Optics & Laser Technology 79 (2016) 164–172

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Review

[INVITED] Signal and noise in Laser Induced Breakdown Spectroscopy: An introductory review ☆

Elisabetta Tognoni *, Gabriele Cristoforetti

National Institute of Optics of the National Research Council (INO-CNR), Via G. Moruzzi 1, 56124 Pisa, Italy

ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form
8 December 2015
Accepted 10 December 2015
Available online 17 December 2015

Keywords:
Laser Induced Breakdown Spectroscopy
Signal
Noise
Fluctuations
Normalization

ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) has become a very popular technique for elemental analysis thanks to its ease of use. However, LIBS users often report poor repeatability of the signal, due to shot-to-shot fluctuations, and consequent not satisfactory limits of detection. In many practical cases, these shortcomings are difficult to control because the signal is affected by several noise sources that cannot be reduced simultaneously. Hopefully, there is a large amount of knowledge, accumulated during several decades, that can provide guidelines to reduce the effect of the single sources of fluctuations. Experimental setup and measurement settings can be optimized on purpose. Spectral data can be processed in order to better exploit the information contained. In the current paper several approaches to improve the analytical figures-of-merit are reviewed and the respective advantages and drawbacks are discussed.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has recently become a very popular technique for elemental analysis. At a first approach, new users may be conquered by LIBS due to its apparent ease of use, versatility, analytical potential. There is no need of a long training to set up a new LIBS apparatus and emission spectra are easily obtained from a sample. Therefore, it is relatively quick to conceive and experimentally carry out LIBS observations, especially if aiming at the qualitative identification of elements.

On the other hand, LIBS is often criticized because of a poor repeatability of the signal observed on a shot-to-shot basis. This characteristic is due to the complexity of the laser-sample and

☆Invited article by the Associate editor : Patrick Dupre

* Corresponding author.
E-mail addresses: elisabetta.tognoni@ino.it (E. Tognoni), gabriele.cristoforetti@cnr.it (G. Cristoforetti).

http://dx.doi.org/10.1016/j.optlastec.2015.12.010
0030-3992/

laser-plasma interactions, to the transient and inhomogeneous nature of the phenomenon observed, to the sensitivity of the plasma toward physical and chemical characteristics of the sample and atmospheric conditions. Experimental data can be poor and highly dispersed, unless experimental settings are optimized in order to reduce possible causes of noise [1]. Some investigations of the noise sources in LIBS measurements are available in the literature. Relying on these seminal works, the present review has been designed as an introduction for new LIBS users, with the aim of suggesting how to better exploit the information contained in the spectra.

The organization of the paper is the following. We first recall in Section 2 the definitions of signal and noise for measurements in this field, as well as the definitions of accuracy, precision and trueness. In Section 3 we briefly describe the different sources of noise in LIBS measurements. Section 4 provides an overview of recent investigations about experimental parameters affecting the analytical figures-of-merit. Three widespread approaches for line intensity normalization are described in Section 5. At end, Section 6 is focused on the processing of single shot spectra.

The discussion of issues regarding quantitative analysis (calibration curves, detection limits) is out of the scope of the present paper. A tutorial review regarding calibration in atomic spectrometry can be found in Ref. [2]. The definition of detection limit and other concepts involved in quantitative analysis are presented in Refs. [3,4].

2. Definitions

We assume that the reader is aware of the origin and physical meaning of the radiation emitted by a laser-induced plasma. Briefly, the analyte signal in LIBS is the radiation emitted by the analyte element in correspondence of a specific atomic or ionic transition (thus, at a given wavelength), and collected by a detector. The plasma emits also a signal, called continuum background, composed of bremsstrahlung radiation from free electrons and recombination emission. Therefore, the detector response (y) observed at a given wavelength in a spectrum is the sum of the analyte signal (S), the signal due to plasma continuum background (B), and the background introduced by the detector (dark current, stray light, etc., D) [5]:

$$y=S+B+D \tag{1}$$

In a first approximation the contribution D given by the detector can be considered negligible. The analyte net signal is obtained from the observed signal after subtraction of the continuum background. Since the background cannot be measured under the analyte line, it is typically measured at wavelengths close to the analyte peak. The signal may be given as peak intensity, when measured at the central wavelength of the emission line, or as integrated intensity, if measured by integrating the intensity over the line width. Similarly, the background can be measured at a given wavelength or as an integrated value over a spectral window.

