Chemometrics and Intelligent Laboratory Systems 167 (2017) 226–231

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemometrics

Determination of carbon and sulfur content in coal by laser induced breakdown spectroscopy combined with kernel-based extreme learning machine

Chunhua Yan[a], Juan Qi[a], Junxiu Ma[a], Hongsheng Tang[a], Tianlong Zhang[a,**], Hua Li[a,b,*]

[a] *Institution of Analytical Science, College of Chemistry & Materials Science, Northwest University, Xi'an, 710069, China*
[b] *College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, 710065, China*

ARTICLE INFO

Keywords:
Laser-induced breakdown spectroscopy
Kernel-based extreme learning machine
Coal
Carbon
Sulfur

ABSTRACT

The carbon and sulfur content is an important index of coal property. In the present work, kernel-based extreme learning machine (K-ELM) model was built and applied to laser induced breakdown spectroscopy (LIBS) to improve the quantitative analysis accuracy of carbon and sulfur in coal. The different preprocessing techniques, input variables and model parameters were optimized by 5-fold cross validation to find which combination can provide an appropriate calibration model. Then the optimized K-ELM model was applied to quantitative analysis of carbon and sulfur content in coal, and a comparison with support vector machine (SVM), least squares support vector machine (LS-SVM) and back propagating artificial neutral net (BP-ANN) was carried out. The three quantitative techniques were evaluated in terms of Root Mean Square Error (RMSE) and correlation coefficients (R^2). The results show that K-ELM model has excellent performance compared to the others both in calibration and prediction set, and the optimum results of the K-ELM model were achieved with RMSE = 0.3762%, $R^2 = 0.9994$ for C and RMSE = 0.7704%, $R^2 = 0.9832$ for S in the prediction set. The overall results sufficiently demonstrate that LIBS coupled with K-ELM method has the potential to measure carbon and sulfur content in coal, and is a promising technique for real-time online, rapid analysis in coal industry.

1. Introduction

Coal is the major fossil energy resource in the world. It has been used as an energy resource, primarily burned for the production of electricity and heat, and is also used for industrial purposes, such as refining metals. As the main composition of organic matter in coal, carbon is a major indicator of coal quality, and can be used to rapidly estimate the calorific value of coal. Sulfur is one of the major and hazardous component of coal. Sulfur dioxide (SO_2) generated during coal combustion not only cause the pipeline and equipments corrosion but also significantly threaten human health and the global environment. In addition, C and S content also influence the commodity prices and affect the chemical combustion properties of coal. The accurate measurement of carbon and sulfur content in coal is contribute to help underpin the chemical assessment of fuel commodities and decision about the suitability of coal [1]. Therefore, it is necessary to develop an efficient method for determination of C and S in coal.

A wide number of analytical techniques have been developed to quantitative analysis of carbon and sulfur, such as volumetry [2], X-ray fluorescence spectrometry (XRF) [3,4], UV–vis spectrometry [5,6], optical emission spectrometry with inductively coupled plasma (ICP-OES) [7–9] and mass spectrometry with inductively coupled plasma (ICP-MS) [10–12]. All of these techniques, except for XRF, require complicated sample preparation procedure including wet acid digestion, which is certainly hinder their application in the case of mineral coal. While XRF method has difficulties in analyzing light elements due to instrumental limitations and low X-ray yields for the light elements. Laser induced breakdown spectroscopy (LIBS) is an optical emission spectroscopy technique with the capacity of fast, multi-elemental analysis, minimal sample preparation, non-destructive analysis and in-situ analysis. These characterization properties make LIBS become a very popular analytical technique in many fields such as environment monitoring [13–15], biomedical and pharmceutical analysis [16,17] and space exploration [18–20].

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[*] Corresponding author. Institution of Analytical Science, College of Chemistry & Materials Science, Northwest University, Xi'an, 710069, China; College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, 710065, China.
[**] Corresponding author.
E-mail address: huali@nwu.edu.cn (H. Li).

http://dx.doi.org/10.1016/j.chemolab.2017.06.006
Received 19 January 2017; Received in revised form 19 May 2017; Accepted 3 June 2017

Since each element has its own set of emission lines, a appropriate analytical method that can be used to quantitatively correlate the LIBS spectral intensity of a specific peak with the elemental content. However, the traditional linear methods may not completely present the relationship between the LIBS spectral intensity and element content because of the uncontrollable fluctuation of the experimental parameters, the inhomogeneity of sample surface and physical and chemical matrix effects. Therefore, it is necessary to develop and apply efficient multivariate nonlinear analysis methods to overcome this problem. In recent years, the chemometric methods such as support vector machines (SVM) [21], random forest (RF) [22,23] and artificial neural network (ANN) [24,25] have been extensively used in LIBS spectra for both quantitative and qualitative analysis. However, these algorithms does involve some inherent questions, which hinders their application in LIBS spectra. For example, most traditional neural networks through a gradient descent algorithm to update its parameters, which make the training process is quite slow and it is easy to fall into local optimum. Therefore, many new algorithms with respect to good generalization performance at extremely fast learning speed have been proposed to overcome these shortcomings.

