Review: Laser-Induced Breakdown spectroscopy (LIBS) a promising technique, its limitations and a proposed method

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REVIEW: LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) A PROMISING TECHNIQUE, ITS LIMITATIONS AND A PROPOSED METHOD

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Abstract. Laser Induced Breakdown spectroscopy (LIBS) is an extremely potential spectroscopic analytical tool. A highly focused laser bean stiochiometerically ablates the surface of the material in the form of a plasma plume. Excited species in the plasma plume emit their characteristic wavelengths upon de-excitation which are collected, dispersed and analyzed for qualitative and quantitative analyses. Basic LIBS setup includes a laser, target sample, optical fiber and a spectrometer. However it has been used in different configurations like single-pulse and double pulse configurations. LIBS has several advantages over other currently practiced analytical techniques in terms of higher resolution, better limit of detection (LOD), negligible sample preparation etc. Despite of all these advantages it is suffering from poor accuracy and reproducibility of results due to uncontrolled atmosphere around the targeted sample and variations in other experimental parameters. In order to improve reliability of LIBS in terms of accuracy and reproducibility we have designed a methodology for experimentation under controlled environmental conditions inside an especially designed ablation chamber. We will make use of multiple simultaneous laser pulses, which are supposed to play a significant role in improving the analytical accuracy of LIBS particularly for non homogeneous samples. In this article we will briefly review the basics of LIBS, its types, common instrumentations, advantages, limitations applications and at the end our proposed methodology.

Keywords: LIBS instrumentation; applications; advantages; limitations; accuracy proposed methodology

Abstrak. Spektroskopi leraian aruhan Laser (LIBS) adalah alat spektroskopi yang berkeupayaan tinggi bagi penganalisaan unsur. Ia mengambil kelebihan dari tenaga laser terfokas padat yang mampu menghasilkan pengkakisan unsur ke atas permukaan sebarang jenis bahan dan membentuk kepulan plasma. Rencam yang teruja dalam kepulan plasma terkakis memancarkan panjang gelombang ciriannya semasa pengujaan diambil, disebar dan dianalisis untuk analisis kualitatif dan kuantitatif. Susunatur paling mudah LIBS adalah terdiri daripada laser, sampel kajian dan spektrometer. Bagaimanapun ianya telah digunakan dalam beberapa susunatur

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berbeza seperti hentaman tunggal dan susunan hentaman berganda. Ia mempunyai beberapa kelebihan berbanding teknik-teknik analisis lain yang diamalkan pada masa kini dari segi resolusi yang lebih tinggi, had pengesanan lebih baik (LOD), penyediaan sampel mudah dan sebagainya. Walaupun dengan semua kelebihan tersebut, teknik ini cuba mendapatkan ketepatan dan kebolehulangan semula keputusan kerana suasana yang tidak boleh dikawal di sekitar sampel sasaran dan perubahan pada parameter eksperimen yang lain, yang mana, akan menjejaskan pelepasan rencam plasma. Dalam usaha untuk meningkatkan kebolehpercayaan LIBS dari segi ketepatan dan kebolehulangan semula, satu kaedah direkabentuk untuk eksperimen suasana terkawal di dalam ruang terutama reka bentuk kebok pengkakisan. Kita akan menggunakan beberapa hentaman laser serentak, yang dipercayai memainkan peranan penting dalam meningkatkan ketepatan analisis LIBS terutamanya untuk sampel bukan homogen. Dalam kertaskerja ini membincangkan secara ringkas asas-asas mengenai LIBS, jenis-jenisnya, instrumen biasa, kelebihan, aplikasi dan pada akhir metodologi yang dicadangkan.

