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1. Introduction

In 2019, the installed capacity of thermal power generation in China was 1.19 billion kilowatts, accounting for 69.5% of the total power generation. The annual consumption of coal was 4.86 billion tons, and the average coal consumption was 305 g $kW^{-1} h^{-1}$. If the coal consumption is reduced by 1 g $kW^{-1} h^{-1}$, 11.9 million tons of coal will be consumed annually in China, which is equivalent to nearly 1 billion dollars, and correspondingly reduces 120 000 tons of sulfur oxides and 100 000 tons of nitrogen oxides.^{1,2} Therefore, the development of optimization control technology for coal blending and combustion in thermal power plants is of great significance for reducing coal consumption and has great economic and social benefits. The key to achieving optimal control of these processes in thermal power generation is to quickly analyze the calorific

Ultra-repeatability measurement of the coal calorific value by XRF assisted LIBS

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The calorific value of coal mainly depends on the content of combustible organic elements and ash, and is a comprehensive indicator of coal quality. It is of great significance to quickly obtain the calorific value of coal entering the boiler for the optimal control of coal blending and combustion in thermal power generation. However, the measurement repeatability of LIBS for the coal calorific value has not yet met the requirement of a standard deviation (SD) of less than 120 J q^{-1} in the Chinese national standard. This paper innovatively proposes an analytical method of XRF-assisted LIBS, which can not only analyze the combustible organic light elements by LIBS, but also can analyze the inorganic ash-forming elements by XRF with high stability, thus greatly improving the measurement repeatability of the coal calorific value. According to the stability of intensity, the elemental emission lines in the LIBS and XRF spectra are selected reasonably, and the prediction model is established through principal component analysis and multiple regression. The experimental results show that the SD of coal calorific values predicted is 72 J q^{-1} , which is one order of magnitude lower than the 700 J q^{-1} of traditional LIBS, and fully meets the requirement of the national standard. It is found that the measurement instability of the calorific value mainly comes from the contribution of the C line, and the SD of the calorific value can be further reduced to 56 J q^{-1} by means of spectral screening. This XRF-assisted LIBS technology with ultrarepeatability is expected to be applied in power plants, coal chemical industries and other industrial fields that need to pay close attention to coal quality.

value of coal entering the boiler and adjust the air-coal proportion in time to achieve full combustion of the coal.

The calorific value of coal is defined as the heat generated by the complete combustion of coal per unit mass, and is a comprehensive indicator of coal quality. It is not only positively correlated with the content of C, H, and S involved in combustion, but also closely negatively correlated with the ash content (oxides of Si, Al, Ca, Fe, Mg, etc.). The traditional calorific value of coal is determined by the oxygen bomb method³⁻⁵ specified in GB/T 213-2008,6 and is calculated by the rise of water temperature caused by combustion of coal in an oxygen bomb. Obviously, it is time-consuming and lags behind the industrial production seriously. The most commonly used rapid analysis method is prompt gamma neutron activation,^{7,8} which uses a neutron source to activate coal and analyzes the gamma ray energy spectra to realize proximate analysis of coal. However, radioactive hazards emanate from the instrument during operation, and the accuracy of the calorific value converted using the empirical formula is poor.

Laser-induced breakdown spectroscopy (LIBS)⁹ as an emerging spectral analysis method has become one of the most potential coal quality analysis technologies at present due to the advantages of being fast and safe and simultaneous multi-

