from [6].

In short, the data acquisition process using LIBS starts by emitting laser pulses from the source. The pulses will hit the material, causing ablation and formation of the plasma plume. In other words, the high-energy laser pulse with an extremely high temperature will heat the material and cause erosion of a very small part of it. The ablated material will transform from its original phase, whether solid, liquid, or gas, to the plasma state. This is due to the atomic excitation because of the laser's high temperature. The exciting material will produce atomic emissions in the form of light with different wavelengths. These emissions are captured by an optical sensor that diffracts the light. After capturing, the spectrum (Figure 4) will be detected and stored in a PC, and quantitative and qualitative analysis algorithms will be applied to the spectrum using computer software. Depending on the set parameters, the result will be a spectrum with a certain range of wavelengths and their intensities [33–37].

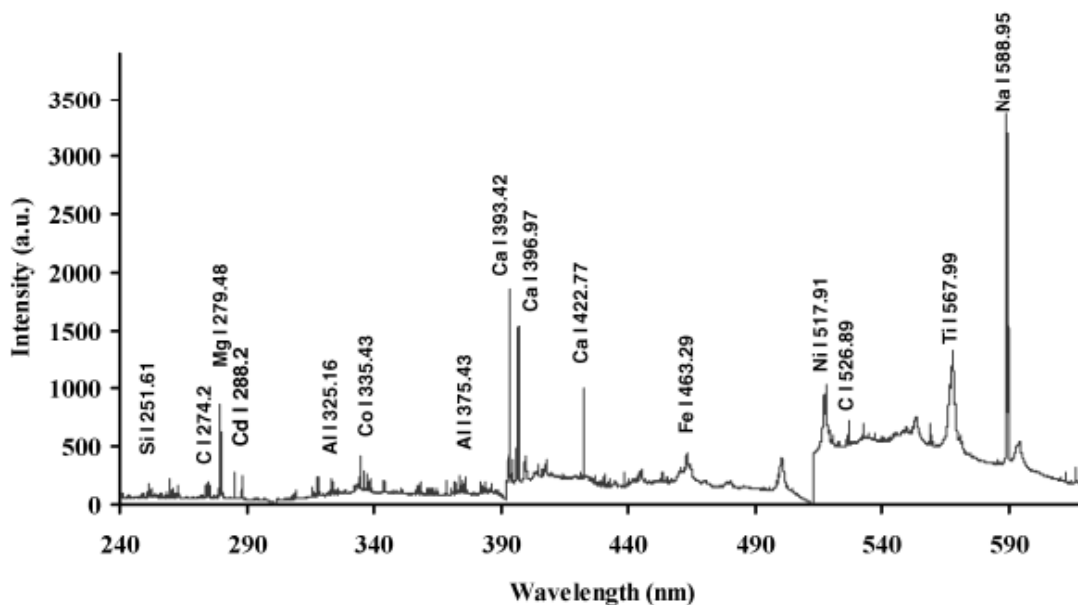


Figure 4 Typical LIBS spectrum showing the measured intensities of some chemical elements for a rock sample. Reprinted from [24].

2.3 Advantages of Laser-Induced Breakdown Spectroscopy in Soil Studies Comparing to Other Techniques

Multiple analytical techniques in physics are used to deal with ground or soil materials. The working mechanisms and expected outcomes are different from one approach to another. For instance, the Scanning Electron Microscope (SEM), which has existed for a while and superseded with a better version of the same machine, is a significant tool for soil studies. The captured microscope images by SEM can be used to investigate the structure and fabrics of the soil particles. This is done with the assistance of an electron beam interacting with the sample under vacuum conditions to achieve the required resolution, which generally ranges from 0.5 to 5 nanometers. Environmental Scanning Electron Microscope (ESEM) was a great breakthrough for soil investigation [38]. Unlike SEM, ESEM can be utilized with wet material, which is crucial for soils since water is a major part of the soil matrix. Among some other differences between SEM and ESEM, the

latter can achieve sufficient image resolution when used with low vacuum or gas conditions. However, both techniques require sample preparation to obtain the best image quality [39].

On another note, X-Ray Diffraction (XRD) is the most utilized method for soil analysis among the other x-ray methods. XRD can provide an effective semi-quantitative soil analysis by measuring the x-ray wave diffraction angle after colliding with a particle. Each unique angle can be related to a specific chemical compound, while the amount of these diffractions per unit of time can be used to determine the concentrations of the measurement. XRD is beneficial in such studies because of the nature of inorganic soil material [40]. Since the soil particles are very fine, with poor crystalline structure in general, XRD is a convenient and reliable method to investigate the minerals in soils. Any testing sample, whether it is soil or not, needs some preparations to obtain the best accurate results. Powder samples are preferably dry with a grain size of 10 μm or less. The raw data requires proper quantitative analysis methods, including fitting methods, to achieve useful information [41].

Multiple Geophysical techniques can be utilized in the field for ground investigation. Reflected radio waves detected by Ground Penetration Radar (GPR) can be used to identify the interfaces of subsurface soil layers. The soil layers are identified with this technology based on the dielectric constant property of the materials. Whenever material property changes in density in general, the constant dielectric changes cause some of the emitted waves to reflect. A typical GPR cart used for ground investigation has an antenna or multiple antennas attached to it to emit the waves [42]. The detection depth and its resolution are based on the frequency of the emitted waves. In some situations, the obtained

data cannot be reliable due to the presence of anomalies. For instance, groundwater tables and metallics significantly affect the reflected waves [43].

Another method used for ground investigation is by utilizing the electric resistivity property of soils. Electrical Resistivity Tomography (ERT) is another in-situ geophysical technique that can explore subsurface conditions by assessing the electrical current flow in the soils. As it is already well known, the electrical resistivity is mostly dependent on the degree of saturation of soils with the pore fluid. Simply, due to the lower electrical resistivity of water, the resistivity of a soil matrix with water as a pore fluid would also decrease. Multiple other factors affect the resistivity of a soil matrix, such as pore connectivity and soil particle gradation, but above all is pore fluid salinity. Assuming that the soil is saturated with some other fluid other than water, say hydrocarbons. Due to the salinity of hydrocarbons, which is higher than water, the electrical resistivity of this material is even lower than water. Some studies showed that the area of contaminated soils with hydrocarbons could be determined with ERT due to the salinity of the fluid, which causes a clear abnormality when imaging a soil profile with ERT.

On a different note, geophysical inversion has limitations due to non-uniqueness and requires diligence to obtain a proper profile [44]. All in all, both GPR and ERT may not give clear quantitative results at this moment. However, they may add great value when combined with other geotechnical tests. The literature shows some interest in replacing conventional geotechnical tests with these geophysical techniques [45].

LIBS is also powerful with such material when comparing LIBS to two of the most common laboratory analytical techniques described earlier in soils. A clear advantage for

LIBS is that pre-prepared samples are not necessarily needed to obtain reliable results. Suppose this advantage is combined with a mobile LIBS setup currently available commercially. In that case, LIBS can be utilized as an in-situ physical technique similar to the two geophysical techniques described earlier. Not only LIBS can be utilized in the field, but lucid quantitative results on the spot can easily be obtained, unlike GPR or ERT.

Similar to the geophysical techniques, some research is considering LIBS to assist or replace conventional geotechnical tests [46]. Nonetheless, LIBS would require developing some correlations with conventional test results to utilize LIBS as a standalone test, which is an approach done for geophysical tests [47]. Mapping data and developing profiles is possible with LIBS; however, unlike GPR and ERT, the entire mapped profile shall be exposed for testing as LIBS cannot generate a results map for the embedded profile since the readings cannot be taken [48]. Finally, LIBS does not require data analysis if the machine is calibrated for properly testing the target soil material. On the contrary, GPR and ERT data need to process their data to make sense of the obtained data [49].

2.4 Laser-Induced Breakdown Spectroscopy Data Processing and Analysis

The matrix effect is a fundamental issue that affects the quantitative analysis in laser-induced breakdown spectroscopic studies. It emanates due to the chemical composition and physical characteristics of the soil samples under investigation. Such effects influence the elemental concentration of the individual elements within the plasma, and thus the measured emission intensity. Matrix effects primarily influence the generated laser plasma and the ablated atoms of the material [50].

2.4.1 Physical Matrix Effects

The physical matrix effects relate to the nature and physical properties of the sample which indicates the amount of the material to be ablated by the incident laser. The surface properties of the specimen i.e., optical transmissibility, thermal conductivity, absorptivity, hardness, texture and roughness, reflectivity, degree of crystallinity, porosity, and grain size) will influence the interaction of the laser with the material surface. The rate of plasma formation would also be affected by the moisture content and presence of organic matter. Elsewhere, it was noted that during LIBS analysis, variation in emission line intensity will occur when dealing with minerals of varying grain sizes [51]. Sample hardness will determine the quantity of the material ablated to generate plasma; surface roughness will influence the laser energy coupling with the surface as well as the emission intensity from the LIBS signal. The plasma temperature (ranging from 5,000 to 14,000 K) depends on the nature and composition of the specimen.

To mediate the complications caused by the matrix effects and understand their influence on LIBS plasma generation, a study was carried out by NASA's Mars Sciences Laboratory in preparation for the deployment of Nasa's ChemCam system. In such a study [52], they employed a simulated Mar's atmosphere (9 mbar CO₂) to investigate the matrix effects on limestone and mafic volcanic rocks at a 3 m distance and formulate an analytical technique to correct them. They observed that the external standard method of normalizing the LIBS signal intensity performs better than the calibration-free and internal normalization approaches.

