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Review

A review of the development of portable laser induced breakdown spectroscopy and its applications

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ABSTRACT

In this review, we present person-transportable laser induced breakdown spectroscopy (LIBS) devices that have previously been developed and reported in the literature as well as their applications. They are compared with X-ray fluorescent (XRF) devices, which represent their strongest competition. Although LIBS devices have advantages over XRF devices, such as sensitivity to the light elements, high spatial resolution and the possibility to distinguish between different layers of the sample, there are also disadvantages and both are discussed here. Furthermore, the essential portable LIBS instrumentation (laser, spectrograph and detector) is presented, and published results related to new laser sources (diode-pumped solid-state, microchip and fiber lasers) used in LIBS are overviewed. Compared to conventional compact flashlamp pumped solid-state lasers, the new laser sources provide higher repetition rates, higher efficiency (less power consumption) and higher beam quality, resulting in higher fluences, even for lower energies, and could potentially increase the figure of merit of portable LIBS instruments. Compact spectrometers used in portable LIBS devices and their parts (spectrograph, detector) are also discussed.

Contents

1. Introduction

When an intensive laser pulse that is focused onto a sample surface is absorbed by the surface, a small amount of the material can be removed (ablated), vaporized and ionized to finally form a plasma

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plume that emits light. The light has a characteristic spectral structure relating to the plasma and the sample composition. The ablation abilities and plasma formation after the interaction of the intensive laser pulse with a material surface have been observed very soon after the invention of the laser. This knowledge, combined with optical emission spectroscopy methods, later resulted in a new analytical technique: laser induced breakdown spectroscopy (LIBS) [1]. Over the past 50 years, thousands of articles, a handful of books [2–8] and a number of reviews [9–29] have been published dealing with LIBS fundamental [9,10,15,16,30], archeological [14], biomedical [26] and geological applications [18], instrumentation and methodology [17,27], fieldable LIBS [11], remote LIBS [25], single pulse LIBS [21] and the LIBS of light elements in steel [19] or in non-conducting materials [20]. Special attention should be paid to Hahn's and Omenetto's extensive two-part review [16,17] which contains close to one thousand references.

The usefulness of LIBS under laboratory conditions has been proven and presented many times since the first application. However, there has always been a demand for sample analysis in the field from where the samples originate. This could increase the speed of the analyses which could be crucial, for example, when analyzing dangerous chemical agents or explosives. Sometimes the nature of the sample does not allow it to be transported to the laboratory. In any case, the elimination of the process of both transporting and storing the sample, and therefore speeding up the analysis, is itself a highly motivating factor in the effort to increase the portability of these analytical devices. Of course, a certain degree of miniaturization of the device depends on the analysis type, relating to some technical implementation, and this is not always possible with the current level of technologies. In 1996, Yamamoto et al. [31] presented design possibilities for a portable LIBS instrument and commenced the development of portable LIBS devices.

As it turns out, recently, the possibilities of miniaturizing LIBS into really lightweight and portable instruments, operated by persons with a minimal training, are in progress. For example, this is seen in the effort to introduce a real handheld LIBS device onto the market by private companies that weighs a couple of kilograms, is easily portable and provides analytical results within a few seconds. Progress is possible due to the miniaturization of the lasers, spectrometers, and computers accompanied by the miniaturization of the electronics and the increase in the storage capacities of the batteries powering the devices.

In 2010, Laserna and Fortes [11] published a review on fieldable LIBS devices, covering most of the fieldable devices developed until the year the review was published. The devices were separated into three groups, whereby for this review the portable LIBS group is the most important one. The goal of this review is to help orientate the reader in the area of portable LIBS instruments and relating publications to those instruments that push the borders toward a higher level of portability. With respect to the interest in a higher level of portability for LIBS devices, the instruments that meet certain additional criteria are described. These criteria naturally appear when someone has to carry the instrument in the field, particularly areas that cannot be reached by a car or with a trolley. With higher portability in mind, the LIBS devices presented here meet the criteria for maximum weight and how they are powered. In this review, we focus on the instruments that weigh up to a maximum of 15 kg, can be carried by one person over a short distance, and with an ability to overcome certain barriers: e.g. stairs. Moreover, the instrument should be powered by batteries; however, there are two exceptions to this: the first portable LIBS instrument [31] and the device developed by Laserna et al. [32–36]. Although there are other possibilities for powering the devices in the field, such as portable generators or solar cells, the use of batteries offers high portability, something that the aforementioned power sources cannot offer.

