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Laser-Induced Plasma Spectroscopy Technology to Estimate Calcium Concentration in Human Fingernails

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Abstract

This paper employs the utilization and the use of technology known as Laser-Induced Breakdown Spectroscopy (LIBS) to diagnose osteoporosis by means of nail analysis and to determine the calcium concentration in human fingernails. The primary objective of the study was to determine the calcium concentration in nails as a means of determining bone density in diagnosing osteoporosis respectively. One healthy individual and five individuals diagnosed with osteoporosis were among the individuals from Medical City Hospital that provided samples for the analysis. The findings demonstrated that nails that are in good health had higher calcium contents in comparison to nails that are afflicted by osteoporosis. The LIBS technology is a potent and accurate instrument that can be used to analyze the elemental composition of nails and may also indicate changes that are associated to diseases. This method can be adopted by medical professionals to enhance their capacity to diagnose and monitor osteoporosis, as well as to recommend the most appropriate treatment. The emission spectrum of elements plasma ranging from 200 nm to 800 nm was recorded. The concentration of calcium sample that detected by LIBS were (0.85, 0.65, 0.8, 0.9, 0.74 and 1.1) and by XRF were (0.39, 0.28, 0.34, 0.71,0.6 and 0.77).

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1. Introduction

Osteoporosis results in a decrease in bone mass and a breakdown of bone tissue, making bones more brittle and increasing the likelihood of fractures. It primarily affects the elderly, but equally affects men and women as well [1]. Osteoporosis can be caused by a number of factors, including but not limited to: hormone changes, age, genetics, lifestyle choices, and certain medical diseases or medications. The decline of estrogen, a hormone that protects bone density especially, puts women at risk once menopause sets in [2]. Element analysis, both qualitative and quantitative, is carried out using laser-induced breakdown spectroscopy (LIBS). Although laser-induced plasma was first observed in 1963 [3], it was only after 1980 that it has received substantial attention from both academics and practitioners. There are multiple approaches to quantitative LIBS analysis [4]. The sample concentration of one or more elements is essential in most materials. The calibration-based technique (CB-LIBS) usually works best in these instances. CB-LIBS requires a reliable relationship between the integral intensity ($\bar{S}$) of a neutral or ionized atom and the concentration (C) of the analyte to determine the concentration of a specific species in a sample. Four standardizing approaches have been used until now: external, internal, addition, and addition-internal combinatorial [5]. The widely used methodology has many advantages over other spectro chemical analysis methods. Laser pulse screening can preserve spatial information on surfaces. Analysis may be done quickly and computerized without experience. However no specific sample preparation is needed. To attain a high spatial resolution target, a laser beam is focused onto the surface of the sample. To this end the research reveals that the majority of elements are unbiased [6]. Although LIBS isn't perfect; no methodology is. Spectroscopic signals becomes unstable due to variations in laser intensity. Plasma properties are affected by variations in gas and air

pressures above the sample. Matrix influences, both physical and chemical, influencing the intensity of spectral lines A publication [7]. Some examples of plasma include the atmosphere and gaseous nebulae, a large portion of interstellar hydrogen, the solar wind, the flash of lightning, the faint glow of the aurora borealis, the gas inside a fluorescent tube or neon sign, and a small amount of ionization in rocket exhaust, among others [8]. Relatively a number of publications have reported on the use of LIBS (Laser-Induced Breakdown Spectroscopy) for elemental analysis of biological materials. Specifically, the technique has been proposed in several studies for analyzing nails, hair, and teeth [8]. Nail bio-samples contain subject biological information. Nails store nutrition, habitat, and other environmental data, it also includes body elements like Ca, Mg, Fe, etc., but at different levels. Nail analysis can also discover body elements not found elsewhere. Nail trace elements imply 2–18 months of hazardous substance exposure [9]. Nail biomarkers have several advantages for elemental analysis. Sample collection is easy and noninvasive, while population studies can be done with a large number of samples. The nail's composition remains intact after collection because its elements are segregated from other metabolic activities in the body. Thus, nail elemental analysis can reveal body element imbalance or toxicity [10]. There is a growing interest in studying human fingernails and hair for trace elements and medical or forensic applications [11]. Hair and nail forensics can help identify evidence at a crime scene. It is also possible to positively identify offenders by comparing their genetic makeup to that found in hair and nail samples taken from crime scenes [12]. Any technique reproducibility concerns will not affect the signal-to-noise ratios of the analyte or internal standard in any standard sample or target since they are treated the same. Addition-internal combinatorial standardization can overcome matrix effects and irreproducibility issues, which often affects measurement results and cause serious determinant errors [13]. Keratins, fibrous structural proteins produced in vertebrate epithelial cells, are insoluble and filament-forming proteins that can be soft or hard dependent on physical, histological, and chemical properties. Hard horn, nails, claws, and hooves contrast with the soft keratin that makes up the epidermis. The adaptation of vertebrates to their external environment relies on the mechanical support and other protective services provided by durable, strong, and nonreactive keratinous materials [14]. Different physiological and pathological variables impact mineral element concentrations in the fingernail keratinous matrix [15]. Nails may indicate long-term mineral metabolism in human life quality due to their slow development rate. Nails can also be acceptable for monitoring dietary imbalances, illnesses, and persistent toxic exposure [16]. This work uses calibration-based laser-induced breakdown spectroscopy to measure fingernail calcium.

