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Precise alignment of the collection fiber assisted by real-time plasma imaging in laser-induced breakdown spectroscopy

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ABSTRACT

Improving the repeatability and the reproducibility of measurement with laser-induced breakdown spectroscopy (LIBS) is one of the actual challenging issues faced by the technique to fit the requirements of precise and accurate quantitative analysis. Among the numerous factors influencing the measurement stability in short and long terms, there are shot-to-shot and day-to-day fluctuations of the morphology of the plasma. Such fluctuations are due to the high sensitivity of laser-induced plasma to experimental conditions including properties of the sample, the laser parameters as well as properties of the ambient gas. In this paper, we demonstrate that precise alignment of the optical fiber for the collection of the plasma emission with respect to the actual morphology of the plasma assisted by real-time imaging, greatly improves the stability of LIBS measurements in short as well as in long terms. The used setup is based on a plasma imaging arrangement using a CCD camera and a real-time image processing. The obtained plasma image is displayed in a 2-dimensional frame where the position of the optical fiber is beforehand calibrated. In addition, the setup provides direct sample surface monitoring, which allows a precise control of the distance between the focusing lens and the sample surface. Test runs with a set of 8 reference samples show very high determination coefficient for calibration curves ($R^2 = 0.9999$), and a long term repeatability and reproducibility of 4.6% (relative standard deviation) over a period of 3 months without any signal normalization. The capacity of the system to automatically correct the sample surface position for a tilted or non-regular sample surface during a surface mapping measurement is also demonstrated.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is currently experiencing a rapid development driven by an increasing number of applications. The simplicity of implementation and the versatility for analysis in all kinds of medium of the technique make it applicable in a wide range of applications such as the environment [1,2], the homeland defense and the security [3,4], industry [5], forensic [6], geology [7,8], underwater exploration [9] as well as biomedical analysis [10]. Rapid expansion of the LIBS application contrasts however with the quantitative analysis ability of the technique which is still considered as its "Achilles' heel" [11]. One of the critical issues concerns its measurement repeatability and reproducibility, which actually appear in general significantly worse compared to other established quantitative analysis techniques. A number of studies emphasize the sensibility of the measurement stability for LIBS to the experimental parameters [12,13]. It is however not really a surprise when we consider the fact that LIBS directly uses the emission from the ablation plasma for spectroscopic analysis, and that the laser-induced plasma as a spectroscopic emission source is far from a stationary and a uniform and homogenous one [14–16] as that used in inductively coupled plasma optical emission spectroscopy (IPC-OES), for example. A breakthrough in the control and the master of the measurement stabilities in short as well as in long terms is indeed one of the actual key actions which would accelerate the maturation of the LIBS technique introduced now since more than 50 years [17,18].

In this paper, we develop the idea of a precise control of the capture of the plasma emission with an optical fiber assisted by, either manually or automatically, real-time imaging of the plasma. We describe an experimental implementation of this idea with a prototype of LIBS instrument. And we demonstrate the high analytical performance, especially in terms of measurement precision, repeatability and reproducibility, allowed by such setup. Additional functionalities offered by the developed setup, such as precise control of the laser beam focus with respect to the sample surface and of the lens-to-sample distance will also be demonstrated. Our purpose is to introduce an efficient configuration of LIBS instrument which offers an advanced level in the control of the geometrical configurations of plasma generation and of plasma emission detection, while keeping the additional complexity in an affordable degree. The described configuration obviously only fits a LIBS instrument for "laboratory type" measurements, but the basic idea of correlating the optical emission capture to the morphology and the structure of the plasma remains general for all types of

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LIBS instruments suitable for all types of measurements. It is also quite obvious that a tighter control in LIBS experiment does not mean a better understanding of the complex physical processes involved in the generation and the evolution of the laser-induced plasma. Our approach is therefore purely empirical and intending to optimize the LIBS detection system with the actual morphological property of the generated plasma. Such approach does not exclude a better understanding of the process of laser-induced plasma allowing its emission being detected in a more stable way and less sensitive to unavoidable experimental parameter fluctuations in short as well as in long terms.

2. Advanced control in a LIBS instrument with real-time plasma imaging: the basic idea and the experimental implementation