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Paper

element measurement.¹⁰ The principle is that plasma is produced by focusing a powerful laser pulse on the target sample and its emission is resolved using a spectrometer to determine the elemental composition and concentration ratio.11 There have been many reports on the measurement of the coal calorific value using LIBS. For example, Li et al.12 combined a back propagation neural network with cluster analysis to analyze the calorific values of 35 coal samples, and the predicted average relative error (ARE) was less than 4.23%. Yuan et al.¹³ established a partial least squares (PLS) model based on the dominant factors, and the root mean square error (RMSEP) of the predicted calorific values was reduced to 1300 J g⁻¹. In our previous work,¹⁴ a fully softwarecontrolled LIBS coal quality analyzer was designed, using the closed-loop negative feedback pulsed laser energy stabilization technology and the support vector machine nonlinear regression method, and the RMSEP of the calorific value reached 850 J g⁻¹. Qin et al.¹⁵ proposed a method of LIBS combined with Fourier transform infrared spectroscopy to simultaneously extract the atomic and molecular information on elements in coal, and the RMSEP of the calorific value was as low as 560 J g^{-1} . By comparing the effects of various spectral pretreatment methods, Li et al.16 selected the quantitative model of 11-point smoothing and second-order derivation, and the RMSEP of the calorific value reduced to 280 J g⁻¹. Hou et al.¹⁷ proposed a set of data processing algorithms including spectral line standardization, spectral line identification, and PLS based on the dominant factors, which further reduced the RMSEP of the calorific value to 70 J g^{-1} . However, the above research mainly focused on the measurement accuracy, but in practice, it pays more attention to whether the measurement repeatability meets the national standards.3 There are few reports on improving the repeatability of LIBS for the coal calorific value. Yao et al.18 combined cluster analysis, artificial neural networks (ANNs) and genetic algorithms (GAs) to analyze the LIBS spectra of coal powder, and the mean standard deviation (SD) of the calorific value was 860 J g⁻¹. Lu et al.¹⁹ also employed ANNs and GAs to perform LIBS measurement of the calorific value, and the reported SD was 380 J g⁻¹. Li et al.²⁰ proposed a fullspectrum quantitative model for spectral correction, and the SD of the calorific value was further reduced to 220 J g^{-1} by PLS variable selection. However, the repeatability of LIBS measurement of the coal calorific value has not yet reached the national standard ($\leq 120 \text{ J g}^{-1}$). This may be due to the inherent fluctuation of pulse energy, the poor representativeness of small focus, and the susceptibility of plasma to the environment,²¹ which greatly limit the LIBS measurement repeatability. How to break through this bottleneck has become the key to the industrial application of LIBS.

In recent years, X-ray fluorescence (XRF) spectrometry^{22,23} has been well applied to the determination of the coal ash composition and ash-forming elements. For example, Parus *et al.*²⁴ and Hicks *et al.*²⁵ used XRF to analyze the ash content of coal, and the SD was only 1.7%. Ma *et al.*²⁶ employed XRF to analyze the content of Si, Al, Fe, Ca, Mg, Na, K, Ti, P and other ash-forming elements in coal, and the measurement

repeatability was far less than the requirement of the national standard.²⁷ The principle of XRF is that when individual atoms are excited using external energy, they will emit X-ray photons with characteristic energy or wavelength and thus realize the quantification of elements.²⁸ Although XRF has excellent repeatability in the measurement of inorganic ash-forming elements and even the ash content in coal, it cannot predict the calorific value of coal. This is because XRF is unable to analyze the light organic elements such as C and H, which are positively related to the calorific value.

Compared with LIBS and XRF, the former can analyze almost all the elements in coal, including C and H, but its measurement repeatability is not ideal, while the latter can only analyze ash-forming elements in coal, but it has high repeatability. It is assumed that if the two methods are combined to form an XRFassisted LIBS technology for coal calorific value analysis, not only organic elements can be detected, but also inorganic elements can be analyzed with high stability. The measurement repeatability is expected to meet the requirement of the national standard. In this work, the XRF and LIBS spectra of dozens of coal samples are combined for modeling and quantitative prediction to verify the repeatability of XRF assisted LIBS in coal calorific value measurement.

