Laser Induced Breakdown Spectroscopy Data Processing Method Based on Wavelet Analysis

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Abstract. In this paper, we present a data processing approach for Laser induced breakdown spectroscopy(LIBS). This method is based on wavelet analysis and pattern matching. First, it uses wavelet transforms to decompose the laser induced spectrum data which comes from the sample and obtain the decomposition coefficient of spectrum, then reconstructs the feature background spectrum by means of low frequency coefficient. Through using pattern cluster method to divide the spectrum data of calibration sample into some subsets, then do the calibration for each spectra data in each subsets. Second, we extract effective measurement pattern class template and calibration parameter from the spectrum subset which has the minimum differ between the result of calibration sample and the reality value. In practical process of measurement, we use effective measurement pattern class template to match the spectra data to identify the effectiveness of the measurement. Therefore, we can calculate element contents with the calibration parameter achieved before. This method can decrease the times of laser excitation and increase the measurement accuracy effectively.

1 Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an analysis technique, in which spectra of laser-produced plasmas were used for qualitative as well as quantitative spectrochemical analysis of material[1]. During the past decade, related technology has produced more reliable lasers, charge coupled detectors, and miniature spectrographs with its capabilities of recording spectra over a wide range of wavelengths. The combination of these technologies has produced unprecedented enhancements in the signal-to-noise ratio. LIBS has rapidly developed into a major analytical technology with the capability of detecting all chemical elements in a sample without any preparation, of real-time response, and of close-contact or stand-off analysis of targets. So it will be used widespread in the future.

But since the spectrum plasma may be disturbed by matrix effect and some objective factors which are difficult to avoid, such as laser intensity fluctuation, characteristics of the sample surface, laser-induced breakdown spectroscopy has some problems which are large random and poor reproducibility and it influence the accuracy of the quantitative analysis.

This paper uses wavelet transform method to obtain the effective measurement pattern class template. Then using this template to match the measured spectra

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data, identify the validity of the spectrum and calculate the element contents of material. It can increase the accuracy of measurement and reduce the stimulating times of laser.

2 Measuring Principle of Laser-Induced Spectroscopy

LIBS uses a beam of intense pulsed laser irradiation to the measuring material after focusing, the focal point of the measurement object ionization and generate high temperature, high-density plasma. In this method, a solid target is vaporized by a powerful laser pulse to form partially ionized plasma that contains atoms and small molecules. In the high temperature system, the fierce collision between the particles makes the molecular or atomic ionized into ions, and the molecular, atomic and ions can distribute on all energy level, high energy level transition to low level so as to make the laser plasma generate strong spectrum. The LIBS system diagram is shown in the Fig. 1.

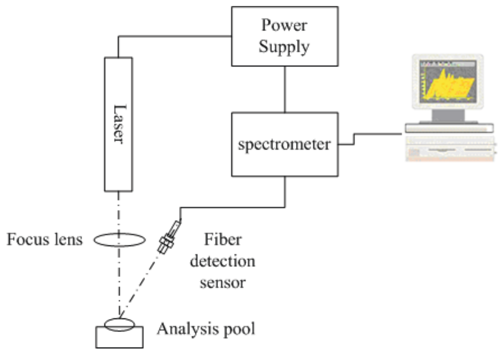


Fig. 1. LIBS system diagram

If local thermodynamic equilibrium (LTE) condition is assumed, the re-absorption effects are negligible (i.e. the plasma is optically thin)[2], the spectrally integrated line intensity, corresponding to the transition between levels E_k and E_i of the generic atomic species with concentration , can be expressed as

$$I_{\lambda}^{K_i} = N_s A_{ki} \frac{g_k e^{-(E_i/K_a T)}}{U_s(T)} \tag{1}$$

where λ is the transition wavelength, N_s is the density of emission atomic, A_{ki} is the transition probability of this spectral line, $U_s(T)$ is the partition function under the plasma temperature, the intensity unit of the line of departure is photon number$/cm^3$, in the actual measurement process, take the efficiency of optical receiver system into consideration, the intensity of experimental spectral line is indicated as[3]

$$\overline{I_\lambda^{K_i}} = FC_sA_{ki}\frac{g_k e^{-(E_i/K_aT)}}{U_s(T)} \tag{2}$$

$\overline{I_\lambda^{K_i}}$is the line intensity of the measurement , C_s is the atomic content correspond to this emission line, F is the experimental system parameters including optics efficiency of the receiving system and plasma temperature and its volume. In order to intensify the intensity of spectrum signal and increase the SNR, it calculates the average value of multi-spectrum. The formula (2) only contains C_s as unknown parameters and C_s is related to the element contents of the measured material, the other parameters are known . So when obtaining the $\overline{I_\lambda^{K_i}}$, the intensity of this correspond spectral line expresses the concentration of the analysis element by using calibration.