2. Experimental Preparing of nail samples

We used a stainless steel nail clipper to collect samples from six individuals at the Medical City Hospital; five of these had osteoporosis and one was healthy. To ensure that no samples were mixed, we placed them in individual plastic containers and labeled them. While maintaining a controlled temperature for 30 seconds, the samples were soaked in acetone, and later rinsed with distilled water to eliminate any remaining pollutants. Since organic solvents like acetone result in less elements loss compared to aqueous detergents and acids, it was chosen to clean nails. After that, they were let to dry at ambient temperature [17]. Instead of grinding the sample before examination, LIBS technology uses a laser to excite it, creating plasma that can be analyzed via spectroscopy. A mortar and pestle were utilized to prepare samples of nails for XRF analysis. The inquiry was governed by the ethical standards outlined in the Declaration of Helsinki. Prior to the collection of the sample, the patient provided verbal and analytical consent. Under document number 2999 (dated 20/11/2024), a local ethics committee examined and authorized the study protocol, subject information, and permission form were also issued.

A. Nd:YAG Laser System

At 1064 nm, a passively Q-switched Nd: YAG laser delivered 100 mJ pulses lasting 10 ns. A 100 mm double-sided convex quartz lens focused laser beams. The lens was placed on the finger nail to create plasma. A 5 mm optical quartz convex lens was held in place by a laser source lens holder. Attached to the base of the laser holder was the test sample. The light from the plasma plume was collected by a small lens that was installed within the multimode silica fiber optic head. An adequate gap of 100 mm was maintained between this fiber optic and the laser-generated plasma plume. Furthermore, ideal angle for collecting the plasma emission in relation to the stone was 45°. A CCD spectrometer model (UVA800-Mux) with a spectral range of 200–800 nm and an optical resolution of 0.5 nm received the plasma emission via fiber optics. The optical emission spectrum was recorded and

analyzed using SpectroGryph1.2 spectroscope software; the experiment setup is shown in Fig.1. The sample was positioned as indicated in Figure (1), with the laser at a 90-degree angle and the fiber optic lens at a 45-degree angle. To verify the system's functionality and the samples homogeneity, the sample was first tested at various surface positions using a laser beam, which suggest that the spectrometer has captured the emission spectrum of the produced plasma.

Figure 1: the experiment setup (LIBS System).

B. X-ray fluorescence:

An analytical technique called X-ray fluorescence (XRF) makes it possible to determine the elemental makeup of different materials without causing any damage. The elemental makeup of the material can be determined by analyzing the distinctive secondary X-rays that are released when it is stimulated with high-energy X-rays or gamma rays. XRF is a rapid, non-destructive method with several uses that is widely used in the examination of rocks, metals, polymers, and minerals.

C. XRF sample analysis:

The first step in analyzing the materials components is samples preparation using XRF equipment located at the Ministry of science and technology.

3. Results and Discussion

Figure (2), (3),(4),(5),(6) and (7) shows the emission spectrum of samples of nails S1,S2,S3,S4,S5 and S6 plasma induced by of Q-Switched Nd: YAG with fundamental wavelength 1064 nm and laser energies (100 mJ). The emission spectrum of elements plasma ranging from 200 nm to 800 nm was recorded. Many spectral emissions can be seen in Figures. For sample 1 figure (2) shows the elements recorded are Ca I , Fe I , and Si II, where there are 7 peaks of Ca I are 318.569,336.46,394.89,397.37,422.67,445.66 nm and 518.88 nm and 3 peaks of Fe I are 249.08,500.4,655.58 nm and peak of Si II 567.17 nm.

