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REVIEW ARTICLE

Research progress in Asia on methods of processing laser-induced breakdown spectroscopy data

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Laser-induced breakdown spectroscopy (LIBS) has attracted much attention in terms of both scientific research and industrial application. An important branch of LIBS research in Asia, the development of data processing methods for LIBS, is reviewed. First, the basic principle of LIBS and the characteristics of spectral data are briefly introduced. Next, two aspects of research on and problems with data processing methods are described: i) the basic principles of data preprocessing methods are elaborated in detail on the basis of the characteristics of spectral data; ii) the performance of data analysis methods in qualitative and quantitative analysis of LIBS is described. Finally, a direction for future development of data processing methods for LIBS is also proposed.

Keywords laser-induced breakdown spectroscopy, data preprocessing, data analysis

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1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical type of atomic emission spectroscopy. Since LIBS was first proposed by Breech and Cross [1] in 1962, it has attracted increasing attention from researchers. Because of its unique features such as little or no sample preparation, remote detection, and rapid online analysis, LIBS has been applied in many fields such as industrial production [2], environmental monitoring [3], medical science [4], food security [5], the military [6], and space exploration [7]. Furthermore, it has shown great potential for application in many other fields [8, 9].

However, compared with conventional chemical analysis methods, LIBS has two main drawbacks: i) detection sensitivity: the limit of detection (LOD) of LIBS is at the parts per million level [10]; ii) quantitative accuracy: it is currently difficult to limit the analytical relative error (RE) to less than 2% [11]. To improve the sensitivity and accuracy of LIBS analysis, approaches such as experimental parameter optimization [12], control of the physical properties of laser-induced plasma [13], varying the mode and environment of the interaction between the laser and the material [14–18], and improving instrument

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performance [19] are adopted by researchers. However, hardware upgrades are costly and limit the further development of LIBS. In contrast, the intrinsic signal can be obtained by noise reduction and correction processes. In fact, the data processing approach can not only improve the signal-to-noise ratio (SNR), but also reduce the signal fluctuations, contributing to the improvement of the detection sensitivity, stability, and reproducibility of LIBS [20]. Because of its unique features such as intelligence, speed, automatic operation, and cost-efficiency, data processing has become an important branch of LIBS research.

Currently, LIBS is being developed rapidly in Asia [21]. In 2014, the eighth international conference on LIBS was held at Tsinghua University. In 2015, the Asian Symposium on LIBS (ASLIBS) was held at Huazhong University of Science & Technology. ASLIBS (2015) focused on new principles and methods of LIBS and novel industrial applications. All of these events show that LIBS research in Asia has become important worldwide. Research on data processing methods in Asia has made tremendous progress in the past ten years. Here the research progress in Asia and problems with LIBS data processing methods are reviewed and described, and future prospects for LIBS data processing methods are discussed.

2 Basic theories

2.1 Fundamentals

A typical LIBS system is shown in Fig. 1. The laser beam from a Q-switched Nd:YAG laser was focused onto the sample surface by a lens. When the sample surface was ablated by the high-energy-density pulsed laser, the materials in the ablation area were vaporized and ionized, and plasmas were produced immediately. The plasmas contained a large number of atoms, ions, and free electrons. Early in the process, the electron bremsstrahlung and ion–electron recombination radiation, which are radiated in a continuous spectrum and produce a continuous background, were strong [22]. To reduce the effect of the continuous background, a digital delay generator was adopted to trigger the laser pulses and control the gate delays and widths of the charge-coupled device. As the laser continued heating the sample, the high-temperature, high-particle-density plasma expanded outward. In this process, the particles in the plasmas absorbed the laser energy and underwent photoionization and thermal ionization. Collisions among particles induced further ionization. Then the plasma plume reached local thermal equilibrium. In the plasma cooling process, atoms and ions in the excited state transitioned down to lower energy levels and radiated photons; then spectral emission was observed. The plasma emission was collected by a light collector, coupled into an optical fiber, and then transmitted to a spectrometer. Finally, the spectral data were analyzed by a computer. From the wavelengths and intensities of the spectral lines, the elements and their concentrations in samples can be deduced.