2.4.2 Chemical Matrix Effects

The chemical matrix effect occurs when one element interferes with the emission characteristics of another element in the plasma. An element may exhibit different LIBS emission intensities when present in two different compounds at the same concentration (such as a trace element in silica mineral and carbonate material). This largely depends on the properties of the individual matrices since each has different melting temperatures under laser radiation and material vaporization. Eppler et al. [53] reported that two main factors, namely compound speciation, and sample composition influence the detection and quantification of Ba and Pb in soil and sand samples. Specifically, Pb emission intensities increased in the order nitrate<sulfate<chloride<carbonate<oxide and Ba emission intensities increased in the order nitrate<chloride<sulfate<oxide<carbonate. A similar matrix effect occurs in specimens of the same material with different compositions where the emission intensity of a minor element is affected by a major element. For example, in research to investigate highly concentrated brines NaCl–CaCl₂ and NaCl–KCl, the emission lines of both Ca and K depend strongly on the NaCl concentration, and matrix interference resulted in a strong decrease in the signal-to-background and increase in signal-to-noise for both emission lines [54].

2.4.3 Spectral Pre-processing

The signal intensity fluctuation is one of the factors affecting the LIBS spectra. Therefore, except when the specimen of interest is a solid inclusion analyzed with a single laser shot or a micrometer-scale fluid, it is a normal trend to combine several laser shots, often 100s [55–57]. To generate high-quality data for chemometrics analysis, this, and many other issues such as sample characteristics, spectral interference, effects from the external

environment, and spectrometer resolution must be addressed. For instance, the baseline drift and the background from the continuum emission can affect the ability to extract the LIBS spectral lines with an optimum degree of accuracy. Therefore, the baseline correction is key to acquiring accurate spectral lines of interest. Noise, which usually forms a component of LIBS emission signal, and affects the desired quantitative analysis can be filtered by spectral smoothing. On the other hand, the contribution from any non-gated background continuum radiation can be reduced through background subtraction [58].

The problem of overlapping peaks is generally solved through decomposition by mathematical analysis. Some of the common approaches used include neural network methods, Fourier deconvolution, wavelet transformation, peak sharpening, and curve fitting. Apart from denoising and wavelength calibration, raw LIBS spectra could pass through five steps of normalization, outlier rejection, baseline correction, spectral averaging, and resolution enhancement to distinguish overlapped peaks. This help to reduce the effects of alternating experimental conditions and physical matrix so that corrected LIBS spectra could be utilized for quantitative analysis and other applications.

There exists a multitude of works regarding spectral preprocessing in LIBS. For example, Segnini et al. [59] developed a straightforward method to reduce the Fe and Al interference on the C usually observed in the LISB studies of some soil samples. They used the method to quantify the amount of carbon present in selected Brazilian soils of varying textures. The quantification process was influenced by both chemical composition and soil texture. Dyar and his team [60] studied different approaches used for baseline correction and evaluated their comparative predictive performance. They considered thirteen elements including (Zn, Ni, Co, Fe, Mn, Cr, Ti, Ca, K, Mg, Na, Si, and Al) that could be of geological interest.

Their investigations found that the traditional trend of applying a single method for baseline removal was not effective for quantitative analysis. They recommend these techniques be applied on an element-by-element and spectrum-by-spectrum basis for improved quantitative determination. Another important spectral preprocessing procedure is the normalization of the spectra. It is critical in reducing matrix effects and mitigating shot-to-shot fluctuations in LIBS signal intensity. Among the many works reported in this regard is that of Chadwick and his colleagues [61]. They found that poor statistics in LIBS analysis were caused by outliers within a set of measurements. They also reported that improved accuracy for quantitative determination was achieved through the normalization of elemental emissions to the total plasma emission intensity. Senesi et al. [62] normalized the line emission intensities of elements of interest to the background signal of the emission spectra in their quantitative determination of Pb, Zn, Cu, Cr, and V in contaminated and pristine soil samples from Italy, while Kwak et al. [63] used the signal-to-noise ratio of an As emission line instead of the intensity in their LIBS study of As in mine tailings sites across South Korea.

2.5 Laser-Induced Breakdown Spectroscopy as a Tool for Quantitative Elemental Analysis

The accuracy and precision of elemental concentration in a particular specimen are critical for quantitative chemical analysis using any analytical method. Several factors can be optimized in LIBS to enhance the analytical performance [64–67]. These include the stability of the laser pulsed energy, lens-to-sample distance, detector characteristics, the system's geometry, and the laser repetition rate. On the other hand, it is cumbersome to optimize sample-dependent properties like the matrix and the sampling method. There are

several methods of elemental quantification with each having its merits and demerits. Some of these methods include chemometrics analysis, calibration method, and calibration-free techniques [68].

2.5.1 The Calibration Curve Approach

In this technique, the elemental concentration in a given specimen can be determined by comparing the LIBS signal intensity of the element of interest with that of the same element from a standard sample whose concentration is known within the expected range of the unknown sample concentration. The calibration curve generally relates the intensity of the elements in the specimen to the mass of the ablated sample in the plasma plume to the standard sample investigated under the same analytical condition. Principally, the concentration-intensity relationship for the elements under investigation is formulated based on standard samples having a similar matrix as the specimen under study. This is simple for some classes of materials such as alloys and metals. However, this could be challenging for GeoLIBS applications where it is difficult to establish a direct match between the chemical and physical properties of the specimen and the standard sample even if the specimen's matrix is known.

Some ways to remedy inhomogeneities caused by the matrix effects include either pulverizing and homogenizing the specimen, studying the specimen by multiple laser shots spread across the sample, or by adopting an algorithm to ignore irrelevant spectra that do not represent the bulk specimen [69–71]. The effects of ambient pressures on the calibration curves developed for 14 elements were investigated by Salle and his team [72]. They studied the curves for Ba, Sr, Ni, Fe, Mn, Cr, Ti, Ca, K, Si, Al, Mg, Na, and Li elements in standard clay and soil pellets. They obtained the best calibration curves at low

pressures with optimum linear regression and repeatability realized at 7 Torr of carbon dioxide gas. Moreover, studies of the calibration curves for clays and soils depict that matrix effects exhibit little influence at lower ambient pressures. Therefore, regardless of the chemical matrices, quantitative LIBS elemental determination would be more favorable in a low-pressure environment [73].

2.5.2 Calibration-free Laser-Induced Breakdown Spectroscopy

The calibration-free technique is a quantitative analysis method that does not employ the use of calibration standards. It was established to address the sample-matrix issue. The method assumes that the local thermodynamic equilibrium condition is reached within the plasma plume, thus allowing the estimation of N_e and T_e , after which the sample's composition can be obtained.

The method requires that the source of the radiation is thin enough to assume that the plasma is a total representative of the sample composition, thus, allowing the determination of the line integral intensity between 2-energy levels of an atomic specie. Provided that each energy level is represented by a different spectral line, the elemental concentration of can be obtained without necessarily calibrating the integral intensities of the lines. It was established, theoretically, that the calibration-free method permits the calculation of the elemental concentration of all the elements present in the specimen up to their detection limits. As discussed by Tognoni et al. [74], the extent to which the calibration-free approach leads to accurate relative concentrations of the elements present is a cumbersome task and depends on the various conditions outlined above.

There have been multiple reports indicating the prominence of the calibration-free approach in the elemental quantification of LIBS specimens. For example, Corsi and his

team [75] have reported a successful elemental quantification of a suite of soils and sediments. However, they realized a substantive difference in the quantification of heavy metals. Tawfik and his colleagues [76] have investigated the matrix effects on the generated plasma from seawater of varying degrees of salinity using calibration-free LIBS. Their results revealed the presence of both the Ne and Te for the three elements Ca, Mg, and Na in the sample matrix, and their concentration was observed to change with matrix composition. These findings implied that Ne and Te formed a compositional fingerprint for a particular sample, therefore, the salinity of the seawater sample could be determined from a single element without necessarily analyzing the rest of the constituents. Elsewhere, Homackova and his colleagues [77] employed the calibration-free LIBS to study a pitchstone to quantitatively analyze a dozen of elements (Ba, Sr, Fe, Mn, Ti, Ca, K, Mg, Na, Si, Al, Li). Their results indicate a good agreement in the detection between the calibration-free and other conventional methods.

2.5.3 Chemometrics in LIBS

In principle, chemometrics involves the application of statistical and mathematical tools to (i) extract some relevant data from the analysis, (ii) identify the relationship between the data acquired from analytical devices and the physical properties or given parameters, and (iii) assist in designing experiments. Given the fact that LIBS can provide large data sets within a short time, it becomes ideal to apply the chemometrics technique in analyzing the LIBS output. Chemometric techniques can be utilized in LIBS for data processing and interpretation, spectral pre-processing, and signal analysis. Owing to its ability to consider multiple variables simultaneously, the method provides many advantages including extraction of enough information from the data, development of calibrations, identification

of outliers, reducing the influence of interfering signals, and reduction in noise. Multivariate techniques have created a new roadmap for quantitative and semiquantitative analysis far beyond the usual univariate method. They have served as a means to utilize the total information enshrined in the LIBS spectra instead of considering only the information localized in a particular portion, and then correlating the information with the sample's composition for discrimination and identification of various elements.

Owing to the increased acceptability of the chemometrics technique in LIBS elemental quantification, several works have been reported describing the merits and demerits of different chemometric tools. The most widely used chemometric tools applied in LIBS for classification, identification, and discrimination purposes are SVM, LASSO, SIMCA, PLSDA, PCR, PCA, KNN, and ANN. The chemometrics techniques are generally formulated based on the idea of the principal components except for the ANN technique. The principal components concept requires that samples are grouped according to the cluster's distribution in the PC space, and the test sample's identity is associated with the closest cluster. The samples that do not identify with any cluster are, however, considered unclassified.

Sirven and his team [78] studied a series of natural rock samples including obsidian, trachyte, trachyandesite, gabbro, limestone, and basalt. They applied three chemometrics techniques (PLSDA, SIMCA, and PCA) to the acquired LIBS spectra. The SIMCA exhibited higher robustness compared to PLSDA in the more realistic situation where spectra of unknown rock samples were investigated. It was also more robust in discriminating rocks of nearly the same composition. However, the PLSDA appeared to be more accurate than SIMCA in the case where all the were taken into consideration for the

calculation, yielding the classification accuracy of 86%. On the other hand, the PCA technique enabled good discrimination of the elements and provided a visual diagnosis of the spectral classes. However, it didn't support any automatic prediction. Finally, they observed that combining SIMCA and PLS-DA techniques yielded 100% classification accuracy with remarkable robustness.

