Hindawi Publishing Corporation
Journal of Chemistry
Volume 2015, Article ID 648385, 10 pages
http://dx.doi.org/10.1155/2015/648385

Review Article

Laser-Induced Breakdown Spectroscopy in Africa

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Received 9 December 2014; Revised 16 February 2015; Accepted 20 February 2015

Academic Editor: Jorge Caceres

Laser-induced breakdown spectroscopy (LIBS), known also as laser-induced plasma spectroscopy (LIPS), is a well-known spectrochemical elemental analysis technique. The field of LIBS has been rapidly matured as a consequence of growing interest in real-time analysis across a broad spectrum of applied sciences and recent development of commercial LIBS analytical systems. In this brief review, we introduce the contributions of the research groups in the African continent in the field of the fundamentals and applications of LIBS. As it will be shown, the fast development of LIBS in Africa during the last decade was mainly due to the broad environmental, industrial, archaeological, and biomedical applications of this technique.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique with a wide variety of applications for the qualitative and quantitative elemental studies. LIBS has been developed since the invention of the laser in 1960 [1]. The idea emerged to develop an analytical method based on laser-induced plasma. The first paper of laser sampling technique with spark excitation was introduced by Brech and Cross at the international conference on spectroscopy (1962) [2]. The technique was called "Microemission Spectroscopy" and marketed as a source unit which could be coupled to any spectrograph. In 1981, Loree and Radziemski [3] introduced the acronym LIBS for the first time by referring to the breakdown of air by laser pulses during the plasma creation. LIBS is a developing and promising technology that has the advantages of simplicity and robustness and the possibility of detecting both low and high atomic number elements [4]. The technique has a far-reaching capability to provide rapid, *in situ* multielement detection of any material, solid, liquid, or gas [4–8]. The numbers of LIBS papers published by groups all over the world are increasing steeply along the last four decades [9]. In fact, as shown in Figure 1, the situation on the African level is the same, although the numbers are not comparable with the international scale.

Detailed description of LIBS and its applications has been given in a number of published review papers and text books [4–9]. Basically, in LIBS, laser pulses from a Q-switched laser source are focused via a suitable focusing lens onto the surface of the sample. Adopting laser pulses of few tens of millijoules and pulse duration of a few nanoseconds leads to an irradiance in the order of some megawatts. Focusing of such huge amount of laser power in a tiny volume results in the evaporation, dissociation, atomization, and ionization of some nanograms to micrograms of the sample surface material. At the end of the laser pulse, we are left with the so-called plasma plume which consists of a collection of positive ions and swirling electrons at very high temperature in the range 6000–10,000 K that depends on the laser pulse energy and the physical properties of the target material (melting point, heat of vaporization, thermal conductivity, surface reflectivity, etc.). As the plasma cools down, recombination and deexcitation of ions and atoms take place in the form of emission of light which is collected and fed to a suitable spectrometer-detector system to obtain the LIBS spectrum. Qualitatively, the spectral lines are the finger print of the atomic species in the plasma and consequently in the target material. Quantitatively, there is a direct proportionality between the intensity of the spectral lines and the concentration of the relevant elements in the target material.

2. LIBS Fundamentals

Fundamental researches to understand the basics of LIBS technique include two branches: the first branch studies the laser-target interaction and related parameters such as laser characteristics and physical parameters of the sample material and the second branch deals with plasma evolution mechanisms which are space and time dependent. To the best of our knowledge, the first LIBS study in Africa was published in the year 2000 by Hanafi et al. [10] in Egypt at the National Institute of Laser Enhanced Science (NILES). It was a study of the spectral emission in laser-induced breakdown spectroscopy of gases. The measurements were carried out on helium, argon, nitrogen, and air irradiated with ruby laser. Helium showed strong line emission in the visible region, whereas argon plasma contained a large number of ionic and atomic lines almost overlapping to form humps of spectral lines in the visible region. EL Sherbini et al. [11] measured the plasma electron density in laser produced plasma utilizing the Stark broadening of the H_α-line at 656.27 nm from the produced plasma of aluminum target in humid air from 10^{18} cm^{-3} down to 6×10^{16} cm^{-3} at longer delay time. The results were in agreement with electron density from the optically thin Al II line at 281.62 nm from the same spectra. This agreement confirms the reliability of utilizing the H_α-line as an electron density standard reference line in LIBS experiments [11]. In the approach of measuring plasma properties, El Sherbini et al. [12] measured plasma properties from the degree of plasma optical opacity at the wavelength of hydrogen H_α-line. The technique used in this approach is called DLAAS, that is, diode laser atomic absorption spectroscopy. The measurement was done for different solid target materials with major elements including aluminum, iron, and titanium and other materials of high hydrogen content like wood and plastic. The results show that the plasma associated with metallic targets is almost optically thin at the H_α-line over all fluences and at delay times $\geq 1\,\mu$s but is rather thick for hydrogen-rich targets (plastic and wood) over all delay times and fluences [12]. Spectral emission lines from the plasma are used to calculate plasma electron temperature. El Sherbini et al. [13] studies emphasize the importance of line intensity correction due to self-absorption before using them. The correction was done from the comparison of the electron densities as deduced from magnesium lines to that evaluated from the optically thin hydrogen H_α-line at 656.27 nm appearing in the same spectra under the same conditions [13], where Mg present as traces in aluminum targets suffering from optical thickness shows scattered points around Saha-Boltzmann line [13].

