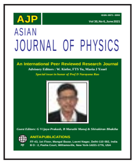

Asian Journal of Physics
Vol. 30, No 6 (2021) 871-888
Available on: www.asianjournalofphysics.com

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Advances in applications of LIBS in India: A Review

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Dedicated to Professor D N Rao for his significant contributions and pioneering works in the fields of spectroscopy, optics, nonlinear optics and photonics

In this review, a comprehensive overview of laser-induced breakdown spectroscopy (LIBS) research work carried out by different groups in India is presented. In the last two decades, it has been extensively explored for a wide range of applications, including estimation of elemental concentration and the classification of materials. LIBS is commonly used for variety of purposes, including environmental monitoring, industrial and nuclear applications, geological and archaeological surveys, defence applications, and biological applications, etc. In these milieu, various analytical methodologies and machine learning algorithms were used for both qualitatively and quantitatively analyzing LIBS data.

Keywords: Laser-Induced Breakdown Spectroscopy (LIBS), Laser-induced plasma (LIP), Pulsed laser.

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is a well-established analytical technique that can instantly provide the qualitative and quantitative chemical information of the sample in any form, be it in solid, liquid, or gas [1,2]. It works by focusing a high-energy pulsed laser onto a sample surface to create laser-induced plasma (LIP) and spectroscopically investigating the light emanating from it provides the information at the atomic level [3,4]. Since the last three decades, many real-time advantages have been recognized, such as simplicity in producing plasma, low cost, portability, and acquiring strong signals with minimal destruction. Significant progress has been made throughout these years for different applications, which include environmental monitoring, remote material assessment in nuclear sites, a geological survey in space exploration, diagnosis of objects in archeology, dentistry and disaster management, homeland security, and standoff detection, etc. Nowadays, LIBS is regarded as an appealing and effective spectroscopic tool when the atomic or chemical information of any material is required.

LIBS has piqued the interest of many researchers from various countries due to its ease of use and numerous on-field advantages such as requiring no or minimal sample preparation, multi-elemental detection, and being capable of *in-situ* and standoff experiments. As a result, the number of research papers published in the field of LIBS has been steadily increasing. Fig 1.a shows the number of LIBS publications from 1989 to 2020, while Fig 1.b shows the publication statistics of the top 15 countries/territories.

From Fig 1. a, it can be seen that the number of publications is very low until early 2000. However, since the beginning of the twenty-first century, the number of publications has been increased rapidly,

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doi: https://doi.org/10.54955/AJP.30.6.2021.871-888

which can be primarily attributed to the advancements in laser and sensor/detector technology facilitating the compact LIBS platform for rapid analysis. Further, the introduction of various analytical algorithms and the application of machine learning tools for analysis revolutionized the LIBS application and reach [5]. Figure 1(b) depicts the research articles published by various countries, in which China and the United States ranked first and second, respectively, and India is ranked eighth among all countries. LIBS research work in India has started relatively late. The initial studies focused on the investigation of aluminum alloy was made by Rai *et al* in 2001 [6]. From then, many research groups began to involve in LIBS research. Figure 2 shows the statistics of LIBS publications from different research groups/institutes in India. The aim of the present study is to provide details of the research progress made by the Indian LIBS research community over the past two decades.

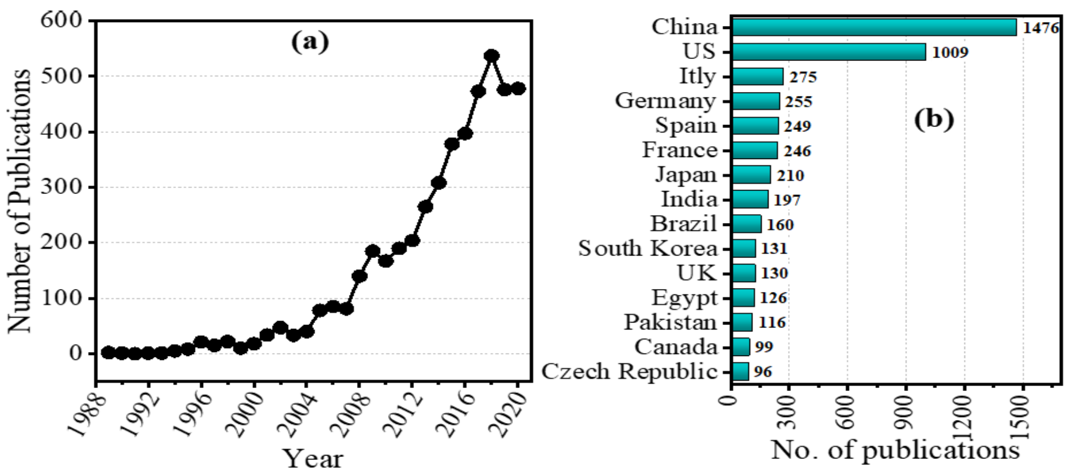

Fig 1. Number of articles published in the field of LIBS (a) with time, (b) in countries/territories (Source: https://www.scopus.com/term/analyzer).