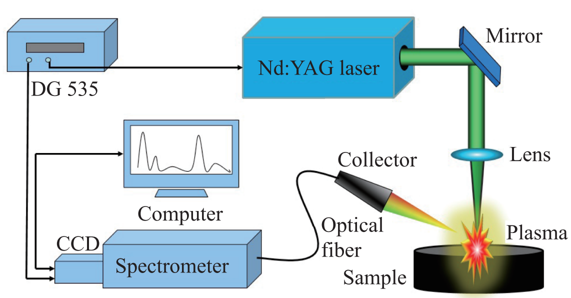

Fig. 1 Schematic diagram of a typical LIBS system.

2.2 Characteristics of spectral data

- **Matrix effect**

It has been found that the forms of chemical compounds and the bulk sample composition strongly affect the emission signals, which is called the "matrix effect" [23]. The matrix effect leads to sample stoichiometry problems in the laser ablation process and variation of the ablation rate. The matrix effect always affects the characteristics of the laser-induced plasma, including the plasma temperature, total number density, and electron density.

- **Self-absorption effect**

Because the atoms at the plasma periphery are usually at a low energy level, the emission light from the plasma center could be reabsorbed by the same type of atoms at the periphery of the plasma, which is called the "self-absorption effect" [24]. The self-absorption effect weakens the peak of a spectral line, so the line's intensity is usually lower than its expected value.

- **Spectral noise**

Noise is unavoidable during spectrum acquisition. Many factors contribute to noise in the spectrum, such as photon shot noise, the dark current of the detector, thermal noise caused by carrier motion, and natural light [25]. Noise in the spectrum is characterized by a wide distribution and stochastic volatility. It leads to a low SNR, which affects the analytical sensitivity and stability.

- **Spectral broadening**

Ideally, the characteristic spectral line should be an infinitely narrow spectral line without broadening. In the process of actual measurement, however, the spectral lines from plasma are broadened (by Stark broadening, Doppler broadening, and natural broadening) and observed by a spectrometer. Because of spectral broadening, the observed spectral lines undergo interference with lines close to them [26]. This interference eventually affects the accuracy of the analytical results.

In summary, interference is caused by four factors in LIBS measurement: i) laser instability: the fluctuation of the laser energy will affect the stability of the interaction between the laser and the sample; ii) the interaction between the laser and the sample: this process is affected by the composition and structure of the sample, which is also related to the matrix effect, continuous background radiation, and self-absorption effect; iii) the ambient conditions of plasma generation: the plasma generation and evolution processes will vary with the ambient conditions such as the gas, pressure, and temperature; iv) spectrum acquisition: other noise will be introduced by natural light, the plasma, and the detector during spectrum acquisition. Thus, spectral signal distortion always exists as a result of the factors described above. LIBS spectral signal distortion results in a poor linear relationship between the concentration of an element and the spectral line intensity, which reduces the accuracy, precision, and stability of LIBS analysis.

3 Data processing methods

The effect of the interference signals on the results of LIBS analysis can be effectively reduced by spectral data preprocessing and analysis. Asian researchers have made great progress in research on LIBS data processing methods. China has contributed significantly to the development of LIBS data processing methods in Asia [11]. Sun's group at Shenyang Institute of Automation, Chinese Academy of Sciences, conducted thorough research on LIBS spectrum denoising, continuous background subtraction, overlapping peak resolution, and self-absorption correction [25, 27–30]. Wang's group at Tsinghua University focused on improving the quantitative performance of LIBS and proposed a set of methods to reduce the measurement uncertainty using a so-called "spectrum standardization" process and to improve measurement accuracy by combining the advantages of a statistics-based multivariate model and a conventional physical-principle-based univariate model [31–42]. Duan's group at Sichuan University focused on the material classification model and studied the performance of the random forest (RF), support vector machine (SVM), and partial least squares discriminant analysis (PLS-DA) in LIBS qualitative analysis [43–46]. Lu's group at South China University of Technology studied the principal component regression, partial least squares regression model, and multivariate analysis methods in coal analysis [47–50]. Research on LIBS data processing methods also draws much attention in other Asian countries. Jeong's group at Gwangju Institute of Science and Technology (Korea) focused on self-absorption correction, spectrum standardization methods, and material classification models [51–53]. Bahreini's group at the Laser and Plasma Research Institute of Shahid Beheshti University (Iran) studied the material classification model and the possibility of its application to thyroidism diagnosis [54, 55].