For sample 2 figure (3) shows the elements recorded are Fe II ,Ca I, Ca II ,Cd I , Si I and Cr II where there are 5 peaks of Ca I 335nm,394.89,397,422.67,518.88 nm and 3 peaks of Fe I 445.26, 592.77, 655.58 nm, peak Fe II 249.19 nm, peak of Si I 567.18 ,peak of Cd I 480.09 nm and peak of Cr II 277.31 nm.

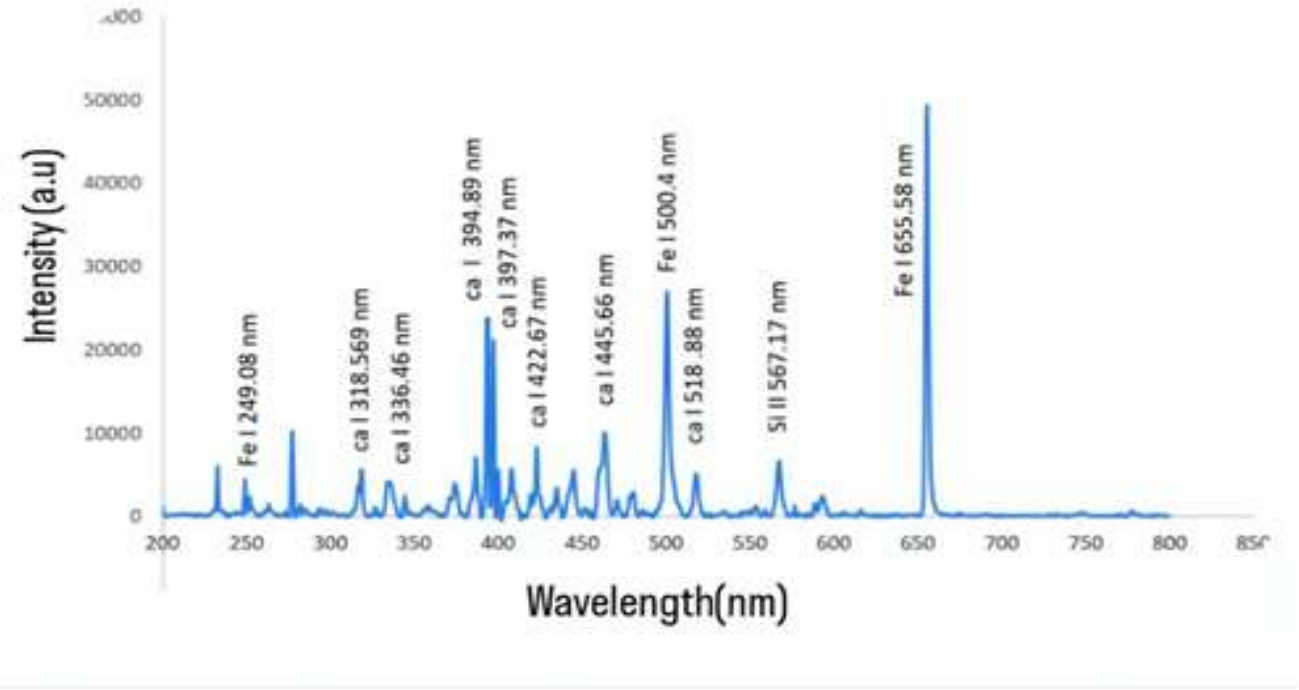

Figure 2: Emission spectrum of sample 1.