Kata kunci: Instrumentasi LIBS, permohonan, kelebihan, kekurangan, ketepatan, kaedah yang dicadangkan

1.0 INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is a promising technique for elemental analysis of any kind of material. It is a versatile technique that can be applied anywhere in any atmosphere [1]. Even it can be applied in hostile environments like furnaces [2] and nuclear reactors [3]. It demands very little or even no sample preparation. Therefore, it is not a demanding technique rather it can be called as a giver; it provides information about the composition of any kind of material without demanding tedious formalities. However, for quantitative analysis all conditions are not suitable because of variations in emission signals from plasma which depend on several factors involving ambient atmosphere, pressure [4], laser pulse energy, gate delay, gate width etc [5,6]. For accurate quantitative analysis we need to optimize all these parameters very carefully. LIBS has been applied to a variety of materials for diverse applications ranging from alloys to artifacts [7] and [11], gases to solids [12], [13], [14], [15], [16], [17] and [18], soils to vegetables [19] and [20], animal tissue to space exploration [21], [22], [23] and[24]. Although it has not yet become a standard technique and is not as mature as ICP-OES, scientists are watching great potentials in it for being a strong competitor in the market [25] and [26]. Lots of work is being done for the improvement of LIBS, however it is still struggling with its accuracy and precision [27] and [28]. Scientists from all around the world are working and contributing to this technique, developing several methods and configurations to get better and reliable results. These mainly include different configurations of single pulse LIBS and multiple-pulse LIBS [29]. Each has its own figures of merits and levels of instrumentations.

Here is presented a brief review of LIBS techniques including our proposed methodology and discussion about their principles, experimentations, advantages and disadvantages. It would be very useful for gaining technical understanding of different configurations of LIBS technique their pros and cons and usefulness for particular applications.

1.1 Basics of Technique

Laser-Induced Breakdown Spectroscopy (LIBS) works on the principle of Optical Emission Spectroscopy. It uses laser produced plasma as a source of atomic and ionic emissions. A highly focused pulsed laser beam produces breakdown on the material surface and ablates the material which takes the form of highly ionized gas named as plasma. Excited species in the plasma give out characteristic radiations upon de-excitation; these radiations behave as spectral signatures for particular elements [1], [29] and [30]. Radiations emitted from the plasma are overlapped with each other, so, to distinguish the emitted wavelengths these radiations should first be separated as individual lines for subsequent analysis. For this purpose a monochromator or spectrometer is used as dispersive element that separates the radiation into its constituent wavelengths that are accumulatively recorded as a spectrum. This spectrum is of inevitable importance, it contains information about the plasma characteristic parameters i.e. electron density, plasma temperature, localized thermal equilibrium etc. and also reveals the presence of various elements and their concentration. The identification of species, within the plasma, is made on the basis of emission wavelengths. Whereas intensity of the emission lines (emitted wavelengths) provide information about plasma temperature and concentration of the particular element. However from width of the emission line electron density in the plasma can be calculated. Boltzmann and saha-boltzmann equations are normally used for the estimation of electron density and plasma temperature respectively [29] and [30].

2.0 TYPES

With the passage of time the technique of LIBS got modifications accounting for improvements and suitability regarding different applications. Two basic types of LIBS are Single-Pulse and Multiple-Pulse LIBS, the later includes from two to several number of laser pulses.

Single-Pulse LIBS (SP LIBS) uses only one laser pulse for the formation of plasma and subsequent spectral analysis, that's why it is named as single-pulse LIBS. It is the simplest and most basic type of this technique. The instrumentation for single-pulse LIBS is very simple, it does not require complex alignment of optical components. Using one laser pulse means the production and usage of only one plasma plume for spectroscopic studies. Since only a few micro-grams [31] of the material ablate in single pulse ablation, so, it can practically be called as a non-destructive technique for material analysis at micro level. Due to its capability of non-destructive testing it finds its applications for delicate and precious samples like antique artifacts [7]. However due to the involvement of very small quantity of mass single-pulse LIBS is not suitable for the analysis of bulk material.

Diverse applications of SP LIBS are found in literature. SP LIBS has its importance in some unique applications. It has got ability of non-destructive analysis of cultural heritage art and artifacts [32]. It can provide answers to several questions about forgery, origin and age of historical samples through material identification or pigment analysis [31]. Some particular applications contain analysis of the historical documents [33], parchment [34], pigment investigation of historical paintings, analysis of restoration process and cleaning of antique items [35] and [36].

