Indian Journal of
Advances in Chemical Science

Article

Review of Recent Advances and Applications of Laser-induced Breakdown Spectroscopy in Environmental Monitoring

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ABSTRACT

Analysis of geological and environmental materials is the current and growing requirement in the recent years. Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic technique based on atomic emission and has been used as an analysis tool of minerals, rocks, soils, sediments, etc. LIBS has the advantage of faster analysis than other techniques with a typical detection limits of elements. Applications of LIBS have been growing rapidly and continue to be extended to a broad range of materials. The paper presents the applications of LIBS exclusively for the analysis of environmental materials. However, before discussing the reviews on LIBS applications on environmental monitoring; a brief overview of the fundamental of the LIBS analytical technique, double-pulse and femtosecond LIBS methods, its instrumentation, sampling techniques and analysis of minerals, rocks, soils, sediments, and other natural materials are presented. LIBS technology is the increasing requirement for the quality control in the environment due to the various pollutants. The review focuses on the most relevant advances and is reported in different sections relative to the analyzed objects.

Key words: Environmental monitoring, Laser-induced breakdown spectroscopy, Neodymium-doped Yttrium Aluminum Garnet laser, Plasma.

1. INTRODUCTION

The applications of laser-induced breakdown spectroscopy (LIBS) have been widely studied in versatile fields such as environmental monitoring [1-4], biomedical applications [5], mars [6,7], and space exploration [8]. LIBS is a form of optical excitation in which the sample is vaporized by a high energy laser pulse and forms a luminous plasma. The light from the plasma is temporally resolved (to discriminate against the continuum emission from the plasma) and wavelength dispersed to obtain information regarding the composition of the material that was laser vaporized. This technique has received considerable attention in recent years as a versatile analytical technique, particularly in environmental applications, as it offers several advantages: (a) Small sample size required for analysis, (b) direct analysis of inhomogeneous materials (without the need for any sample preparation), and (c) small turnaround time between sample submission and analysis. All the above advantages become particularly attractive in the analysis of environmental samples. In this method, the sample is first vaporized by a focused, high energy laser pulse. Usually the fundamental (1064 nm) or the second harmonic (532 nm) of a YAG laser, with pulse energies in the realm of 20–50 mJ/pulse is used. Emission from the laser plasma is sampled through a collection lens and focused onto a spectrometer. As emission in the first ~100 ns after the laser pulse, is dominated by the continuum emission from the plasma, the detection must be delayed, for this light to decay. The latter part of the emission is dominated by emission from the elements of interest in the analyte sample, which must be selectively detected. The detection system of the spectrometer must therefore be equipped to gate the observation suitably. Further, for the detection system to have multielement capabilities, an array type detector, such as a charge-coupled device array is necessary (instead of a single channel photomultiplier). The elemental composition determined by the wet chemical analysis process has major limitations such as the detection limit, time consuming, and does not provide an immediate feed-back to the environmentalist. The environmental monitoring groups thus to be supported by developing an online process for the estimation of elements. The elements that were estimated included transition metals, lanthanides, noble metals, and p-block elements, with detection limits in the realm of 100–500 ppm. Any analytical method employed for the environmental monitoring must possess the following desirable characteristics: Speed of analysis, on-line capability, amenable for remote operation, user-friendly, accuracy, and precision. In addition to these characteristics, LIBS has also been used for the analysis of samples of any state such as solid [9], liquid [10], or gas [11].

2. EXPERIMENTAL

2.1. Experimental setup

Figure 1 shows the schematic of the experimental setup. It may be noted that the laser, lenses, beam steering optics, X-Y table for sample restoring, and the multichannel spectrometer are required for the LIBS set-up.

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ISSN NO: 2320-0898 (p); 2320-0928 (e)
DOI: 10.22607/IJACS.2023.1104001

Received: 22th July 2023;
Revised: 28th October 2023;
Accepted: 26th November 2023.

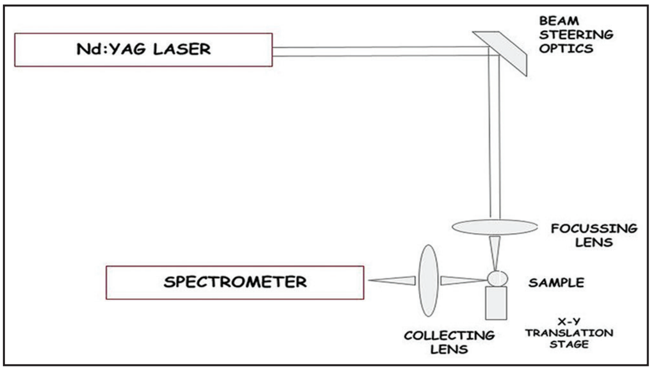

Figure 1: Schematic representation of a typical laser-induced breakdown spectroscopy set-up.