2. Experimental

2.1 Samples

A total of 49 powdered coal samples certified by China Coal Research Institute (CCRI) were used in this experiment, with a calorific value ranging from 2.28 \times 10³ J g⁻¹ to 32.50 \times 10³ J g^{-1} (Table 1). The C1, C2, and V1 samples with lower calorific values belong to coal gangue, the C17, C21, C22, C27, C28, C29, C32, V12 and V14 samples are anthracite coal, and the rest are bituminous coal. These three types of coal were employed to test the performance of the prediction model and the applicability of the proposed method. Each coal sample was pressed into a tablet with a radius of 33 mm and a thickness of 6 mm using an electric press machine (DY-30) under a pressure of 20 tons for 3 minutes. All the coal samples were divided into a calibration set with 33 samples (denoted as C1-C33) and a validation set with 16 samples (denoted as V1-V16). The spectra of the calibration set were used to establish the prediction model, while those of the validation set were used to validate the quantitative performance. Here, in order to ensure the applicability of the prediction model and the representativeness of the validation set, all the samples were sorted according to the calorific values, and one out of three was selected for validation.

2.2 LIBS setup

The LIBS setup used in the experiment has been shown in detail in our previous work,²⁹ and it mainly consisted of a laser source, spectrometer, beam expander, sample stage, stepper motor and computer. A Q-switched Nd:YAG laser (INDI-HG-20S) operating at 1064 nm was employed as the ablation source, with a fixed energy of 38 mJ per pulse and a pulse width of 8 ns. After three times of beam expansion, the laser was focused on the surface

Table 1 Certified calorific values of 49 coal samples. Here, the italic font represents the coal gangue and the bold font indicates the anthracite coal

Sample no.	Calorific value $(\times 10^3 \text{ J g}^{-1})$	Sample no.	Calorific value $(\times 10^3 \text{ J g}^{-1})$	Sample no.	Calorific value $(\times 10^3 \text{ J g}^{-1})$
<i>C1</i>	2.28	C2	7.60	C3	18.16
C4	19.54	C5	20.05	C6	20.98
C7	20.99	C8	21.39	C9	21.64
C10	23.72	C11	24.35	C12	25.24
C13	25.42	C14	25.57	C15	25.72
C16	25.95	C17	26.76	C18	28.85
C19	29.44	C20	29.72	C21	29.80
C22	30.00	C23	30.03	C24	30.45
C25	30.51	C26	30.57	C27	31.09
C28	31.20	C29	31.23	C30	31.40
C31	31.73	C32	32.16	C33	32.50
V1	4.94	V2	19.42	V3	20.65
V4	21.33	V5	22.45	V6	24.36
V7	25.55	V8	25.80	V9	26.85
V10	29.50	V11	29.93	V12	30.28
V13	30.56	V14	31.19	V15	31.25
V16	31.86				

of the coal tablet using a flat convex lens with a focal length of 150 mm to generate plasmas. Here, the tablet was placed on an X-Y-Z translation stage controlled using a function generator (33522A-Keysight). The plasma spectra were collected using an optical fiber and then coupled into a three-channel spectrometer (Avs-Desktop-USB2) for spectroscopic detection. Here, the spectral ranges of the three channels were 200-450 nm, 450-680 nm and 680-1000 nm, the spectral resolution was 0.15 nm, and the integration time was set to the minimum 1 ms. The spectral intensity was calibrated using a powerful deuterium halogen source (Avantes, AvaLight-DH-S-BAL). As the laser hit the coal sample, dust was generated, which interfered with the collected plasma fluorescence. Therefore, a negative pressure tube was placed on the surface of the coal sample to quickly suck away the dust. In order to eliminate the interference of water vapor in the air on the H line in the LIBS spectrum, a dehumidifier in the laboratory was used to ensure that the relative ambient humidity is around 25%. In order to eliminate the adverse effects of sample heterogeneity on the results, 100 repeated spectra at different positions on the sample surface were collected, normalized and averaged.

2.3 XRF setup

In our experiment, the X-ray fluorescence spectra of the coal samples were collected using a commercial energy dispersive XRF (ED-XRF) spectrometer (DF-1000), in which a rhodium anode sealed X-ray tube operated at 12 kV/200 μ A and the internal filament operated at 0.5 V/0.8 A provided the X-ray source. The generated X-ray hit the samples, and the fluorescence signals were collected using a silicon drift detector (VICO-DV H20) with a time constant of 2 μ s and magnification of 7. The ambient temperature of the laboratory was maintained at 26 °C, and each coal sample was measured in a vacuum environment of 50 Pa for 100 s.