Mathuthu et al. from Zimbabwe demonstrated that laser-induced breakdown spectroscopy could be a useful and versatile tool for density, phase velocity, plasma frequency, and refractive index measurements in air plasma [14]. The results confirm previous experimental results that the plasma counteracts higher energy deposits by expanding instead of getting hotter. The electron density at the center of the plasma plume is slightly hollow probably due to the effect of the shock wave. From the measured parameters, the behavior of plasma frequency and laser phase velocity change was determined.

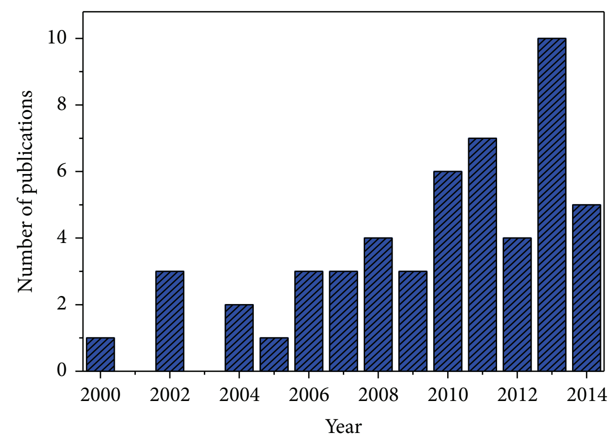

Figure 1: Number of LIBS publications in Africa since the year 2000.

Laser phase velocity changes are due to a decrease in the real part of the refractive index, which in turn is caused by radial electron density gradients. The laser-induced air plasma has a concave parabolic-shaped electron density and a convex parabolic-shaped refractive index near the laser axis, that is, around a diameter of 0.5 mm [14].

