An Improving Method for Background Correction in Laser Induced Breakdown Spectroscopy

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Abstract. Background correction is an essential part in LIBS signal analysis. The interpolation method of background correction has major drawbacks. This paper introduces an interpolation method to overcome the shortcomings of linear and cubic spline interpolation methods. Finally, we compare different interpolation methods to verify the proposed interpolation method.

Introduction

As a noninvasive optical technique, Laser induced breakdown spectroscopy (LIBS) has become a very popular analytical method in multiple industrial applications, including material sorting, material process control and quality assurance.\cite{1-2} One of the basic problems in the analysis of LIBS signals is the separation of useful information contained in peaks from the useless information (background and noise). Background estimation, as the indispensable preprocessing step of spectra, critically influences subsequent analysis steps. The accuracy and reliability of the background analysis depend critically on the treatment in order to estimate spectral line intensity for the quantitative spectral analysis.

Some methods for background estimation are designed with the goal for the efficient performance. The approaches to the background treatment cover Fourier transform digital filters, wavelet transform and polynomial fitting. Fourier transform is an accurate method for background estimation, but it depends on direct human intervention to manually specify the upper and lower limits in the frequency domain.\cite{3} Not only is this time consuming, but the limits also differ from case to case. A zero-area Gaussian filter is proposed by Janssens that also led to the elimination of the continuum background.\cite{4} The use of digital filters implies a prior knowledge of the spectrometer instrument function. The wavelet transform is accurate when the frequency domain of the peaks and background are distinguishable.\cite{5} In this way, it might lose some useful information of the spectra and cause distortion at some part of the spectra. It can be clearly seen from the above discussion that each of the background correction methods has its strong points and also certain shortcomings. In addition, the primary advantage of polynomial fitting is its simplicity and effectiveness. It is faster than other methods and has been widely used for LIBS. The weakness of polynomial fitting is its dependence on the interpolation method.\cite{6} Lanxiang Sun presents a method of background correction based on linear interpolation, which may result in obvious break points and poor smoothness of background.

In this paper, we present an interpolation method to improve the defects resulted from linear interpolation concerning LIBS background. Furthermore, different interpolation methods for LIBS background correction are compared in terms of calibration curve.

Algorithms

The background correction method in \cite{6} includes three key steps: firstly, select several initial predicted points from all the minima on the spectra by a proper threshold. Secondly, expand the predicted points by linear interpolation. Finally, draw polynomial with optimal power through the
expanded predicted points. As shown in Fig.1, the cubic spline and linear interpolation methods are used to interpolate for expanding the predicted points. The cubic spline interpolation may cause overshoot and undershoot because this interpolation algorithm is not flexible enough, while the linear interpretation may cause the obvious break points, which is not expected by background correction. To solve this problem, we first introduce the parabolic parameter spline interpolation algorithm (PPSI).

![Fig.1 Different interpolation methods of background correction for LIBS.](image)

For interpolation points \( P_1, P_2, \ldots, P_n \), the process of the PPSI is interpolating three arbitrary adjacent points \( P_{i-1}, P_i, P_{i+1} \) and \( P_i, P_{i+1}, P_{i+2} \) with a parabolic spline. Based on the principle of parabolic parameter spline, we propose the segment power function algorithm. According to the subsection smooth theorem, suppose \( P_1(x_1, y_1), P_2(x_2, y_2), P_3(x_3, y_3), P_4(x_4, y_4) \) are four points in the same plane, and \( x_1 \leq x_2 \leq x_3 \leq x_4 \), \( S_2(x) \), \( S_3(x) \) are single-valued smooth curves interpolated by \( P_1, P_2, P_3, P_4 \), then curve \( S(x) = \frac{x_3 - x}{x_3 - x_2} S_2(x) + \frac{x - x_2}{x_3 - x_2} S_3(x) \) is first smooth in the interval \((x_1, x_4)\). The process of segment power function algorithm is similar to the parabolic parameter spline interpolation algorithm except that it uses a power function method to interpolate adjacent points \( P_{i-1}, P_i, P_{i+1} \) and \( P_i, P_{i+1}, P_{i+2} \) among interpolation points \( P_1, P_2, \ldots, P_n \), and then splice the two curves. The method of interpolating three optional points \( P_1, P_2, P_3 \) in segment power function algorithm is as shown in Fig.3(a), suppose the line crossing point \( P_2 \) and parallel to \( P_1P_3 \) intersects line \( x = x_1 \) and \( x = x_3 \), respectively, at points A and B. First construct power function \( y=x^\alpha (\alpha>1) \). Then construct function

\[
y = \begin{cases} 
\frac{A' P_1}{A' C} x^\alpha, & x \leq 0 \\
\frac{B' P_3}{B' D} x^\alpha, & x \geq 0 
\end{cases}
\]