Dimensions, weight and power consumption are key features for portable instruments. These parameters depend on the most important parts of the device: the laser and spectrometer. Up until now, flashlamp pumped solid state lasers (FLPSS) were commonly used in the devices. However these days, new laser sources represented by small diode-pumped solid-state (DPSS), microchip and fiber lasers are available for use in LIBS devices. The lasers rapidly improve their performance and although they have been already used in LIBS studies, suggesting their usefulness in portable LIBS devices, they are not widely used. The authors of this work hypothesize that implementation of the new laser sources in the devices could help to further progress in the portable LIBS area. Therefore, the present article provides a review of published results relating to LIBS studies dealing with the new laser sources, followed by a discussion that addresses their usefulness. The spectrometer is another important part of the instrument, the parameters of which strongly influence the figure of merit of the overall instrument. Although there have not been as many technological improvements compared to the laser sources, we discuss the spectrographs and detectors that can help in the design of the portable LIBS instrument.

2. Notes on the portable LIBS instrumentation

Portable LIBS devices are commonly composed of a probe and a control unit (see Fig. 1). The sample is examined by the probe part which is held in the hand. In order to make the probe part lightweight, with acceptable dimensions, the probe part and control part are separated and placed in two different boxes. The probe part contains a laser and collecting optics. The other part, such as a spectrometer, computer, electronics, batteries, pump or gas purge, and which do not need to be placed close to the laser, are placed in the control unit box. Thus for spectral analyses of laser induced plasma (LIP), the light is collected in the probe and delivered to the spectrometer in the control unit via an optical fiber. The obtained spectra are further treated by the computer, which is also located in the control unit.

For the devices reviewed in Table 2, there are two versions of the probe and two versions of the control unit. Fig. 1 shows the possible configurations of the probes, called type 1 and type 2. Type 1 is destined for general use whereas type 2 is more suitable for the analysis of samples located on a floor or high on a wall. It can have a longer reach due to the longer laser light path to the focusing lens (type 2a) or by placing the laser with a focusing lens on a long handle (type 2b).

Fig. 1 also presents four common configurations of the collecting optics, labeled A–D. In A–C, the collected light is focused onto the fiber and therefore the light only contains spatially limited spectral information about a portion of the volume of the LIP plume. Conversely, in the case of D, the light is spatially integrated from the LIP volume given that the light entering the fiber is only limited by an angle described by the numerical aperture of the fiber. The spatial integration of the light also means that there is a spatial integration of parameters such as the temperature and density of the different LIP species, which may make it difficult to interpret these parameters. They are more meaningful for the spectra originating from a small LIP volume and are important, for example, in calibration free analyses. Although the interpretation of these parameters is not important for most of the portable LIBS devices, a collecting optics is used as it can result in a higher signal due to more light being collected. This can be important, especially for weak emission lines.

The two versions of the control units used are shown in Fig. 2. The backpack version can be considered as being more portable than the suitcase version. An interesting design of the portable LIBS instrument was presented in [37], where the instrument parts are integrated within a multi-pocketed flak vest.

The laser and spectrometer are two key parts of the LIBS system and their performance influences the capabilities of the overall instrument. Unlike laboratory systems and bigger portable or transportable LIBS systems, in this review, the laser's and spectrometer's performance is limited due to the weight and dimension restrictions. Therefore, the question regarding a compromise in the laser's and spectrometer's parameters is more essential.

The laser's function is to initiate the breakdown, ablate sample material, heat it and form the plasma plume. These processes are induced by the intensive laser pulse, focused onto the sample surface and of course,