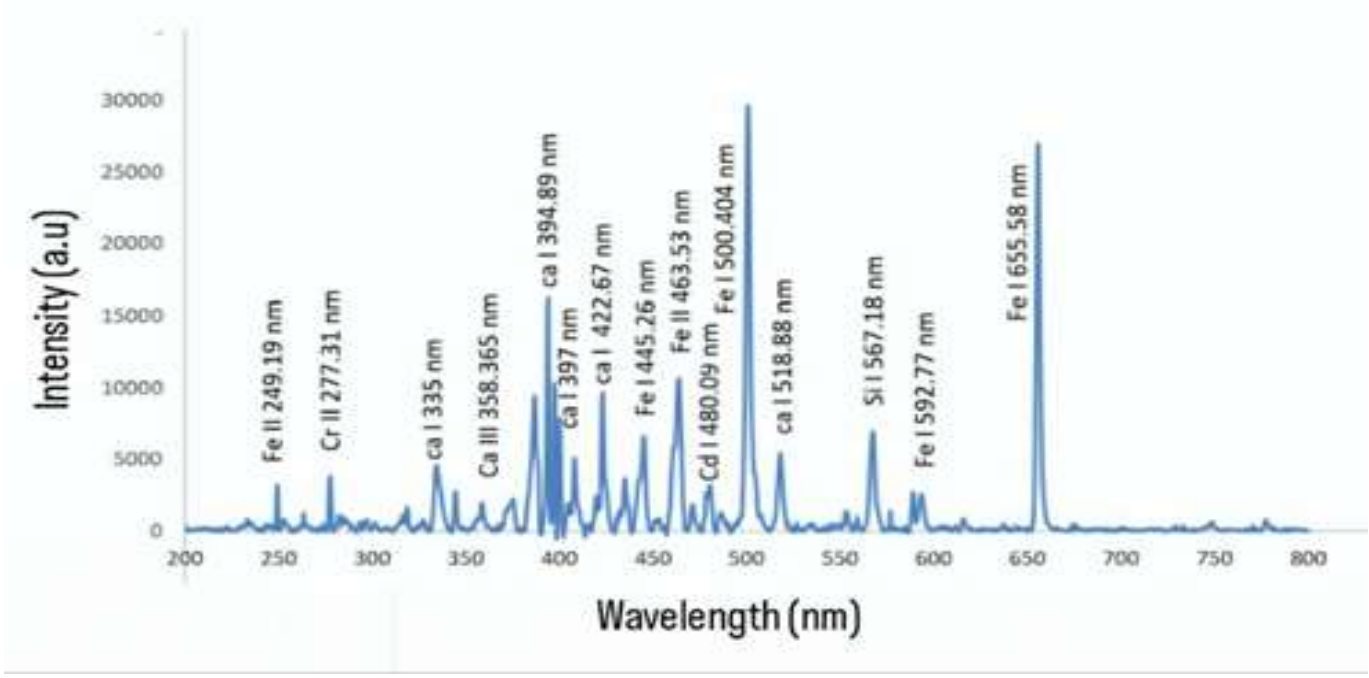

Figure 3; Emission spectrum of sample 2.

For sample 3 figure (4.3) shows the elements recorded are Fe I ,Ca I, Co II ,Th I , Zn I, F I, O II , K II and Cr II where there is one peak of Ca I 518 nm, and 2 peaks of Th I 422.99 ,444.538 nm , peak Fe I 249.12 nm , peak of O II 463.88 ,peak of CoI 232.78 nm, peak of Cr II 277.31, Peak of Zn I 334.31 and peak of K II 500.77 nm.