In our experiments, the XRF measurement on each coal sample was performed prior to the LIBS measurement. This is because LIBS is a micro-loss technique, while XRF is a nondestructive one. Performing XRF measurement first will not affect the LIBS measurement results.

2.4 Evaluation method

The following describes the evaluation methods of spectral line stability, measurement accuracy and repeatability in the experiment. The evaluation of spectral line stability is to select the most stable spectral line of the same element from the LIBS and XRF spectra for modeling. Here, the RSD was used for evaluation, which is defined as:

$$RSD = \frac{\sqrt{\sum_{q=1}^{p} (Z_q - Z_k)^2}}{\frac{p-1}{Z_k}},$$
(1)

where *Z* is the line intensity of an element, Z_k is the average line intensity, *q* is the measurement order of the same sample, and *p* is the total number of repeated measurements of the same sample. The smaller the RSD, the better the stability of the spectral line.

The measurement accuracy is to evaluate the closeness between the measurement results and the true values. The determination coefficient of the prediction curve (R^2), root mean square error of prediction (RMSEP) and average relative deviation (ARE) were used to evaluate the quantitative performance. Here, the expressions of R^2 , RMSEP and ARE are as follows:

$$R^{2} = 1 - \frac{\sum_{j=1}^{m} (y_{aj} - y_{cj}) (y_{bj} - y_{dj})}{\sum_{j=1}^{m} (y_{aj} - y_{cj}) \sum_{j=1}^{m} (y_{bj} - y_{dj})},$$
(2)

$$\mathbf{RMSEP} = \sqrt{\frac{\sum_{i}^{n} (y_{aj} - y_{bj})^{2}}{n}},$$
(3)

$$ARE = \frac{1}{m} \sum_{j=1}^{m} \frac{|y_{aj} - y_{bj}|}{y_{aj}} \times 100\%,$$
(4)

where y_a and y_b are the true and predicted values of the calorific value, y_c and y_d are the average of the true and predicted values of all the coal samples, *j* is the sample order, *m* is the total number of coal samples, *i* is the sample order of the validation set, and *n* is the total number of the validation set. The closer R^2 is to 1, the better the linearity of the prediction model. And the closer RMSEP and ARE are to 0, the smaller the deviation between the predicted results and the true values.

The measurement repeatability is to evaluate the degree of consistency between the repeated measurement results of the same sample. The SD was used to judge the stability of the calorific value predicted for the same sample:

$$\mathbf{SD} = \sqrt{\frac{\sum\limits_{q=1}^{p} \left(V_q - V_k\right)^2}{p-1}},$$
(5)

where V is the calorific value of the sample, and V_k is the average calorific value of the same sample during repeated measurement. The smaller the SD, the better the measurement repeatability of the calorific value.

3. Results and discussion

3.1 Spectral line selection

In order to fully combine the LIBS and XRF spectra to build a stable prediction model, it was necessary to select appropriate spectral lines. The two typical spectra of coal obtained in the experiment are shown in Fig. 1. In the LIBS spectrum shown in Fig. 1(a), the spectral lines of 11 elements related to the calorific value of coal, including C, Mg, Mn, Si, Al, Ti, Fe, Ca, Na, H, and K, were marked. However, there was no spectral line of S because not only its excitation potential is too high to be excited, but also its characteristic lines are located in the ultraviolet or near-infrared region, which is beyond the wavelength range of this spectrometer. In the XRF spectrum shown

Table 2Spectral lines of the elements in the LIBS and XRF spectra.Here, the lines selected for modeling are shown in bold