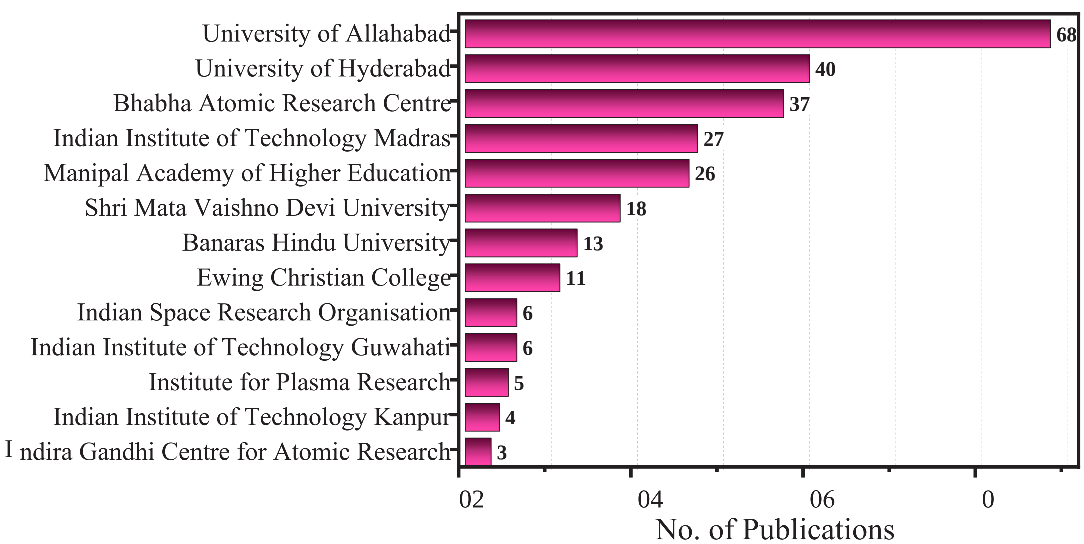

Fig 2. Institute/university wise LIBS research publications in India.

2 Details of the LIBS instrumentation

One of the salient features of this technique is the relatively simple instrumentation. In this technique, first pulsed laser light of sufficient intensity is focused on the sample to produce laser induced plasma (LIP) and then the emission intensities of the LIP are investigated. The essential components of any LIBS system are [4],

a) A pulsed laser to ablate the sample and produce LIP,
b) Optics to route and focus the light from the laser to sample surface,
c) A lens to focus the light onto the sample surface,
d) Collection optics to collect the light emitted from the plasma,
e) A spectrograph to disperse the emitted light, and finally,
f) A detector camera to convert the emitted light into signal counts.

A typical LIBS experimental setup schematic can be found in many of the LIBS articles [7,8]. Different types of LIBS experimental configurations are reported by different groups in India. A configuration here implies the combination of the type of laser, spectrometer, and detector. Table 1 summarizes these configurations. A pulsed nanosecond (ns) Nd:YAG laser has been the overwhelming choice as a light source; however, some researchers also used femtosecond (fs) and picosecond lasers [9-11]. It is well known that the pulse duration of light can influence the properties of the generated plasma and its evolution [12]. While thermal vaporization is the primary ablation mechanism when ns laser is used, Coulomb explosion is dominant with an fs laser. In comparison to the LIP formed by an ns laser, fs LIP has a shorter lifetime and low plasma temperature. In LIBS, to produce LIP, usually a laser beam is focused on the surface of the sample in an ambient atmosphere or in a controlled environment (argon/ nitrogen); and after the formation of plasma, the plasma emissions are collected using collection optics and subject to investigation. Depending on the specific application, other types of experimental configurations have also been employed. For example, Rai *et al* employed a fiber-optic probe to generate the plasma of a molten Al alloy and as well to collect the emission from LIP [13]. Further, in this case the laser was not focused on the surface of the sample but, it was focused inside the molten alloy by inserting the probe inside it. Rai *et al* also investigated industrial water by making a small modification in the LIBS experimental setup [14]. Instead of directly focusing the laser beam onto the surface of the water; they used a liquid jet configuration in which the water was dropped from a height, and the laser was focused onto the flow of water. The laminar flow of water was controlled by a jet pump connected to the tube containing water. Some groups used a standoff geometry where the light was focused on the sample situated at 5-10 m away from the laser source [15].

Table 1 includes the information about the different types of spectrographs used by various groups. Primarily, two different types of spectrometers are utilized, viz; Echelle and Czerny-Turner depending on the application of interest. Several parameters such as spectral range, spectral resolution, and dispersion, gated or non-gated configurations can greatly influence the performance of the LIBS instrumentation. Among these, the Echelle spectrograph which has a higher resolution compared to the Czerny-Turner is a preferred choice. Further, two types of detectors were used by most of the researchers: - charge-coupled device (CCD) and intensified CCD (ICCD) [3,7]. The temporal resolution of the spectrometer is very crucial, especially for quantitative elemental analysis using CF-LIBS and for other temporal studies. An ICCD, though a great choice, as it provides time-gated detection with higher resolution, is costly. However, a CCD is quite less expensive and is smaller in size than the ICCD, but has a tradeoff with resolution. The typical resolution of ~ 0.1 nm is routinely achievable with ICCD-based detectors and of the order 1-2 nm by using the Czerny-Turner spectrographs. Hence, for general-purpose real-time analysis, CCD is convenient. In the initial days, ICCD was preferred; however, in order to make this technique feasible for the applications, it became necessary to develop portable, low-cost systems. Hence, Czerny-Turner based handheld spectrometers were used and found suitable. Junjuri *et al* performed a detailed experiment and showed CCD to be more effective than ICCD for the identification of plastics [20].