2.1. Correlating the detection of plasma emission to the actual plasma morphology

The basic idea is to introduce a correlation between the morphology (size, position, shape and structure) of the plasma and the alignment of the collection optical fiber in a LIBS arrangement where a fiber is used to capture a part of the emission from the plasma [19]. Such consideration implicitly assumes that the size of the plasma at the moment when its emission is detected is significantly too large so that only the emission from one part of it can be captured by the fiber. It is often the case for laboratory type of LIBS measurements except the specific case of micro-LIBS. The morphology of the plasma can fluctuate shot-to-shot and day-to-day as a function of the ensemble of the experimental parameters. The relation between the causes and the effect can be very complicated, but the purpose here is to adjust the signal collection system in a LIBS measurement as a function of the actual morphology of the plasma in order to rule out the signal fluctuation caused by the fluctuation of the plasma morphology whatever the cause. A real-time imaging and image processing provide shot-to-shot and day-to-day information about the morphology of the plasma. Such information is thus used to measure any deviation of the actual plasma with respect to a “reference” one for an ensemble of given experimental parameters. The correction on the alignment of the fiber can be applied either manually by the operator or automatically by a servo system [19]. Notice that this correction can be performed for a plasma based on the information extracted from the image of the previous plasma due to the time required for the image processing (~15 ms) and the finite displacement speed of the *x*–*y* translation stages holding the fiber. Such correction can be applied laser shot after laser shot during a measurement (automatically), or each time a new series of measurement starts (manually).

A possible realization of this idea is illustrated in Fig. 1, where the real-time imaging of the plasma is performed along the direction perpendicular to the laser propagation axis, i.e. the *z*-axis. Correspondently, the plasma emission is collected along the same axis with an optical fiber. This choice is justified by the fact that in general, the plasma undergoes an axial propagation [20] leading to an amplified fluctuation of its morphology along the axial direction. A lateral image of the plasma is therefore formed by an optical arrangement including two lenses. It is furthermore duplicated by the insertion of a beam splitter which deviates a part of the plasma emission collimated by the first lens (L_1) to an orthogonal direction (*x*-axis). With the help of two lenses, L_2 and L_3, two correlated images of the plasma are formed. A CCD camera (C_1) is used to record one of the images, while an optical fiber F_1 placed on the image plane of the second image and mounted on motorized *x*–*y* stages, collects the emission from a part of the plasma. In Fig. 1b, a typical image of the plasma recorded by the C_1 camera is shown in a 2-dimensional frame. A false color scale is used in the picture to represent the emission intensity from the plasma. Due to the conjugated nature of the two images, it is possible to calibrate the *x*–*y* displacements of the fiber in the frame of the plasma image. Such calibration allows placing the fiber with precise coordinates with respect to the shape of the plasma as shown in Fig. 1b. It is also possible with image processing and a well-defined algorithm to place the fiber according to the plasma properties, for example with respect to the barycenter of the emissivity of a given species. In this configuration, when the morphology of the plasma

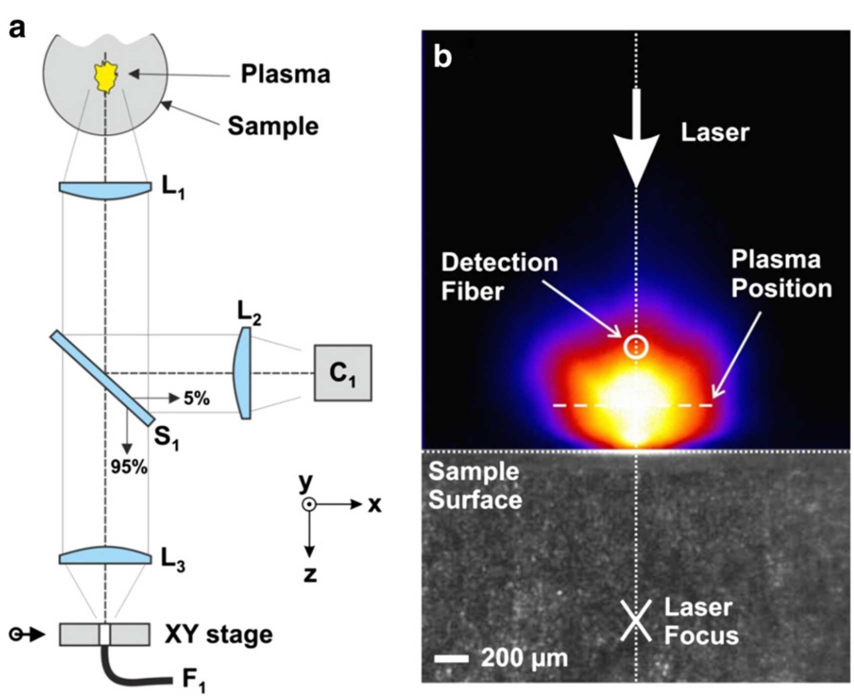

Fig. 1. Correlation between the collection of plasma emission by an optical fiber and the morphology of the plasma. a) Implementation of the basic idea with a lateral imaging system where the use of a beam splitter (S_1) in the optical system leads to two correlated images of the plasma. One of them is directly recorded by a CCD camera. An optical fiber mounted on *x*–*y* stages captures the emission from a part of the second image. b) A 2-dimensional frame corresponding to a picture taken with the C_1 camera. The image of the plasma is displayed on the frame. The motorized displacements of the fiber are calibrated with the coordinates of the frame in such way one can represent the fiber (with the real size of its entrance) on the frame. The sample surface as well as the laser beam focus is also represented on the frame.