There are two types of data processing methods: data preprocessing methods and data analysis methods. Data preprocessing methods are aimed at eliminating the effect of the interference information in the original spectra and providing high-quality spectra for subsequent qualitative and quantitative analysis. There is a relationship between the spectral line intensity and the concentration, which ideally are proportional. Data analysis methods are aimed at obtaining the relationship between the spectral line intensity and the concentration; then the elemental composition of the sample can be determined qualitatively and quantitatively.

3.1 Data preprocessing methods

Data preprocessing can provide high-quality spectra, which are effective for improving the analytical accuracy and precision of LIBS. Data preprocessing methods are aimed at eliminating the effect of noise, continuous background radiation, interference between overlapping peaks, self-absorption, and spectral line intensity fluctuation.

3.1.1 Denoising

Noise contributes to poor SNR of spectra and limits the LOD in LIBS analysis. The effect of noise can be reduced by upgrading the hardware facilities, but hardware upgrades are prohibitively expensive. Thus, denoising based on data processing methods is an economic and effective solution. With the development of more sophisticated Fourier analysis, local characterization in both the time and frequency domains has been improved greatly by wavelet analysis, which is an effective noise suppression approach for nonstationary signals such as LIBS spectra. An increasing number of researchers are introducing wavelet analysis to LIBS spectrum preprocessing. Zhang *et al.* [27] proposed the double threshold optimization model on the basis of wavelet semisoft threshold denoising. The results showed that the LOD values were reduced by more than 50%, and the SNR values were improved by a factor of 2. Yuan *et al.* [40] studied the performance of wavelet hard threshold de-

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noising, and the SNR values of the 247.86 nm C line under air, argon, and helium ambient gases improved by 2, 2, and 3 times, respectively. Zhang *et al.* [25] used entropy analysis to determine the optimal decomposition level of wavelet threshold denoising, and the LOD values were reduced by more than 50% when the proposed method was used.

3.1.2 Continuous background removal

The continuous background is distributed throughout the spectral range. Although the continuous background decays quickly, and spectra with a high signal-to-background ratio (SBR) can be obtained by controlling the delay time and gate width of the detector, the effect of the continuous background cannot be eliminated completely. By using data preprocessing methods, the continuous background can be removed effectively, and a higher SBR can be obtained. Sun and Yu [28] set a proper threshold to find the reasonable minima and then used polynomial functions to approximate the continuous background, realizing automatic estimation of varying continuum background emission. By using the proposed method, the correlation coefficient of the linear calibration curve of Si in Al alloy samples was improved from 0.7837 to 0.8227. Yuan *et al.* [40] realized continuous background removal by deducting the low-frequency components of the spectrum after wavelet transform, and the root mean square error of prediction (RMSEP) was considered as the optimization goal. Zou *et al.* [56] proposed a modified algorithm of background removal in wavelet transform. The scaling factor γ was introduced to modify the conventional algorithm. The results showed that overfitting phenomena can be effectively avoided and the accuracy of the regression model can be improved by using the proposed method. Hu *et al.* [57] studied the sliding window integral slope algorithm for removing the continuous background. By using the proposed method, the SBR values for lead and copper were increased by 5.7 and 1.95 times, respectively. The relative standard deviations (RSDs) were reduced by 2% and 2.5%, respectively.