3. Factors Affecting LIBS

Factors affecting the nature and the characteristics of the laser produced plasma were studied. These factors could be grouped in (i) laser parameters including (energy, wavelength, and pulse duration), (ii) optical parameters or focusing properties, (iii) ambient conditions of surrounding atmosphere in composition, pressure, electric field, and temperature, and (iv) physical properties of the material under investigations including reflectivity of the surface, density, specific heat, and boiling point of the target. Abdellatif and Imam [15] studied laser wavelength effect on the produced aluminum plasma. Measurements were done using Q-switched Nd:YAG laser at wavelengths 1064, 532, and 355 nm. The plasma electron temperature was calculated using the Boltzmann plot for the Al II lines. The spatial profile of the electron density using Stark broadening formula was estimated. Assuming LTE (local thermal equilibrium) conditions, they found that the maximum attainable value of the spatial electron temperature depends on the laser wavelength and the electron density reaches its highest value near the target surface [15]. Later on, Galmed and Harith [16] studies showed that the emission line intensities increase by increasing the laser pulse energy until they level off due to self-absorption. The line intensities decrease exponentially as the delay time increases due to plasma expansion [16]. Calculated plasma parameters show that electron density (N_e) at different laser energies and for different samples has the same values, while plasma excitation temperatures (T_{exc}) increase on increasing the laser pulse energy to stabilize at higher laser energy due to spectral line self-absorption in the plasma plume. They deduce that the LTE conditions are not fulfilled for lower laser fluences but only at higher laser fluences. This may be as a result of the effect of the initial plasma conditions that depend on the incident laser pulse energy [16]. Another study for the same group showed that, for high energies (150–750 mJ), electron density increases with increasing the laser energy while they decrease with increasing the delay time [17]. From the previous results, it can be concluded that plasma parameters depend strongly on the laser wavelength, laser energy, and delay time [15–17]. The effect of laser irradiance in depth profile measurements was studied by Abdelhamid et al. [18]. They studied the effect of irradiance on intersection point (the number of laser pulses required to reach the interface between two layers), average ablation rate, the crater depth, and depth resolution. Lowering the irradiance, the average ablation rate decreases and the depth of the crater becomes less. They found that, for all the layered specimens of Au and Ag grown onto Cu substrates, as the working distance (difference between the lens-to-sample distance and the focal length of the lens) increases, the intersection point value between the two layered materials increases, while both the average ablation rate and crater depth are decreasing [18]. Elhassan et al. [19] demonstrated the effect of applied electric field on plasma parameters and LIBS signal emitted. They used pure aluminum impeded in one of two copper electrodes. They show that electric field had a pronounced effect on the emission intensities of the ionic lines under forward biasing (negative target) where the emission of the ionic lines grew exponentially. In case of reversed biasing, the line intensity deteriorated with respect to the zero field value. Plasma temperature was slightly affected by increasing the electric field in both directions. On the other hand, the electron number density was found to decrease slightly in the case of forward biasing, with a much stronger decrease (about one order of magnitude) in the case of reversed biasing. They found that signal-to-noise (S/N) ratio and the limit of detection (LOD) were improved in case of forward biasing electric field [19]. Electric field was found to have no effect on laser-induced shock wave (SW) velocity, which depends mainly on the laser parameters, such as pulse energy and spot size. Different research groups from Egypt and Algeria investigated the dynamics of plasma expansion in vacuum [20–22]. Imam et al. investigated spatially the dynamics of plasma expansion velocity, as well as its composition in vacuum [20]. Moreover, modeling and theoretical analysis of the experimental data allowed the study of nonequilibrium processes in the laser-induced plasmas. Investigation of the plasma expansion in a vacuum revealed a departure from equilibrium which has been explained in terms of the three-body recombination effect. The corresponding rate constant of such effect was measured and the obtained results were in good agreement with the corresponding theoretical estimates. Finally, deviations from the Saha balance were found. An explanation of the phenomenon was given in terms of radiative effects and three-body recombination [20]. The excitation temperature of the core of the plasma plume is measured in vacuum using Boltzmann plots. It is found that, in the core of the plume, the excitation temperature T_{exc} is 9900 K in vacuum (at the distance 0.6 mm from the target). The density of electrons is determined from the Stark broadened line width. It is found that the electrons in the core of the plume have a density of $1.8 \sim 10^{16}$ cm^{-3} in vacuum at a distance 0.6 mm from the target [21]. The temperature increases with distance from the target until a distance of 0.6 mm; after that, it decreases. This is due to the enhancement of the cooling rate in the outer part of the plasma. The decrease of the electron density after 0.6 mm may be due to the shielding of the target by the plasma, which prevents further interaction of the laser radiation with the target. Moreover, it might be due to the enhancement of the recombination processes [21]. Plasma diagnostics in vacuum for different oxygen pressures were accomplished by both fast imaging and optical emission spectroscopy [22]. The former approach showed a splitting of the plasma under different oxygen pressures that were in the range from 0.02 to 1 mbar and started for time delays varying from 550 to 190 ns, respectively. The plasma appeared to have, at the early stage, a monodimensional expansion, followed by a tridimensional expansion into vacuum and under oxygen atmosphere. The drag model was found to describe well the spatial-temporal behavior of the plume for 0.02, 0.1, 0.5, 1, and 5 mbar of oxygen pressure. The estimation of the stopping distance of the plasma plume by the drag model was necessary when choosing the substrate target distance. The spectroscopic analysis of the emission spectrum of the alumina plasma, recorded between 200 and 600 nm into vacuum and under different O_2 pressures, suggested that the plume of alumina was composed of emitting species as Al I, Al II, Al III, and AlO where no oxygen emission line was observed. The band head of AlO emission at 484.21 nm appears only in oxygen ambiance. As oxygen pressure increased, the AlO molecular band emission became distinct. In vacuum, the conversion of plasma plume from the thermal energy into the kinetic one was shown as a consequence of the decrease in the electron temperature along the distance from 1.69 to 0.52 eV [22]. Laser emitted plasma at nitrogen ambient gas was studied [23, 24]. For different pressures, results show that, at lower ambient pressure values of N_2, the intensities of Ti spectral lines last only for a few hundreds of nanoseconds even not more than 500 ns at 15 Torr. As the ambient pressure is increased, the intensities of the lines can last for up to several microseconds and even reach about 25 μs at 760 Torr [23]. However, it is observed that the intensities of the spectral lines increase with increasing ambient N_2 pressures, especially at the higher values of the ambient N_2 pressure where the intensities of the lines increase rapidly. Continuum radiation results from collisions of electrons with heavy particles, neutrals, and ions and is also due to recombination of the electrons with ions. Thus, it can be inferred that, at the initial stage of the plasma near the ablated surface, there are a large number of electrons, ions, and neutrals in the excited states [23]. Laser ablated carbon plasma under nitrogen ambience at different laser fluence (12, 25, and 32 J/cm^2) shows that CN and C_2 emission intensity did not depend on the laser fluence, while CII and NII emission intensity increases continuously with the rise of the fluence. The spatiotemporal evolution of CN follows the C_2 one at the vicinity of the target surface, whereas, for greater distances, it follows the CII one. These investigations also demonstrated that there are different chemical reactions leading to the CN formation, by stating that, at the neighborhood of the target surface, CN molecules come directly from this surface or from the bimolecular reaction between C_2 and N_2 in the gas phase. However, at greater distances, CN molecules are mainly produced by a three-body reaction between the atomic species C and N [24].