(1)

where \( A' P_1 = AP_1 \), \( B' P_3 = BP_3 \) and \( C, D \) are, respectively, the crossing points of line \( y=x^\alpha \) with lines \( x=x_1-x_2 \) and \( x=x_3-x_2 \) as shown in Fig.3(b).
Fig. 2 Power function interpolating method.

Suppose the equation of line crossing point \(P_2\) and parallel to \(P_1P_3\) to be \(g(x)\), and the function of Eq.(1) to be \(f(x)\), then interpolate points \(P_1\), \(P_2\), \(P_3\) with the formula as follows: 

\[ y = f(x-x_0) + g(x) \]  

that is

\[
S_2(x) = \begin{cases} 
\frac{(x-x_2)}{x_1-x_2}AP_1 + \frac{(y_3-y_1)}{x_3-x_1}(x-x_2) + y_2, & x \leq x_2 \\
\frac{(x-x_2)}{x_3-x_2}AP_1 + \frac{(y_3-y_1)}{x_3-x_1}(x-x_2) + y_2, & x \geq x_2 
\end{cases}
\]

(3) where \(AP_1 = (x_3-x_2)y_1-(x_2-x_1)y_3 \) and \(S_2(x)\) is a single-valued and smooth curve.

**Experiment**

To demonstrate the feasibility of the proposed method for background correction, LIBS experimental setup is prepared to test and verify the proposed method in practical applications. The LIBS experimental setup used for obtaining spectral data in this work is schematically shown in Fig. 1. The laser source is a Q-switched Nd:YAG laser (CFR200 Nd:YAG from Big Sky Laser) with maximum pulse energy of 200mJ, pulse width of 12-15ns, wavelength of 1064 nm, and repetition rate of 1-15Hz. The sample is placed on a three-dimensional manually controlled stage, and the laser beam is focused on the sample surface by a convergent lens of 75mm focal length. The spectrometer is ESA 4000 from LLA Instruments GmbH for analysis. In a wavelength range of 200nm to 780nm and with a resolution of a few picometers spectra are recorded by an ICCD camera. The samples used in experiment are some national standard copper alloy samples, and their serial number is GSB 04-2416-2008. In the measurement, the laser pulse energy is 100mJ, the laser fluence on sample is 50J/cm2, and the single laser pulse frequency is 5Hz. Because LIBS data are influenced by a variety of experimental factors in the test process, the repeatability is low. For this reason, we use the average of multi-measurement to reduce the error caused by the uneven distribution of inner components. We measured each sample for 10 times in five different positions. All experiments are under the conditions of normal atmospheric pressure and 25 degree centigrade.
Results and discussion

As shown in Fig. 4, the background correction with different interpolation methods demonstrates the different effects on background estimation. The background correction with linear interpolation has the obvious break points, and the background correction with cubic spline interpolation has overshoot and undershoot. The background correction with the proposed interpolation method can be used to obtain a compromise between these two drawbacks.

Fig. 4 Different interpolation methods for LIBS background correction.
For the qualitative investigation of the copper samples by LIBS, we are in a position to determine the most suitable conditions for quantitative analysis of these copper samples. We have tried to avoid the experimental fluctuations and several types of interference to observe calibration curves for the main elements with good linearity and lower detection limits than obtained before. Fig. 5 gives a comparison of calibration curves results for Ni with different interpolation methods. The quality of the calibration curves with the proposed interpolation method is better than that of linear interpolation in sensitivity and correlation coefficients.

![Calibration Curves Comparison](image)

**Fig. 5** The comparison of calibration curves with different interpolation methods for background correction.

**Summary**

In this paper, the proposed interpolation method is applied to background correction for LIBS. The linear and cubic spline interpolation methods have obvious drawbacks for background correction. The proposed interpolation method shows good performances than the other interpolation methods for background correction. Therefore, for improved background estimation accuracy, the proposed interpolation method is suggested.

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References


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10.4028/www.sciemtific.net/AMM.751.86