3.1.3 Spectral peak recognition and overlapping peak resolution

Peak overlap leads to severe distortion of the intensities of spectral lines and results in low analytical accuracy and precision in LIBS. Thus, spectral peak recognition and overlapping peak resolution play an important role in LIBS spectral data preprocessing research. Li *et al.* [58] proposed a symmetrical zero-area transformation method for peak seeking. The experimental results showed that the proposed method possesses strong adaptability to volatility. Its ability to recognize weak peaks was close to, or even better than, that of artificial recognition. Chen *et al.* [59] proposed an automatic peak detection method based on continuous wavelet transform to eliminate the effect of the background and noise. The proposed method realized highly accurate peak detection and exhibited a strong ability to recognize overlapping peaks. Zhang *et al.* [29] studied a method for resolving overlapping peaks using curve fitting. The proposed method determined appropriate initial values for curve fitting according to fractional differential theory, and then the Levenberg–Marquardt method was used to optimize the curve fitting. High efficiency and accuracy were obtained in both simulated and experimental results. The ultimate aim of overlapping peak resolution and peak recognition is to provide spectral lines with high quality for qualitative and quantitative analysis. Analytical line selection methods have also been studied. Yang *et al.* [60] proposed a method that can select analytical lines automatically according to the intrinsic characteristics of spectral lines such as the intensity, wavelength, and width at half-height.

3.1.4 Self-absorption correction

Because of the self-absorption effect, the intensity of spectral lines is lower than its expected value, which contributes to the poor accuracy of quantitative analysis. The analytical accuracy can be improved to a certain extent by using data preprocessing method to correct the spectral line for self-absorption. The conventional curve-of-growth method requires a large amount of calculation and computational complexity, so its performance is unsatisfactory [61]. Sun and Yu [30] proposed an internal reference for self-correction (IRSAC) method, which used a regressive algorithm to estimate and correct the self-absorption. In *et al.* [51] introduced the spectral line intensity ratio into the self-absorption correction model. Ni *et al.* studied the very fast simulated annealing algorithm and proposed a self-absorption correction algorithm based on multiparticle spectra [62]. The accuracy of quantitative analysis in calibration-free LIBS (CF-LIBS) can be improved effectively by self-absorption correction. High-precision CF-LIBS analysis is generally needed for commercialization of LIBS instruments. Data preprocessing methods have been demonstrated to be a good choice to correct the self-absorption owing to their high efficiency and low cost.

3.1.5 Spectrum standardization

Spectrum standardization can be used to reduce the effect of spectral signal intensity fluctuations, and it has become a routine tool in data preprocessing. The basic procedure in conventional spectrum standardization methods is to select an internal reference line and normalize it, or standardize it, using spectral line intensity ratios. The principle of this method is the use of the ratio of two or more spectral lines' intensities to compensate for spectral line intensity fluctuations. Hou *et al.* [33] proposed a combined atomic and ionic line algorithm to improve data stability. Because the intensities of an atomic line and an ionic line change in opposite directions in response to changes in the plasma temperature, the signal fluctuation caused by the plasma temperature variation can be compensated. In *et al.* [52] introduced spectral line intensity ratios into the calibration model, which can effectively eliminate the effect of the spectral line intensity fluctuation on the analysis results.

To reduce the effect of signal fluctuation further, Wang *et al.* [31] proposed a new spectrum standardization method. The basic principle of the method is as follows. Assuming there exists a "standard state" characterized by a standard plasma temperature, electron number density, and total number density, the standardization model can be obtained by converting the spectral line intensity to the intensity in the standard state. To avoid the complicated calculation of the plasma temperature and electron number density, Li *et al.* [32] proposed a simplified spectrum standardization method in which Taylor expansion is applied to compensate for the fluctuations caused by variations in the plasma temperature, electron number density, and total number density. On the basis of the simplified spectrum standardization method, Li *et al.* [37] studied the performance of a combination PLS and spectrum normalization model that used the information of multiple lines in quantitative analysis. Compared with the simplified standardization model, the PLS-based spectrum normalization model can improve the RSD, the standard error, R^2, the RMSEP, and the maximum relative error (MRE) by about 38%, 38%, 0.6%, 11%, and 38%, respectively. In contrast to conventional spectrum standardization methods, complicated calculation is avoided, the effect of signal fluctuations is effectively reduced, and the stability of LIBS analysis is improved by using the "standard state" method.

Because the formation mechanisms of interference information in LIBS spectra are complex, it is difficult to completely eliminate the effect of the interference information. Thus, to further improve the quality of spectra using data preprocessing methods, the formation mechanism of plasma should be considered.