Method	С	Mg	Si	Al	Ti	Fe
LIBS (nm)	247.9	279.6	288.2	309.3	334.9	388.3
XRF (keV)		1.25	1.84	1.56	4.51	7.11
Method	Ca	Mn	Na	Н	К	S
LIBS (nm)	393.5	404.7	589.1	657.9	770.0	
XRF (keV)	4.04	6.54	1.04	—	3.61	2.47

in Fig. 1(b), the horizontal axis is the energy, and the vertical axis is the line intensity. It can be seen that there are 16 spectral lines, in which 10 elements of interest including Mg, Al, Si, S, K, Ca, Ti, Na, Mn, and Fe are marked in red. Among them, the line intensities of Mg and Na were relatively small, which was due to the poor excitation efficiency of XRF for light elements, while those of Al, Si, Fe, and especially S were high. Here, all the spectral lines marked in Fig. 1 are listed in Table 2. It can be seen that there are spectral lines of Al, Ca, Si, Fe, Mg, K, Ti, Mn and Na in the two spectra. Next, we will calculate and compare the stability of different lines of these elements in the XRF and LIBS spectra, so as to make an appropriate selection of spectral lines.

Fig. 2 and Table 3 show the comparison of the RSDs of each element using the two methods. It can be seen that the RSDs of Al, Ca, Si, Fe, Mg, K, Ti, and Mn measured by XRF were much smaller than those by LIBS, while the RSD of Na measured by LIBS was smaller than that by XRF. This shows that XRF has good stability in measuring Al, Ca, Si, Fe, Mg, K, Ti and Mn, while LIBS has better stability in measuring Na. Considering the elements S, C and H, the prediction model of the coal calorific value was established by using Al, Ca, Si, Fe, Mg, K, Ti, Mn, and S lines in the XRF spectra and C, H, and Na lines in the LIBS spectra (Table 2).

3.2 Performance evaluation

The performance of XRF assisted LIBS was evaluated by using the four parameters R^2 , RMSEP, ARE and SD, and was compared with that of traditional single LIBS. Before multiple linear



Fig. 1 Typical spectra of coal using two methods: (a) LIBS spectrum, and (b) XRF spectrum.



Fig. 2 A comparison of the RSDs of each element in coal measured by LIBS and XRF.

Table 3 A comparison of the RSDs (%) of each element in coal measured by LIBS and XRF

Method	Al	Ca	Si	Fe	Mg	K	Ti	Mn	Na
LIBS (%)	$\begin{array}{c} 1.10\\ 0.22 \end{array}$	3.90	1.65	2.28	2.74	3.12	2.60	2.88	2.67
XRF (%)		0.04	0.33	0.32	0.57	0.33	0.18	0.24	3.28

regression, the principal component analysis (PCA) was used to reduce the interference between the spectral lines of different elements. Therefore, the input variables of the model by XRFassisted LIBS were the principal components obtained after PCA of the 9 elemental spectral lines in the XRF spectra and the 3 elemental spectral lines in the LIBS spectra, while those by LIBS were principal components obtained after PCA of 11 elemental lines in the LIBS spectra.

Fig. 3(a) and (b) show the consistency between the predicted values and certified values of the calorific value of all the coal samples by using this method and LIBS, respectively. The horizontal axis is the certified calorific value of the coal samples, the vertical axis is the predicted calorific value of the coal samples, the

blue triangles represent the calibration set, and the red circles represent the validation set. It can be seen that compared with those of LIBS, the linear correlation R^2 of the fitting curve was increased from 0.926 to 0.983, the RMSEP of the coal calorific value was reduced from 2.8×10^3 J g⁻¹ to 0.9×10^3 J g⁻¹, and the ARE was reduced from 5.6% to 3.2%. This indicates that the prediction results of the proposed XRF-assisted LIBS are closer to the true values, and the measurement accuracy of the coal calorific value has been effectively improved. In addition, the error bars of the prediction results of the validation set were also marked in the figures, which show that each pair of error bars of this method was almost coincident and difficult to distinguish, while that of LIBS was extremely obvious.