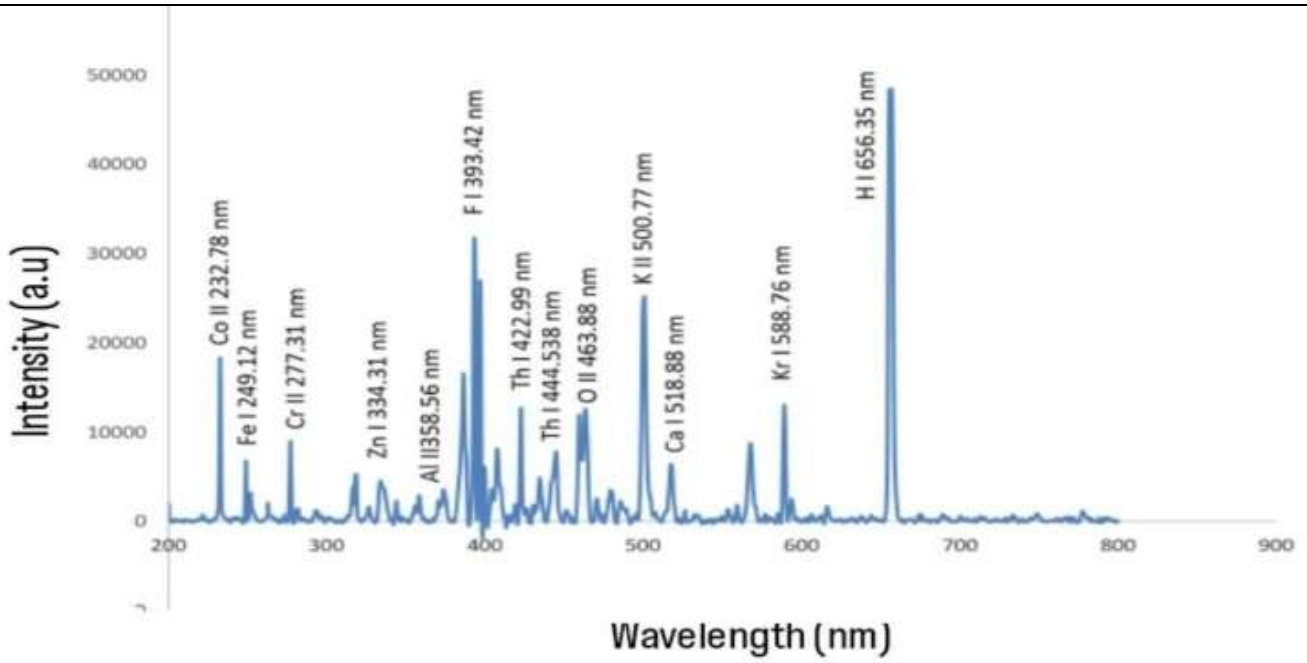

Figure 4: Emission spectrum of sample 3

For sample 4 figure (5) shows the elements recorded are Fe I ,Ca I, Ca II, Cu II ,C II ,Cr I, Cr II and Zr I where there is 3 peak of Ca I 422.83,445.32,518 nm, and Two peaks of Ca II 393.46 ,397.03 nm , peak Fe I 249.07 nm , peak of Zr I 335.36 nm ,peak of C II 588.71 nm, peak of Cu II 615.71, Peak of Cr I 655.58nm,peak of Cr II 277.31nm.

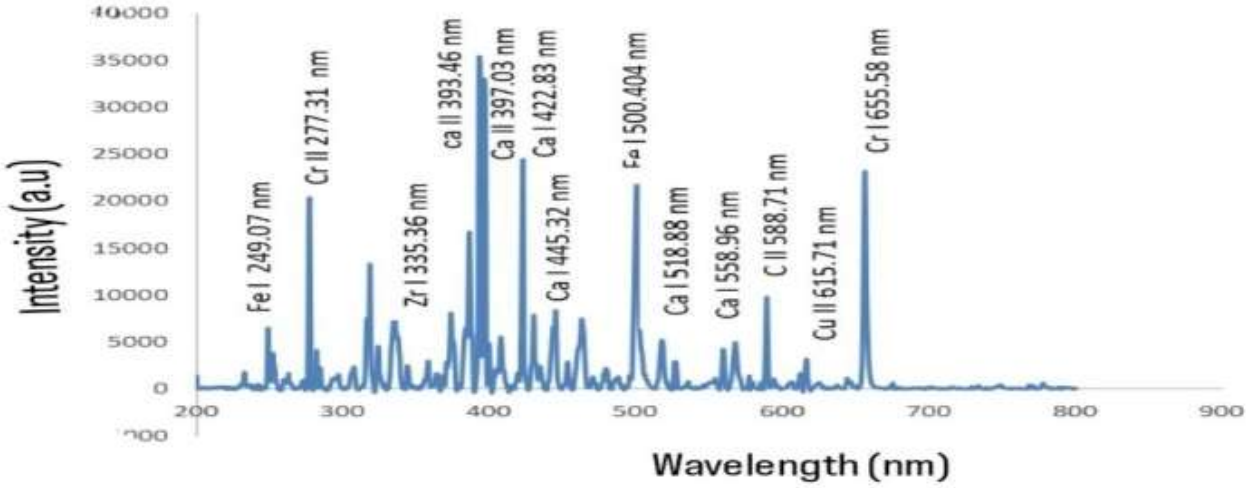

Figure 5: Emission spectrum of sample 4.