Table 1. Details of the LIBS systems reported by different research groups in India

S.No	Institute	Laser (Wavelength, Pulse Duration)	Spectrograph	Detector	Reference
1	University of Allahabad	Nd: YAG (1064/532 nm, ~ 4 ns)	Echelle	ICCD	[16, 17]
			Czerny-Turner	CCD	[18, 19]
2	University of Hyderabad	Nd: YAG (1064/532 nm, ~7 ns,)	Echelle	ICCD	[7, 8]
		Nd: YAG (1064/532 nm, ~7 ns)	Czerny-Turner	CCD	[15, 20]
		Ti: Sapphire (800 nm, ~100 fs)	Echelle	ICCD	[9, 21]
		Nd:YAG(532,~30ps)	Czerny-Turner	CCD	[22]
3	Bhabha Atomic Research Center	Nd: YAG (1064/532 nm, ~7 ns,)	Echelle	ICCD	[23]
4	Indian Institute of Technology Madras	Nd: YAG (1064 nm, ~ 6 ns)	Czerny-Turner	CCD	[24]
5	Manipal Academy of Higher Education	Nd: YAG (1064/532 nm, ~ 6 ns)	Echelle	ICCD	[25]
6	Banaras Hindu University	Nd: YAG (532 nm, ~ 4 ns)	Czerny-Turner	CCD	[26]
7	Indian Space Research Organization	Nd: YAG (1064 nm, ~ 7 ns)	Monochromator	NMOS	[27]
		Diode pumped solid state (1540 nm, ~7ns)	Ablation-corrected holographic reflection	CCD	[28]
8	Indian Institute of Technology Guwahati	Nd: YAG (532 nm, ~10 ns)	Monochromator	PMT	[29]
9	Institute for Plasma Research	Nd: YAG (1064 nm, ~5 ns)	Echelle	ICCD	[30]
10	Indian Institute of Technology Kanpur	Nd: YAG (1064 nm, ~8 ns)	Echelle	ICCD	[31]
11	Indira Gandhi Centre for Atomic Research	Nd: YAG (532 nm, 8 – 10 ns)	Echelle	CCD	[32]

3 Applications

3.1 Quantitative elemental analysis

LIBS is an ideal choice to find out the presence of all the elements in a given sample in a single step by using just an ns laser pulse. However, the concentration of the element must be of the order of ppm or more. Many applications require either the presence of or absence of a particular element in a sample. For example, in toys, heavy elements like Hg are not supposed to be present more than a recommended level, and essential elements like Mg, Fe are required to be present in food items. However, at the next level of applications, the quantitative elemental analysis of different elements present in the sample (parts per million), the absolute mass of each species (ng in a sample), or a surface concentration (nm/cm^2) is needed. Quantitative elemental analysis with LIBS can be accomplished in two ways:- either with calibration curve LIBS or with calibration-free LIBS (CF-LIBS). Here, we review the advances made by Indian researchers on calibration curve LIBS and CF-LIBS.

3.1.1 Calibration curve analysis

LIBS calibration curve represents the relationship between the absolute mass (percentage of concentration) of element and intensity of its emission. Once the calibration curve is constructed, it can be used for quantitative elemental analysis of unknown samples. However, there is a major limitation of the calibration curve LIBS, that the unknown sample should have the same matrix as that of the samples used in constructing calibration curve. Several research articles have been published describing the applications of calibration curve LIBS in various areas. Using the calibration curve technique, Singh *et al* found the elemental contents of species present in human kidney stones [33]. They have considered different stoichiometric samples as reference sample having 50 – 5000 ppm of Cu, Mn, Zn, and Sr in the matrix of calcium oxalate ($CaC_2O_4H_2O$) for the construction of the calibration curve and approximated their elemental concentrations with limit of detections (LODs) 9, 8.5, 17, and 10 ppm, respectively. Pb can be easily absorbed by vegetables and crops via their roots or foliage and, therefore, its quantification is important. Pandhija and Rai quantified the amount of toxic element (Pb) present in the soil sample [34]. They considered pure $Pb(NO_3)_2$ compound as a reference sample to construct the calibration curve and estimated the concentration of Pb with a LOD of ~45 ppm. Calibration curve LIBS has shown to be an effective tool for trace detection not only for solids but also for the elements present in the liquids. The generation and release of toxic wastewater produced in industries is hazardous for the environment. The removal of toxic elements present in the water is vital to make the environment eco-friendly. To troubleshoot this problem, it is crucial to quantify the amount of heavy metals and potentially toxic elements present in the industrial wastewater. To estimate the presence of Cr in the industrial wastewater, Rai and Rai [14] recoded LIBS spectra of 9 different standard Cr samples for the calibration curve, and then estimated elemental concentration of Cr present in the wastewater with LOD of 30 ppm. This result demonstrates the sensitivity of calibration LIBS technique towards the trace detection in liquid samples. Rai *et al* also used the calibration LIBS technique for the accurate detection of elemental concentration of molten Al alloy [6]. They also demonstrated the difference between the molten Al alloy and solid Al alloy by investigating the ratio of the elemental concentrations of both the samples and comparing it with the intensity ratio. In the calibration LIBS, LOD is the most important parameter to be optimized/ improved in order to consider this technique in real-time applications. To improve the LOD of calibration LIBS method, Pandhija *et al* performed an experiment on soil samples for quantification of Cd [35]. Instead of using atomic or ionic emission lines for the calibration curve, they used both atomic and ionic emission intensities of Cd, and it was demonstrated that the LOD is better in this case.