Motto-Ros and his colleagues [79] employed the chemometrics technique to investigate four different rock samples extracted from a particular meteorite impact area in Egypt. They employed a processing technique based on the artificial neural network to perform the quantitative analysis. The specimens consist of volcanic glass, sandstone, and two impact glasses all depicting the analogs of the Martian surface rocks. A number of powdered specimens including soils, andesite, and basalt were previously used to train and validate the ANN algorithm. A mean deviation of less than 15% was observed in the elemental concentrations of Fe, Mn, Ti, Si, Al, Ca, and Mg measured using LIBS when compared to the data obtained through X-ray fluorescence. Their results further signify the remarkable potential of the ANN method in accounting for the overlap of spectral lines and matrix effects. Elsewhere, Chen et al. [80] reported the benefits of using a 2D convolutional neural network in the quantification and discrimination of different rock samples. They studied various rock samples including shales, mudstones, limestones, granites, and dolomites. Their results revealed a high classification accuracy of more than 99% for the test and validation sets compared to other identification techniques. In another study, Muckano and his team employed ANN and PLS to investigate soil and rock samples collected from geothermal areas typically characterized by an increased content of As and high background radiation. Their investigations revealed that the ANN technique was more

accurate than PLS in solving the matrix effects problem in the rock samples for the elements Pb, As, Cu, Cr, and Ti. This is perhaps due to its ability to model the spectral non-linearity and hence, improve the performance.

In their effort to implement LIBS for practical applications, Koujelev et al. [81] collected 41 certified mineral specimens consisting of rock powders and 14 natural rocks of varying origins including ores, dolomite, granite, obsidian, basalts, and andesites. Their research concentrates on three basic issues (i) Studying the possibility of applying the algorithms in inhomogeneous and weathered field rocks of different homogeneity and texture; (ii) The possibility of identifying new samples by training the model using a few balanced samples; and (iii) The power of the model to distinguish between similar specimens and its ability to associate a new specimen to any known sample. The developed algorithm was then run on a set of unknown specimens not included in the training dataset. Despite some small variations in chemical compositions and surface texture of the tested rock samples with regard to the training dataset, an identification rate of 88% was achieved in the validation stage. These observations further demonstrate the capacity of the modified ANN in accommodating the variations of samples and its ability to identify unknown specimens. El-Haddad et al. [82] employed the LIBS technique for the in-situ determination of Cu, Fe, Ca, and Al in soil samples. They used linear regression for the quantification analysis which yielded unsatisfactory performance due to self-absorption and the complex soil matrix composition. However, they recorded marvelous quantitative determination results when they used the dataset constituting a set of elements as input variables instead of using data from a single element. Zhu et al. [32] studied 16 marine sedimentary rock specimens including limestone, marl, and mudstone using LIBS. They used both the PLSDA and

SVM chemometric techniques for the classification and discrimination of the elements. Their results revealed that SVM outperformed PLSDA in classification strength. Boucher and his colleagues [83] carried out a comprehensive investigation using LIBS on a suite of 100 spectra extracted from different igneous and meta-igneous rocks. They used multiple machine learning algorithms and compared the relative performance of each of them. To identify the most effective machine learning models for estimating the elemental concentration, several linear methods such as linear support vector regression, elastic net, LASSO regression, PCR, and PLS were utilized. They also adopted some non-linear techniques such as support vector regression with polynomial kernel and K-nearest neighbor algorithms. They observed that applying the concept of dimensionality reduction on the dataset as a preprocessing step significantly enhances the performance of the linear models. They concluded that the linear models possess better predictive performance compared to the non-linear ones that often suffer over-fitting and hence yield more error-inclined predictions. They also proposed that a combination of two or more models could achieve a higher prediction error.

2.6 Applications of Laser-Induced Breakdown Spectroscopy

This section gives an overview of the ways LIBS can be utilized as a potential geochemical tool in geosciences while also demonstrating via specified examples how its analytical application has been and might be explored in this field for real-time analysis. The following applications of LIBS have been emphasized: (i) for elemental analysis; (ii) for geochemical mapping at the microscale level; (iii) to determine the amount of a chemical in a sample; and (iv) for quick differentiation of samples that have similar characteristics by comparing the spectral features within a designated spectral library.

Throughout the past few decades, LIBS has been considered a technique for carrying out research in the laboratory. Researchers were able to focus light and collect optics, couple systems from lasers, and spectrograph/detect components in various configurations with the goal to (i) demonstrate the effectiveness of LIBS in the analysis of various types of materials or (ii) conduct a unique experiment focused at understanding breakdown occurrence in contrasting media, laser-material interaction or specific detail of plasma physics. However, the invention of the first commercial LIBS laboratory has changed this situation for the last 15 years which was then subsequently followed by the development of commercial hLIBS analyzers and fpLIBS systems [6,84]. Nowadays, there exist at least six different instrument producers that can offer hLIBS analyzers commercially to successfully detect elements in the range of $\mu\text{g/g}$ or better in the field [6,84]. The use of software to control the operation of this analysis coupled with the ability to process the signal in real time has computerized the whole process and advanced its utilization for quantitative analysis, depth profiling, spectral matching, and surface mapping. The choice of wavelength, laser type, pulse rate and laser power, selection of a single-pulse in contrast to double-pulse means, and conditions for spectrometer light collection could be utilized to improve the analytical conditions in the studies considered in the subsequent sections that utilize such automated laboratory systems for LIBS analysis. Meanwhile, the commercial laboratory hLIBS analyzers and LIBS systems are considered to adapt less in their analytical ability.

2.6.1 Applications in Civil Engineering

Although there are many applications for LIBS in civil engineering, the technology is currently being utilized in two major fields. The first field is the detection of aggressive

chemicals for concrete/cement samples, while the other defines the cement type. The main aggressive chemical elements which they are affecting the concrete quality (i.e. the durability of reinforced concrete) are Chloride and Sulfur. The literature has a major interest in Chloride since it heavily controls steel corrosion in reinforced concrete structures [85]. In contrast, Sulfur content controls the Sulfate attack phenomena, which causes the concrete itself to deteriorate significantly, starting from concrete cracking to delamination and spalling [86].

It is already known that each chemical element emits multiple lines with different wavelengths. For instance, chlorine has many persistent lines that can be detected along with a wide spectrum range. To set a target chemical element to be used for investigation in certain applications, the best atomic line(s) shall be determined. The logic behind this is to establish the base grounds for obtaining the most reliable wavelength for that chemical element in that certain application. However, the practicality and effectiveness of each line are different from one application to another. Hence, optimization studies are considering narrowing the number of atomic lines used to identify certain elements based on the application. This is being done by investigating the sensitivity of atomic lines of interest; the selection of such lines is based on testing, for a certain application, a set of samples with pre-known different concentrations of the target element. All possible lines are investigated, and the most varying lines with varying concentrations of the target chemical elements are considered sensitive lines and used for detection.

It is worth mentioning that the sensitive lines have to show a clear and logical pattern for the concentration of the target element before considering them as control lines used for the detection. It has been found that the atomic line of chlorine at 594.8 nm has high

sensitivity behavior (Figure 5), even though its intensity is relatively low compared to other emission lines such as 837.5 nm. This is due to the higher signal-to-noise ratio in the 594.8 nm line due to the absence of reabsorption or self-absorption of the emissions on the concrete samples [87]. Thus, a good correlation (Figure 6) has been found between the chlorine content in concrete samples using the sensitive line of 594.8 nm. The same line has been studied again using a dual-pulsed LIBS system to further investigate the line in concern. For concrete specimens, it has been noticed that rich emissions come from calcium atoms with high absorption activity in the 800-900 nm range. A conclusion was drawn that the 594.8 nm line interferes less with the calcium lines, unlike the 837.5 nm chlorine line. Hence, the sensitivity is higher in the former. This can be justified as it is well-known that concrete materials have an ample amount of calcium [88].

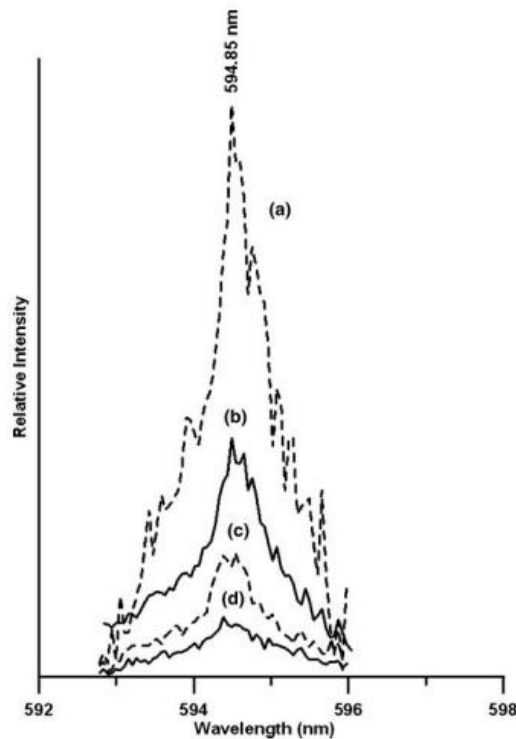


Figure 5 Investigating the sensitivity of the emission line of 594.85 nm with different chlorine content in a concrete sample: (a) 3.5% (b) 1.5% (c) 1% and (d) 0.4. by weight. Adapted from [87].