For sample 5 figure (6) shows the elements recorded are Fe I ,Fe II ,Ca I, Ca II, Cu II ,C II ,Th II and Si II where there is 2 peaks of Ca I 422.82, 518.88 nm, and Two peaks of Fe I 248.95 ,344.27 nm ,3 peaks of Fe II 445.2,463.37, 500.006nm , peak of CaII 393.36 nm ,two peaks of Cu II 276.97,318.57 nm, two peaks of Th II 386.43,656.005, Peak of CII 588.75nm,peak of Si II 567.19nm.

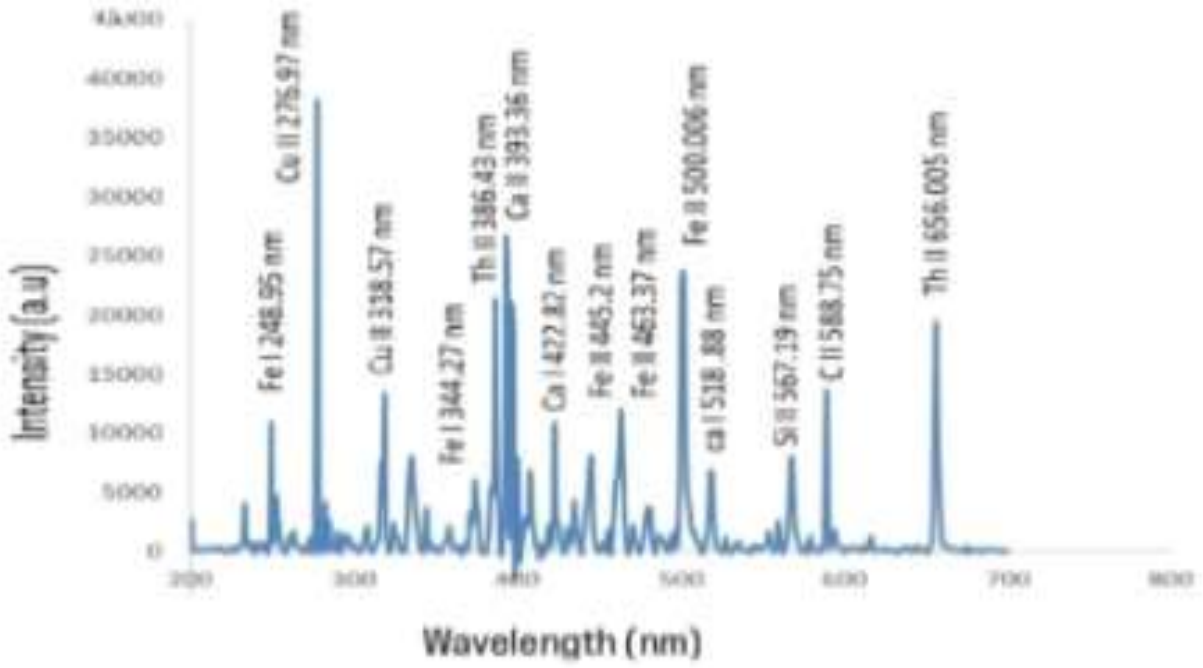

Figure (6) Emission spectrum of sample 5.

For sample 6 figure (7) shows the elements recorded are Fe I ,Ca I, Ca II, Cr II ,C II ,Th II , Si II and O I where there is 2 peaks of Ca I 430.38, 518.88 nm, peak of F e I 249.02 nm , peak of Cr II 277.31 nm two peaks of Th II 334.65 ,363.52 nm, peak of Ca II 373.81nm , peak of Cr I 655.582 nm, peak of Si II 567.23 nm, Peak of C II 588.73nm.

