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**REVIEW**

# Progress of Chemometrics in Laser-induced Breakdown Spectroscopy Analysis

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**Abstract:** Laser-induced breakdown spectroscopy (LIBS), a new type of element analytical technique with the advantages such as real-time, online, non-contact and multiple elements simultaneous analysis, is a frontier analytical technique in spectral analysis. However, it is still the main problem for LIBS technique to improve the accuracy of qualitative and quantitative analysis by extracting the useful information from a large number of complex LIBS data. Chemometrics is a chemical sub-discipline of multi-interdisciplinary, which has the advantages in date processing, signal analysis and pattern recognition. It can solve some complicated problems which are difficult for traditional chemical methods. In the paper, we reviewed the research progress of chemometrics methods in LIBS from the spectral data pre-processing, qualitative and quantitative analysis in recent years.

**Key Words:** Chemometrics; Laser-induced breakdown spectroscopy; Data pre-processing; Qualitative analysis; Quantitative analysis; Review

## 1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is a potential technique for material and elemental analysis on the basis of atomic emission spectroscopy (AES)[1–5]. In LIBS, a low-energy pulse laser (typically tens to hundreds of mJ per pulse) launched by laser device is reflected by plane mirror and focused by plano-convex lens onto samples surface, and then a plasma with high temperature is generated; the light with different frequencies is radiated during the plasma cooling process, and collected by a optic fiber and coupled to spectrometer; the qualitative and quantitative analysis of LIBS can be carried out by detecting the wavelength and integrated intensity of spectral line. LIBS technique is originated from the invention of ruby crystal laser[6], and has become a great concern in many scientific fields due to its high energy density, monochromaticity, coherence and so on. Since LIBS technique was first reported by Brech and Crossin in 1962[7], it has become a research focus in the field of spectroscopy with the development of laser and optical detection techniques. At present, the review articles on LIBS is increasing year by year[8], however, the review about chemometrics in LIBS analysis is very few. In comparison with the conventional analytical techniques, LIBS bears the advantages such as fast, real time, on-site, nondestructive, remote analysis and simultaneous multi-elements detection[9–13], and thus has been widely used in materials, metallurgy, combustion, environment, archeology, space exploration, medicine, military and so on[14–21].

Because LIBS technique can be used to obtain the composition information and content of the sample in a short time, it is one of the rapid multi-elements analysis methods. However, large number of complex analytical data would be generated in the sample determination by LIBS technique due to the diversity of analysis samples and the complexity of their

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chemical composition. Thus it is still the main problem for LIBS technology to improve the accuracy of qualitative and quantitative analysis by extracting the useful information from a large number of complex LIBS data and reducing subjective explanation. Chemometrics is one of the key analysis tool and main research field due to its stability and reliability in processing the large data collected in the determination by LIBS technique[22]. Chemometrics as a new multidisciplinary chemistry can be used to extract the maximum useful information from large raw data with the aid of computer sciences and mathematics by designing and selecting the optimized measurement procedures and experimental methods. Chemometrics has seeped into the various fields of analytical chemistry, and becomes an indispensable tool for modern analyst. The main tasks for chemometrics include the selection of optimal experimental conditions and the maximum extraction of useful information. Chemometrics has gradually played its advantages in the related LIBS research field, but the research review about chemometrics for LIBS analysis was not reported yet. In this article, we summarized the research progress of chemometrics methods in spectral data preprocessing, qualitative and quantitative analysis by LIBS technique in recent years, and forecasted the application prospects in LIBS technique.

## 2 Spectral data preprocessing

Because of the fluctuations of laser pulse energy, the difference of spectrometer resolution, and the effect from external environment and inhomogeneity of sample, there are always coexist with a great deal of interference information and effective information in LIBS data. Consequently, the spectral data preprocessing is an important part of spectral analysis. Chemometrics method can be used to eliminate or reduce the error generated by random factors in spectrum and the influence of variety of non-target factor to the spectrum. For spectral data preprocessing, it is not only necessary to extract the effective information from interference information for analysis, but also to obtain the feature information from the effective information, select the data variables, optimize the input spectral range and provide the reliable and accurate data foundation to construct a more precise and robust training (or calibration) model between the LIBS spectrum and the classes (for classification analysis) or the concentration (for quantitative analysis) of complicated samples to provide the concentration of unknown component or the property of samples. The data processing methods for LIBS mainly consist of baseline correction, noise filtering, overlapping peak resolution, and data compression.

### 2.1 Baseline correction

Baseline correction as a key data preprocess for LIBS is directly related to the quality of analysis, hence it has been received a great attention of many scholars. The target of LIBS analysis is the emission spectral line of atoms or ions. Because of the presence of blackbody radiation, bremsstrahlung, load radiation[23] and some of the molecular radiation, there are a larger continuous background interference and baseline drift in LIBS analysis, which leads to a serious influence on the accurate extract of characteristic spectral lines. Thus, the baseline correction could be carried out by mean of deducting background intensity. Lazic *et al*[24] proposed an approach based on rejecting the spectral line with very weak integrated intensities or stronger background noise to achieve baseline correction. Li *et al*[25] performed background subtraction by fitting the background continuous spectrum around the characteristic spectral lines within a relatively narrow band. Gornushkin *et al*[26] split LIBS spectrum into N sub-groups to fit the continuous background by high order polynomial function based on local minimum. On the basis of this, Sun *et al*[27] used a threshold based on a signal variance ratio to deduct all "unsuitable" minima and to reduce computational time. If the threshold was overestimated, the resulting background intensity would also be overestimated, and vice versa. Yaroshchyk *et al*[28] proposed model-free algorithm to realize the automatic continuous background correction of LIBS data. The proposed method did not require input variables, and the window size not depended on the complexity and type of the spectrum, also the method was more robust and easy to realize automation. The LIBS spectral line broadening mainly consists of Doppler broadening (Gaussian linear), natural broadening and collision broadening (Lorentz linear), of which the broadening contours is the convolution of Gaussian and Lorentz function, and the Stark broadening caused by electron and ion collisions plays a dominant role in the spectral line broadening[29]. Liu *et al*[30] employed Levenberg-Marquardt(L-M) algorithm to optimize and evaluate the undetermined parameters of theoretical Lorentz model, excluded the continuous background of the spectral signal, and corrected and reduced the wavelength and spectral intensity. Wavelet transform (WT) is a novelty signal processing method, but there is no a serial of systematic research work in terms of background subtraction of LIBS signal. Yuan *et al*[31] utilized the wavelet coefficients instead of the spectral information reconstructed to subtract the background of LIBS spectra based on WT, and improved the quantitative analysis accuracy of high-concentration carbon in coal. Zou *et al*[32] optimized wavelet function, decomposition level and scaling factor to realize the background subtraction of LIBS signal.

### 2.2 Noise filtration

Noise is a significant part of LIBS signal, and the noise seriously impacts quantitative analysis. The random noise