One of the main issues with SP LIBS is lacking of shot to shot reproducibility. Several factors cause fluctuations in the measurements with single pulse. These mainly include the laser pulse coupling with the sample surface and variations in the plasma temperature [31]. Along with lacking in reproducibility single pulse LIBS provides greater limits of detection and comparatively poor precision [29]. The problems mentioned above are disadvantageous for quantitative analysis, however do not impose any limitation on qualitative analysis.

Multiple-Pulse LIBS makes use of two or more laser pulses for plasma production and excitation. The use of double or multiple pulses in LIBS is of higher interest because it results in significant enhancements in signal intensities. It is tried in various configurations and geometrical arrangements. These comprise:

1. Multiple pulses within the same flash lamp pulse
2. Collinear beams from two lasers focused on the same spot in the target
3. Orthogonal beams, typically with one beam perpendicular and one parallel to the surface
    i. Where the pulse for the beam parallel to the surface is first in time forming an air spark (pre-ablative)
    ii. Where the pulse for the beam parallel to the surface is second, and reheats the material ablated by the first pulse (reheating)

Schematic illustration of two configurations of double-pulse LIBS is depicted in Figure1. One pulse is used for the production of plasma while the other is used to excite it. This enhances the signal intensities a great deal as compared to single-pulse LIBS [37]. The interpulse duration is of great importance in this technique. Improvements, as compared to single pulse configuration, in terms of signal enhancements, signal to background ratio, matrix dependency and other figures of merit have been observed in double pulse configuration as for example demonstrated in ref [38] and the references therein. Another benefit of double-pulse LIBS, when used in pre-ablative configuration, is the greater mass removal as compared to that quantity removed with two individual laser pulses of same energy [29].

3.0 ADVANTAGES

LIBS is a very useful technique for elemental analysis of any type of material under any atmosphere. It requires very small or even no sample preparation. Although it is suffering from low accuracy but still it possesses the ability of easy and rapid quantitative analysis. One of its attractive features is the simultaneous multi-elemental analysis that it can perform with high resolution scanning of the material. It is very sensitivity technique and capable of producing low limits of detection (LOD). LIBS can be considered as a non-destructive technique since it involves negligible amount of mass for analysis (micro). LIBS can, in principle, be applied in any atmosphere, even in hostile environments, therefore, it is very handy for in-situ analysis and in-process monitoring of the product. Besides all other advantages there are two other unique features of LIBS, namely remote and stand-off. These enable the LIBS to analyze materials at remote locations (e.g. around the obstacles or in physically in-accessible locations) and also those in the line of sight but several meters away from the equipment [1], [29] and [30].

These abilities of LIBS raise its worth among other analytical techniques and make it a very attractive analytical tool. With such great advantages it pulls the attention of scientist's community around the world for performing experimentations to further explore and improve its features.

