Calibration-free laser-induced breakdown spectroscopy: Remaining challenges

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Calibration-free laser-induced breakdown spectroscopy has been under development for more than two decades. The first approach, based on the multi-elemental Boltzmann plot, gained popularity due its ease of implementation [1]. However, its analytical performance was limited, as the assumption of an optically thin plasma in local thermodynamic equilibrium was rarely fully satisfied. Consequently, several improved approaches have been proposed [2,3], most of them aimed to compensate for self-absorption - considered a major source of performance lowering [4]. Due to the complexity of their implementation, they were often neglected in practice, and calibration-free LIBS analyses were frequently performed by selecting spectral lines with negligible optical thickness [5,6].

Later, spectrum simulation-based methods emerged [7-9]. By solving the radiation transfer equation, these methods are particularly attractive, as they inherently account for self-absorption [10]. Simplified analytical solutions of the radiation transfer problem appear especially promising, as they allow rapid computations suitable for iterative modeling. Additionally, comparing simulated and measured line shapes provides valuable feedback for model validation, and helps to identify the experimental conditions form most accurate LIBS emission modeling [11].

This presentation aims to provide a critical an overview of the development of calibration-free LIBS for elemental analysis and its analytical performance. Special emphasis will be placed on the impact of self-absorption on measurement uncertainty, which is a key criterion in selecting the most suitable analytical transitions. The main sources of uncertainty in calibration-free LIBS will be reviewed, along with strategies for improving analytical performance. Finally, we will identify the remaining challenges to bring calibration-free LIBS up to the standards required for industrial applications.

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