3.2 Data analysis methods

Data analysis is demonstrated to be of crucial importance in LIBS analysis. It is well known that there is much elemental information in LIBS spectra. The aim of data analysis methods is to obtain the key information on the elemental composition of samples with higher accuracy and precision. There are two types of data analysis methods: qualitative analysis and quantitative analysis. Many types of analytical models are established in data analysis methods to realize qualitative and quantitative analyses.

3.2.1 Qualitative analysis

The aim of qualitative analysis is to identify and classify samples without providing accurate concentrations of the constituent elements. The most common qualitative analysis is classification, including unsupervised pattern recognition and supervised pattern recognition. The most commonly used unsupervised pattern recognition method is principal component analysis (PCA) [63]. Commonly used supervised pattern recognition methods include PLS-DA [64], SVM [65], RF [43], and artificial neural network (ANN) [66].

- **Principal component analysis**

PCA is a multivariate statistical analysis method that can be used to extract the important variables by linear transformation. The spectral lines in LIBS spectra represent many variables. PCA can be used in LIBS data analysis to extract the most important variables that can describe the spectral characteristics. Liu *et al.* [67] classified four plastic materials (high-density polyethylene, low-density polyethylene, polyethylene terephthalate, and nylon) using PCA combined with cross-validation.

- **Partial least squares discriminant analysis**

PLS-DA is a discriminant analysis method based on PLS. Discriminant analysis determines how to classify the samples on the basis of several measured variables. PLS-DA is similar to PCA, but PLS-DA is a supervised pattern recognition method, which means that a learning process is necessary before unknown samples can be identified. Gazmeh *et al.* [54] discriminated healthy and carious tooth tissues using PLS-DA. The proposed method yielded 100% accuracy for prediction of unknown samples of dentin and enamel. The classification of unknown samples requires only a few seconds after the model is constructed.

- **Support vector machine**

SVM is a trainable learning machine based on statistical learning theory and the structural risk minimum principle. It has many advantages for resolving small sample sizes and nonlinear and high-dimensional pattern recognition, so it is widely applied in LIBS data analysis. Yu *et al.* [68] identified 11 types of plastics with SVM and obtained an average correct identification rate of 98.73%. Liang *et al.* [45] classified nine types of round steel using a multiclassification method based on SVM. The basic principle of the classification model is as follows. The samples are first classified by a one-against-all model, and if all the samples are classified successfully, the classification process is complete; if the one-against-all model fails to classify all the samples, the one-against-one model is used to classify the unclassified samples further.

PLS-DA and SVM are linear and nonlinear analytical methods, respectively. Some researchers have compared the performance of the two methods in LIBS data analysis. Tian *et al.* [69] investigated the identification of geological cuttings using PLS-DA and SVM. The experimental results showed that SVM performs significantly better than PLS-DA, with a correct classification rate of 91.67% as compared to 68.34% and an unclassified rate of 3.33% as compared to 28.33%. Zhu *et al.* [46] compared the performance of PLS-DA and SVM in sedimentary rock classification. The experimental results suggested that SVM outperforms PLS-DA, with a correct classification rate of 93.1% as compared to 91.9%. Because of the nonlinear relationships in LIBS spectra, the nonlinear SVM method is more suitable for LIBS spectral data analysis than PLS-DA.

- **Random forest**

RF is a classifier with multiple decision trees. The output is determined by the mode of the outputs of the decision trees. It has specific features such as the ability to handle a large number of input variables, a fast learning process, and high classification accuracy. RF has also been applied in LIBS spectral data analysis. Sheng *et al.* [43] studied the identification and discrimination of ten iron ore grades using RF. The experimental results showed that the average predicted accuracy rate of RF is 100%, whereas that of SVM is 96%.

Under some circumstances, better results will be achieved by combining two or more algorithms. Wang *et al.* [70] classified seven types of plastics using a model combining PCA and an ANN, and obtained a classification accuracy of 97.5%. Tian *et al.* [69] used a combined PLS-DA and SVM model to classify geological cutting samples. Compared with the results obtained using SVM alone, the correct classification rate improved to 95% from 91.67%. Selecting the analytical lines by analyzing the correlation between elements in a sample is an effective auxiliary method. Lee *et al.* [53] determined the input variables of the classification model by intensity correlation analysis of the emission lines. The results were consistent with those of PCA and PLS-DA, which showed that correlation analysis was helpful for constructing a simple and efficient classification model.

