Research and Analysis of LIBS Spectra for Qualitative Data

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Abstract. As the qualitative analysis software of laser induced breakdown spectra (LIBS) mainly relies on the principle of proximity and artificial identification, we developed a spectral data processing software, which manages background subtracting, filtering, peak searching and elements identifying, etc. The spectra database contains LIBS emission lines from the National Institute of Standards and Technology (NIST). The user can edit the database such as addition, correction or deletion of data. Using Cosine Similarity algorithm and combining of the database, the system is capable of being straight and fast in the determination the composition of the material by calculating the potential elemental composition of the sample, and will be a useful tool for LIBS.

1 Introduction

Laser-induced breakdown spectroscopy (short for LIBS) is a spectrum technology using plasma to obtain the chemical element, a typical atomic emission spectroscopy. The principle is that high-energy laser pulse is focused on the sample surface, burning sample and producing high-temperature plasma, by gathering and analyzing plasma spectrum so as to determine the composition and content of the elements contained in the measured sample. LIBS device is featured by compact dimension, low cost, no mandatory sample-preparation, less amount of analyzed samples, and rapid detection process, suitable for the simultaneous analysis of whole element, thus getting increasing attention.

Currently, as to the research of LIBS technique, numerous studies have been made in optimization and quantitative analysis of instrument parameter, while there is less research in qualitative analysis . Yaroshchyk et al. has established analysis model using spectrum simulation and has achieved semi-quantitative analysis software, but the function of the spectral simulation cannot be used for unknown samples. MP Mateo et al. has developed SALIPS software with spectral analysis and spectral-mode capabilities, and the software requires manual identification of the original constituent elements in order to conduct follow-up treatment. Tu Cai et al. has developed LIBS analysis software by VC + 6.0, including two parts of spectral analysis and spectral database, and has achieved functions of peak searching, baseline correction, automatic spectral-line analysis and spectral-line extension, spectral storage and others. Hu Zhiyu et al has developed spectrum recognition software based on LabVIEW, and the software can automatically identify spectral line of LIBS, able to achieve substrate attenuation of spectral data, automatic peak-searching, element recognition and other functions. Software developed in literatureand using proximity principle elements in the judgment of element affiliation does not apply to complex spectral lines. Based on the literature, this paper has introduced cosine similarity algorithm in process of determination of element affiliation, to determine whether the element exists or not through the similarity value, and has developed data processing software using C # development tools and SQLite3 embedded database to achieve a qualitative elemental analysis.

2 Design of Data Processing Software

Data processing software includes background subtraction, smoothing filtering, peak searching, element recognition and other functions, as shown in Figure1.
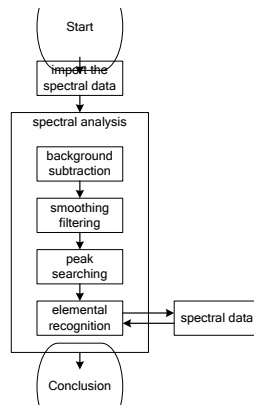
Figure 1 flow chart of spectral data processing software

2.1 Background subtraction

Background of laser-induced breakdown spectroscopy mainly stems from blank noise and continuous radiated noise. Blank noise can be directly removed by collecting a blank spectrum through by the instrument, and the main purpose of background subtraction is to reduce the influence of continuous radiated noise. Iterative method is adopted in background subtraction of the software, and the user needs to select an appropriate half-width and height, as shown in equation (1).

$$B_i = \frac{1}{2}\left(P_{i-\mathrm{FWHM}} + P_{i+\mathrm{FWHM}}\right) \tag{1}$$

2.2 Smoothing filtering

Smoothing is the most common means to enhancing signal-to-noise ratio in spectral data processing, and Savitzky-Golay is a universal way of moving window smoothing, and its working principle is the fitting of window data into polynomial using least square method, and the use of all values taken by polynomial fitting as the intensity value after smoothing. Smoothing filtering at points of 3, 5,7,9,11,13 and 15 are available in software. The larger the window is, the higher the signal-to-noise ratio after smoothing will be, but the signal distortion will be more serious as well, and the window default in software is 9.

2.3 Peak searching

Peak searching includes two modes, namely, manual peak searching and automatic peak searching. Manual peak searching identifies peak with the eyes in the spectrum to add peak position via mouse or input of wavelength location. Automatic peak searching is ridgeline peak searching, conducting continuous wavelet transform using Mexh mother wavelet, turning one-dimensional spectrum into two-dimensional ridgelines for peak searching. This method can skip steps of background subtraction and smoothing filtering, performing peak searching directly, no need to input parameters, able to identify weak peaks and overlapping peaks.

2.4 Element identification

Recognition is the determination of element affiliation of spectral peaks to be analyzed by comparing wavelength of spectral peaks and database of atomic emission line. Due to issues of insufficient precision in spectrometer and wavelength drift, there may be numerous alternative elements in a spectral peak, and at this time, aided analysis must be made relying on other spectral peaks and related rules. Identification process of software is as follows:

1) The spectral peaks are arranged according to the intensity, with wavelength into array intensity, to record maximum wavelength of lambdaMax and minimum wavelength of lambdaMin in spectral peaks.