4. LIBS in Aqueous Medium

LIBS in aqueous medium did not develop rapidly like in solid and gas. The reason was primarily attributable to the technical difficulties encountered in performing LIBS experiments in liquids and the short lifetime of in-bulk generated laser-induced plasma making the interpretation of the obtained spectra not significant and consequently preventing the extraction of plasma parameters. Liquids, in addition, must be transparent at the laser wavelength and the emitting wavelengths of the monitored species; another experimental difficulty arises when laser-induced plasma is produced on the surface of the liquid. The splashing of the liquid and shock waves which produced ripples on its surface represent obstacles in this case. The first normally leads to the opacity of the light collection optics in the vicinity, while the second defocuses the laser beam on the liquid surface. In the year 2002, a detailed experimental study of laser-induced breakdown spectroscopy in water was performed by Charfi and Harith [25] where the aqueous plasma has been studied temporally and spatially. Aqueous solutions of different Na and Mg concentrations were used to construct calibration curves and estimate the limit of detection (LOD) in pure solution and mixed solutions of different matrices. The lowest detection limits were 1 and 2 $\mu g\,mL^{-1}$, respectively, in pure solutions while they were slightly higher (1.2 and 2.5 $\mu g\,mL^{-1}$) in mixed solution. The differences in the LIBS limit of detection of the same element in different matrices could be correlated with the compatibility of the physical properties of the elements existing in the same matrix. Approximately, similar electronic structures may facilitate better conditions for energy transfer within the matrix consequently raising the technique sensitivity. The target physical properties play an important role in the obtained values of the laser-induced plasma temperature T_e and electron density N_e. These, in turn, affect the spectral characteristics of each element in the same matrix [26]. Another study shows that the detection limits are a function of the element studied [27]. Ben Ahmed et al. [28] studied the kinetics of plasma produced in aqueous solution and they proposed a model based on electron-ion recombination that was compared with the experimental results obtained from plasma on the surface of water solutions of $MgCl_2$. They proposed that the recombination of the electrons created at the beginning of the interaction with the laser pulse, with ions ejected from the solution, could be the origin of the observed excited species. Further experimental results reported on the temporal characteristics of laser generated plasma in Na and Cu aqueous solutions that exhibit fluorescence signal on the decaying edge of plasma emission at their respective characteristic resonance lines. The potential of the laser plasma spectroscopy for *in situ* pollution monitoring in natural and waste water was discussed [29]. Spatial and temporal evolution of the plasma produced on the distilled water surface was discussed. The temporal evolution from 200 ns after the plasma creation to 2200 ns of the H_α and H_β lines is reported. Supposing LTE, electron density and temperature were determined, including the influence of the self-absorption on its measurements [30].

5. LIBS Applications

5.1. Surface Hardness Measurement. Laser-induced plasma spectroscopy can be exploited not only as elemental analysis techniques, but also as the estimation of the surface hardness of solid targets; it has been found that there is a remarkable correlation between the ionic to atomic spectral lines emission ratio and the surface hardness of solid targets. This phenomenon is related to the repulsive force of the laser-induced shock waves. LIBS used to measure the hardness for different objects from metal alloys to calcified biological samples. The measured shock wave front speeds in case of the three investigated calcified tissues confirm that the harder the target the higher the SW fronts speed and the higher ionic to the atomic line ratio of Mg [31]. Kasem et al. [32] found it possible to discriminate between bones from different dynasties from the results of the surface hardness measurement by evaluating calcium ionic to atomic spectral line intensity ratios in the relevant LIBS spectra. LIBS used to estimate the age of broiler breeders by measuring the surface hardness of their eggshell on two different strains, Arbor Acres Plus (AAP) and Hubbard Classic (HC) [33]. In case of steel, alloys are treated thermally to have different surface hardness. ZrII/ZrI line ratios used to investigate hardness [34]. Aberkane et al. [35] from Algeria showed the correlation between plasma temperature and surface hardness for Fe-$V_{18\%}$-$C_{1\%}$ alloys. Samples have the same ferrite composition but different surface hardness measured by Vicker method. The differences in hardness values were attributed to the crystallite size changes due to different heat treatment. The results showed a linear relationship between the Vickers surface hardness and the plasma temperature. The relation between ionic and atomic line ratio for vanadium (VII/VI) provided good linear results too [35].