For a clearer comparison, Fig. 4 shows a SD histogram of the calorific values of 16 validation coal samples measured by the two methods. The blue horizontal line represents the mean SD of the calorific values predicted by LIBS, the black horizontal line represents the SD of the coal calorific value specified in the Chinese national standard, and the red horizontal line represents the mean SD of the calorific values predicted by XRF-assisted LIBS. It shows that the SDs of calorific values of most



Fig. 4 Comparison between the SDs of LIBS and XRF assisted LIBS for calorific value prediction and the national standard.



Fig. 3 Quantitative results of the calorific value by (a) XRF assisted LIBS and (b) LIBS.

of the coal samples (except for V9, V12 and V14) determined by XRF assisted LIBS were lower than the national standard (\leq 120 J g⁻¹), and the difference between the SDs of the coal samples was very small. The average SD of XRF assisted LIBS was 72 J g⁻¹, which had met the requirement of the Chinese national standard. In contrast, all the SDs of the calorific values of the validation samples measured by LIBS were much higher than the national standard, and the SDs of the coal samples varied greatly. The average SD of LIBS was 700 J g⁻¹, which is nearly 5 times higher than the national standard. This illustrates that the SD of XRF-assisted LIBS has been reduced by an order of magnitude compared to that of single LIBS, and this ultrarepeatability fully meets the requirement of the national standard.

3.3 Instability analysis

In order to further explore the contribution of fluctuation of the spectral line intensity of the elements to the SD of the calorific values predicted, we conducted the following instability analysis. By substituting the RSD corresponding to the spectral line of each element into the above prediction model for calculation, the contribution rate graph shown in Fig. 5 was obtained. It can be seen that the total contribution rate of the RSDs of the spectral lines of C, Mg and Mn to the SD of the calorific value exceeded 90%, especially the C line was more than half. Therefore, the key to improving the measurement repeatability was to further reduce the RSDs of these three spectral lines. Since the Mg and Mn lines were derived from the ultra-high stable XRF spectra, it was almost impossible to reduce the RSD. In this way, we could only reduce the RSD of the C 247.9 nm line from the LIBS spectra. The instability of the C line was mainly due to plasma shaped variation because of cracking, gas dynamics and others, so it was inevitable to collect a few poor spectra. Here we set a signal-to-background ratio threshold of 3 to eliminate these spectra. After spectral screening, the RSD of the C line has decreased from 10.4% to 6.2%, and the SD of the predicted calorific value has been further reduced from 72 J g^{-1} to 56 J g^{-1} .



Fig. 5 RSD of the line intensity of each element and its contribution to the SD of the calorific value.

4. Conclusions

In this paper, a novel XRF-assisted LIBS method for ultrarepeatability measurement of the coal calorific value was proposed based on the advantages of the good stability of X-ray fluorescence for the determination of inorganic elements, and the prediction accuracy and repeatability were evaluated using R^2 , RMSEP, ARE and SD. According to the RSDs of the intensity of lines, the optimal lines of the elements in the XRF and LIBS spectra were selected. The C, H, and Na lines from the LIBS spectra and Al, Ca, Si, Fe, Mg, Ti, Mn, S, and K lines from the XRF spectra were used in the prediction model. The preliminary experimental results showed that the R^2 , RMSEP and ARE of XRF-assisted LIBS were better than those of single LIBS, indicating that this new method can improve the measurement accuracy. More importantly, the SD of the coal calorific value predicted by XRF-assisted LIBS was merely 72 J g^{-1} , which is an order of magnitude lower than that of LIBS, and fully met the requirement of less than 120 J g^{-1} as specified in the national standard. In addition, we also studied the influence of the stability of line intensity on the measurement repeatability, and found that the SD of the calorific value was mainly contributed by the RSD of the C line and could be further reduced to 56 J g^{-1} by spectral screening. This XRF-assisted LIBS technique is expected to be widely promoted in coal-fired enterprises and coal chemical industries. Next, we will strive to develop prototypes for industrial field testing.