Table 1 summarizes the features of algorithms exploited for qualitative analysis in LIBS.

A large number of variables are represented in LIBS spectral data, and the relationship among them is generally nonlinear. There are two key tasks for achieving high classification accuracy: construction of the identification model and determination of the input variables. Pattern recognition methods have become relatively mature. The model should be constructed on the basis of pattern recognition and take into account the characteristics of LIBS spectra. The efficiency and accuracy of the model are affected by the input variables. Determining the input variables on the basis of the physical characteristics of the laser-induced plasma is the key to improving the performance of the model.

3.2.2 Quantitative analysis

To determine the elemental concentrations by analyzing the intensity of spectral lines is the core of LIBS quan-

Table 1 Algorithms exploited for qualitative analysis in LIBS.

Algorithm	Features	Performance	Reference
PCA	Unsupervised; intuitive; data dimension reduction	4 kinds of plastics: more than 75% average accuracy	[67]
PLS-DA	Supervised; linear; reduce the multicollinearity effect	dentin and enamel: 100% average predicted accuracy	[54]
SVM	Supervised; nonlinear; small sample and high dimensional pattern recognition	Round steel: 92.78% average accuracy Sedimentary rocks: 93.1% average accuracy 11 kinds of plastics: 98.73% average accuracy Geological cuttings: 91.67% average accuracy	[45] [46] [68] [69]
RF	Supervised; a large number of input variables processing capacity; fast learning process	Iron ore: 100% average predicted accuracy	[43]
PCA+ANN	Supervised; self-learning; calculation reduction; nonlinear problem processing	7 kinds of plastics: 97.5% average accuracy	[70]
PLS-DA+SVM	Supervised; simple combination of PLS-DA and SVM	geological cuttings: 95% average accuracy	[69]

titative analysis. Quantitative analysis methods include calibration-free [71] and calibration-curve methods.

CF-LIBS is based on plasma spectroscopy theory, which makes it possible to deduce the elemental composition quantitatively without a standard sample. It is the ideal method in practical applications. Because of the assumption of optical thinness and the uncertainty of concentration normalization and parameter calculation, the precision of CF-LIBS is unsatisfactory. Self-absorption correction is one of main bottlenecks in CF-LIBS. Sun and Yu [30] proposed the IRSAC method. Compared with conventional CF-LIBS, the accuracy of quantitative analysis with IRSAC was better and the calculation was simpler, but the proposed method can be utilized only as a semiquantitative method owing to the limited analysis precision. To further improve the accuracy of CF-LIBS, it is necessary to study the physical mechanism of self-absorption, on the basis of which the uncertainty of theoretical calculations can be reduced.

Calibration-curve methods can be used to construct the mapping relationships between the elemental concentrations and spectral line intensities for standard samples. This method includes univariate analysis and multivariate analysis. Univariate analysis is a conventional analysis method including standard calibration [72] and internal calibration [73]. Because the influence of the matrix effect cannot be eliminated by univariate analysis, the analytical accuracy is limited. The effect of the nonlinear relationships among the variables of the spectral data can be reduced by multivariate analysis, including multiple linear regression (MLR) [74], PLS [75], dominant-factor-based PLS [34], support vector regression (SVR) [76], ANN [77], RF [44], and relevance vector machine (RVM) [78].

• Multiple linear regression

MLR is a conventional multivariate analysis method. Because of the limited number of independent variables, MLR is suitable only when the mapping relationships between independent variables and dependent variables are linear and there is no multicollinearity between the independent variables. Yao *et al.* [49] analyzed unburned carbon in fly ash using internal calibration and MLR. Using the MLR can reduce the influence of the matrix effect to a certain extent and improve the performance of the quantitative analysis model compared to that obtained using univariate analysis.