5.2. Depth Profiling. LIBS is a relatively novel technique that is being applied to the characterization of interfaces in layered materials. LIBS technique with relatively high laser pulse energy (50 mJ/pulse) is reliable to investigate layered specimens of different metallic elements via depth profiling procedure at fixed experimental conditions [18]. Kiros et al. [36] studied rock of hewn churches from Lalibela, Ethiopia. The elemental composition of both the bulk rock materials and their external layers, exposed to the environmental factors, was analyzed. Depth profile shows a lower content of potassium on the surface together with increasing oxygen intensity in depth which was observed. Variations in depth of these two elements, which are clearly anticorrelated, may reflect changes in abundance of clay minerals and feldspar due to alteration of the basalt. They established relationship between loss of cations and the high presence of hydrogen in the samples collected from external wall of the churches and in-depth profile of weathered basalt. Since cations are lost from the constituent, primary minerals are replaced by H^+; this process disrupts the lattice structure and causes a marked loss of strength. Khedr et al. [37] from Egypt studied ancient Egyptian glazed ceramic samples. Depth profiling allowed differentiation between the dirty layer, the glaze surface, and the ceramic body. Galmed et al. [38] studied Ti thin film using femtosecond LIBS. Titanium of thickness 213 nm was deposited onto a silicon substrate before and after thermal annealing. Femtosecond laser was unable to differentiate between the annealed and nonannealed samples because of the lack of energy homogeneity throughout the laser pulse cross-section. Studies by the same group also showed that spectral line choice was not significant as long as the spectral lines are fulfilling the LIBS spectral lines conditions. The normalization of the lines was able to improve the LIBS results to be more reproducible [39, 40].

6. Cultural Heritage and Archaeology

LIBS has been applied for the analysis of Egyptian Islamic glaze ceramic sample from Fatimid period Fatimid period. The analysis of contaminated pottery sample has been performed to draw mapping for the elemental compositions. Results show that one of the most important constituents in the glaze was copper, which suggests that the green glaze pigment was made from copper compounds. However, the presence of tin in the samples revealed the assumption of using bronze (copper-tin alloy) in the green pigment preparation [37]. LIBS used to evaluate cleaning of corroded Egyptian copper embroidery threads on archaeological textiles using laser cleaning method and two modified recipes of wet cleaning methods. This was done by following up the copper signal before and after cleaning. It was found that laser cleaning is the most effective cleaning method without any damage to both metal strips and fibrous core [41]. Ahmed and Nassef [42] studied mummy's linen wrapping textile dated back to the Ptolemaic period (305 BC-30 AD). LIBS qualitative results were comparable to those of SEM-EDX results. Roberts et al. from South Africa studied the 2 million-year-old fossils and rocks in surrounding recovered from the Cradle of Mankind site at Malapa. They found that the phosphorus content is significant enough to discriminate fossil bones with relative ease from the surrounding rock which had no significant phosphorus content. The rock lines in the same spectral region were shown to be mainly from silicon, iron, and manganese. They quantify the damage to the fossils during laser removal of rock; the depth of fossil removal was measured as a function of laser fluence. The threshold fluence for maximum rock removal of depth $d = 40\,\mu m$ was $600\,Jcm^{-2}$ [43]. Kasem et al. [32] used LIBS for interpretation of archeological bone samples from different ancient Egyptian dynasties. They found that buried bones are susceptible to minerals diffusion from the surrounding soil that has undergone careful analysis (Figure 2). Diagenesis or postmortem effects must be taken into consideration on studying dietary habits and/or toxicity levels via analysis of ancient bones.

7. Environmental and Chemical Studies

Environmental studies for tropical forest in Ethiopia were done by Dilbetigle Assefa et al. [44]. They employed calibration-free LIBS to determine the concentration of elements in the rock samples. Area under study showed high concentrations of iron, neodymium, Zn, and Pt which means greater potential for mining of these elements. The concentration of Cr, Mn, and Fe in sediment samples collected from Tinishu Akaki River (TAR), Addis Ababa, Ethiopia, was determined using LIBS. Areas with less number of industries (such as Biheretsigie and Gefersa) had the lowest concentrations while those with large number of industries (such as AA TAR Kolfe and AA Melkaqurani) had the highest concentrations of the selected metals which indicated an increase in anthropogenic effects around the investigated areas. Results showed that LIBS can be applied as an alternative technique to other existing methods, like flame-atomic absorption spectroscopy (F-AAS) and does not require a sample decomposition step which is time consuming and expensive and may result in contamination of samples and the environment itself [45]. Mukhono et al. [46] used Multivariate chemometrics in spectroanalysis and characterization of environmental matrices. Multivariate calibration strategies were applied for prediction of the trace elements in the geothermal field samples. It was found that geothermal areas were characterized by elevated content of arsenic while at the same time its concentrations were normally distributed in the field samples. Exploratory data analysis using principal components analysis (PCA) and soft independent modeling of class analogy (SIMCA) were successfully applied to classify and distinguish the origin of the geothermal field matrices (HBRA or NBRA) based on LIBS atomic signatures in a manner applicable to geothermal resource characterization and environmental impact modeling. Mukhono and coworkers [46] concluded that LIBS spectra provide vital information, for example, spectral signatures of Ca, Mg, Fe and Si which can be used in routine monitoring analysis for variations in soils from three sources: (i) high background radiation area- (HBRA-) geothermal, (ii) HBRA-nongeothermal, or (iii) normal background radiation area- (NBRA-) geothermal field. Femtosecond LIBS has been used by Roberts et al. [47] in the detection of metallic silver on chemical vapor deposited (CVD) grown silicon carbide (SiC) and in pebble bed modular reactor (PBMR). Samples used were tristructural isotropic (TRISO) coated with $500\,\mu m$ diameter zirconium oxide surrogate kernel. The SiC layer of the TRISO coated particle is the main barrier to metallic and gaseous fission products. They concluded that the LIBS technique is a good alternative for a remote analytical technique and that femto-LIBS can achieve good surface spatial resolution and good depth resolution in experimental coated particles [47]. LIBS was used by Elnasharty et al. in Egypt [48] for the estimation of consumption and/or combustion of motor oil during routine engine operation. This has been performed by following up the intensities of molecular emission lines cyanide (CN)