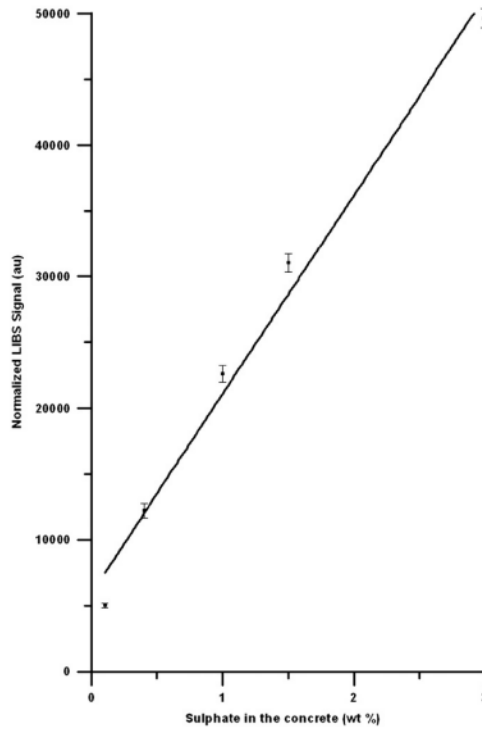


Figure 6 A proposed sample correlation for sulfur content in concrete based on the intensity measurements of the wavelength 545.38 nm (S II) in a concrete sample [89].

In the same way, detecting sulfate in concrete is being done by seeking the emission lines of sulfur. Similar to chlorine, sulfur lines may be heavily affected by some other elements present in concrete. In this case, it has been found that sulfur is highly reactive with oxygen, which is in abundance in concrete. Detecting sulfur is associated with another challenge which is detecting strong emission lines. Like most other chemical elements, strong emission lines for sulfur can be detected in vacuumed space. This is another obstacle as the testing environment will heavily affect the intensities of the measured lines. However, there are multiple attempts to assess sulfur emission lines in the literature, with few studies related to concrete samples. To further validate the studies with single-pulsed LIBS experiments, a double-pulsed LIBS (Figure 7) was used to evaluate the emission lines of sulfur on concrete. It has been found that strong sulfur lines cannot be obtained from the

range of 200 nm to 900 nm [89]. Hence, it was further validated that the strong sulfur lines can be obtained from either the UV region below 200 nm or the Infrared region higher than 900 nm. However, this does not mean that the weak lines from the ascribed range cannot be used for detection. The wavelength of 545.38 nm can be used for such detection, taking into account the detection limit based on statistical analysis.

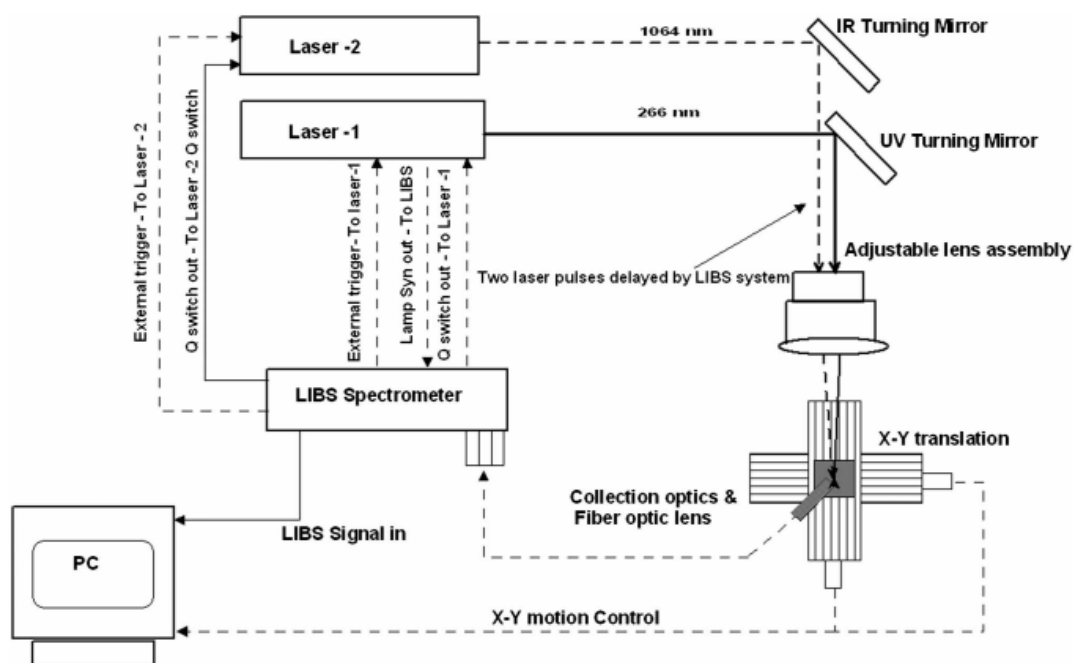


Figure 7 A schematic diagram for a double pulsed laser while testing a sample in atmospheric pressure. Reprinted from [14].

All in all, sulfur detection is similar to chlorine's but with the difference that strong and/or sensitive lines cannot be obtained from the usual attainable range. In such a case, sulfur detection in concrete samples is not practical at this moment unless the UV and Infrared ranges can be measured effectively with convenient testing conditions and affordable laser sources [90]. On a different note, sulfate detection can go beyond measuring the value of sulfur content at each testing point in a concrete sample. Depth profiles can be acquired by

combining all results of multiple testing points using element distributions per area. This is being tested by testing many points of a cross-section of a concrete sample to determine the depth of sulfate penetration in concrete. It is safe to assume that it is possible to map the concentration of any other aggressive chemical elements on a concrete surface once the intensities of these elements can be captured with great confidence [91]. This can put the mapping feature (Figure 8) using LIBS and Tomography in a similar place where the difference between them is based on how the data is acquired. In LIBS, mapping data are based on the data acquired from only the surface of the material using pulsed lasers, while in Tomography mapping, data are collected from the surface and within the material cluster using penetrating waves. All in all, the mapping feature is based on combining all collected data of a certain surface or profile using discrete mathematics such as finite difference [92].

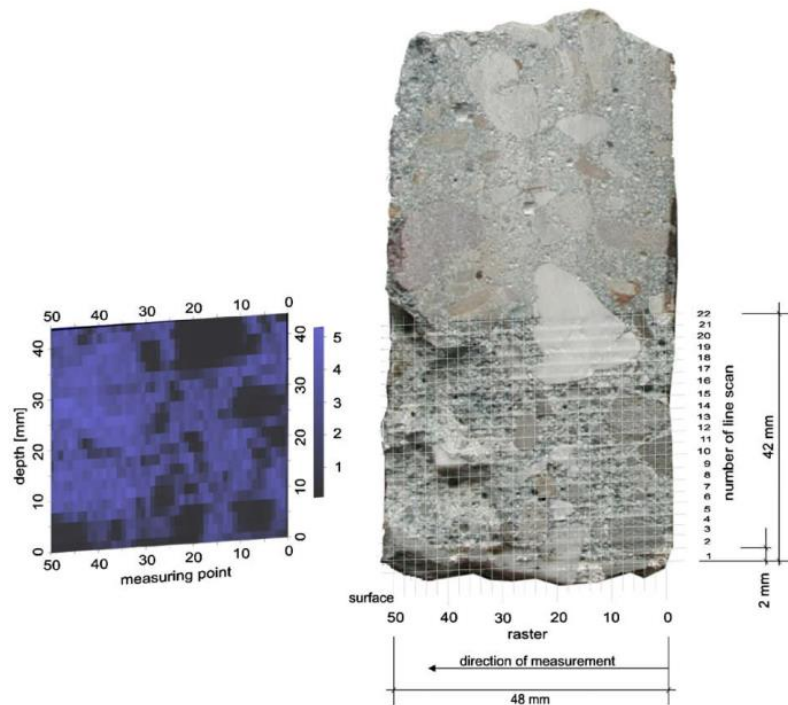


Figure 8 Spatially resolved analysis of sulfur content based on the elemental distribution for the measured data at multiple points on a concrete sample. Adapted from [91].

The last major application of LIBS in civil engineering is determining the cement type as per the standard classification. The methodology rests on assigning a controlled data set for each known and standardized cement type with the concentration of certain elements. Once the intensities of these elements are determined, the tested cement sample will be classified after comparing its measurements to the controlled dataset [93]. Overall, LIBS can utilize powder or intact concrete samples for analysis.

2.6.2 Applications in Soil Analysis

In the past few decades, soil mineralogy has partaken a great part of the literature with many studies. The relative change of the soils' physical behavior with the variation of their chemical characteristics has indicated the significance of soil mineralogy [95]. The geotechnical characteristics of soils are usually investigated with regard to each other [96]. However, studies have shown that these soil parameters, such as specific gravity, consolidation, shear strength, and permeability, are quite related to the chemistry of soils which sometimes may be overlooked in the industry [97]. This is because people tend to follow the usual practices assuming that the soil within the area has the same origins, making it behave similarly. Although Scandinavian countries have a lot of clay soils which were investigated a lot and may set the basis for some guidelines for clays, the usual practice for such soils cannot be entirely used with other soils say Sabkha soils in the Arabian Peninsula, even though both types of soils may be considered as soft soils. This is generally because of the different chemical structures and atomic bonds in Sabkha soil due to the presence of salts that may not be available in the other soil. In addition, pore fluid chemistry is an important factor that affects soil behavior and heavily influences soil mineralogy [98]. It is unlikely to have the same engineering characteristics for soil in which

its pores are filled with Sabkha brine, natural seawater, or freshwater since the soil matrix is different in each scenario. Not to mention that different pore-fluids may change the structure of soils if long-term effects are considered, such as chemical weathering [99]. As many researchers tend to study the mineralogical properties of soils, some of these studies are used to assess artificial soils as their approaches are based on certain properties that can be obtained at the time. In the older days, the investigation of the effect of soil's chemical structure was based on the basic geological parameters for the parent rocks, such as color, cleavage planes, hardness, etc., which might be considered a better classification approach compared to the existing one [100]. With the creation and evolvement of various technologies, the composition of soils, particle formation, and atomic structures were used to classify further and categorize soils based on their expected behavior.