As aforementioned, calibration curve LIBS can be considered as an efficient tool for quantitative elemental analysis, albeit it has many limitations, which are responsible to the failure of concentration estimation in some scenarios. Primarily, it is not possible to obtain a suitable matrix-matched reference sample for every sample. Secondly, the calibration curve measurements strongly depend on the LIBS experimental conditions, which should be similar when an unknown sample is analyzed. However, sometimes it is difficult to attain exact experimental conditions as many factors are involved in it. The calibration LIBS results can be affected by variation in the pulse-to-pulse laser energy, detector gain and linearity, lens-to-sample distance (LSTD), and other experimental factors. Changes in environmental conditions in the atmosphere around the sample or in the path of laser light can also affect the calibration curve. Matrix effect also involves the ablation mechanism, production of plasma, absorption of the laser by plasma, smoothness of the sample surface, etc., which can also affect the calibration curve. Many attempts were made to correct the calibration curve for the matrix effect [36-38], but still, this technique has shortcomings for the implementation in real-time measurements.

3.1.2 CF-LIBS analysis

As an alternative, in contrast to calibration curve LIBS, CF-LIBS has been introduced in the year 1999 to overcome the matrix problem [5]. This technique doesn’t require any matrix-matched standards and can analyze the elemental concentration of the given sample directly. Instead of the calibration curve, this method involves the measurement of plasma electron temperature and electron density for concentration estimation. The CF-LIBS algorithm has been described briefly in the literature [5]. With the passage of time, many advances have been made in the CF-LIBS algorithm, and it was accepted as a valuable tool for many analytical problems, especially for rapid quantitative screening of unknown samples. The potential of CF-LIBS has been demonstrated by applying it to a different set of samples as well as by comparing the results with the standard techniques, although accuracy was poor in some cases. Because of a lack of accuracy and precision, it is not yet ready for real-time use. From a general perspective, CF-LIBS can become a valuable tool for the rapid screening of unknown samples, particularly alloys. In India, various applications of CF-LIBS have been reported, and the details are summarized in Table 2.

Table 2. Quantitative CF-LIBS results for different samples

Sl. No.	Sample	Element	Concentration			Ref
			CF-LIBS	Standard values	Standard type	
1	Dergaon Meteorite	H, N, O, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Co, Ni	(0.27, 0.69, 33.50, 0.77, 13.44, 1.70, 17.42, 0.09, 1.77, 0.07, 0.55, 0.31, 27.90, 0.07, 1.30) wt%	(NA, NA, NA, 0.67, 14.23, 1.20, 17.30, 0.07, 1.19, 0.04, 0.03, NA, 27.73, NA 1.75) wt%	XRF*	[16]
2	Tokamak	Fe, Cr, Ni, Mo, Cu, Mn, Ca, Mg, C	(55.25, 13.96, 10.77, 2.30, 2.24, 2.93, 9.02, 2.71, 0.82) wt%	NA	NA*	[43]
3	Industrial waste (S1)	Cr, Pb	(3413, 907) ppm	(2815, 823) ppm	Calibration LIBS	[46]
	Industrial waste (S2)	Cr, Pb	(2416, 481) ppm	(2400, 500) ppm		
	Industrial waste (S3)	Cr, Pb	(1433, 445) ppm	(1012, 410) ppm		
	Industrial waste (S4)	Cr, Pb	(1058, 323) ppm	(1036, 330) ppm		
	Industrial waste (S5)	Cr, Pb	(8, 382) ppm	(15, 350) ppm		
4	Food supplements (Brand A)	Ca, Mg, Zn, Cu, P, Fe, Cr, Mn, Na, K	(55.54, 20.06, 3.59, 1.15, 9.41, 2.24, 0.57, 2.65, 2.05, 2.75) wt%	(53.85, 23.92, 4.04, 0.54, 12.12, 1.88, 0.03, 0.54, NA, NA) wt%	Certified value	[42]
	Food supplements (Brand B)	Ca, Mg, Ti, Na, K	(64.53, 33.85, 0.26, 0.59, 0.75) wt%	(65, 35, NA, NA, NA) wt%		
5	Lona Salt	Na, K	(22.43, 37.94) wt%	(19.8, 26.9) wt%	AAS*	[47]
	Saindha Salt	Na, K	(37.75, 5.39) wt%	(35.75, 7.9) wt%		
	Tata Salt	Na, K	(67.8, 9.7) wt%	NA		
	Ordinary Salt	Na, K	(51.57, 8.92) wt%	NA		

*NA = Not available, XRF = X-ray fluorescence, AAS = Atomic absorption spectrometry

Usually, CF-LIBS analyses are performed by acquiring the LIBS signal at a particular time delay. Instead of considering a specific temporal delay, Mal *et al* performed the CF-LIBS analysis by acquiring signal at multiple time delays and demonstrated the effect of the temporal window on the quantitative analysis of Cu alloy [39]. They optimized the temporal window for suitable implementation of CF-LIBS by characterizing the transient behaviour of LIP. The experiment was performed in the 0.5 – 5 µs temporal window in steps of uniform temporal delays and observed that 2 – 4 µs is most suitable for the implementation of CF-LIBS.