LIBS requires the measuring system under a strict stable environment, such as the laser energetic and point focusing must stand stable[4]. Unfortunate the system cannot keep stable under numbers of conditions in the actual measurement, so it will make a difference between every stimulate results and the simple average method cannot make the efficient handling.

3 The Method Based on Wavelet Feature Extraction

Because the laser induced spectrum contains many spectrum lines, so it is hard to classify and identify the effective or not. In order to solve this problem, we use wavelet decomposition and reconstruction to obtain the background spectrum. After that we classify the background spectrum and obtain the effective measurement pattern, which is used as a template to judge effective of measurement data. And next, we extract the calibration parameters which come from the effective schema. In the actual measuring process, we use the template as the criteria to determine each measurement result whether it is effective or not. If the data set is effective, then calculate the element content via calibration parameters. It is important that this method can obtain effective measuring data in a few excitation processes and increase the measuring accuracy. The data handle process is shown as Fig. 2.

3.1 Wavelet Decomposition and Reconstruction

Recently, the wavelet transform has received considerable attention from researchers in many areas such as signal processing, image processing, pattern recognition, communication, etc. The primary attractive feature of wavelet transform is its capacity for multiresolution analysis. It achieves low-frequency resolution and high time resolution in the high-frequency band, and high-frequency resolution and low time resolution in the low-frequency bands in an adaptive manner. at the same time,Wavelet transform (WT) exhibits very attractive features that make it ideal for studying spectrum signals,so in recent year,wavelet has been used widely in spectrum data processing[6][7][8].

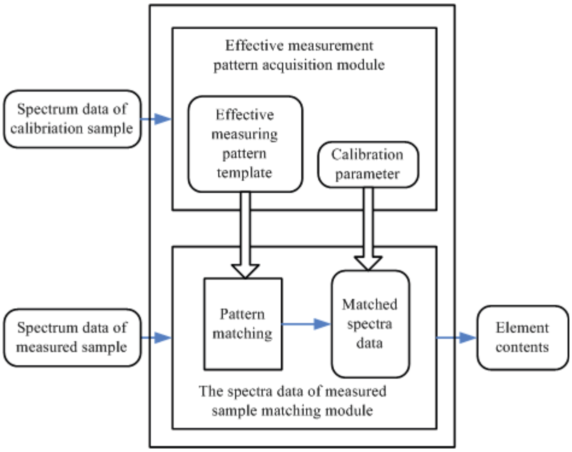


Fig. 2. Diagram of LIBS spectra data processing

Wavelet transform decomposes a signal into localized contributions labeled by a scale and a position parameter. And each of the contributions at different scale represents the information of different frequency contained in the original signal. The discrete wavelet transform(DWT) decomposes the time record $x(t)$ (t=1,2, . . . , N) into dyadic wavelet functions $\psi_{j,k}(t)$ and scaling functions $\varphi_{j,k}(t)$. The basis for this decomposition is formed from mother wavelet $\psi(t)$ and father wavelet $\varphi(t)$, by translating in time and dilating in scale[5].

$$\begin{aligned}\psi_{j,k}(t) &= 2^{-j/2}\psi\left(2^{-j}t-k\right)\\ \varphi_{j,k}(t) &= 2^{-j/2}\varphi\left(2^{-j}t-k\right), \qquad j,k\in Z\end{aligned} \tag{3}$$

where k=1, 2, . . . , $N/2$, N is the length of data queue . j=1, 2, . . . ,J, J is often a natural number, Z is the set of integers. Wavelet decomposition produces a family of hierarchically organized decompositions.

At each level j, the j-level approximation $A_j(t)$, and a deviation signal called the j-level detail $D_j(t)$ can be calculated according to the following equations.

$$D_j\left(t\right) = \sum_{k\in Z} W(j,k)\psi_{j,k}(t) \qquad j,k\in Z \tag{4}$$

where, $W(\ j,\ k)$ is the wavelet coefficients, and

$$W(j,k) = \int_{-\infty}^{+\infty} x(t)\psi_{j,k}(t)dt \tag{5}$$

The signal $x(t)$ is the sum of all the details:

$$x(t) = \sum_{j\in Z} D_j(t) \tag{6}$$

Then, take a reference level called J; there are two sorts of details. Those associated with indices $j \leq J$ correspond to the fine details, the others, which correspond to $j > J$, are the coarser details, we group these latter details into

$$A_J(t) = \sum_{j>J} D_j(t) \tag{7}$$

which defines what is called an approximation of the signal $x(t)$ Apparently, with the increase of the level J, the resolution defined as 2^{-J}decreases, and $A_J(t)$ will only contain the "lower frequency" components of $x(t)$[5].