2) Probable elements are found from database in intensity successively, and detection range of wavelength is ± δ. Probable elements retrieved are put into the list of elements by the structure of (element name, the wavelength in database, and current value of intensity);

3) Elements are grouped by the element names, sorted according to wavelength, to identify possible elements;

4) With data excluded, the possible data are excluded for each group of elements in elements from the changeable energy-level of database. For instance, the two characteristic lines of Al are 396.152nm (112.061-25347.756cm-1) and 394.4006nm (0.0-25347. 756cm-1), with the relative intensity of 500 and 1000 respectively. With similar changeable energy-level, when the peak appears near 394.4006nm, if there is aluminum in the sample, then the peak of 396.152nm annex must exist at the same time. If there is none, the peak near the 394.4006nm can only be possible peak of the other elements, and then the data is removed from the group Al.

5) The various constituent elements (wavelength, intensity) are extracted to the list of pk, and all the characteristic wavelengths and relative intensities of the elements between lambdaMin to lambdaMax are found from the database, then placed into the db list by the same structure. With aligned length, pk and db have the same wavelength values, and the added intensity value is represented by 0. The intensity values in pk and db are used to get the cosine similarity, as shown in equation (2), with the similarity range from -1 to 1: -1 means that the pointing direction of the two vectors is exactly opposite; 1 indicates that their pointing is identical; 0 usually means that they are independent. The threshold value is represented by T in software by, the value greater than T indicates that this element exists, and the default value of T is 0.5.

$$\cos(A,B) = \frac{A \cdot B}{\|A\| \times \|B\|} = \frac{\sum\limits_{i=1}^{n} A_i \times B_i}{\sqrt{\sum\limits_{i=1}^{n} (A_i)^2} \times \sqrt{\sum\limits_{i=1}^{n} (B_i)^2}} \tag{2}$$

2.5 Spectral database

Spectrum database stores the characteristic spectrum line of common elements so as to provide data for element identification. Spectral wavelength ranges from 180nm to 1100nm, covering the vast majority of wavelength measured by laser-induced breakdown spectroscopy technology. Field includes wavelength, the relative strength, the element name, the degree of ionization and the sequence numbering of energy difference. Data in database are extracted from strong characteristic spectrum line in NIST atomic spectroscopy database, and the degree of ionization is the secondary ionization at most, and the value is set in allusion to high-low energy level difference in the sequence numbering of energy difference. Software provides the interface so as to modify, add and delete records.

3 Experiment and Result Analysis

In the environment of Windows7, spectral data processing software has been developed with C # language in platform of Visual Studio 2010. Database is stored with Sqlite3, called by System.Data.SQLite library.
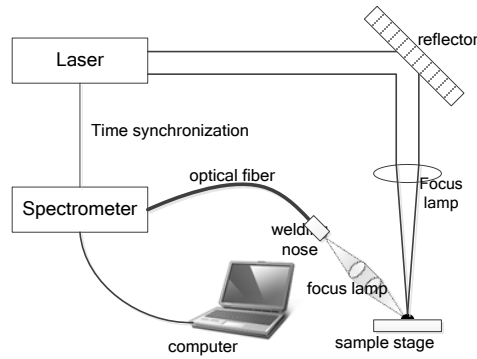
Figure 2 Experimental setup

LIBS experiment is conducted for spectral standard sample with known components (BYG1916-1), and specific component elements and contents of the sample are shown in Table 1. The experimental apparatus is shown in Figure 2, starting from the laser, pulse laser enters perpendicular to the surface of the sample through the reflection of mirror, and approximately 150μm facula emerges on the sample surface through focusing lens, burning sample, with plasma produced. Spectrometer collects the emission spectroscopy of plasma, and spectrum analysis is made after uploading data to computer. Laser (Litron Nano SG 120-10) parameters: Wavelength of 1064nm, repetition frequency of 5Hz, laser energy of 50mJ; spectrometer (AvaSpec-ULSi-series) parameters: spectral range 200-940nm, spectral resolution of 0.1nm (200-320 nm) and 0.6nm (320-940nm), the delay time of spectrometer of 0.8μs, and integration time of 380ms. Spectral lines obtained are input into the software, and the display of initial screen is shown in Figure 3, and the recognition effect obtained after analysis and process is shown in Figure 4, the report data as shown in Table 2.

In accordance with the method used in the step of element identification in this paper, the elements with similarity greater than or equal to 0.5 include Al, Cu, Mn and Fe elements, while V, Cd and Ce are excluded due to smaller similarity. Therefore, the four elements Al, Cu, Mn and Fe are detected, conforming to the composition elements of the sample.

Table 1 Sample component elements and contents

Element	Al	Fe	Mn	Cu
Content	7.76%	4.94%	2.63%	Allowance

Table 2 Element recognition results

Element	Similarity	The effective number of spectral peaks	Characteristic peak number in database
Al	0.7728183979970240	3	9
Cu	0.7147938813031590	7	21
Mn	0.5661561960377700	6	16
Fe	0.5160242753606580	8	33
V	0.3795373905398040	1	30
Cd	0.3739134322353400	1	15
Ce	0.3100006283066680	2	26

4 Conclusion

Based on the process of element identification, combined with database technology and cosine similarity, this paper has determined the likelihood of the presence of the element by calculating the similarity value, which has provided a way of quantization for the element identification, with fast and accurate recognition results. With the C # language, spectral data processing software has been developed, able to assist the laboratory personnel in the rapid completion of qualitative analysis so as to identify the composition of substances, which has certain practical value.

5 Acknowledge

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