The proposed utilization of X-ray techniques for quantitative analysis in the late 70s with proper calibration curves has revolutionized soils' mineralogical and chemical analysis. It has been found that the content of certain minerals is a major factor that controls the grain size, particle shape, and both physical and chemical behavior. This discovery opened the doors to enrich soil mechanics further. It can be argued that research with regard to geotechnical designs has reached its peaks. Undoubtedly, whatever comes after the design and construction of any civil engineering structure has to be studied [101]. It has been reported that some current studies are investigating the long-term effect of heavy structures on the supporting soil to ensure longevity and safe operating conditions for these structures. The key for these studies is to assess both the nature and behavior of the soils using mineralogical analysis [41]. Like the X-ray technique, LIBS may revolutionize this field as it may be considered a great tool for such problems if utilized properly [102]. This can

be supported by research that indicates its effectiveness with soils. LIBS can take advantage of different samples, such as powdered (prepared) samples, natural (unprepared) samples, wet or dry samples, etc [103]. In the end, LIBS can be used for field assessment if a mobile system can be utilized. This technology has some great advantages compared to other existing techniques if calibrated properly [104].

Several reasons have made it necessary to understand soil elemental composition and its variation through time and depth. This includes maximizing agricultural produce, understanding water storage, and soil fertility, and identifying anthropogenic contamination. Global warming and extensive land use have made the accurate measurement of certain physical parameters necessary to improve agricultural yield. These parameters include inherent spatial heterogeneity of soil C content, soil organic C stocks for CO₂ sequestration present in the terrestrial environment, and intrinsic temporal and spatial soil C heterogeneities. Also, among the sources of N and P in growing crops are fertilizer, manure, and soil which might cause leaching. This risk of leaching is a result of intensive agricultural practice due to the accumulation of P in the soil. LIBS has been explored by various researchers to rapidly and effectively determine the chemical composition of soil to help improve the estimation of these parameters [105–113].

Soil analysis using LIBS started with the investigation of pressed pellets obtained from the Rio Grande site located in southern Patagonia (Argentina) within the spectral region of 390 to 420 nm. It was carried out to detect emission lines, Ba II and Ca II, and develop a Ca calibration curve that is based on the ratio of Ba/Ca intensity [114]. Arctic soils from Svalbard in Norway were analyzed using a laboratory LIBS system to measure the composition of elements and Ar gas flow to improve the emission intensities. Fourteen

elements (Pb, Ba, Cu, Fe, Mn, Ca, K, Si, Al, Mg, Na, O, C, H) were observed to be present in the pelletized soils that were obtained in and around Ny-Ålesund, which is considered to be the Earth's most northerly human settlement [115]. Figure 9 shows that the elemental distribution of these Arctic soils when processed through PCA are dissimilar for local areas and are also compositionally distinct from soils extracted from urban and abandoned mining sites in Korea.

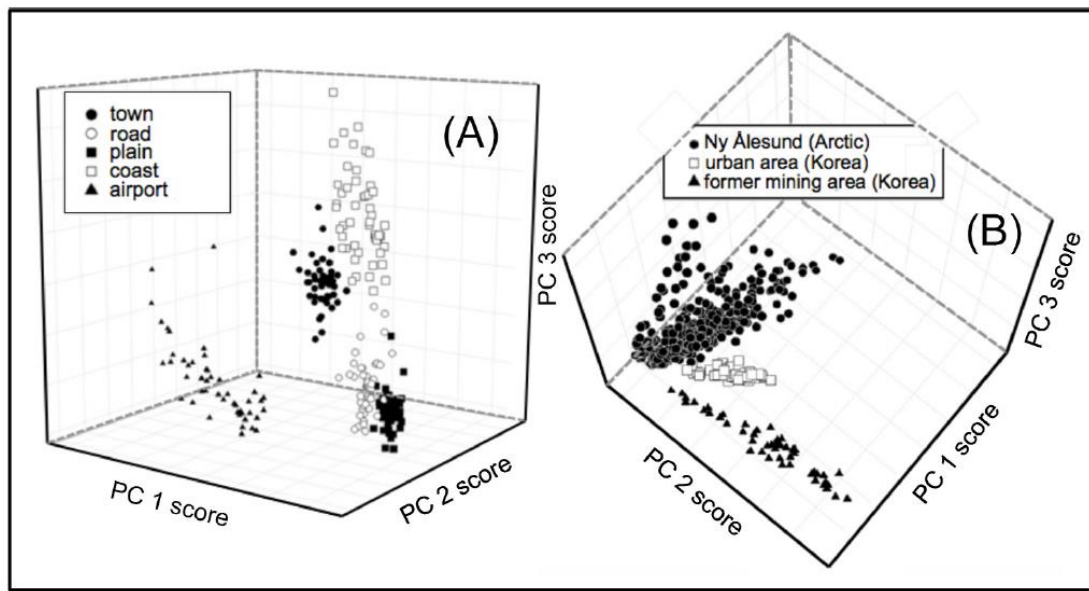


Figure 9 PCA score plots for Arctic soil near the Ny-Ålesund region of Svalbard, Norway (A) and PCA score plots comparing the Ny-Ålesund soil with that of an urban and abandoned mine area in Korea. Adapted from [111].

Erler et al. [116] investigated homogenized and pelletized samples of topsoil from 0 to 30 cm depth for 137 samples from two agricultural fields close to Wilmersdorf in Germany made of loamy sand, sandy loam, or sand formed from parent material consisting of calcareous glacial till covered by a non-stratified layer of sand and rocks. The total mass fractions of the major (K, Ca, Mg, P, and N) and minor (Fe and Mn) nutritional elements, the amount of humus, the pH of the soil, and the amount of P that is available to plants

were all calculated. Three multivariate regression methods (GPR, LASSO, and PLSR) were used to decrease the impacts of the soil matrix on the LIBS broadband spectra spanning the 200-900 nm spectral range that were obtained in the lab using a commercial LIBS analyzer. The results were then tested for calibration and prediction. Recently, a type of deep learning approach with the advantage of end-to-end was utilized to predict soil type and soil properties based on the non-preprocessed LIBS spectra. The results showed, when compared to conventional partial least squares (PLS), that the CNN models presented equal classification accuracy, but they decreased the root mean square error in the validation set (RMSEV) by 2.90%, 10.05%, 9.56%, 4.97%, and 1.48% for total potassium (TK), total phosphorus (TP), total nitrogen (TN), soil organic matter (SOM), and pH, respectively. In addition, the CNN models performed better in avoiding overfitting than the conventional PLS coupled with different spectral preprocessing techniques [117].

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 Overview

There is no doubt that soils are non-uniform materials that vary from one location to another [118,119]. Due to this fact, soils must be investigated prior to construction to assess the subsurface conditions and obtain the necessary parameters for design. This is currently done using standardized tests followed throughout the globe. This study considers an alternative approach for soil assessment using Laser Induced Breakdown Spectroscopy (LIBS). The technique is considered for its possibility to be utilized in laboratory or field tests in a way that is faster, cheaper, and less time-consuming compared with conventional tests. LIBS is a non-destructive technique that uses electromagnetic waves in the form of a pulsed laser to evaluate the chemical elements.

A typical LIBS setup consists of Nd:YAG laser source, reflecting prism, focusing lens, and spectrometer attached to a computing unit, as shown in Figure 10 [120]. When the laser pulses get in contact with the testing material, the temperature of the contact surface will increase drastically causing the material, whether solid, liquid, or gas, to transfer into a plasma state. Depending on the LIBS setup, the formed plasma plume can be produced in a vacuumed environment, as can be seen in Figure 10, or in ambient pressure, as can be seen in Figure 2. However, when the ambient pressure environment is considered, some of the gas elements, such as oxygen and hydrogen, may be excited as well when the plasma plume of the tested material is formed. Upon the cooling down of the plasma plume, the

excited ions tend to emit light with multiple wavelengths [121,25]. The emissions are captured with fiber optics to transmit the light to a spectrometer that usually uses Charged Coupled Detector (CCD) sensors. Certain wavelengths can be ascribed to certain chemical elements through a set of atomic spectroscopic data such as the National Institute of Standards and Technology's (NIST) data set [31]. Nonetheless, it requires some diligence and basic information about the nature of the tested material as multiple wavelengths are assigned to a single chemical element. The end result of LIBS testing is to obtain the intensity of a certain wavelength or to obtain the intensity spectrum for a range of wavelengths.

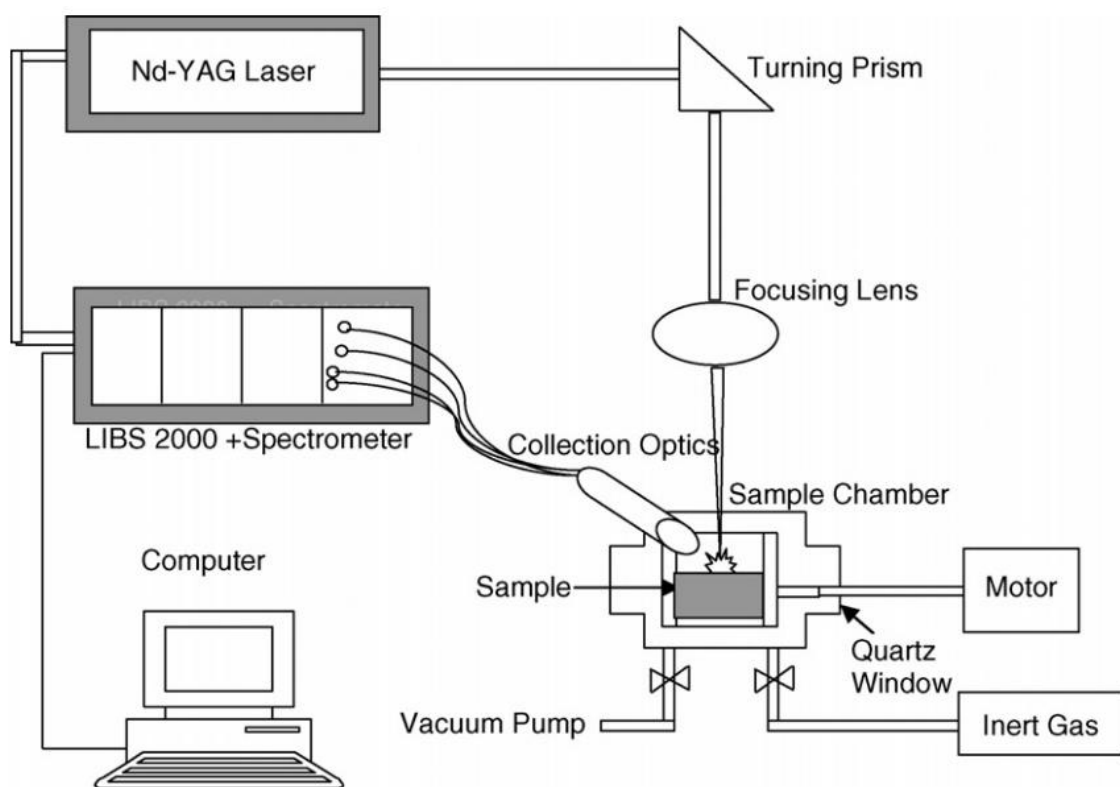


Figure 10 Typical single-pulse LIBS setup with vacuumed chamber. Adapted from [3].