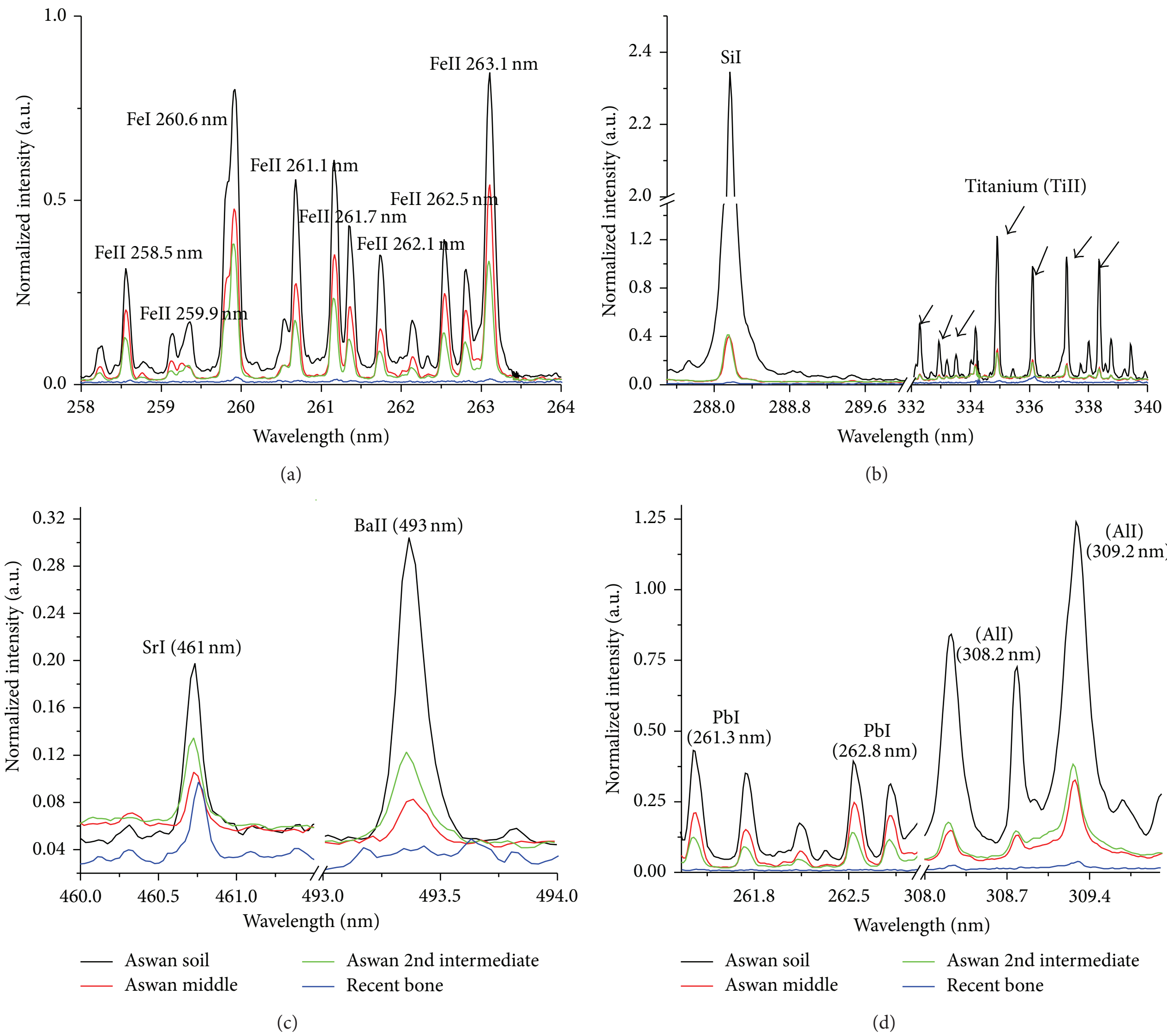

Figure 2: LIBS spectra of ancient bones from different historical eras and recent bones compared to spectra of soil samples [32].