• Partial least squares (PLS)

PLS is a multiple-statistic data analysis method that was developed on the basis of PCA. When the principal components are extracted using PLS, the correlations among the dependent and independent variables are taken into account, realizing data structure simplification, correlation analysis among the variables, and regression modeling. When conventional PLS methods were introduced to the analysis of coal [40, 50], metal [79], plants [80], and fertilizer [48], quantitative analysis results with high accuracy were obtained. Zou *et al.* [81] used a genetic algorithm (GA) to select the variables and constructed a GA-PLS model. For most of the elements in soil, the prediction ability of the GA-PLS model was better than that of PLS methods.

• Dominant-factor-based PLS

Basically, PLS is only a linear correlation statistical regression method that ignores the physical background. Further, a univariate model provide more robust results over a wider range owing to its grounding in physical principles, but its quantitative performance is not as good as that of a multivariate model because only a few spectral lines are used for analysis. To combine the advantages of these two methods, Wang *et al.* [35, 36] proposed the dominant-factor-based PLS model. A multivariate model was established on the basis of the dominant factor model and the physical background, possibly considering nonlinearity [36], and PLS was used to compensate for the residual errors of the dominant factor model and further improve its performance. The results showed that both the measurement reproducibility and accuracy were greatly improved when this model was applied to coal analysis [34, 38, 42].

• Support vector regression

SVR is an SVM method that can realize linear regression by constructing a linear decision function in a higher-dimensional feature space according to structural risk minimization. The fit and complexity of the training samples are considered in SVR. Wang *et al.* [82] studied the quantitative analysis models of MLR, neural network regression, and SVR on the basis of an analysis of the heavy metal Ni in water. The experimental results showed that the SVR model exhibited the best performance. The average RSD and average relative error were both less than 3%. The performance of SVM and PLS has also been compared. Shi *et al.* [83] and Zhang *et al.* [84] both studied the performance of SVR and PLS in quantitative analysis. The experimental results showed that the effect of self-absorption can be effectively eliminated by using SVR; thus, more accurate quantitative analysis can be obtained.

• Artificial neural networks

The model constructed by an ANN is based on a simulation of the human neural network, which is suitable for establishing the nonlinear relationships among the independent and dependent variables. Nonlinear effects such as the self-absorption and matrix effects can be corrected to a certain extent by using an ANN. Sun *et al.* [85] studied the effect of different inputs on the performance of the ANN model and compared it with the internal standard method. The experimental results showed that the RSD values for Mn and Si decreased to less than 8% from more than 10% when the ANN model was used. Li *et al.* [86] proposed a multi-spectral-line calibration method based on ANN, which used the intensity ratios of multiple spectral lines of interest and matrix elements to train an ANN. Shen *et al.* [87] used a GA to optimize the weights and thresholds of an ANN. Compared with the results obtained using a back-propagation ANN model, the MRE values for Ba and Ni in soil decreased to 4.15% and 6.06% from 7.91% and 10.5%, respectively, when the neural–genetic method was used. A large number of training samples and long training time are needed in ANN modeling, which is also sensitive to the incompleteness and error of the samples, so the application of ANN in on-line analysis is limited.

- **Random forest**

RF regression is based on the multivariate regression tree. It has a high noise tolerance, which can be useful for reducing overfitting phenomena. Zhang *et al.* [44] studied the performance of the RF regression model in quantitative analysis of multiple elements in steel. The RF regression model outperformed PLS and SVM models, with an RMSE of 0.69 as compared to 1.76 or 0.726, respectively. High precision and a faster learning process can be obtained by using an RF regression model. Therefore, RF has great potential for use in LIBS quantitative analysis.

- **Relevance vector machine**

RVM is a sparse probabilistic model that is similar to SVM. The calculation of the kernel function is much simpler when RVM is used than when SVM is used. Yang *et al.* [78] studied an RVM quantitative analysis model. The experimental results showed that the RVM model had strong generalization ability. The RMSE was 0.71% when RVM was used, whereas it was 0.92%, 1.31%, and 1.39% when PLS, ANN, and SVM, respectively, were used. RVM can yield higher accuracy and better robustness than PLS, ANN, and the standard SVM model.

Table 2 summarizes the features of algorithms exploited for quantitative analysis in LIBS.