Author contributions

X. L. L. and L. Z. designed the experiments and conducted the calculations. X. L. L., L. Z., Z. H. T., and Y. B. performed the experiments. S. Q. W., J. H. H., G. F. X., W. G. M., L. D., W. B. Y., L. T. X., and S. T. J. guided the setup of experimental protocols and supervised the completion of the experiments and papers. All the authors read and approved the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

1 S. Nazari, O. Shahhoseini, A. Sohrabi-Kashani, S. Davari, R. Paydar and Z. Delavar-Moghadam, Experimental determination and analysis of CO_2 , SO_2 and NO_x emission factors in Iran's thermal power plants, *Energy*, 2010, 35, 2992–2998.

- 2 S. H. Lee, S. J. Yoon, H. W. Ra, Y. I. Son, J. C. Hong and J. G. Lee, Gasification characteristics of coke and mixture with coal in an entrained-flow gasifier, *Energy*, 2010, 35, 3239–3244.
- 3 S. Sheta, M. S. Afgan, Z. Y. Hou, S. C. Yao, L. Zhang, Z. Li and Z. Wang, Coal analysis by laser-induced breakdown spectroscopy: a tutorial review, *J. Anal. At. Spectrom.*, 2019, **34**, 1047–1082.
- 4 P. Lindahl and A. Bishop, Determination of trace elements in coal by an oxygen bomb combustion/atomic absorption spectrophotometric method, *Fuel*, 1982, **61**, 658–662.
- 5 C. N. Standards, *Determination of calorific value of coal*, https://www.cnis.ac.cn/.
- 6 N. K. Mandavgade, S. B. Jaju and R. R. Lakhe, Determination of Uncertainty in Gross Calorific Value of Coal Using Bomb Calorimeter, *International Journal of Measurement Technologies and Instrumentation Engineering*, 2011, 1, 45–52.
- 7 C. He, Z. Yang, L. Chen, G. Huang and L. Han, Influencing factors of on-line measurement of straw-coal blends using near infrared spectroscopy, *Trans. Chin. Soc. Agric. Eng.*, 2014, **30**, 192–200.
- 8 J. X. Zhang, The application and safety management of coalscan 2500 ash-admeasuring apparatus, *Sci/tech Information development & economy*, 2005, vol. 15, pp. 269–270.
- 9 Q. Yu, X. H. Ma, R. Wang and H. F. Zhao, Research on fast classification based on LIBS technology and principle component analyses, *Spectrosc. Spectr. Anal.*, 2014, 34, 3095–3099.
- 10 M. P. Mateo, G. Nicolas and A. Yaiiez, Characterization of inorganic species in coal by laser-induced breakdown spectroscopy using UV and IR radiations, *Appl. Surf. Sci.*, 2007, 254, 868–872.
- 11 M. Gondal, M. Siddiqui and M. Nasr, Detection of trace metals in asphaltenes using an advanced laser-induced breakdown spectroscopy (LIBS) technique, *Energy Fuels*, 2010, 24, 1099–1105.
- 12 Y. S. Li, W. Y. Lu, J. B. Zhao, G. X. Feng and Z. M. Lu, Detection of caloric value of coal using laser-induced breakdown spectroscopy combined with BP neural networks, *Spectrosc. Spectr. Anal.*, 2017, **37**, 2575–2579.
- 13 T. B. Yuan, Z. Wang, S. L. Lui, Y. T. Fu, Z. Li, J. M. Liu and W. D. Ni, Coal property analysis using laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2013, 28, 1045–1053.
- 14 L. Zhang, Y. Gong, Y. F. Li, X. Wang, J. J. Fan, L. Dong, W. G. Ma, W. B. Yin and S. T. Jia, Development of a coal quality analyzer for application to power plants based on laser-induced breakdown spectroscopy, *Spectrochim. Acta, Part B*, 2015, **113**, 167–173.
- 15 H. Q. Qin, Z. M. Lu, S. C. Yao, Z. H. Li and J. D. Lu, Combining laser-induced breakdown spectroscopy and Fourier-transform infrared spectroscopy for the analysis of coal properties, *J. Anal. At. Spectrom.*, 2019, **34**, 347–355.