and carbon (C_2) relevant to the main compounds of oil in its LIBS spectra, while the oil undergoes a range of chemical and physical transformations during consumption. The results showed that the trend of integral intensity values of CN and C_2 emission lines versus the mileage at all selected wavelengths is similar and can be described by an exponentially decaying curve (Figure 3). The rates of dissociation for CN and C_2 contents in oil samples were calculated to be taken as indicator for consequent depletion of engine oil. Additionally, the ratios for the integrated emission intensity of CN to C_2 have been calculated and found to be proportional to the corresponding mileage. Furthermore, they concluded that the obtained trend can be used as prognostic approach for normal degradation of engine oil [48].

Another Egyptian group [49] studied the feasibility of LIBS technique in a turbulent combustion environment and signal enhancement by applying an orthogonal dual-pulse arrangement for air-fuel mixture. The data showed that the signal is slightly higher in the double pulse mode as compared to the same application in a solid material [49]. LIBS has been used to identify the constituents of Sudanese crude oil from Adaril oilfield. Almuslet and Mohamed [50] showed organic compounds specific spectral features including sequences of the CN violet system and the C_2 Swan system and H, C, N, and O atomic and ionic lines. The principle for identification of organic compounds was based on their spectral features and on the integrated intensity ratios of the molecular bands (CN and C_2) and atomic lines (H_α and C) [50]. Calibration-free LIBS at 2nd harmonic laser excitation (532 nm) has been used for semiquantitative analysis of different species of T_{eff} seeds (Red, White, and *Sirgegna*) of Ethiopia [51]. The differences in relative concentrations were demonstrated. Red species shows the highest Ca content but the lowest in Mg, while, for the other two species, it was the contrary. Spectrochemical analysis of organic liquid media such as vegetable oils and sweetened water characterized by two

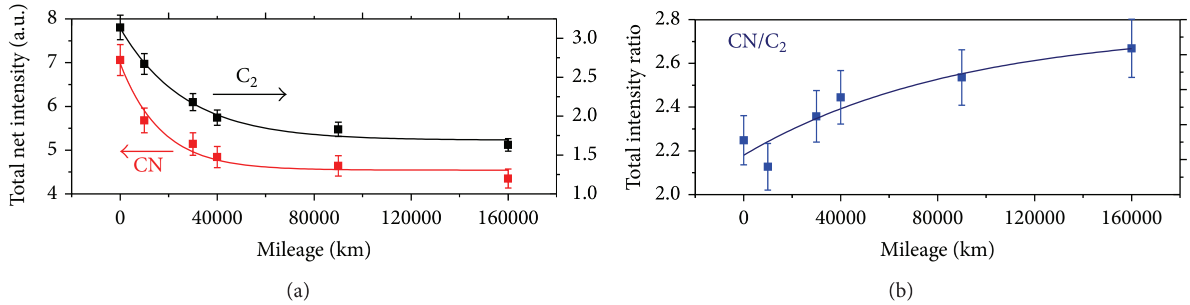

FIGURE 3: Trends of summation of integrated line intensities for (a) CN and C_2 peaks and (b) CN/C_2 ratio at different mileage [48].

types of molecules, saccharose (cyclic) and linear chain fatty acids, were performed with the use of LIBS by a Tunisian research group [52]. The absence of C_2 emission in plasma of sweetened water was observed. This present work suggested that the C_2 emission depends on the form of the molecule constituting the pulverized sample to create plasma. It seems that there is emission of C_2 if the molecule contains at least one carbon-carbon linear band. It was also shown that oil containing more saturated fatty acids emits more C_2 compared to CI but shows no correlation with the number of double bonds. A statistical analysis was performed based on the ANOVA test on the single parameter C_2/CI which was used for classification of vegetable oils according to their saturated fatty acid content [52]. El Sherbini et al. [53] observed LIBS signal enhancement from the nanostructured ZnO compared to bulk material signal. They suggested that the surface plasmon resonance dependence on the electron density is the major effect acting to enhance the radiation field. In order to get the highest signal enhancement from the nanostructured samples, the lowest possible fluence at the largest delay time with shortest laser wavelength was the possible choice [53].