3.2 Extraction of Effective Model Class

In experiment, We uses laser to excite m times to each sample which comes from a set of calibration samples of n, every spectra data denoted as $G_{i,j}$,$i = 1, 2, \cdots, n, j = 1, 2, \cdots, m$, and it forms the calibration sample measuring spectra data set $\mathbf{G} = \{G_{i,j}\}$. Every spectrum data sequence is expressed as $G_{i,j}(k) = [X_1, X_2, \cdots, X_k, \cdots X_N]$, N is the length of the spectrum data sequence. The flowchart of extracting effective pattern is shown in Fig. 3.

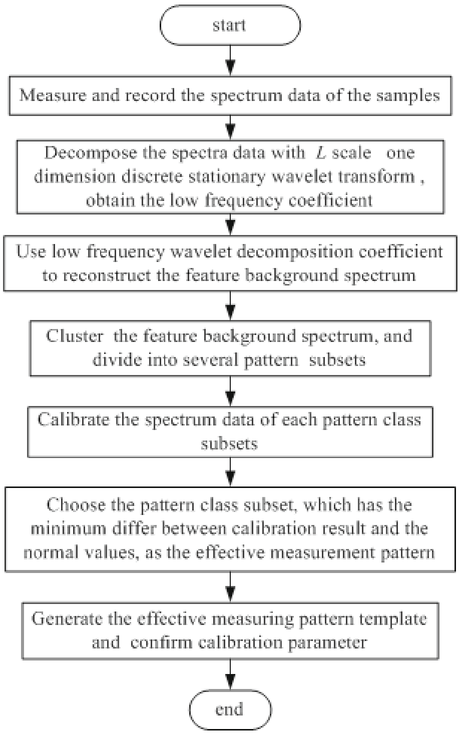


Fig. 3. Flowchart of extracting effective measurement pattern

(1) It decompose each spectrum data sequence $G_{i,j}$, which in the calibration sample spectrum data set, by using L scale one-dimension discrete stationary wavelet and obtains low frequency decomposition coefficient $W_{i,j}^{a} = [w_{l,k}^{a}]_{L\times N}$.

(2) Using low frequency decomposition coefficient $W_{i,j}^{a}$ to reconstruct the spectrum and obtain the feature background spectrum $G_{i,j}^{b}$ correspond to the spectrum $G_{i,j}$. The feature background data sequence $G_{i,j}^{b}$ can express as $G_{i,j}^{b}(k) = [X_1^b, X_2^b, \cdots, X_k^b, \cdots, X_N^b]$. All of the feature background spectrum $G_{i,j}^{b}$ compose the feature background spectrum set $\mathbf{G}^b = \{G_{i,j}^{b}\}$.

(3) Carries on the cluster analysis to the background spectrum data $G_{i,j}^{b}$ in the feature background spectrum data set $\mathbf{G}^b$, and dividing the feature background spectrum data set into several pattern class subsets $\mathbf{G}_h^b$, that is $\mathbf{G}^b = \{\mathbf{G}_1^b, \mathbf{G}_2^b, \cdots, \mathbf{G}_h^b, \cdots, \mathbf{G}_H^b\}$, $h = 1, 2, \cdots, H$. Here H is the number of pattern class subsets which are obtained by analyzing the feature background spectrum data set. According to the correspondence relationship between the spectrum measuring data $G_{i,j}$ and the feature background spectrum data $G_{i,j}^{b}$, and the partition of background spectrum data set $\mathbf{G}^b = \{G_{i,j}^{b}\}$, we can divide the calibration sample spectrum measuring data set $\boldsymbol{G}$ into several pattern class subsets $\mathbf{G}_h$ which are correspond to the pattern class subset $\mathbf{G}_h^b$ of feature background data set $\mathbf{G}^b$, that is $\mathbf{G}{=}\{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_h, \cdots, \mathbf{G}_H\}$.

