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Detection and correction of laser induced breakdown spectroscopy spectral background based on spline interpolation method

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that has gained increasing attention because of many applications. The production of continuous background in LIBS is inevitable because of factors associated with laser energy, gate width, time delay, and experimental environment. The continuous background significantly influences the analysis of the spectrum. Researchers have proposed several background correction methods, such as polynomial fitting, Lorenz fitting and model-free methods. However, less of them apply these methods in the field of LIBS Technology, particularly in qualitative and quantitative analyses. This study proposes a method based on spline interpolation for detecting and estimating the continuous background spectrum according to its smooth property characteristic. Experiment on the background correction simulation indicated that, the spline interpolation method acquired the largest signal-to-background ratio (SBR) over polynomial fitting, Lorenz fitting and model-free method after background correction. These background correction methods all acquire larger SBR values than that acquired before background correction (The SBR value before background correction is 10.0992, whereas the SBR values after background correction by spline interpolation, polynomial fitting, Lorentz fitting, and model-free methods are 26.9576, 24.6828, 18.9770, and 25.6273 respectively). After adding random noise with different kinds of signal-to-noise ratio to the spectrum, spline interpolation method acquires large SBR value, whereas polynomial fitting and model-free method obtain low SBR values. All of the background correction methods exhibit improved quantitative results of Cu than those acquired before background correction (The linear correlation coefficient value before background correction is 0.9776. Moreover, the linear correlation coefficient values after background correction using spline interpolation, polynomial fitting, Lorentz fitting, and model-free methods are 0.9998, 0.9915, 0.9895, and 0.9940 respectively). The proposed spline interpolation method exhibits better linear correlation and smaller error in the results of the quantitative analysis of Cu compared with polynomial fitting, Lorentz fitting and model-free methods, The simulation and quantitative experimental results show that the spline interpolation method can effectively detect and correct the continuous background.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a rapid spectrum detection technology for detection of the substance of various states (i.e. solid, liquid and gas) [1–7]. This technology exhibits many advantages, including non-destructive (or micro-destructive) detection, multiple-elements synchronous detection, and quick and real-time analysis. LIBS is widely used in many fields, such as industry, environment, agriculture, and food [8–11]. The number and variety of LIBS applications for elemental analysis have rapidly increased because of technological improvements [12–14]. Studies have used LIBS for quantitative analysis of elemental contents in various samples [15–17]. In the experiment, the laser acts on the object surface to produce a plasma. In the early stages of plasma evolution, the LIBS spectrum usually exits continuous background which common generates duo to the Bremsstrahlung radiation, recombination radiation and experiment environment [18]. The strength of the continuous background directly affects the accuracy of the results if the spectral signal of the measured element is weak in quantitative analysis. Generally, the optimal time delay and gate width are selected through preliminary experiment to reduce the continuous background. The experimental parameters cannot be easily adjusted to correct the background because different elements are affected by different experimental parameters. Therefore, scholars must develop an effective, universal and rapid method for background correction.

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Several methods have been established for detecting and correcting the continuous background of the LIBS spectrum. Gornushkin et al. [19] proposed a method that uses polynomial fitting to estimate the continuous background. In this method, all the minima of the spectral data are determined; then the spectral data of the full wavelength are divided into several groups; and the minimum points in each group are fitted by least square method. The final fitting result is estimated as the continuous background of the group. However, this method always over-estimated background in each group [20,21]. Moreover, the background value of the connection points between adjacent groups is discontinuous. Sun [22] improved this method and named it as minimal point screening (MPS). The first step is to find all the minimum points in the spectral data, followed by selecting appropriate minimum points through a large number of complex LIBS signal to conclude the characteristics of the background; finally, least square piecewise polynomial fitting of the minima is used to estimate the continuous background. In this method, concluding the characteristics of the background is extremely difficult [20,21]. Yaroshchyk [23] proposed a model-free algorithm to estimate the continuous background. First, all the minima of the spectral data are determined. Second, the continuous background of every pixel in the spectrum is determined by the minima in the vicinity of the pixel. This method can effectively estimate the continuous background and exhibits robustness to noise. Nevertheless, calculating the mean value as the continuous background of a pixel by using the minima in the vicinity of the pixel may also over-estimate the background. Other researchers also describe the use of Lorenz fitting to estimate the continuous background [24,25]; this method can be used to detect and correct the continuous background within a spectral peak region but cannot be easily applied to the full wavelength.

The above-mentioned methods exhibit a better background correction result for spectral data but also present some limitations. In this regard, this paper proposes a continuous background estimation method based on spline interpolation. Most of the existing correction methods have not been applied to quantitative and qualitative analyses of LIBS technology to verify their reliability. As such, Section 3.2 presents a quantitative experiment of Cu to verify the reliability of each method.

A window function is defined for preliminary processing of data. A simulation experiment was used to verify the practicability of the proposed background correction method. The simulation data are used to calculate SBR after background correction using polynomial fitting, spline interpolation, Lorentz fitting and model-free methods. The simulation results show a large SBR value after background correction by spline interpolation. A quantitative experiment of Cu is also performed and quantitative result used as standard to judge the practicability of various background correction methods. In the quantitative experiment, spline interpolation method is compared with polynomial fitting, Lorenz fitting, and model-free methods. Based on the experimental results, the proposed method based on spline interpolation exhibits a high linear correlation and small quantitative error in the quantitative analysis.