Because of the effect of factors such as the self-absorption and matrix effects, poor accuracy is a problem for both CF-LIBS and standard calibration methods. During the development of LIBS data analysis methods, researchers selected or constructed models suitable for LIBS analysis, for instance: i) the dominant-factor-based PLS model, which combines the advantages of the uni-

Table 2 Algorithms exploited for quantitative analysis in LIBS.

Algorithm	Features	Performance	Reference
MLR	Multivariate analysis; simple and convenient; linear problem	C (one kind of coal): $R^2 = 0.994$, AE $= 0.04 \sim 0.78\%$; C (different kinds of coal): $R^2 = 0.981$, AE $= 0.23 \sim 0.85\%$	[49]
PLS	Data structure simplification; correlation analysis; reduce the multicollinearity effect	Fertilizer sample: P_2O_5: RSD = 2.55%, AE = 0.31%; K_2O: RSD = 0.92%, AE = 0.63% Ash in coal: RSD = 8.5%, LOD = 1.73%	[48] [50]
Dominant factor based on PLS	Nonlinear transformation; residual errors compensation; physical mechanism consideration;	Brass sample: Cu: $R^2 = 0.999$, RMSEP = 2.33%, RMSE = 1.27% Cu: $R^2 = 0.999$, RMSEP = 1.97%, RMSE = 1.05%	[35] [36]
SVR	High dimensional feature space; structural risk minimization; fit and complexity consideration	Sedimentary rock sample: Si: RMSEP = 1.0352%; Ca: RMSEP = 1.4541%; Mg: RMSEP = 0.3237%; Fe: RMSEP = 0.4157%; Slag sample: F_2O_3: RMSE = 2.43%; TiO_2: RMSE = 7.83%; CaO: RMSE = 6.22%;	[83] [84]
ANN	Simulating human neural network; self-learning; correcting nonlinear effects	Steel sample: Cr: RMSECV = 0.01%, ARSD = 6.4%, MRSD = 7.4%; Ni: RMSECV = 0.023%, ARSD = 12.9%, MRSD = 20.1%;	[86]
RF	Multivariate regression tree; high noise-tolerance; fast learning process;	Steel sample: Si: RMSEP = 1.8657%; Mn: RMSEP = 0.8324%; Cr: RMSEP = 0.7395%; Ni: RMSEP = 0.6892%;	[44]
RVM	Sparse probabilistic; calculation simplified; strong robustness;	High-alloy steel sample: Cr: RMSE = 0.71%, MRE = 4.01%; Ni: RMSE = 0.92%, MRE = 4.98%; Mn: RMSE = 1.54%, MRE = 6.21%;	[78]

variate and multivariate models, can be used to obtain better results than PLS; ii) analysis models such as SVR and ANN, which consider the self-absorption and matrix effects, can be used to improve the analytical accuracy notably; iii) RF and RVM, which were recently introduced to LIBS analysis, have more potential for LIBS data analysis. Two key factors determine the performance of the quantitative analysis model: the input of the model and the model parameters. If the full spectrum is selected as the input, too much interference information will be introduced, which will increase the computational complexity and affect the analytical accuracy. Thus, the input of the model should be selected reasonably. Because the complexity, computation time and the performance of analysis model are mainly determined by the model parameters, when selecting the model parameters, nonlinear effects such as the self-absorption and matrix effects in LIBS should be considered.

4 Conclusions

Data processing, which is an indispensable part of LIBS analysis, is an effective method for improving the accuracy and precision. This paper reviews research progress on two aspects of LIBS data processing: data preprocessing methods and data analysis methods. In research on both of these aspects, researchers in Asia have made great progress.

Although the performance of LIBS can be improved to a certain extent by using data processing methods, a performance gap still exists between LIBS and conventional analysis methods. The potential for improving the accuracy and precision of LIBS can be revealed by using data processing methods. Data preprocessing methods should take into account the formation mechanism of laser-induced plasma and the characteristics of spectral data, as well as the processing of spectral data using appropriate mathematical methods. Data analysis methods should construct a simple and efficient model that considers nonlinear factors such as the self-absorption and matrix effects. The market for applications of LIBS techniques has recently broadened both in Asia and worldwide. To realize commercialization of LIBS, its accuracy, precision, and repeatability must be further improved.

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