Pandhija and Rai extended the CF-LIBS application to study coral skeleton [40]. The coral skeleton contains organic constituents identical to the human skeleton. The quantitative results revealed that the CF-LIBS could be useful for *in situ* applications in the field of archeology, forensic science, disaster management, and in other fields where elemental analysis of human bone is required. Further, this technique has been exploited for quantitative analysis in biological/medical/food applications such as human kidney stones (gallstones) [41], appropriate edible salts for kidney patients [33], and food supplements [42]. CF-LIBS has been applied to investigate geological and extraterrestrial materials. Rai *et al* performed the quantitative analysis of dergaon meteorite [16]. CF-LIBS was also employed in the nuclear sectors. Several studies were performed on the various parts of tokamak to quantify the deposition of impurities at different layers [43-45]. Apart from these, CF-LIBS has been applied for environmental monitoring. Solving the water pollution problem is a primary challenge to humankind. Industrial wastewater can pollute the sea and rivers at an extreme level because it contains toxic elements and other hazardous by-products. Thus, CF-LIBS can become an important tool for monitoring the concentration level of heavy metals and potentially toxic elements.

Indian researchers have reported some environmental applications of CF-LIBS in determining the elemental concentrations of toxic elements in various mediums. Kumar *et al* performed the CF-LIBS analysis on industrial wastewater to quantify the presence of toxic elements like Cr and Pb [46]. This particular application of CF-LIBS is very important as it provides the quantitative investigation of impurities present in water and can be useful to study other liquids. Rai *et al* demonstrated CF-LIBS as a powerful tool for estimating the concentration of trace elements trapped in snow collected from different regions of the greater Himalayan range [48].

3.2 Application of machine learning to LIBS data

Various machine learning (ML) approaches for interpreting LIBS data demonstrated it as an excellent tool not only for identification and classification of materials but also elemental analysis for a wide range of applications. The former application is of interest where there is a class of materials, and the objective is identifying a material based on the LIBS spectrum. Such application can range from identification of the type of plastic, identification of the type of rocks, or identification of a high-energy material (HEM). Unlike the elemental analysis, this task is possible with the application of machine learning to the LIBS data. Complex LIBS data has been analyzed using many techniques, including artificial neural network (ANN), principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), support vector machine (SVM), and soft independent modelling of class analogies (SIMCA). As part of its operation, ML constructs a mathematical model using LIBS spectra corresponding to a class of samples. When the identity of an unknown sample's has to be established, its spectrum is presented to the algorithm which generally gives a probability as output. Based on the maximum probability, the class of the unknown sample is given. This is a data-driven approach. In order to take care of the uncertainties that can arise in the data, multiple spectra of all the samples under study are collected. Hence, unlike the CF-LIBS, which can estimate the concentrations of all elements using a single spectrum, this needs multiple spectra i.e., typically more than 30 for better accuracy in the prediction. This type of application is particularly appealing wherever there is a set of samples belonging to a class and the spectra cannot directly distinguish their identity. For example, samples of organic nature that contain Carbon, Hydrogen, Nitrogen and Oxygen as their primary elemental constituents will produce similar-looking spectra with differences only in the intensities. This approach has been exploited in many areas like Geology, waste management, explosive detection and biology etc.

3.2.1 Geological and Extraterrestrial application

Geological and extraterrestrial objects often require real-time investigation. However, in some instances, it can be challenging to use chemical procedures for sample preparation in an uncontrolled outdoor environment. Hence, these kinds of applications require an effective analytical tool for *in situ* examination. LIBS is one of the most suitable techniques for such kinds of applications, because it does not require any sample preparation and is a nearly non-destructive technique capable of real-time applications. LIBS can detect trace elements quantitatively present in the rocks, soil, and water, etc. Further, the standoff detection capability of LIBS makes it worthy for geological and extraterrestrial applications. It can also work in different environmental conditions, including air, argon, vacuum, etc. [7,49,50]. The application of LIBS towards geological and planetary samples was mainly explored by the research group of University of Allahabad, India. ISRO researchers demonstrated compact standoff and portable LIBS system for real-time detection. The setup was placed on Chandrayan-2 rover lunched to investigate the elemental composition of the lunar regolith and pebbles present on the moon surface [28].

Rai *et al* performed quantitative elemental analysis on meteorites [16]. The meteorite is the portion of asteroids that reached the surface of the earth from outer space. A meteorite was recovered from Dergaon village (96°46'48'; 26°46'32") in Assam State, India. The meteorite was subjected to quantitative elemental analysis using LIBS to quantify the elements present in it. For this purpose, CF-LIBS was employed on it, and the concentration of each element present in that meteorite was estimated as mentioned in Table 2. Cd is one of the most toxic heavy metal present in the soil, which can contaminate the vegetable corps and ultimately affects human health. Hence, quantification of Cd present in the soil, especially in the industrial area, is essential. Pandhija *et al* collected soil sample from the industrial area of Kanpur city, India, and performed calibration curve LIBS analysis to quantify the amount of Cd present in the soil [51]. After performing calibration LIBS analysis, they observed that the amount of Cd present in the soil was more than the standard value set by Environmental Protection Agency (EPA). Therefore, it was suggested that it can affect the health of the people residing nearby places through food chain.

Scientists and researchers all over the world are now working on finding life on Mars. Gypsum provides ideal habitat to microbial organisms by protecting them from UV radiations and supporting them for growth and development under critical arctic conditions . Based on some terrestrial evidences, scientists predict the possible presence of microbial life on Mars. Hence, more understanding of the gypsum is essential at the atomic level. Rai *et al* performed a LIBS experiment on different samples of gypsum collected from different geographical locations and environments of formation [52]. The LIBS spectral analysis revealed that all five gypsum samples have similar atomic constituents, making difficult to discriminate them at first glance. To distinguish between them, PCA analysis was performed, which shows a clear separation between them. Further, PLSR analysis was performed to predict the elemental concentrations of major elements (Ca, S) present in the gypsum. Abhishek *et al* reported the analysis of moldavite observed in parts of Central Europe. It is a shocked silica-rich glass formed due to the collision of a chondritic meteorite. The spectroscopic analysis provides the information of the chronology of impact event, nature of source material and the type of impactor (meteorite). PCA has been applied to the LIBS data to demonstrate the classification of chemically diverse geological materials [53].