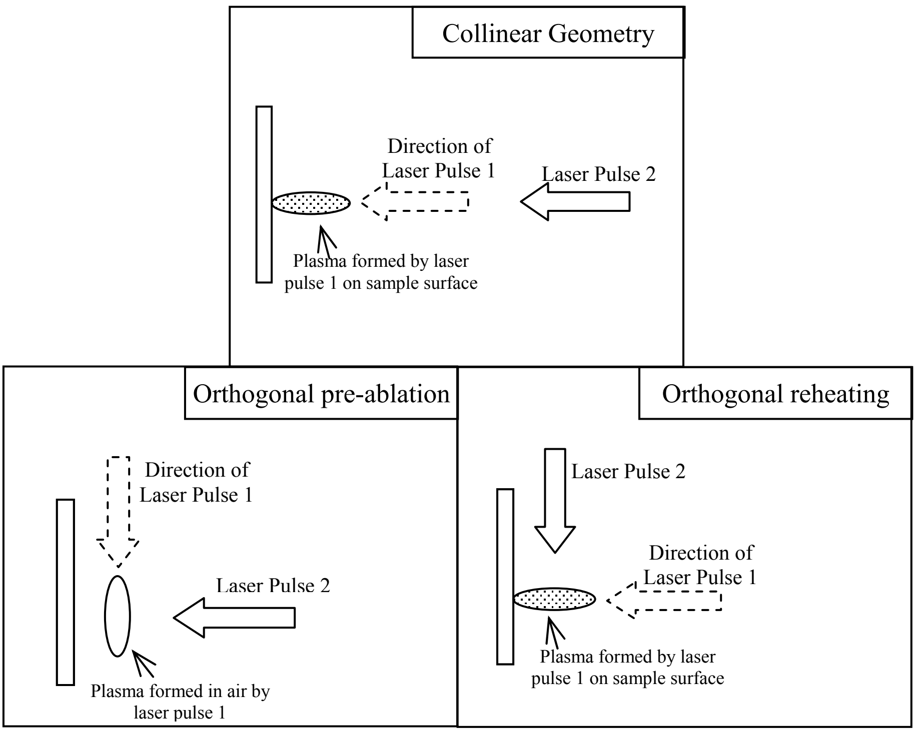

Figure 1 Geometry of double pulse LIBS in different configurations as mentioned with each

4.0 LIMITATIONS

Laser induced breakdown spectroscopy is no doubt has potentials of being excellent technique for multi-elemental, high resolution analysis of any kind of material. However it has got some limitations that are biggest constraints in the path of LIBS for reliable analysis. These include accuracy and precision, these should be seriously tackled to make this technique a standard tool for authentic analysis. The involvement of very small amount of mass is quite valuable for micro analysis, but for bulk analysis it becomes problematic especially for inhomogeneous samples.

There are several factors that impose limitations on accuracy and precision of this valuable technique. Ambient conditions, experimental parameters for spectral measurements, matrix of the sample are the factors that are responsible for obtaining informative or useless spectra. Experimental parameters like laser pulse energy, gate delay, gate length are very important for getting reliable results.

5.0 PROPOSED METHODOLOGY

We are working on LIBS to study the possible improvement in its accuracy and precision. Here we propose to study the LIBS in a controlled environment using multiple simultaneous laser pulses. It would be very useful in carefully studying several factors hindering the accurate responses of LIBS for precise results. We will be able to study the best ambient conditions involving nature of the medium, its pressure and flow rate, best timing parameters including gate delay and gate width, useful lens to sample distance (LTSD) and most suitable position of the fiber optic cable (FOC) for efficient light collection.

For gaining control over the ambient atmosphere a specially designed sample chamber would be very beneficent. The sample chamber must include sufficient utilities to allow us to change the ambient gas, its pressure and flow rate. The schematic diagram of a sample chamber is shown in Figure 2. It has an optical bench inside, three laser/view ports, one electrical connections port and nozzles for connecting gas cylinder and vacuum pump.