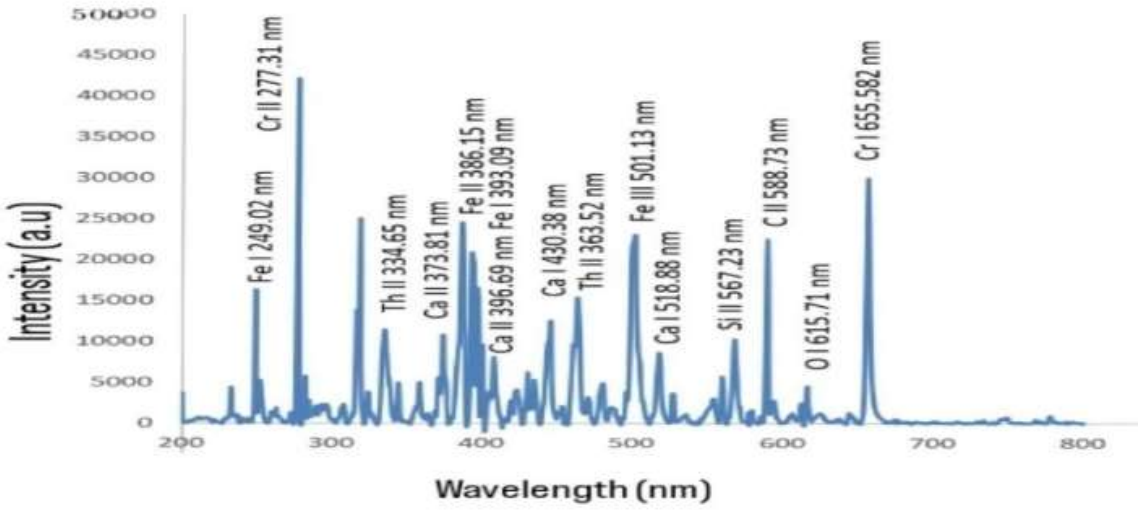

Figure 7: Emission spectrum of sample 6(healthy).

Concentration of calcium in the sample by LIBS and XRF : The samples are tested by two techniques which are LIBS and XRF to be sure of the equality data. The concentration of the six samples is shown in the table 1.

Table 1: Concentration of calcium in the sample by LIBS and XRF method

Sample	First line electron density (cm^{-3})	Second line electron density (cm^{-3})	Concentration % by LIBS	Concentration % by XRF
1	0.944×10^{18}	1.111×10^{18}	0.85	0.39
2	0.833×10^{18}	1.278×10^{18}	0.65	0.28
3	0.889×10^{18}	1.111×10^{18}	0.8	0.34
4	1×10^{18}	1.111×10^{18}	0.9	0.71
5	0.944×10^{18}	1.278×10^{18}	0.74	0.6
6	1.222×10^{18}	1.111×10^{18}	1.1	0.77

3.1. Correlation coefficient

The study showed significant strong positive correlation between LIBS and XRF values (r=0.7555, P=0.0113) as shown in figure 8.

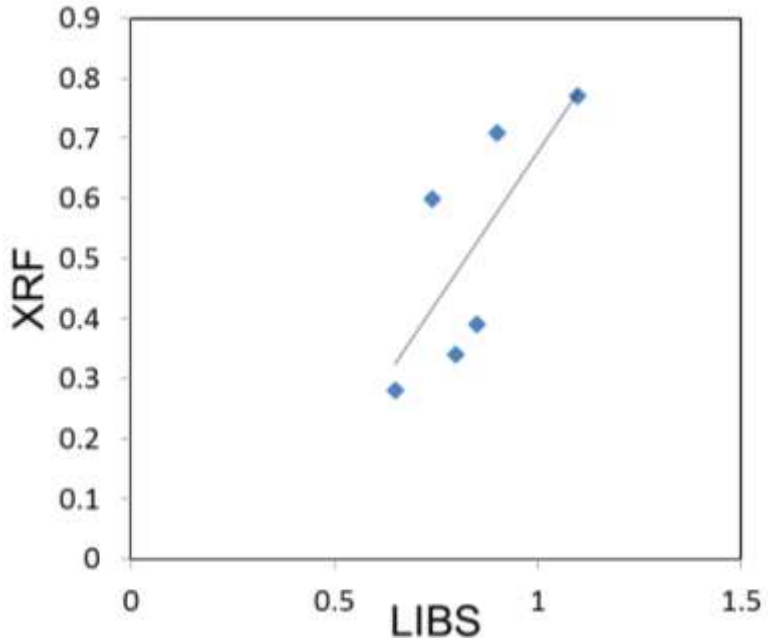

Figure 8: Correlation coefficient between XRF and LIBS

4. Conclusions

Spectral line, providing important element data. Shows a proportionate ratio of an element in the emission spectrum is calculated by dividing its concentration by the sum of all element concentrations and multiplying by 100. This ratio shows the elements spectrum contribution. Calcium (Ca) dominates nail samples. Calcium emissions are 1.1% in health and 0.78% in injury. These results imply LIBS nail analysis is reliable and acceptable. It can accurately measure sample elemental composition and concentrations, revealing nail chemical makeup for diagnostic and health monitoring.

Conflict of interest: The authors declare no conflict of interest regarding this work.

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