The elemental composition of planetary surface materials provides information about the present and past conditions under which minerals were evolved. The developing an instrument capable of doing the job for planetary missions is quite difficult becuase, the instrument has to be compact and capable of functioning in changing environmental conditions. Laxmiprasad *et al* at ISRO developed a compact, portable and standoff LIBS instrument which was flown in Chandrayan-2 mission for the elemental investigation of the moon surface [28]. The instrument was primarily developed for both *in situ* and standoff investigation of lunar regolith and pebble's elemental composition present on the moon surface. The instrument was developed by considering all the internal and external factors that can affect the on-field measurements. The instrument was designed to be compact with a total weight of ~1.1 kg and volume (180 mm×150 mm×80 mm) and was placed on the rover. Three major units: (i) ablation unit (AU), (ii) plasma emission detection unit (PEDU), and (iii) processing unit (PU) were combined to form the instrument. The AU comprises of a compact diode-pumped solid state laser delivering energy of 3.5 mJ with 1540 nm wavelength and 7 ns pulse duration for producing LIP. The PEDU includes a compact optical unit having 3-lenses, 2-mirrors and a CCD spectrograph unit to collect and investigate the plasma emission. The function of PU is to decode the command received by the rover, trigger LIBS electronics, capture and process the CCD image. The instrument was subjected to different functional testing like thermo-vacuum recycling test, thermal soak test, vibration test, shock test, etc. after development. The instrument developed can be operated at a temperature (working temperature) of –20 ^{o}C to +55 ^{o}C, and its storage temperature is–40 ^{o}C to +70 ^{o}C.

3.2.2 Environmental monitoring and waste management

With the increase in population, the deposition of hazardous waste products increase significantly in which many are toxic and harmful to the environment. For example, the plastic consumption has risen steadily, and its deposition harms the ecosystem. Industrial waste is hazardous and harmful, which generally pollutes the rivers and sea. Hence, resolution of such a problem is essential. The first step towards solving these problems is to identify hazardous materials and classify them from others. In this application, LIBS can be useful as it can identify and classify different materials at trace levels and with similar chemical compositions, respectively.

Toxic elements present in the water are very harmful to the environment and, hence, to human beings if consumed directly by drinking or through vegetable crops cultivated with the same water. Rai *et al* quantitatively estimated the concentration of toxic elements like Cr present in the industrial wastewater [14]. They used the calibration curve LIBS technique for this purpose and found the concentration of Cr to be 1500 ppm in the wastewater collected from the Cr-electroplating industry. Further, the same group estimated the concentration of Cr in tannery water collected from Kanpur, India. They observed that the amount of Cr is higher than the permissible limit set by U.S. EPA for drinking water [54]. Karpate *et al* optimized the LIBS experimental setup for the detection of elements inside water and demonstrated the usefulness of LIBS for analyzing elements of wastewater pollutants from industries and agriculture fields [55]. Plastic is another environmental pollutant that is nondegradable. With the time the use of plastics per capita in almost every country is increasing rapidly [20]. As it is very difficult to avoid the use of plastics; hence, the only alternative is recycling them to make the environment eco-friendly. In order to recycle, it is essential to distinguish/ sort different plastics; because mixing different types of plastics will lead to chemical reactions between them, resulting in the release of toxic elements, which again can pollute the air. In order to solve this problem, *Junjuri et al* demonstrated a low-cost LIBS experimental setup for real-time sorting of post-consumer plastics [20]. They collected different kinds of post-consumer plastics used in daily life from a local recycling unit. They used various machine learning algorithms like PCA, ANN, etc., with LIBS to identify particular plastic and distinguish them from others. The time duration for the testing was demonstrated to be very less (in order of milliseconds), making the LIBS a fast and low-cost system for sorting of plastics. Moreover, they also demonstrated the potential of femtosecond LIBS combined with various machine learning algorithms for the identification and classification of post-consumer plastics and achieved an identification rate of more than 97% [21]. The assessment of contamination of top soil at urbanized interfluve region of Indo-Gangetic plains has been reported by Rai *et al* [56]. Principal least square regression analysis has been used to predict the concentration of the constituents. Different wavelength regions have been chosen for the calibration models and the results were compared with the concentration obtained from magnetic susceptibility measurements [56].