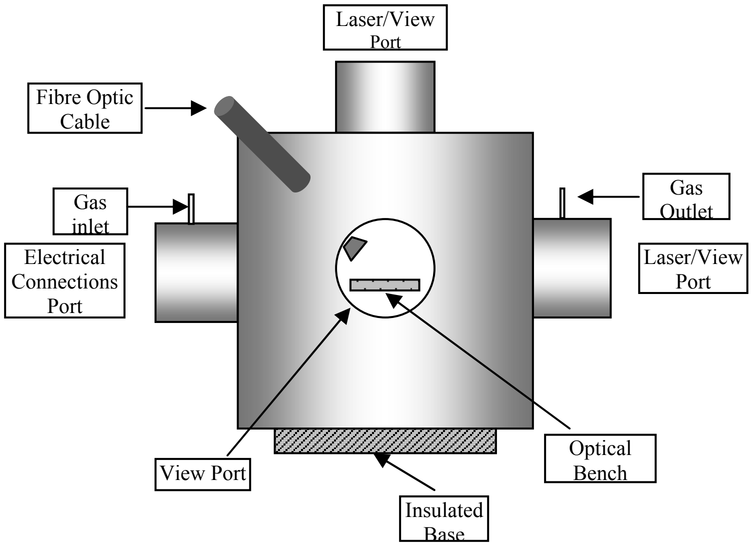

Figure 2 Schematic diagram of the chamber designed for our experiment

Nd:YAG laser can be used for ablation of a wide range of materials and is very frequently used in experiments involving laser ablation. One of its benefits is that it belongs to the class of solid state lasers and, contrary to gas lasers, it shows stability against pulse to pulse energy fluctuations. Therefore, in our methodology we propose the use of Nd:YAG (1064nm, 250mJ, 4ns, 50MW) laser for generation of multiple simultaneous pulses and collection of analyte material from different sites of the sample surface through ablation. Sample ablation and collection of the resultant spectra would be performed under stable ambient conditions inside the chamber for each measurement, and measurements will be made for different sets of parameters of ambient atmosphere. To study the precision the procedure will be replicated with identical experimental conditions for every iteration. A specialty of this experimental study lies in the use of only one laser and splitting its beam into two or more pulses (nearly equal in energy) depending upon the laser pulse energy. Schematic diagram of the experimental setup is given in Figure 3.

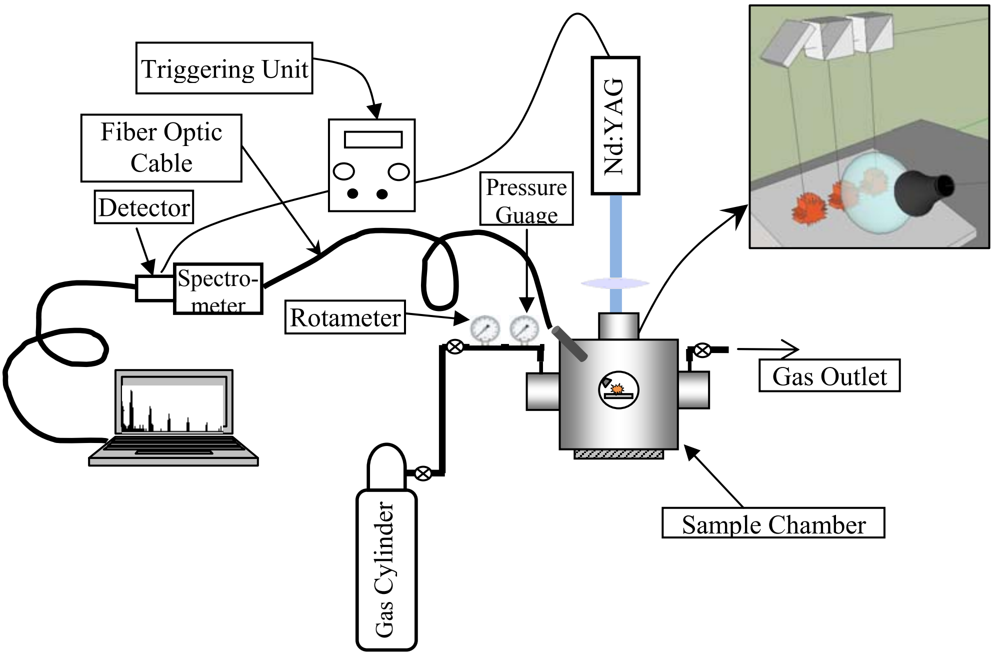

Figure 3 Schematic diagram of experimental setup, inset describes the geometry inside the chamber

6.0 SUMMARY AND CONCLUSION

Summarizing the above discussion, laser induced breakdown spectroscopy is an attractive technique for elemental analysis of materials. It is under the process of evolution since the advent of laser. LIBS has single pulse LIBS as the fundamental while and during evolution it finds different configurations of double and multiple pulse LIBS, which provide even better results for analysis. Its different configurations possess their own importance in their field of applications. Single pulse LIBS owns unique significance for qualitative analysis in delicate applications in nearly non-destructive way. LIBS, generally, is finding its applications everywhere in applied sciences like medicine, agriculture, dentistry, space exploration, heritage reservation etc. From last couple of decades it has been into extensive research in different forms, under various subjects, from diverse aspects for a wide range of applications. It has great potentials yet to be explored for its deployment as a mature technique with matchless capabilities.

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