Extreme learning machine (ELM) [26] as a relatively new nonlinear method, has shown its excellent performance in classification [27] and regression [28] problems. Different from most learning algorithms with gradient descent, ELM randomly initializes the weights and biases between the input layer and hidden layer, while the weights between the hidden layer and output layer are selected by minimal norm least square method. Therefore, ELM can effectively avoid the slow training speed and over-fitting problems suffered by traditional neural network training algorithms. Furthermore, it possesses similar high generalization performance compared to other conventional learning algorithms such as back propagation artificial neural network (BP-ANN) [29] and support vector machine (SVM) [30]. However, ELM produces a large variation in result with the same number of hidden nodes due to the randomly assigned input weights and bias. A kernel-based extreme learning machine (K-ELM) [31] has been developed lately to solve this problem, and in which the hidden layer of ELM was replaced with a kernel function.

In the present article, LIBS combined with K-ELM was used to measure carbon and sulfur content in coal. At first, the different preprocessing techniques, input variables and model parameters were studied in detail to find which combination can provide an appropriate calibration model. Then, carbon and sulfur content in coal were measured by K-ELM model and the results were compared with SVM, LS-SVM and BP-ANN models. The performance of the four quantitative techniques were evaluated by RMSE and R^2 values.

2. Material and methods

2.1. LIBS setup

LIBS measurements were obtained using a 8 ns Q-switched Nd: YAG laser (Beamtech Optronics Co., Ltd., Dawa-300) operating at 1064 nm, with energy of 90 mJ and a maximum repetition rate of 10 Hz. The sample was placed directly on an X-Y-Z manual micrometric stage. The laser beam was focused on the sample surface using an objective with 50 mm of focal length to create the plasma, and the resulting ablating spot diameter was 0.2 mm. Then the light emitted from the plasma was collected through a collecting lens at a 45° angle with respect to the laser beam, and an optical fiber was then delivered it to a spectrometer (MX2500-3PLUS, Ocean Optics, USA) which is equipped with a CCD camera. The delay time was set to be 3 μs and gate width was set to be 100 μs. All measurements were performed in air at atmospheric pressure. The quantitative analysis of carbon and sulfur content in coal sample were carried out using MATLAB (2010b).

2.2. Coal samples

Twenty-six coal standard samples from Jinan Zhongbiao Technologies Co Ltd in the form of powder were used in this study. Table 1 shows the carbon and sulfur content of the coal samples. Each powdered sample was pressed into a pellet with a pressure of 100 MPa for 5 min, and 20 different positions were randomly selected and measured for each pellet. Furthermore, in order to reduce the influences of shot to shot fluctuations and improve the signal-to-noise ratio, each measured spectrum was obtained by the accumulation of 10 laser pulses. In this work, the analytical spectra for each coal sample were the average of 20 spectra, and 26 (one LIBS spectra for each coal sample) analytical spectra were acquired from the 26 coal samples. Eighteen samples were randomly selected to

Table 1
The reference elemental content (wt.%) of the coal samples used in this work.

No.	CRM-No.	Sample-No.	Carbon (%)	Sulfur (%)
1[a]	–	ZBM091	79.70	1.93
2	–	ZBM092	76.21	3.85
3[a]	GSB06-2105-2007	ZBM095	81.44	0.35
4	GSB06-2106-2007	ZBM096	81.45	0.40
5	GSB06-2108-2007	ZBM098	78.50	1.70
6[a]	GSB06-2109-2007	ZBM099	79.60	0.66
7	GSB06-2181-2008-1	ZBM100	47.02	1.40
8[a]	GSB06-2181-2008-3	ZBM102	58.00	1.26
9	GSB06-2181-2008-4	ZBM103	59.40	2.90
10	GSB06-2181-2008-5	ZBM104	53.63	4.35
11[a]	GSB06-2181-2008-6	ZBM105	53.43	6.45
12	GSB06-2110-2007	ZBM106	72.65	0.57
13	–	ZBM107	80.00	1.54
14	GSB06-2111-2007	ZBM108	79.02	0.58
15	–	ZBM109	70.90	0.45
16[a]	GSB06-2112-2007	ZBM111A	74.16	0.81
17	GSB06-2112-2007	ZBM111B	72.05	0.88
18	GSB06-2114-2007	ZBM113	78.64	2.07
19	GSB06-2115-2007	ZBM114	74.70	0.27
20	GSB06-2116-2007	ZBM115	76.50	0.20
21[a]	GSB06-2117-2007	ZBM120	77.28	0.42
22	GSB06-2118-2007	ZBM121A	75.34	0.50
23	–	ZBM122	82.30	1.30
24	–	ZBM123	79.77	0.51
25	–	ZBM124	76.57	2.50
26[a]	–	ZBM130	80.79	0.87

[a] Selected for prediction sample.