3.2.3 Industrial applications

LIBS has received great attention from the Indian LIBS community towards the industrial applications owing to its intrinsic properties such as fast response and non-contact nature. It explored different areas, for example, plastic waste recycling, which has a huge impact on the environment and usage of natural resources [20,21,57,58]. The studies have shown that a low-cost LIBS system can detect ten types of plastics [20]. Another study on plastics by Shameem *et al* proposed and demonstrated a hybrid Raman LIBS model for improved classification performance [59]. They also explored the use of this system/configuration for the archeological applications [25]. Its standoff capability has an added advantage for probing the samples in harsh environments such as nuclear plants/industry [23,60,61] and steel manufacturing industry/metallurgy [22,62,63]. Further, the high spatial resolution feature serves as a promising analytical method in metallurgy where mapping of elemental concentration provides the crucial information of the material quality during the production process. It is revealed that optimization of the experimental conditions such as gate delay and energy of the laser pulse is necessary to improve the concentration measurements [64]. Aparna *et al* reported that LIBS could be a useful spectroscopic tool to monitor the high voltage transformer health by determining the copper contamination in the transformer oil [65]. They adopted LIBS to investigate the diffusion of copper sulfide into the insulation of the pressboard and to estimate the diffusion depth [66]. Further, the thermal ageing performance of epoxy aluminium nitride nanocomposites was also studied [67], and machine learning (ML) algorithms were utilized for the classification of thermally aged and virgin pressboard specimens [68]. Another research group explored LIBS to measure ash content in coal refineries [69,70]. They also studied the effect of the surrounding environment/gases such as N_2, Ar, He, & atmospheric air and their flow rate on the characterization of the coal samples. It has been demonstrated that the accuracies of the carbon measurements are higher in the presence of Ar [70]. Quantification of dopants and impurities in glass by LIBS is another area of research explored by a research team from Manipal academy of higher education. LIBS is an essential diagnostic tool for the glass manufacturing industries [71,72]. Devangad *et al* employed a UV Nd:YAG laser (ns) as the excitation source for studying the homogeneous distribution of Mn in glasses and for the concentrations measurements [73,74]. They have also characterized the rare-earth-doped glasses using LIBS [75].

Quantitation of constituents of the nuclear waste [23], fuel [76], and diagnosis of fusion plasma-facing components (PFCs) are primarily explored by the Indian researchers. BARC group has mainly focused on the first two aspects and the last one was explored by the researchers from the University of Allahabad. Singh *et al* have quantified the Uranium in the nuclear waste glass [23]. This study mainly focused on the application of the univariate and multivariate data analysis techniques for Uranium quantification. It has been demonstrated that the analytical merit for the univariate model is superior for the data recorded with the Czerny turner spectrometer, whereas Echelle spectrograph data has shown better results for the multivariate analysis. Singh *et al* have also presented the characterization of the power reactor thoria reprocessing facility waste glass using the PLSR algorithm. It has been demonstrated that the analytical capability can be increased by truncating the spectrum to only utilize relevant pixel intensities based on the relative PLSR coefficients [77]. Further, LIBS calibration curve measurements were performed to estimate the Uranium in thorium-uranium mixed oxide fuel samples which is an important step in chemical quality assurance of nuclear fuel materials [78]. They have also explored the dependencies of laser wavelengths (1064, 532, and 266 nm) on the composition measurements. It is revealed that 266 nm excitation has shown better results and achieved accuracy satisfied the nuclear industry acceptance criteria range [76].

Plasma interacts with the walls during the discharge process in fusion devices and leads to the erosion of PFCs. These eroded materials get accumulated which need to be analyzed and removed from the reactor for better performance. *Maurya et al* critically reviewed the application of LIBS for the analysis of PFCs [79]. Various impurities such as Ni, Cr, Fe, Mn, Ca, Mo, Cu, and Mg on the Aditya tokamak flange surface were detected. The experiment was performed by focusing twelve successive laser pulses on the flange to analyze the different layers formed on it. Further, the concentration measurements were also performed by using the CF-LIBS algorithms and the results were in good agreement with the concentrations of the tokamak wall constituents [44]. The mapping of these chemical constituents on the different parts of the flange is also reported [80]. Moreover, Maurya *et al* have also proposed and demonstrated a new LIBS experimental design/setup for online analysis of the impurities on the PFCs of a tokamak [81].

3.2.4 Defence applications and standoff detection

Terrorist operations can be prevented and countered by identifying high energy materials (HEMs) and explosives, which play a vital role in protecting the population of any nation [8,82]. The application of LIBS for the separation of explosives was explored by two research groups in India at the University of Hyderabad [10,15]. Most of explosives such as RDX, TNT, HMX, and NTO, etc., are organic compounds that have similar atomic constituents in their chemical structure, and the spectra look the same, and consequently, their identification becomes a challenging task. Moreover, the interaction of the plasma species with the ambient environment further complicates the problem. However, various analytical approaches such as intensity ratios [83], scatter plots [15], and ML algorithms [8] are explored to tackle the problem of explosive detection. Also, the effect of the surrounding environment on plasma formation has been studied using LIBS to understand the plasma reaction pathways [84-86]. It has been reported that molecular emissions observed in the earlier times of the plasma expansion are prominent in fs LIBS. CN/C_2 molecular intensity ratio elucidated the effect of functional groups position on the molecular emissions. These correlation studies enhance the knowledge of plasma formation routes and improve the classification rates of explosives with similar atomic signature [86]. Also, an attempt has been made to understand the decay mechanisms with respect to the molecular species formation pathways in various ambiances. It has been found that CN/C and CN/N ratios were prominent in air and nitrogen atmospheres [84]. A comparative study based on the ns and fs LIBS has suggested that the fragmentation or atomization ratio can serve as a good performance metric for the discrimination of HEMs [87].