2.2. Double-pulse LIBS and femtosecond LIBS

The double-pulse LIBS technique has been used for the analysis of synthetic glasses, rocks, and steels [12]. The group has combined two Neodymium-doped Yttrium Aluminum Garnet lasers emitting at 532 nm in the collinear beam geometry to carry out double-pulse experiments. The suitability of the double-pulse LIBS for different materials has been analyzed based on the advantages and the limitations of the double-pulse LIBS for analytical purpose. The trace level detection of carbon has been measured in standard steel samples using single-pulse LIBS (SP-LIBS) and long-short double-pulse LIBS (LS-DP-LIBS) [13]. The quantitative analysis of carbon in steel samples has been achieved by, long-short double-pulse LIBS (LS-DP-LIBS) with pretreatment pulses. The quantitative analysis of Pb heavy metal in soil has been analyzed using a femtosecond-nanosecond double-pulsed LIBS (fs-ns DP-LIBS) with a delay of 800 µs between the two lasers [14].

The femtosecond LIBS (fs-LIBS) of Cu with the sample preheated to different temperatures (22–120°C) has been reported Wang *et al.* [15]. They have observed the dependence of the spectral intensity of the plasma emission with the target temperature and thus the enhanced the detection sensitivity of femtosecond LIBS. Zhao *et al.* studied the femtosecond laser filamentation-induced breakdown spectroscopy (FIBS) combined with chemometrics methods for soil contamination monitoring application and thus improved the accuracy of heavy metal soil quantitative analysis [16]. The influence of femtosecond pulses in the analysis of solid samples such as brass, copper, aluminum, and silicon (with different buffer gas and pressure) has been reported by Mateo *et al.* [17]. The spectra recorded under air or argon atmosphere showed line broadening particularly at high ambient pressure.

3. ENVIRONMENTAL MONITORING APPLICATIONS PERCEIVED WITH LIBS

LIBS as a tool for environmental monitoring also finds wide application, in addition to industrial and nuclear applications [18], geological [19] and archeological surveys [20], and defense applications [21]. Viana *et al.* used the LIBS technique for the detection of bioaccumulated Fe and Pb in scales of aquatic species, *Salminus brasiliensis*, *and Prochilodus lineatus*; which showed the technique as a promising tool for environmental monitoring [22]. The analysis of impurity elements such as molybdenum (Mo), tungsten (W), carbon (C), copper (Cu), lithium (Li), titanium (Ti), silicon (Si), iron (Fe), and chromium (Cr) deposited on the test tiles was studied [23]. LIBS has showed effective in the depth-resolved identification of impurities deposited on the tiles. The analysis of solid fertilizer samples for the different contaminants (Cd, Cr, and Pb) and other micronutrient elements (B, Cu, Mn, Zn, Ca, and Mg) has been studied using LIBS [24]. One of the major applications studied with this equipment is the evaluation of elemental composition such as minerals and metal on vegetal tissues [25]. While remote online analysis can be estimated using pulsed excimer laser ArF, fiber optics, and a high resolution spectrometer, univariate and multivariate analysis exists for in-depth information from the LIBS experiment. Hence, this technique is attractive as it has the potential to be adapted for a remote, on-line measurement. In addition to the above major application, there are various other applications related to the industries that have been described in the literature, some of which are mentioned below.

Trautner *et al.* demonstrated that the vulcanizing system of rubber can be quantified under ambient conditions with LIBS and the technique as process analytical sensor by itself [26]. Another application of interest to industries is the measurement of coal composition through the analysis of spectral features corresponding to the various classifications of coals [27]. LIBS has been used for the analysis of trace heavy metals in soils [28]. LIBS-assisted by laser-induced fluorescence (LIBS-LIF) was utilized for the selective enhancement effect of spectral intensities of the interfered lines. Likewise, estimation of Pb in soils has been reported with detection limits in the range of 0.6 ppm. LIBS has also been employed for the analysis of elemental composition changes in battery electrode materials to establish the quantitative elemental ratios of Ni, Mn, Co and trace transition metals, Cr, Mo in cathode material samples, allowing, therefore, for process control and quality assurance of the battery electrode materials involved in automotive and various electronic devices [9]. Analysis of proteins in wheat flour and whole meal samples melts has also been achieved using LIBS, which has application as a quality parameter in terms of price, nutritional value, and labeling in industries [29]. LIBS has also been used for monitoring elements in waste printed circuit boards (PCB) as recycling source [30]. The elements that were estimated, included Al and Pb and the sample analyzed contain Al in the realm of 3 and 55 g/Kg. Isotopic analysis of Li and U was estimated by LIBS and laser ablation-tuneable diode laser absorption spectroscopy (LA-TDLAS) [31]. For example, $^{235}U/^{238}U$ ratios have been measured using this method and thus the possibility of rapid elemental and isotopic analysis across the nuclear fuel cycle. A portable LIBS spectrometer is also available for field analysis [32].

4. CONCLUSION

The detection of elements at trace level has been reported in various works. The major highlight of the review is the observation of spectral lines of elements by suitably tailoring the ambient conditions such as spectral interferences using time-delayed detection, thus serving as an environmental monitoring tool. The result on the effect of hybrid LIBS such as LA-TDLAS and LIBS-LIF on the spectral measurements has greatly aided in extending the applications of environmental monitoring. This review reports the use of LIBS for the application of the technique in environmental monitoring.

5. ACKNOWLEDGMENT

The author would like to acknowledge fruitful discussions with research scholars from the research group of the Radiochemistry Laboratory, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu.

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