(4) Using reality element content to calibrate the spectrum data contained in each subset $\mathbf{G}_h$, each subset $\mathbf{G}_h$ can obtain a set of calibration parameter β_h and calibration calculating result. Choosing the subset which has the minimum differ between the calibration calculation result and reality value, then extract the feature parameters of this pattern class to form effective measuring pattern G_m. The method of extract effective measuring pattern G_m as fellows:

Suppose the subset $\mathbf{G}_h$ has the minimum differ between the calculated result and reality value. The calibration sample measuring data subset $\mathbf{G}_h$ correspond to the feature background spectrum subset $\mathbf{G}_h^b$ which has E numbers feature background spectrum and the sequence length of each feature background spectrum data is N. Choosing the maximum value of the k locations among all the spectrum sequence of $\mathbf{G}_h^b$ as the higher limit of the effective measuring pattern class sequence $G_h^m(k)$, and choosing the minimum value of the k locations among all the spectrum sequence of $\mathbf{G}_h^b$ as the lower limit of the effective measuring pattern class sequence $G_l^m(k)$, programming language described by the following:

for k = 1 to N

$$G_h^m(k) = \max_{i=1}^{E}(G_i^b(k)); \qquad G_l^m(k) = \min_{i=1}^{E}(G_i^b(k));$$

end

The effective measuring pattern class model defined as $G_m = [G_l^m(k), G_h^m(k)]$.

(5) Choosing the calibration results of $\mathbf{G} = \{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_h, \cdots, \mathbf{G}_H\}$ and the calibration parameter β_h (correspond to the subset $\mathbf{G}_h$ which has minimum differ between the results and calibration sample element content reality value) as the calibration parameter used in the actual measuring, and involved in calculating the measured sample element content.

3.3 The Application of Effective Pattern Template

Excite the actual sample to obtain the single laser induced spectrum data G_j, $j = 1, 2, \cdots$.

(1) Process L scale one-dimension discrete stationary wavelet transform to decompose the laser induced spectrum data and obtain the low frequency decomposition coefficient $W^a_{i,j} = [w^a_{l,k}]_{L\times N}$.

(2) Use low frequency wavelet decomposition coefficients W^a_j to reconstruct the spectrum and obtain the feature background spectrum G^b_j which is correspond to the spectrum G_j .

(3) Use effective measuring pattern class template to match the feature background spectrum G^b_j, if this feature background spectrum G^b_j belongs to the effective measuring pattern class, this measured spectrum data is regarded as effective. Feature background spectrum G^b_j and the effective measuring pattern class template matching method is: If the data (location k) in the feature background spectrum data sequence $G^b_j(k)$ fulfill the condition $G^m_l(k) \le G^b_j(k) \le G^m_h(k)$,then match the feature background spectrum G^b_j and the effective measuring pattern class template.

(4) Excite the measured sample until the numbers of effective measuring spectrum data beyond the predefined numbers.

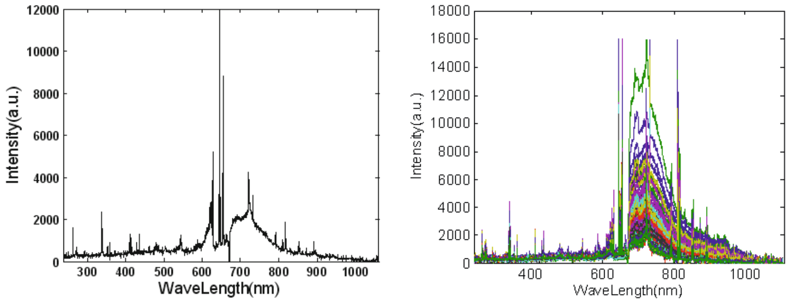
(5) Calculate the element content of the obtained effective measuring spectrum data according to the calibration parameters and use the average value of measured results as the analysis output results.

4 Experiment and Analysis

This paper use LIBS to measure the unburned carbon contents of fly ashes in the thermal power plant. The experiment uses passively Q-type Nd:YAG laser, center wavelength is 1064nm, pulse width is 10ns, pulse repetition frequency is 1∼10 Hz, laser energetic are 120∼160 mJ/Pulse. The spectrograph is AvaSpec-2048FT, communicate with the computer through the USB interface to transfer spectrum data and receive the control order. The spectrograph sends trigger signal to control laser.

We collect 70 fly ash samples from different regions. Before measure the samples, we grind and stir the samples to make them equality. Then we choose 20 kinds of samples as the calibration samples and performing 100 times laser induced spectrum measuring to each calibration samples and obtain 20×100 laser induced spectrum data. Fig. 4(a) is the spectrum of one time exciting to sample, Fig. 4(b) is the laser induced spectra sets of 100 times exciting to one sample, we can see from the Fig. 4(b) that the random factor and laser energetic fluctuation can affect the stability of spectrum data.