Also, a ratio-metric approach involving various atomic intensity ratios such as O/N, H/N, O/H, and H/N corresponding to different samples were investigated and a 3D classification model was developed for the identification of the explosives. Finally, a 3D classification model was developed for the identification of the three explosives [83]. In another study, C/H and H/O ratios were evaluated for the discrimination among the samples and H/O has shown better correlation compared to the C/H ratio [8]. A new approach, i.e., synthesizing the spectra based on the few experimental LIBS spectra combined with ML algorithms are proposed and examined for the classification of five explosives with consuming minimal amount of sample. It has a huge impact on the reduction of the sample consumption, which is a limiting factor especially for the explosives [88]. In another investigation, a judicious feature selection approach based on the genetic algorithm and prerequisite knowledge of the sample stoichiometric composition has shown promising classification of the five explosives [89]. This feature selection approach has shown the feasibility of utilizing a discrete filter-based detector and thereby enabling a compact and cheaper LIBS system for field operations.

Standoff identification plays an essential role in the real-time analysis of the explosives, where the proximity of the sample to the operator is a serious concern because of safety precautions. Different standoff LIBS (ST-LIBS) configurations were investigated depending on the application of interest [8,10, 15]. Conventional ns laser beam suffers from diffraction and adversely affects the signal-to-noise ratio (SNR) of LIBS measurements. On the contrary, fs laser pulses can propagate into long distances and capable of delivering higher energies via the phenomenon of filamentation. Fs LIBS has demonstrated the identification of a set of HEMs in standoff mode where PCA has shown excellent separation among the samples [10]. However, the high cost and comparably larger size of the fs laser system makes it difficult to use in real-time applications. Rajendhar *et al* performed an ns ST-LIBS measurement at 1 m and the spectral emissions were collected with a single lens and Echelle spectrograph equipped with an ICCD. These initial studies have shown the classification of five explosives [8]. Further, they have extended the probing distance to 6.5 m and investigated ST LIBS on various samples (5 explosives and 19 non-explosives) [15]. To develop a low-cost, compact detection system, a handheld non-gated Czerny turner CCD spectrometer is utilized. A systematic evaluation and optimization of focusing and collection systems have been done for improving the performance of the developed ST-LIBS system. The identification accuracies of over 98 % were achieved among the explosives with the ANN algorithm. Despite the huge similarities in the spectral features of the explosives and non-explosives, the correct labelling rates ~ 97 % were demonstrated [15].

3.3 Biological and biomedical application

The elemental information of many samples such as calcified tissues, pharmaceuticals, plants, seeds, and fruits, etc. is extremely useful for biological and biomedical applications of LIBS. In such cases LIBS can be used to make the analysis easier and faster. Several advancements towards these applications made by Indian researchers are summarized below.

LIBS can help in the detection of the carious tooth and distinguishing it from the healthy tooth by quantifying the amount of Ca, Ph, Ca, Mg, Cu, Zn, Sr, H, and O, etc., present in the human tooth [90]. In addition, identification of the carious affected part of a particular tooth is also possible with LIBS [91]. Simultaneously, morphological and anatomical studies of human kidney stones (gallstones) at the atomic level are possible using LIBS [33,49,92-94]. For kidney patients, the choice of suitable edible salt can be made by quantitative analysis of different salts using LIBS [47]. It has also been observed that LIBS can be useful for diabetic management in various ways [19,95-98].

The analysis of plant samples is generally difficult because they involve an acid digestion-based sample preparation process for accurate analysis of micronutrients. LIBS can act as a fast and accurate tool for micro-logical and micro-algal investigation of various plant samples [17,18,99-103]. The toxic and antioxidant elements present in the plants and seeds can also be quantified [97,104]. The presence of minor and major elements in the seeds/ fruits/leaves/ roots of various plants like *Emblica Officinalis*, *Cynodon dactylon, Momordica charantia,* etc., can be detected and quantified [98,103,104]. Moreover, deposition of trace amount of Si on the leaf of the Saccharum species can be identified using this technique. Tripathi *et al* investigated the deposition of Pb and Si on different parts of the wheat seedling [102]. They observed that the Pb accumulation is greater in the roots.

Quantification of approved limits of Toxic elements present in any food item is essential. LIBS can be useful to detect toxic elements present in any food item even at a trace level [105]. Since LIBS is capable of identifying and quantifying elements present in any food item, therefore it can be considered as a useful tool in the food sector industry. Indian researchers performed some experiments for detecting and quantifying the toxic elements present in the foodmaterials [105,106]. Tripathi *et al* detected and measured the elemental concentration of Si and Cr accumulation in the wheat seeds [105]. Agrawal *et al* investigated the impurities present in the different colors of ice balls [106]. They also quantitatively estimated the elements present in different food supplements [107].

4 Conclusion

LIBS is in a state of great vitality as an analytical tool, particularly for industrial, environmental, biological, and defence applications. This article provides a review of advances made by the Indian research community towards various LIBS applications and as well describes also the improvements made in the experimental setup and analytical strategies for various real-time applications. This technology can be put in practical use in environmental monitoring and waste management to identify harmful substances in industrial waste and sort disposal plastics for recycling. Additionally, it can also be utilized in environments like nuclear plants/industries and steel manufacturing/metallurgy to detect contaminates and dangerous substances. Among other uses, it can be used to diagnose diseases, provide online feedback for surgery, and monitor trace elements present in the human teeth and other calcified tissues. Further, LIBS may also be used to detect the components in biological plant samples without any sample preparation, to monitor the presence of harmful substances in food products. and as well to categorize HEMs and explosives with a 95% accuracy rate. LIBS standoff detection capacity, makes it the most reliable tool for remote detection of explosives and HEMs.

Acknowledgement

Authors acknowledge Defense Research and Development Organization (DRDO), India for funding.

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[*Received*: 01.06.2021; *revised recd*: 25.06.2021; *accepted*: 30.06.2021]

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