LIBS may also be used for quantitative analysis based on the measured intensities of the light emissions [122,123]. Due to this fact, there are multiple applications for soil assessment using LIBS with regard to the chemical characteristics. These applications are either for evaluating the concentration of certain chemical elements directly or indirectly utilizing the intensities to develop certain correlations. Nonetheless, there are not so many applications that consider the assessment of the physical and mechanical characteristics of soils [62,102,16,124,15]. Hence, this experimental work was designed to investigate the possibility of relating LIBS outcomes with one of the most widely used standardized soil test, namely the Unconfined Compressive Strength (UCS) test [125-127]. In order to achieve this objective, empirical relations are considered since this approach is commonly used in geotechnical engineering. This research is based on the fact that the mineralogy of soils is somehow contributing to their physical characteristics. However, there are many challenges ascribed to soils when developing such correlations. In fact, the performance of LIBS depends on the size of the data set, correlations with standardized tests, and the accuracy of the model. Actually, any empirical model will face these challenges. Due to the fact that soils are often heterogeneous, intermittent, and with unknown material. Soil characteristics tend to significantly vary based on their existing condition such as confinement, moisture content, and density as compared with other materials such as concrete or steel.

Several studies showed that the engineering properties of soils can be enhanced through different stabilization techniques, one of which is chemical stabilization. There are multiple stabilizing agents used with soils; the most common ones are cement and calcium hydroxide also identified as lime. These agents are commercially available at low-cost in

many locations, which resulted in numerous studies regarding their utilization in soil. These studies happen to be considered a practical solution to enhance the soil properties one of which is the strength [128]. The industry nowadays is making use of cement when sands or coarse-grained soils need to be treated. On the other hand, lime is mostly considered for the treatment of clays or fine-grained soils in general. Since adding foreign elements to soils may significantly change the elemental composition when investigated with LIBS, more efforts would be needed to determine the contributing chemical elements for certain soil characteristics such as strength. This can be done by the means of a thorough peak analysis for LIBS results [132-133]. The outcome of this analysis is to determine the common and contributing elements that are presented in the soil sample, whether the soil is chemically stabilized or not.

This experimental work was set to present, from an engineering perspective, as well as the preparation process for the standardized soil specimens to be tested for both LIBS and UCS. Further, it was planned to assess the dominant chemical elements for normal and stabilized soils with cement and lime through the peak analysis of LIBS data. Finally, based on the obtained relations of both tests using linear regression by the least square method will be presented. Details of the designed experiment, testing procedure, and results discussion are presented in the following sections.

3.1.1 Material Planning

Thirteen different soils were collected from shallow depths at different locations in Saudi Arabia, mostly from the Eastern Province. Each soil has a distinct color and texture compared to the others and is assumed to have varying chemical compositions. The classification for the obtained soils is generally ranging from sands to sands with fines such

as silts or clays, as presented in Table 1. Bentonite clay with high plasticity was utilized as well in this study and also used to be mixed with other soils in the lab to investigate to produce new soils with possible different characteristics. Soils No. 1 to No. 10 are natural soils collected from the field and tested as is, while soils No. 11 to No. 13 consist of two soils, one of which is bentonite, mixed together in the laboratory. Six specimens for each soil to be cast. However, soil No. 1 is a non-cohesive granular soil that cannot be used to prepare a cylindrical specimen as they are collapsing immediately upon demolding. Since this limitation is related to the corresponding standardized test, which is used solely for cohesive soils, this soil was no longer considered in this study. Hence, the total number of specimens prepared from the natural and man-made soils is 72 with 6 specimens per soil. It was not possible to prepare specimens for soil No.1 due to its nature; however, it was used for preparing another soil (soil No. 12) that is utilized in this study.

Table 1 Summary of the basic engineering classification of the soils.

Soil No.	Liquid Limit	Plastic Limit	AASHTO Group	USCS Group	Optimum Moisture Content (%)	Percentage passing sieve #200	Description
1	NA	NA	A-3	SP	NA	0.7	Yellow sweet sand
2	16	11	A-2-4	SP-SM	7	16.12	Orange sandy marl
3	33.5	12.63	A-2-6	SP-SC	19	9.7	Greenish clayey sand
4	35.25	10.41	A-2-4	SW-SM	20	34.28	Dark gray sandy soil
5	42.25	14.55	A-2-7	SW-SM	22	15.2	Red sandy soil
6	28	5.41	A-2-5	SW-SM	18	14.08	White sandy silt
7	30	11.02	A-6	SW-SC	19	42.46	Light gray sandy soil
8	300	267	A-7-5	CH	45	51.42	Brown bentonite clay with high plasticity
9	NA	NA	A-3	SP	7	18.46	Pinky sand with fines
10	40	25	A-2-7	SW-SC	20	12.88	Bright yellow clayey sand
11	205	153.73	A-7-5	SW-SC	18	37.8	Sandy marl with bentonite
12	105	53.8	A-2-7	SP-SC	39	20.94	Sweet sand with bentonite

Soil No.	Liquid Limit	Plastic Limit	AASHTO Group	USCS Group	Optimum Moisture Content (%)	Percentage passing sieve #200	Description
13	145	115.75	A-7-5	SW-SC	51	41.5	Yellowish clayey sand with bentonite

In this experimental program, only two out of the thirteen soils were used for preparing stabilized soil specimens. Soils No. 2 and No. 3 were selected to investigate the behavior of stabilized soil with LIBS due to their abundance in this study and in the region in general. Figure 11 is presenting the criteria for preparing the stabilized soils as there are many factors affecting the quality of the stabilized soil such as the amount of the stabilizing agent (type and dosage) and curing time. The process starts with the selection of soil either soil No. 2 or No. 3 to be stabilized, followed by selecting the stabilizing agent which in this case is either cement or lime. Then, the soil is divided into three categories in which the soil is stabilized with either cement or lime with a dosage of 3%, 6%, or 9% by weight. Further, the soil is subcategorized once again for the curing period as some specimens were cured for 7 days, 14 days, and 28 days before testing. The assigned days are based on the norm followed by researchers and the industry. This experimental program was planned for preparing six stabilized soil specimens for each subcategory (curing age), with eighteen specimens for each category (dosage), and fifty-four specimens for each stabilizing agent in each soil. The overall number of stabilized soil specimens was 216 for both the soils and stabilizing agents.

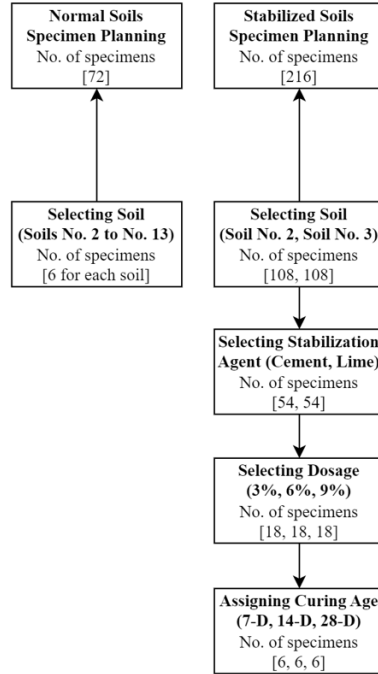


Figure 11 A flow chart for the planned soil specimens for both normal and stabilized soils.

3.1.2 Sample Preparation

Standardized cylindrical-shaped steel molds with a diameter of 3.8 cm (1.5 inches) and 7.6 cm (3 inches) in height were used. The preparation of soil specimens followed the ASTM D2166 standard for the unconfined compressive strength of cohesive soil. The steel mold was filled in three layers, each layer was compacted using a standardized tamping hammer. The soil matrix was air-dried in a 100 °C oven for 72 hours prior to the preparation of the specimens. At the time of preparation, the soil was mixed with the optimum percentage of water in order to achieve the maximum dry density and to avoid crumpling of the soil specimen. Moreover, the prepared specimens were placed in air-tight plastic bags to avoid drying till the testing time, as shown in Figure 12.



(a)

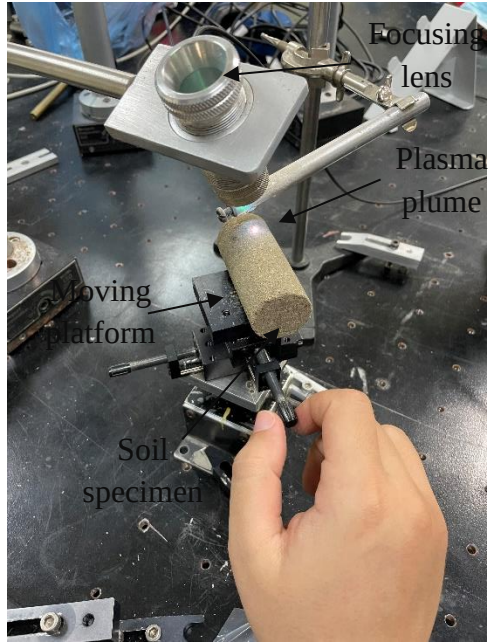


(b)

Figure 12 (a) Soil being compacted in standard UCS mold to prepare a testing specimen. (b) Soil specimen after demolding and placing it inside an air tight bag to preserve the water content.