The analyte signal and the plasma background are accompanied by noise (N), defined as the random deviation from the average. Thus, for a single spectrum [5]:

$$\begin{cases} y = \bar{y} + N_y \\ S = \bar{S} + N_S \\ B = \bar{B} + N_B \end{cases} \tag{2}$$

where $\bar{y}$, $\bar{S}$ and $\bar{B}$ are the average values of total response, analyte signal and continuum background, respectively, as obtained from multiple spectra. Generally the noise is assumed to have normal distribution, with zero mean and standard deviation σ. However, different statistical distributions have been observed in particular cases (see Section 6). During LIBS measurements, spectra can be recorded on a shot-to-shot basis or after accumulation of the signal obtained from multiple shots. Depending on the approach, the background noise can be obtained from the dispersion of its values measured at a single wavelength over a series of single shot spectra, or from the dispersion measured over a wavelength interval, in a single spectrum.

Two indicators of the quality of a measurement are mostly used in LIBS practice: the peak-to-base ratio, defined as the ratio of the signal to the background, and the signal-to-noise ratio, defined as the ratio of the signal to the noise standard deviation. It is worth to mention that the signal-to-noise ratio is, by definition, the reciprocal of the relative standard deviation of the signal [6,5].

Regarding the signal-to-noise ratio, several combinations of y, S, σ_y, σ_S and σ_B have been used in the analytical literature, of course with different meaning and implications. For example, the ratio y/σ_y is a measure of repeatability (see its definition below). On the other hand, the ratio S/σ_B is the one used in the definition of the limit of detection (LOD) [5]. Therefore, when using the signal-to-noise ratio, it is important to specify whether the noise refers to the signal or to the background, in order to make clear the meaning of this indicator. The same applies to the peak-to-base ratio. However, for simplicity and for consistency with the literature, in the following we use the symbols S/B and S/N as abbreviations for the generic peak-to-base ratio and signal-to-noise ratio, respectively.

We want to briefly recall here the definition of accuracy, trueness and precision, pointing the reader to the references where these concepts are deeply discussed [3]. The currently accepted definitions have been issued by the International Organization for Standardization (ISO) in 1993. Even though some slight differences in the definitions contained in different ISO documents exist, accuracy can be defined as the closeness of agreement between the result of a single measurement and the accepted reference value [7]. Trueness is the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value [8]. Therefore, trueness is related to systematic errors [3].

Precision, which is related to random errors, includes both repeatability and reproducibility. Repeatability is the closeness of the agreement between the results of successive measurements of the same measurand under the same conditions of measurement: same observer, same procedure, same instrument under the same conditions, etc. [7]. Repeatability is therefore the measure of shot-to-shot variability with a given sample [1]. Reproducibility, instead, is the closeness of the agreement between the results of successive measurements of the same measurand under changed conditions of measurement (instrument, observer, location, time, etc.) [7]. In summary, accuracy is the sum of trueness and precision.

Precision is quantified by means of standard deviation (SD) or relative standard deviation (RSD). It should be noted that the quality of the estimation of the standard deviation is a function of the statistical sample population, so that a low number of replicates leads to poor estimation of the standard deviation. However, statistical methods may help to estimate the uncertainty affecting the standard deviation [3].

3. Sources of noise

The description of the sources of noise in the LIBS tutorial literature is not as common as the topic would deserve. The list of the main sources of noise in LIBS spectra can be found, for