- 16 W. B. Li, J. D. Lu, M. R. Dong, S. Z. Lu, J. H. Yu, S. S. Li, J. W. Huang and J. Liu, Quantitative analysis of calorific value of coal based on spectral preprocessing by laserinduced breakdown spectroscopy (LIBS), *Energy Fuels*, 2018, **32**, 24–32.
- 17 Z. Y. Hou, Z. Wang, T. B. Yua, J. M. Liu, Z. Li and W. D. Ni, A hybrid quantification model and its application for coal analysis using laser induced-breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2016, **31**, 722–736.
- 18 S. C. Yao, J. H. Mo, J. B. Zhao, Y. S. Li, X. Zhang, W. Y. Lu and Z. M. Lu, Development of a rapid coal analyzer using laserinduced breakdown spectroscopy (LIBS), *Appl. Spectrosc.*, 2018, 72, 1225–1233.
- 19 Z. Lu, J. h. Mo, S. C. Yao, J. B. Zhao and J. D. Lu, Rapid determination of the gross calorific value of coal using laser-induced breakdown spectroscopy coupled with artificial neural networks and genetic algorithm, *Energy Fuels*, 2017, **31**, 3849–3855.
- 20 W. B. Li, M. R. Dong, S. Z. Lu, S. S. Li, J. W. Huang and J. D. Lu, Improved measurement on calorific value of pulverized coal particle flow by laser-induced breakdown spectroscopy (LIBS), *Anal. Methods*, 2019, **11**, 4471–4480.
- 21 T. A. Labutin, A. M. Popov, S. N. Raikov, S. M. Zaytsev, N. A. Labutina and N. B. Zorov, Determination of chlorine in concrete by laser-induced breakdown spectroscopy in air, *J. Appl. Spectrosc.*, 2013, **80**, 315–318.
- 22 U. Stephan, Quantitative XRF of solid samples using an iterative matrix correction code, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1986, **242**, 550–557.
- 23 P. J. Potts, A. T. Ellis, P. Kregsamer, C. Streli, C. Vanhoof, M. West and P. Wobrauschek, Atomic spectrometry update X-ray fluorescence spectrometry, *J. Anal. At. Spectrom.*, 2006, 21, 1076–1107.
- 24 L. Wawrzonek and J. L. Parus, Application of multivariate linear regression for determination of ash content in coal by XRF analysis, *Isot. Environ. Health Stud.*, 1988, 24, 82–84.
- 25 D. G. Hicks, J. E. Reilly and D. W. Kopenaal, On the rapid estimation of % ash in coal from silicon content obtained via FNAA, XRF, or Slurry-injection AA, *American Institute of Physics Conference Series*, 1981, vol. 454, DOI: 10.1063/ 1.32925.
- 26 K. F. Ma, *Experimental study on determination of major elements in coal ash by X-ray fluorescence spectrometry*, Coal Quality Technology, 2019, vol. 2, pp. 32–35.
- 27 Y. Song, F. Guo and S. H. Gu, Determination of 12 elements in coal ash by X-ray fluorescence spectrometry, *Spectrosc. Spectr. Anal.*, 2008, **28**, 1430–1434.
- 28 S. J. Kelloway, C. R. Ward, C. E. Marjo, I. E. Wainwright and D. R. Cohen, Calibration for ED-XRF profiling of coal cores for the Itrax Core Scanner, *Powder Diffr.*, 2014, 9, 28–34.
- 29 J. J. Hou, L. Zhang, W. B. Yin, Y. Zhao, W. G. Ma, L. Dong, G. Y. Yang, L. T. Xiao and S. T. Jia, Investigation on spatial distribution of optically thin condition in laser-induced aluminum plasma and its relationship with temporal evolution of plasma characteristics, *J. Anal. At. Spectrom.*, 2017, 32, 1519–1526.