2. Method

Interpolation method uses a number of points within a certain range of function values to obtain the appropriate specific function; the calculated value of this specific function is used as approximate value in the interval of the other points [26]. This method is widely used for advection-diffusion equation which is related to mass transport in river, lakes, oceans, and groundwater [27,28].

2.1. Algorithm principle

Interpolation method mainly aims to establish a curve connected by a number of cubic polynomials. The function as well as its first- and second-order derivatives are continuous at the connection point. A region (A, B) is divided into n regions$X_0, X_1 \ldots X_n (A < X_i < X_{i+1} < B, i = 0, 1 \ldots n\text{-}1)$. Assuming that the polynomial established by interpolation method is as follows:

$$S(x) = \begin{cases} S_0(x) & x \in [x_0, x_1] \\ S_1(x) & x \in [x_1, x_2] \\ \vdots & \vdots \\ S_i(x) & x \in [x_i, x_{i+1}] \\ S_{n-1}(x) & x \in [x_{n-1}, x_n] \end{cases} \tag{1}$$

where $S(x)$ is the function expression in the region of (a, b):

$$S_i(x) = a_i + b_i(x - x_i) + c_i(x - x_i)^2 + d_i(x - x_i)^3 \tag{2}$$

Which $S_i(x)$ is piecewise polynomial between two points in the region of (a, b) and $i = 0, 1, \ldots n - 1$. The polynomial has n cubic functions; thus, the polynomial has $4*n$ coefficients to be calculated. If we want the polynomial and its first- and second- order derivatives to be continuous at the connection point between two adjacent cubic functions, then the following conditions are required:

$$\begin{cases} S_i(x_i) = y_i & i = 0, 1, \ldots n - 1 \\ S_i(x_{i+1}) = y_{i+1} & i = 0, 1, \ldots n - 1 \\ \lim\limits_{x \to x_i^-} S_i'(x_{i+1}) = \lim\limits_{x \to x_i^+} S_{i+1}'(x_{i+1}) & i = 0, 1, \ldots n - 2 \\ \lim\limits_{x \to x_i^-} S_i''(x_{i+1}) = \lim\limits_{x \to x_i^+} S_{i+1}''(x_{i+1}) & i = 0, 1, \ldots n - 2 \end{cases} \tag{3}$$

where y_i is the function value of each point.

From Eq. (3) can get $4*n\text{-}2$ conditions; therefore, we need two other conditions to calculate all the coefficients. Both start and end points are ignored when considering the continuity of polynomials; as such, some condition constraints possibly exist between start and end points. The two other conditions can be determined by their first derivative.

$$\begin{cases} S_0'(x_0) = y_0' \\ S_{n-1}'(x_n) = y_n' \end{cases} \tag{4}$$

Based on Eqs. (2) and (3):

$$\begin{cases} a_i = y_i \\ a_i + h_i b_i + h_i^2 c_i + h_i^3 d_i = y_{i+1} & i = 0, 1, \ldots n - 2 \\ b_i + 2h_i c_i + 3h_i^2 d_i - b_{i+1} = 0 \\ 2c_i + 6h_i d_i - 2c_{i+1} = 0 \end{cases} \tag{5}$$

where$h_i = x_{i+1} - x_i$.

If $m_i = 2c_i$, then Eq. (6) can be obtained using Eq. (5):

$$\begin{cases} a_i = y_i \\ b_i = \dfrac{y_{i+1} - y_i}{h_i} - \dfrac{h_i}{2} m_i - \dfrac{h_i}{6}(m_{i+1} - m_i) \\ c_i = \dfrac{m_i}{2} & i = 0, 1, \ldots n - 2 \\ d_i = \dfrac{m_{i+1} - m_i}{6h_i} \end{cases} \tag{6}$$

If the value of m_i is calculated, then the value of a_i, b_i, c_i, d_i can also obtained from Eq. (6). The value of m_i is then calculated. By incorporating b_i, c_i, d_i in Eq. (6) into $b_i + 2h_i c_i + 3h_i^2 d_i - b_{i+1} = 0$ in Eq. (5), then the following equation can be obtained:

$$h_i m_i + 2(h_i + h_{i+1}) m_{i+1} + h_{i+1} m_{i+2} = 6\left[\frac{y_{i+2} - y_{i+1}}{h_{i+1}} - \frac{y_{i+1} - y_i}{h_i}\right] (i = 0, 1, \ldots n - 2) \tag{7}$$

The two other conditions can be acquired using Eqs. (2), (4), and (6):

$$\begin{cases} 2h_0 m_0 + h_0 m_1 = 6\left[\dfrac{y_1 - y_0}{h_0} - y_0'\right] \\ h_{n-1} m_{n-1} + 2h_{n-1} m_n = 6\left[y_n' - \dfrac{y_n - y_{n-1}}{h_{n-1}}\right] \end{cases} \tag{8}$$