



Review

Sample treatment and preparation for laser-induced breakdown spectroscopy



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ABSTRACT

One of the most widely cited advantages of laser-induced breakdown spectroscopy (LIBS) is that it does not require sample preparation, but this may also be the biggest factor holding it back from becoming a mature analytical technique like LA-ICP-MS, ICP-OES, or XRF. While there are certain specimen types that have enjoyed excellent LIBS results without any sample treatment (mostly homogeneous solids such as metals, glass, and polymers), the possible applications of LIBS have been greatly expanded through the use of sample preparation techniques that have resulted in analytical performance (i.e., limits of detection, accuracy, and repeatability) on par with XRF, ICP-OES, and often ICP-MS.

This review highlights the work of many LIBS researchers who have developed, adapted, and improved upon sample preparation techniques for various specimen types in order to improve the quality of the analytical data that LIBS can produce in a large number of research domains. Strategies, not only for solids, but also liquids, gases, and aerosols are discussed, including newly developed nanoparticle enhancement and biological imaging and tagging techniques.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been widely investigated in recent decades for different applications ranging from space exploration to biological specimens. The success of LIBS is due to a set of advantages that makes this analytical technique unique such as multi-element analysis, fast response, remote sensing, little to no sample treatment, the attractive cost of the instrumentation, and its ease of use [1,2]. Although LIBS was born as a field technique, the improvement in instrumental capabilities and knowledge on fundamental aspects of laser-induced plasma spectroscopy has allowed for a large expansion into laboratory applications. As a result, LIBS is now competing with other conventional laboratory techniques, still holding some of the advantages mentioned above, but at the same time the analytical performance (i.e., accuracy, repeatability, and reproducibility) could be improved in order to really be competitive with other well-established techniques. As with any ordinary analytical tool, the laboratory setting introduces the possibility of tighter control of LIBS experimental conditions and the use of more sophisticated analysis protocols that may include microscopic techniques, controlled background atmosphere, combination of excitation techniques (i.e. double pulse, plasma supported, fluorescence, etc.) and sample treatment [3–5].

In general, LIBS performance may be enhanced using two main approaches: a) improving the plasma emission signal and b) modifying the specimens. Until now the LIBS community has focused its efforts on enhancing the plasma emission, largely avoiding sample treatment, as is demonstrated in several papers [3–6]. One drawback of this approach is that it increases the cost by adding components (e.g., additional lasers, high performance detectors) and calls for specific expertise in the fields of plasma physical chemistry and laser technology. For these reasons this approach, although very interesting, does not meet the requirements of the majority of scientists and operators who want to use LIBS just as they would any other classical analytical tool. However, keeping in mind that enhancement of signal is mainly linked to the number of emitters more than to the plasma parameters, which are generally difficult to control, the main question becomes: how does the laser energy affect material ejection and, in turn, ablation efficiency? Therefore the manipulation of specimens in order to make them more suitable for laser ablation and LIBS is gaining interest for two reasons. First, to decrease the limits of detection (LOD) in already established LIBS applications and second, to expand the capability of LIBS to those applications where heterogeneity and/or matrix effects had limited its use. It is therefore wise to weigh the operational cost of sample treatment against the advantage of applying LIBS analysis instead of another analytical technique, keeping in mind that most conventional analytical techniques inherently require significant manipulation of specimens to achieve good results.

Sample treatment may be approached in different ways. The simplest manipulation concerns mechanical treatment like polishing the surface for improving the reproducibility of the measurements or increasing the roughness to improve the laser coupling. Deeper treatment may include changing the physical state of the specimen or the chemistry of the sample. In these cases, disadvantages may include alteration of the original chemical composition of the specimen, an increase in the analysis time, destruction of the original specimen, and possible contamination of the sample. It is clear, therefore, that to treat the sample is to give up one of the most attractive advantages of the LIBS technique, thus the crucial question of this paper: “why use sample preparation in LIBS?”

2. A brief theoretical background

Laser-induced breakdown spectroscopy is based on the optical emission spectroscopy of the plasma produced by laser–matter interaction and so the efficiency of the analytical performance is related to two different aspects: one is directly related to the laser–matter interaction and therefore to the coupling of the laser pulse energy with the physico-chemical properties of the specimen [7]; the other is related to the effects of plasma parameters on the optical emission characteristics of the species in the plasma [8]. Indeed these two aspects are strongly linked, as the plasma itself is the result of excitation by electronic impacts on the particles (i.e., atomic and ionic species) ablated by the laser pulse. It stands to reason that optimizing the energy transfer of the laser pulse to the sample is critical for obtaining a suitable emission spectrum for the chemical analysis. In general, assuming at first approximation that the plasma is optically thin, the emission intensity, I_{ul} , of a line is given by the following equation [9]:

$$I_{ul} = 4\pi Gh\nu_{ul}A_{ul}g_uN_u \quad (1)$$

where G is an experimental factor taking into account the probing volume and the instrumental efficiency, ν_{ul} is the frequency of the considered transition, A_{ul} is the spontaneous emission rate, g_u is the degeneracy of the emitting level and N_u is the population number density in the emitting level u .

Although the equilibrium condition in LIBS plasmas requires a deeper discussion [10,11], the Boltzmann distribution may generally be assumed for the emitting species so that Eq. (1) becomes:

$$I_{ul} = \frac{4\pi Gh\nu_{ul}A_{ul}g_uN_0}{Z(T)} \exp\left(-\frac{E_u}{kT}\right) \quad (2)$$

where N_0 is the total number density of the species, T is the excitation temperature and $Z(T)$ and E_u are the partition function and the energy of the emitting level, respectively. From Eq. (2) it is clear that the intensity of the emission line depends linearly on the number density of

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