8. Biomedical and Biological Applications

LIBS is probably the most versatile method of elemental analysis currently in use for many biomedical applications. Studies about the possible correlation between some elements and disease are often among the medicine experts and biologists interesting. El-Hussein et al. [54] from Egypt have used LIBS to identify and characterize human malignancies. The study depended on in vitro relative abundance of calcium and magnesium in malignant tissues with respect to the nonneoplastic tissues. Measurements have been performed under vacuum (10^{-2} Torr) and the samples were frozen down to -196°C (liquid nitrogen temperature) to improve signal from the soft biological samples. They found significant discriminating results in case of breast and colorectal cancers. Another Egyptian group [55] had also used the Ca and Mg levels to monitor tumor photodynamic therapy (PDT) in malignant tissues. Tissues were injected with methylene blue photosensitizer with concentrations 0.5%, 1%, and 2%. The results showed a decrease in tissue elements content after PDT application for both calcium and magnesium compared to before PDT [55]. Hamzaoui et al. [56] from Tunisia had used LIBS for the first time as a potential method for analysis of pathological nails. They found a distinct difference in LIBS spectra of normal and pathological nails in the spectral intensity distribution of calcium, sodium, and potassium of normal and pathological nails. The CN band emission spectrum was used for the estimation of the transient temperature of the plasma plume and consequently of the sample surface. The elemental content of the superficial and inner enamel as well as that of dentin was analyzed using LIBS and X-ray photoelectron spectroscopy (XPS) of bleached and unbleached tooth specimens [57]. LIBS revealed a slight reduction in the calcium levels in the bleached specimens compared to the control ones in all the different bleaching groups and in both enamel and dentin. Good correlation has been found between the LIBS and XPS results which demonstrated the possibility of using LIBS technique for detection of minor loss in calcium and phosphorus in enamel and dentin [57]. LIBS multielemental analysis of horse hair was found to be potential in revealing retrospective information about nutritional status using hair as a biomarker [58]. Longitudinal segments of the hair may reflect the body burden during growth. In the field of poultry science, Abdel-Salam et al. [59] investigated elemental composition of egg shell before and after hatching; depth profile measurements were carried out to follow up different elements throughout the shell. They found that calcium distribution is not homogenous throughout the shell thickness while Mg and Na concentrations in the internal layers of the egg shell before hatching were higher than those after hatching. The results were interpreted due to consumption of inner layer contents by the embryo during its development. Increase in magnesium content is directly related to an increase in shell hardness. In the field of animal production, characterization of semen samples from buffalo bulls (*Bubalus bubalis*) was studied by Abdel-Salam and Harith [60]. LIBS provided information about the elemental seasonal variation in the seminal plasma. The obtained results demonstrated that buffalo seminal plasma contents of Ca, Mg, Zn, and Fe are higher in winter (high season) than in summer (low season). Such elements have direct relation to the sperm parameters, that is, sperm count and motility, and, consequently, LIBS can be used to assess parameters indirectly [60]. Interesting results were found from the evaluation of the nutrients in maternal milk and commercially available infant formulas using LIBS technique by the same Egyptian research group [61]. They found high

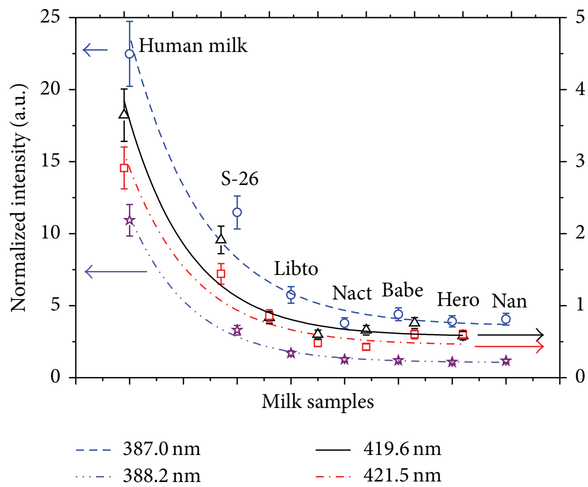

Figure 4: Trends of integrated intensity values for different violet CN emission bands for maternal milk and six types of commercial infant formulas [61].

elemental and protein content of the maternal milk compared with the commercial formulas samples (Figure 4).

9. Conclusion

LIBS is a rapidly developing spectrochemical analytical technique. It is an attractive and promising technology for a large number of applications. LIBS has the advantages of simplicity and robustness and the possibility of detecting both low and high atomic number elements in different types of materials. Besides, portable LIBS systems can be used to perform real-time and *in situ* measurements. In this paper, LIBS fundamental and applications in African countries were reviewed. Through the review, the growing interest in LIBS during the last decade was shown. LIBS has been applied in Africa extensively in the environmental field, archaeology, and cultural heritage studies and in the biomedical and biological field studies. Some of the African research groups are now worldwide well known by their pioneering research works in these fields. The number of papers published is remarkably increasing each year. The 1st Euro-Mediterranean Symposium on LIBS (EMSLIBS 2001) and the 7th international conference on LIBS (LIBS 2012) have been hosted in Africa, namely, in Egypt in the years 2001 and 2012, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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