3.1.3 Testing Procedure

Since this study requires testing the soil specimens twice to obtain the necessary data from two different tests, the goal of the testing procedure was set to maintain the integrity of each specimen till LIBS and UCS testing are performed for the exact specimen. Seeing that LIBS is considered a non-destructive technique; the prepared specimens were set to be tested by LIBS first. Then, each specimen was returned to its original plastic bag till testing to maintain similar moisture content when testing the same specimen once again for UCS using the compressive testing machine as presented in Figure 13.



(a)



(b)

Figure 13 (a) Soil specimen tested under LIBS. (b) Another soil specimen tested for UCS after LIBS.

3.1.4 Laser-Induced Breakdown Spectroscopy Setup

Even though there are multiple studies reporting that double-pulsed laser setups are more effective when testing soil specimens as compared to single-pulsed ones, this study considered a single-pulsed system to test soil specimens in the ambient air conditions to somehow imitate the testing of soils in field conditions [134-135]. It should be noted that some signal noises were detected while calibrating LIBS. This can be ascribed to two major points; one was related to the moisture present within the soil specimens. The other may be due to the fact that the used specimens consist of natural-grained soils and not powdered material. After calibration, it was found that the values corresponding to the laser energy delay time, and pulse duration are best to be set for 24.5 mJ, 200 ns, and 8 ns, respectively, for soils used in this study.

3.2 Results and Discussion

3.2.1 Peak Analysis

In order to correlate both raw data obtained from LIBS to any of the standardized soil tests, one must determine the contributing chemical elements in order to develop proper correlations. Only three out of six specimens in each planned subcategory were tested using LIBS. A total of 144 spectra from the range of 200 nm to 900 nm were studied in order to find the most dominant chemical elements in each of the tested soils. This process starts by identifying the peaks in every spectrum, similar to Figure 14, by the means of determining all wavelengths that have the highest intensities along each soil specimen spectrum. Then, the obtained peaks were compared to all specimens to determine their frequency in this study using the statistical mode for every considered peak to determine the peaks with the highest repetition in the data set. A summary of the dominant peaks and their corresponding chemical elements based on NIST's database is presented in Table 2. It should be noted that the presented peaks in this study are based on the characteristics of the tested soils only and may not be generalized for all soils on earth.

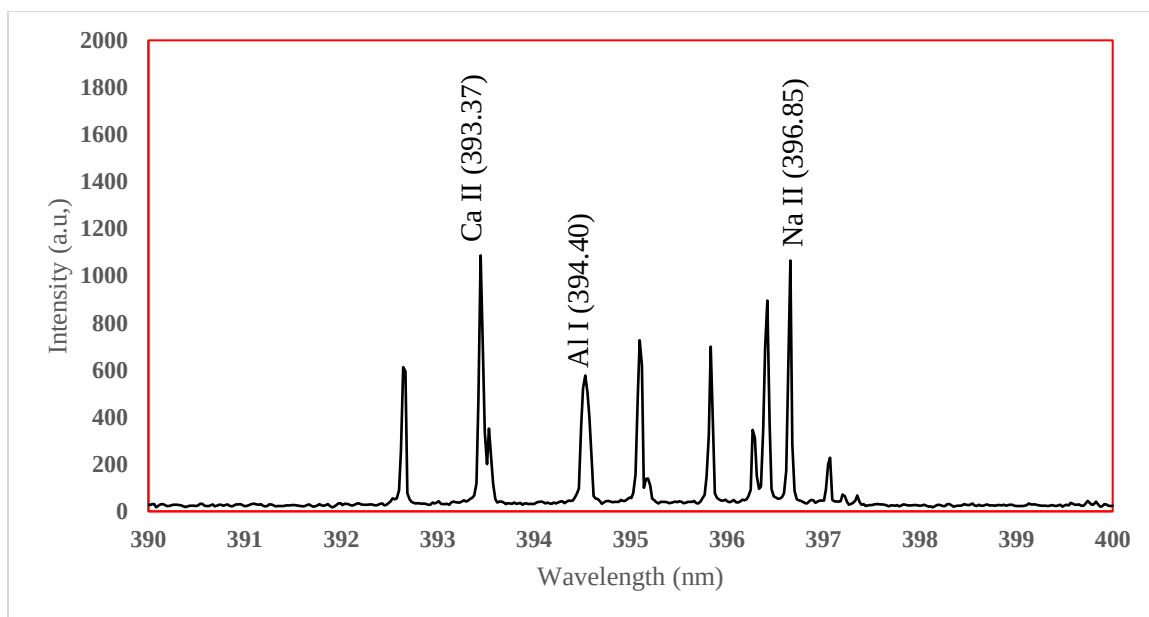


Figure 14 A spectral line for a soil specimen marking some of the common peaks in the tested soils.

Table 2 Results summary of the peak analysis for all soil specimens.

Dominant Peaks in Soil Samples					
Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)	Element
251.92	Si I	396.43	Ti I	590.34	In II
252.74	Fe I	*396.85	Ca II	*612.22	Ca I
263.1	Fe II	397.01	H I	616.22	Ca I
266.1	Na II	*397.33	O II	643.9	Ca I
279.8	Mg II	404.87	K I	766.49	K I
280.45	Fe I	422.67	Ca I		
288.12	Na II	427.46	Ti I		
373.71	Fe I	443.5	Ca I		
383.23	Mg I	445.66	Ca I		
383.83	Mg I	*517.27	Mg I		
390.55	Si I	518.36	Mg I		
393.37	Ca II	589	Na I		
394.4	Al I	589.44	Zn II		
394.73	O I	589.59	Na I		
396.15	Al I	589.93	Ti I		

*Dominant peaks found only in stabilized specimens with Cement or Lime.

3.2.2 Normal Soil Results

It was observed from the peak analysis that a single chemical ion can have multiple wavelengths that can be used for mathematical correlations. To narrow down the possibilities of obtaining unreliable correlations with no statistical significance, only one wavelength is considered for each chemical ion. This was done by determining the wavelength that results in higher average intensity compared to the other wavelengths of the same chemical ion. In addition, there are chemical ions that are not usually present in soil samples and these wavelengths tend to have low average intensity values compared to other wavelengths; hence, these ions were no longer considered for statistical analysis. A summary of the assigned dominant wavelength for each ion and the corresponding statistical significance analysis is presented in Table 3. Given that the 95% confidence level is considered for all collected data for all soils, normal and stabilized, it can be noted that only five wavelengths out of fifteen demonstrate that there is a statistical relationship between the intensity obtained from LIBS and the UCS data. The assigned chemical elements for the corresponding five wavelengths are Si I, Mg II, Mg I, and Ca I; notwithstanding, these elements are generally available in most soils which can be considered a promising outcome.

Table 3 Summary of the dominant wavelengths in their corresponding statistical significance results for 95% confidence.

Significance Analysis for the Selected Chemical Ions for 95% Confidence						
Element	Wavelength (nm)	Observations	P-value	Lower 95%	Upper 95%	Remarks
Si I	251.92	192	0.001985	0.001535019	0.006739964	Reject Null
Fe II	263.1	192	0.544759	-0.00404568	0.007640052	Accept Null
Mg II	279.8	192	0.027757	0.000136975	0.002340652	Reject Null

Significance Analysis for the Selected Chemical Ions for 95% Confidence						
Fe I	280.45	192	0.097266	-0.00019148	0.00227696	Accept Null
Na II	288.12	192	0.07669	-0.00011896	0.002317481	Accept Null
Mg I	383.83	192	0.00224	0.00135217	0.006089538	Reject Null
O I	394.73	192	0.33829	-0.00092397	0.002675944	Accept Null
Al I	396.15	192	0.038115	0.00017474	0.006135617	Reject Null
Ca II	396.43	192	0.157867	-0.00042746	0.002612879	Accept Null
K I	404.84	192	0.600068	-0.00807894	0.004681489	Accept Null
Ca I	422.67	192	5.25E-07	0.002573421	0.005723793	Reject Null
Na	589	192	0.219504	-0.00330191	0.000763141	Accept Null
Zn II	589.44	192	0.271318	-0.00388380	0.001097658	Accept Null
Ti I	589.93	192	0.804354	-0.00188004	0.002420918	Accept Null
In II	590.34	192	0.692238	-0.00655887	0.004363734	Accept Null

Linear regression was considered to provide mathematical correlations for this study. When considering developing a relationship for all soils, no mathematical relations were found, thus, considering this approach tends to give correlations with very low accuracy at all times. This can be ascribed to the fact that soils are heterogeneous materials that have many causes for variation from each other as ascribed earlier. Hence, this study is to the point that developing any relation for all soils is not a viable option when considering linear regression. Thus, linear regression was performed for each soil separately. The results of the one-element regression analysis are presented in Table 4 for each normal soil considered in this study. The accuracy of the results is dependent on the type of soil and wavelength used. For example, Si I (251.92 nm) tend to perform better with soils no. 2, 4, 9, 10, and 11 compared to the rest of the tested soils. The same behavior was observed for

Mg II (279.8 nm) as the results for soils no. 2, no. 5, no. 10, no. 11, and no. 12 show good correlations. On the other hand, the performance of the other Magnesium ion, Mg I (383.83 nm), was found to be good for soils no. 5, no. 9, no. 10, and no. 12. The performance for the peak corresponding to Al I (396.15 nm) varies from very good for soils no. 2 and no. 9 to relatively acceptable for soil no. 10. Finally, the correlations using Ca I (422.67 nm) were found to give good results only for soils no. 2, no. 4, no. 5, and no. 9. It can also be noticed from the same table that soil no. 1 was eliminated from the study since it is physically not possible to cast soil specimens with sand due to the lack of cohesion. In addition, no correlations were found with the ascribed five wavelengths for soils no. 3, no. 7, no. 8, and no. 13. It can be noticed that these four soils contain a relatively large number of fine-grained soils, thus, the corresponding five wavelengths seem to not represent soil soils with fine materials such as silts and clays. Therefore, it might be necessary to identify the peaks using a separate peak analysis for soils with fine grains.

