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RESEARCH HIGHLIGHT

Understanding the source of signal fluctuations in laser-induced breakdown spectroscopy analytical applications

A recent paper [1] by the group of Prof. Zhe Wang, Beijing, China reveals the physical mechanism responsible of the signal fluctuations in laser-induced breakdown spectroscopy analysis.

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Exactly 20 years ago, today, I officially started the First International Conference on Laser-Induced Breakdown Spectroscopy (LIBS), in Pisa, Italy. This event gathered, for the first time, the LIBS community in an International Conference and gave a substantial boost to the research on the spectroscopic study of Laser-Induced Plasmas [2], as well as to a number of applications, ranging from industrial diagnostics [3], environmental studies [4], biomedicine [5], cultural heritage [6], etc..

In fact, the LIBS technique has many unique characteristics, including the robustness and simplicity of the equipment and the capability of operating without any treatment of the samples, which makes it the election technique for in situ applications [7]. On the other hand, the laboratory analytical applications of LIBS did not grow at the same rate of the out-of-the-lab applications; the LIBS plasmas are far from ideal for spectroanalytical measurements: they are non-stationary, non-homogeneous and out of thermal equilibrium [8] for most of their lifetime. Self-absorption [9] and matrix effects make difficult the correlation of the line emission intensity with the concentration of the analyte(s), and the use of the laser for both ablation and excitation of the sample material limits strongly the possibility of optimizing separately the two processes. The minimal quantity of mass analysed in a single measurement reflects in strong signal fluctuations and high Limits of Detection for most of the elements of applicative interest.

In the last 20 years, several important studies have pointed out the need for a better understanding of the mechanism of laser-sample and laser-plasma interaction aimed to improving the performances of the LIBS technique in the laboratory. In 1998, the group of Prof. Sabsabi in Canada proposed the idea of using a sequence of pulses [10] for improving the signal-to-background ratio in LIBS analysis. In 1999, we proposed in Pisa a new method for standard-less LIBS analysis, called Calibration-Free LIBS (CF-LIBS) [11–13], to overcome matrix and self-absorption effects. More recently, in 2013 the group of Prof. De Giacomo in Bari, Italy, developed the idea of using metallic nanoparticles [14,15] for enhancing the LIBS signal and improving its analytical performances. These three key improvements towards the enhancement of LIBS analytical figures of merit in the laboratory were developed in North America and Europe, reflecting the fact that, up to the first decade of the 21st century, the LIBS research was dominated by USA, Canada and European countries. However, the situation started to change in 2014 when, for the first time, the LIBS International Conference went outside the American and Euro-Mediterranean areas to reach Beijing, China. The success of the International LIBS event certified the huge progresses of Asian research in fundamental studies and applications of LIBS.

The paper published by Prof. Wang's group in *Frontier of Physics* [1] is the result of many years of hard work and important investments, which have brought the Laboratory at Tsinghua University, Beijing, China to the top level, among the most impacting LIBS research groups in the world. Prof. Wang set up an experiment which is probably one the most expensive in LIBS history, perhaps only second to the space application of LIBS on Mars [16]. He and his coworkers used three intensified CMOS cameras for the imaging of the laser-induced plasma, with an additional one connected to an Echelle spectrometer for time-resolved spectral acquisition, which enabled them to investigate the plasma evolution and its impact on LIBS signal in a clearer way.

This impressive experimental setup evidenced the onset of instabilities in the plasma, at a critical time delay about 140–170 ns after the laser pulse [1]. The authors individuated in this instability the major source of fluc-

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tuation and uncertainty in LIBS analytical applications. They also explained the physical mechanism which initiated the plasma instability in the recoil of the plasma, pushed back by the gas pressure behind the laser-induced shock wave [17], which amplified the small morphological variations at the earlier stage and resulted in unavoidable LIBS signal uncertainty.

This finding has important analytical implications for the optimization of the experimental conditions (acquisition time, ambient gas, laser pulse duration and beam shaping, etc.), which is to obtain more repeatable LIBS signals by attenuating the drastic plasma frontier pushing-back process or minimizing the impact of this key process. The work of Prof. Wang's group represents a major step in LIBS quantification: they have demonstrated that the fluctuation of the plasma morphology is the main source for LIBS signal uncertainties [18] and the effective way to improve signal repeatability is to reduce the impact of the total number density variation of the measurement species by either data processing method [19] or plasma modulation to obtain more stable plasma [20], and now revealed the key process leading to the morphological variation; all of the above make the quantification method an integrated set. Further research on this topic is envisaged by the authors on this promising topic, which could be a fundamental advance towards a larger diffusion of LIBS as a laboratory analytical technique.

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