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Technical note

Effect of experimental parameters and resulting analytical signal statistics in laser-induced breakdown spectroscopy☆

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ABSTRACT

The purpose of this work is to provide detailed study of statistical behavior of different types of analytical signals in typical of Laser-Induced Breakdown Spectroscopy (LIBS) measurements. The main goal of this work is to justify usage of arithmetic mean and standard deviation as statistical estimates of expected value of selected analytical signal. In contrary to the general assumption that LIBS data show Gaussian distribution, this paper deals with the hypothesis that the data rather demonstrate Generalized Extreme Value Distribution. The study is realized on 10 selected lines measured on NIST glass standard. In order to cover wide range of possible applications three different spectra internal standardization techniques and their influence on distribution were studied. Finally, assuming that the data comes from a single distribution and the central limit theorem is valid, the influence of accumulations on the line distribution is examined and discussed. Statistical tools used and described in this paper can be utilized by other researchers to confirm their hypotheses and verify utilization of Gaussian distribution or even novel data processing methods.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) [1,2] is a promising analytical technique with an increasing number of applications. Along with LIBS popularity the demands on the method are rising [2], particularly the demands on the laser energy stability and high repetition rate, sensitivity and resolution of spectral detectors and quality of collection and focusing optics. LIBS has many advantages (in comparison with other spectroscopic methods) such as instrumentation robustness, virtually no sample preparation, the possibility to study samples in solid, liquid and gaseous state of matter, high repetition rate and fine spatial resolution. The last mentioned brings the possibility of elemental mapping [3]. One of LIBS drawbacks, namely the fact that it is quasi-non-destructive method, is crucial for elemental shot-to-shot analysis and even mapping suggesting that each shot is a unique measurement and cannot be repeated. Therefore it is important to study the repeatability of the experiment and the statistics involved in the so called shot-to-shot LIBS measurement.

The aforementioned shot-to-shot statistics of emission signal could be found important also in other LIBS experiments, especially in aerosol examination [4] and particle size determination [5]. The need for single shot analysis is briefly reviewed in the work of Michel et al. [6]. The important statistical value in majority of applications is the standard deviation of the analytical signal, which is always considered as fluctuation or instability of the experiment, i.e. the measure of accuracy. Further, researchers investigated possible sources of variability. Castle et al. [7] studied multiple variables influencing the standard deviation of selected analytical signals including: stage movement speed, laser energy fluctuation, pulse accumulation and surface roughness. Other works concern the influence of variability of instrumentation, namely shot noise in detector [8] or sample to lens distance [9].

Apart from elimination of the instrumental variations, there are some options to improve the experimental stability and influence the standard deviation. The most common is spectra standardization [10,11] and outliers filtering [12]. The most commonly employed method to our knowledge is the representation of the analytical signal as a ratio of the line under investigation and the certain reference line i.e. internal standard. This technique, along with the guide to line selection, is described in the work of Zorov et al. [10]. This particular work also describes some standardization methods utilizing various external properties of laser-induced plasma (LIP): acoustic signal, electrical current, ablated mass and crater parameters. Recent work of Castro and Pereira-Filho [11] brings twelve different approaches to spectral features standardization as a preprocessing step prior to the quantitative analysis. Pořízka et al. [12] brought comprehensive study and literature research on outliers filtering methods, showing increase of classification accuracy. More computationally intensive is the approach of Wang et al. [13], as they suggest calculation of the “standard state” of LIP. Plasma temperature of such state is then used to scale all measured spectra reducing the overall standard deviation. Differently, Carranza and Hahn

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[4] use filtering algorithm to reduce the overall shot-to-shot variability, however removing 60–70% of the single-shot spectra. This approach is though not usable in elemental mapping.

This paper studies the work submitted by Michel and Chave [14] in more detail concerning the statistics of the analytical signal. In simple terms, Michel points out that data calculated from emission signal does not follow the Gaussian distribution. Hence the calculation of mean and standard deviation is biased (or even variance does not exist). Furthermore, they suggest using another type of distribution to describe the data called Generalized Extreme Value Distribution (GEVD). This fact is supported by the quantile-quantile plot diagrams and measurements performed on both solids and liquids. Nevertheless, the aforementioned work misses direct comparison of the Gaussian distribution and GEVD distribution. Eventually they try to identify the sources of variations (where applicable) and suggest that the laser energy fluctuation influences the variability.

In this paper the topic of statistical distribution of analytical signal is revised. The direct comparison between performance of GEVD and Gaussian distribution is performed by utilizing the Kolmogorov-Smirnov test. Additionally, the influence of spectra standardization and data processing on the resulting analytical signal is discussed. As a final point the accumulation of spectra is brought to attention and taken into consideration as the data processing tool.

2. Methods

2.1. Extreme value distribution

The merit of extreme value theory is the statistical behavior of maximal values taken from a sequence of independent random variables with identical distribution. Historically there are three types of extreme value distributions: Weibull, Gumbel and Frechet, but they were unified into GEVD [15]. The resulting density function is:

$$G(z) = \exp\left(-\left(1+\xi\left(\frac{z-\mu}{\sigma}\right)\right)^{-\frac{1}{\xi}}\right)$$

where μ is location parameter, σ is a scale parameter (similar to the mean and standard deviation in Gaussian distribution respectively) and ξ is the shape parameter. The value of shape parameter defines the three aforementioned distribution types: Weibull, Gumbel and Frechet for $\xi<0$, $\xi=0$ and $\xi>0$ respectively.