Table 4 Summary of the basic engineering classification of the soils.

One-Element Linear Regression Results for Normal Soils			
Soil No.	Observations	Equation	R-square
2	3	UCS = -0.001[Si I]+5.14	0.853
		UCS = -0.001[Mg II]+5.079	0.993
		UCS = -0.002[Al I]+6.051	0.913
		UCS = -0.001[Ca I]+5.414	0.814
4	3	UCS = -0.002[Si I]+13.322	0.712
		UCS = -0.001[Ca I]+13.861	0.595
5	3	UCS = 0.002[Mg II]+5.659	0.777
		UCS = 0.003[Mg I]+6.031	0.856
		UCS = 0.001[Ca I]+6.226	0.882
9	3	UCS = 0.003[Si I]+5.958	0.763
		UCS = 0.002[Mg I]+5.418	0.882
		UCS = 0.003[Al I]+5.198	0.983
		UCS = 0.001[Ca I]+4.99	0.873
10	3	UCS = -0.004[Si I]+17.729	0.994
		UCS = -0.001[Mg II]+17.917	0.704
		UCS = -0.003[Mg I]+17.928	0.624
		UCS = -0.001[Al I]+17.597	0.525
11	3	UCS = 0.000[Si I]+3.096	0.737
		UCS = 0.000[Mg II]+3.191	0.850
12	3	UCS = -0.001[Mg II]+9.402	0.902
		UCS = 0.001[Mg I]+2.858	0.674

• The Corresponding wavelength for Si I, Mg II, Mg I, Al I, Ca I are 251.92, 279.8, 383.83, 396.15, and 422.67 nm, respectively.

• UCS unit is (kPa), while the intensity for each wavelength is (a. u.) based on the exact LIBS setup and testing conditions for this study.

3.2.3 Stabilized Soil Results

In Table 5 the same five peaks used for investigating the natural soils were also considered for stabilized soils with cement and lime. In addition, four other peaks were found for stabilized soils. These four peaks are 280.45 nm, 589 nm, 589.44 nm, and 589.93 nm which correspond to the chemical ions: Fe I, Na I, Zn II, and Ti I, respectively. Instead of investigating the correlations for each soil as done in the previous section, the stabilized soils were categorized based on their stabilizing agent content and curing age. Furthermore, to investigate the effect of the chemical agents, the developed correlations considered

investigating the performance of all stabilized soils together and not each soil separately as done in the previous section. It can be noticed that correlations with the five peaks used for normal soils are also giving acceptable results for soils stabilized with Cement. On the other hand, soils stabilized with lime tend to have, in general, correlations with peaks corresponding to 280.45 nm, 589 nm, 589.44 nm, and 589.93 nm. It can be noticed from the same table 4, that the performance of certain wavelengths for the same dosage varies for each curing age subcategory. For instance, the peak corresponding to the chemical ion Na I was performing very well for stabilized soil with 6% cement at the curing age of 7 days. However, this peak does not indicate any correlation for the material at the curing age of 14 and 28 days. Overall, the correlations for the selected peaks seem to be less accurate when considering general peaks for both cement and lime. Hence, it can be concluded that there is a minimal effect due to the added chemicals and the actual cause of poor relation is the assigned peaks for multiple different soils. Therefore, it is required to investigate the peaks for each soil type separately, rather than for each chemical agent.

Table 5 Summary of the one-element linear regression investigation for stabilized soils with Cement and Lime.

One-Element Linear Regression Results for Stabilized Soils					
Stabilizing Agent	Dosage	Curing Age	Observations	Equation	R-square
Cement	3%	7 Days	6	UCS = -0.01[Si I]+42.514	0.678
				UCS = -0.011[Fe I]+47.219	0.891
				UCS = -0.015[Na I]+44.403	0.605
		28 Days	6	UCS = -0.011[Na I]+109.982	0.798
				UCS = -0.016[Zn II]+114.792	0.512
	6%	7 Days	6	UCS = -0.037[Mg I]+121.766	0.558
				UCS = -0.028[Ca I]+125.039	0.680
				UCS = -0.043[Na I]+108.635	0.907
				UCS = -0.051[Zn II]+95.059	0.531
				UCS = -0.021[Ti I]+109.55	0.916
				14 Days	6
	9%	7 Days	5	UCS = -0.018[Al I]+104.296	0.824
				UCS = -0.011[Na I]+113.4	0.637
				UCS = -0.009[Zn II]+96.575	0.508
				UCS = -0.007[Ti I]+101.235	0.583
14 Days		6	UCS = 0.013[Ca I]+58.878	0.500	
Lime	3%	7 Days	5	UCS = 0.006[Ca I]+69.758	0.542
				UCS = 0.002[Ti I]+5.644	0.932
		28 Days	6	UCS = -0.003[Ti I]+36.442	0.517
	6%	7 Days	5	UCS = 0.002[Fe I]+7.333	0.983
				UCS = 0.004[Ti I]+5.463	0.703
		14 Days	6	UCS = 0.003[Mg I]+17.09	0.553
				28 Days	6
	9%	7 Days	6	UCS = 0.003[Fe I]+6.059	0.507
		14 Days	6	UCS = 0.017[Na I]+-20.138	0.933
				UCS = 0.015[Ti I]+-31.981	0.853
		28 Days	6	UCS = 0.006[Mg I]+19.056	0.601
				UCS = 0.006[Al I]+18.486	0.831
				UCS = 0.008[Zn II]+24.665	0.519
• The Corresponding wavelength for Si I, Mg II, Mg I, Al I, Ca I, Fe I, Na I, Zn II, Ti I are 251.92, 279.8, 383.83, 396.15, 422.67 nm, 280.45 nm, 589 nm, 589.44 nm, and 589.93 nm respectively.					
• UCS unit is (kPa), while the intensity for each wavelength is (a. u.) based on the exact LIBS setup and testing conditions for this study.					

3.2.4 Remarks

The assigned correlations in Table 4 and Table 5 are limited to the investigated soils in this study with the specified testing condition. Hence, the presented correlations shall not be used as a generalized empirical model for all soils. Furthermore, the tested soil specimens were not dried out during the study, thus, LIBS is giving a promising result to be utilized for field (in-situ) testing for soils with moisture. It should be noted that distilled water was used in this study when preparing the specimens, therefore, the performance of LIBS still needs to be investigated for soil samples prepared with saline groundwater such as sabkha brine. Regardless of the LIBS setup such as whether single or doubled pulse laser setups were used, the laser energy and delay time might be needed to be calibrated for each testing condition to obtain better readings with low noise. In addition, it was observed that the soil material is too soft for the applied pulsed laser, hence, the soil specimen had to steadily and slowly move while testing, as shown in Figure 13 (a), to maintain a consistent plasma plume while testing. On a final note, the considered approach of correlations in terms of linear regressions using the Linear Square Method was set for the general assessment of LIBS only; therefore, if one needs to utilize the full potential of correlations with LIBS data, it is suggested to consider more detailed regression approaches based on machine learning such as Polynomial Regression and Bayesian Linear Regression.

CHAPTER 4

EPILOGUE

4.1 CONCLUSION

In summary, this research presents the recent advancements and challenges in the use of laser-induced breakdown spectroscopy for geotechnical applications with sufficient details to introduce the technique to this field. The research elucidates the principles of LIBS and highlights the strengths that qualified it as an excellent candidate for soil studies. It takes some diligence to investigate the most sensitive emission lines within soil materials to set a proper basis for correlations with other soil parameters. Different LIBS setups can be used for such applications. However, dual-pulsed laser setups tend to give the best results with soils. Several factors affecting the quality of the acquired spectra such as matrix effects were discussed. The potentials of LIBS as a remarkable quantification analysis technique using both the calibration curve and calibration-free approaches were also presented. In this study, laser-induced breakdown spectroscopy and single linear regression methods were employed to develop a correlation between the elemental intensities of the soil specimens and their soil unconfined compressive strength. Our results revealed that compacted soil specimens can be used for assessment of the elemental composition using LIBS instead of powdered soil samples. The result of peak analysis showed dominant peaks at the wavelengths 251.92, 279.8, 383.83, 396.15, and 422.67 nm corresponding to elements Si I, Mg II, Mg I, Al I, and Ca I. Moreover, the addition of foreign elements to the soils seems to have an insignificant effect on the peak analysis results, thus, the

dominant peaks for the soils will control the accuracy of the correlations whether stabilizing chemical agents are added or not. This was confirmed after stabilizing some selected soil samples with lime and cement. Therefore, this work showed that LIBS applications can be extended to both mechanical and physical characteristics of soils using empirical correlations and standardized soil specimens.

4.2 PATH FORWARD FOR FUTURE WORK

This research work has introduced LIBS to a new field in which it will be required to establish the fundamentals for practical applications in Geotechnical Engineering. It is believed that this objective can be accomplished considering the following.

- 1- Further investigating the factors affecting the signal-to-noise ratio for soil testing in the field using mobile LIBS setups.
- 2- Investigating the patterns of LIBS data for soils to determine the most proper and practical regression techniques to develop the correlations.

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This research program was the origin of the published review paper namely Applications of Laser Induced Breakdown Spectroscopy in Geotechnical Engineering: A Critical Review of Recent Developments, Perspectives and Challenges by (O. A. Al-Najjar et al., 2022), and will set the basis for a research paper titled Assessment of Unconfined Compressive Strength of Normal and Chemically Stabilized Soils using Laser-Induced Breakdown Spectroscopy. This research program will contribute to an interdisciplinary research paper titled Laser-Induced Based Prediction of Soil Unconfined Compressive Strength: A Machine Learning Approach and a patent titled A novel Laser-induced method for the estimation of soil unconfined compressive strength to be published by their respective authors.