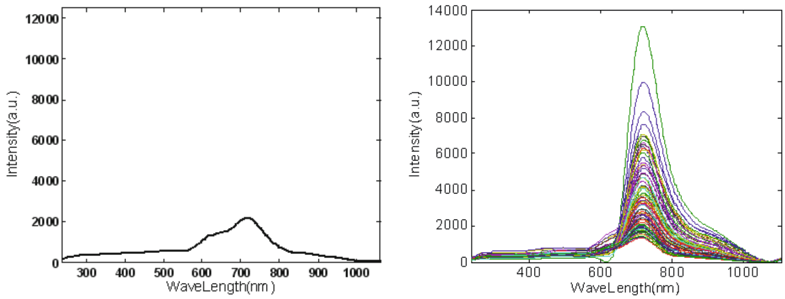
According to this method, a feature background spectrum is reconstructed shown in Fig. 5(a),which corresponding to Fig. 4(a). Fig. 5(b) is the feature background spectrum sets corresponding to Fig. 4(b). Following the next step, the effective measurement pattern template is achieved, which is shown in Fig. 6.



(a) Laser induced spectrum of a single measurement

(b) Laser induced spectrum of 100 times measurement to one sample

Fig. 4. Laser induced spectrum of one fly ash sample



(a) Feature background spectrum corresponding to Fig. 4(a)

(b) Feature background spectrum corresponding to Fig. 4(b)

Fig. 5. Feature background spectrum of one fly ash sample

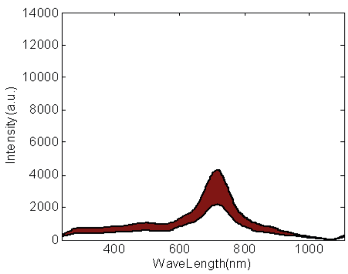
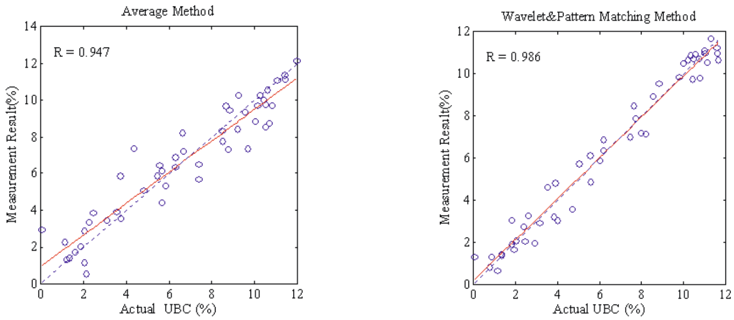


Fig. 6. Sketch map of effective pattern class template

In the measuring process, we use the effective pattern class template to match the measuring data, and if the laser induced spectrum we obtained is effective, then using relevant calibration parameters to calculate the element content. In order to check the effectiveness of this method, we compare the method with the traditional data average method. The traditional method process 50 times measurement and wipe out 5maximum values and 5 minimum values, then using the 40 remaining measurement results to calculate the average value, the linear regression result is shown in Fig. 7(a). The method in this paper is using 10 pattern class templates matching effective results to calculate the average, the linear regression result is shown in Fig. 7(b). Comparing Fig. 7(a) and Fig. 7(b), we can clearly figure out that the method of this paper is effective than the average method, also the laser excite times to 50 samples are decrease from 2500 to 956, so it can not only increase the measurement efficiency , but also extend life span of the laser at the same time.



(a) Average Method Result (b) Wavelet&Pattern Matching Method

Fig. 7. Result comparison

5 Conclusion

LIBS is widely used in qualitative and quantitative analysis the element contents of various kinds of subjects and LIBS has great practical value. But it has lots of factors which are difficult to avoid, such as laser intensity pulse, feature of sample surface and cardinal effect, so the consequence is that it has large randomness and negative repeatability and the accuracy of quantitative analysis will also be affected. On one hand, we can improve the method by improving the hardware device, on the other hand we can take some proper technique method to process the data of laser induced spectrum. This paper uses wavelet analysis and pattern recognition method to obtain the laser induced spectrum and pick up the effective measuring pattern template and correspond calibration parameter. In measuring process, this paper uses template matching method to identify the effectiveness of measuring data and calculate the effective data. This improvement can increase the measurement effective and accuracy, also can decrease the stimulate times of laser and increase the life span of laser at the same time. The experiment indicate the this method is effective.

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