To obtain GEVD parameters one should perform Maximum Likelihood Estimation. This problem was studied in detail by Smith [16], who found out limitations of this procedure, namely the fact that for $\xi<-0.5$ the results can be biased. It is worthwhile to bring to attention the evidence [14] that for $\xi>0.5$ the variance of the GEVD distribution is undefined and that the mean value is undefined for $\xi>1.0$.

2.2. Kolmogorov-Smirnov test

According to Stephens [17] the empirical distribution function (EDF) can be used to test the goodness-of-fit [18]. One sample Kolmogorov-Smirnov (KS) test is based on comparison of EDF with cumulative distribution function (CDF) of fitted distribution. The KS statistic is defined as:

$$D_n = \sup|F_n(x) - F(x)|$$

where $F_n(x)$ is a EDF, $F(x)$ is a CDF and sup is a supremum of the set of distances. The null hypothesis states that the data is drawn from the same distributions against the alternate hypothesis that they are not. At 0.95 level there is the critical value ($K_{0.95}$) for D_n equal to 0.134 for 100 realizations, this means that the null hypothesis is rejected if the tested statistics exceeds the critical value. The D value will be onwards considered as the measure of distribution correctness, stating that distribution fit with lower D describes the experimental value distribution more precisely.

3. Experimental setup

Measurements were performed using Sci-Trace (AtomTrace, CZ), the comprehensive LIBS apparatus, under atmospheric pressure. High energy Nd:YAG laser LF121(SOL Instruments, BY), operating at its fundamental mode (1064 nm, 12 ns pulse duration), was introduced into the chamber by a set of mirrors. The laser pulse was focused on the surface of a sample with a 40 mm focal length best form spherical lens (Thorlabs, USA) referenced hereafter as “primary lens”. Radiation of luminous laser-induced plasma (LIP) was collected with reflective optics CC52 (Andor, UK) and by optical fiber (Ø40 μm, Thorlabs, USA) directed into an echelle spectrometer Mechelle 5000 (Andor, UK; 200–975 nm, F/7, 6000 λ/Δλ). Echellogram was recorded using ICCD camera iStar 734i (Andor, UK; 1024 × 1024 pixels, effective pixel size 19.5 × 19.5 μm). Timing of the experiment is controlled using a pulse generator DG535 (Stanford Research System, US) and a signal inhibitor developed in the laboratory of Brno University of Technology.

Flat homogeneous sample of soft borosilicate glass SRM 1411, a certified reference material from National Institute of Standards and Technology (NIST), was chosen. The glass sample consists mostly of SiO_2 (58.04%), Na_2O (10.14%), B_2O_3 (10.94%) and then of ZnO (3.85%) CaO (2.18%) BaO (5.00%) K_2O (2.97%) and as minor compounds MgO (0.33%) and SrO (0.09%). Under optimal conditions (highest obtained signal) the laser irradiance was 3.75 GW·cm^{-2}. The total number of 270 measurements was performed with spacing 1.5 mm with respect to measured spot size of 500 μm. The detector gate delay was set to 1000 ns and the gate width was 10 μs. Obtained echellograms were not saturated.

The data were processed in the statistical program R [19], graphs were plotted using the *ggplot2* package and the Maximal Likelihood Estimation of GEVD was calculated using the *evd* package.

4. Results and discussion

Each of the selected line (see Table 1) was fitted with pseudo-Voight profile (with constant baseline correction) using AtomAnalyzer (AtomTrace, CZ) software, the numerical integral of the fitted peak was considered as an analytical signal. Table 1 shows calculated

Table 1

The analysis of selected spectral line distribution, λ_0 is the central wavelength of selected line, E_i and E_k are the lower energy and upper energy level respectively (taken from [20]). Underlined values of D are higher than the critical value $K_{0.95}$. Values emphasized by bold font have lower D value suggesting better statistical description of the experimental distribution. Lines marked with number 1 are used in further investigation.

Element	Mg II[1]	Mg II	Si I	Al I[1]	Ca II[1]	Ca II	Sr II	Ba II	Na I[1]	K I
λ_0 [nm]	279.55	280.27	288.16	309.27	393.37	396.85	421.55	493.41	589.00	766.49
E_i [eV]	0.000	0.000	0.781	0.014	0.000	0.000	0.000	0.000	0.000	0.000
E_k [eV]	4.434	4.422	5.082	4.022	3.151	3.123	2.940	2.512	2.104	1.617
D_{GEVD}	**0.069**	**0.044**	**0.043**	0.035	0.048	**0.066**	**0.052**	0.039	**0.027**	**0.030**
D_{Gauss}	0.095	0.067	0.044	**0.034**	**0.036**	0.086	0.080	**0.028**	0.058	0.095
μ_{GEVD}	3396	3601	3924	677	16,012	30,473	1859	26,961	5761	1006
μ_{Gauss}	3622	3907	4146	756	16,666	30,904	2047	28,142	6210	1168
σ_{GEVD}	496	604	631	173	1879	1900	394	3904	925	277
σ_{Gauss}	545	721	623	190	1841	1762	450	3739	1053	359
ξ	-0.11	-0.06	-0.28	-0.14	-0.28	-0.50	-0.09	-0.36	-0.09	0.01