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REVIEW ARTICLE

Review of methodological and experimental LIBS techniques for coal analysis and their application in power plants in China

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Laser-induced breakdown spectroscopy (LIBS) is an emerging analytical spectroscopy technique. This review presents the main recent developments in China regarding the implementation of LIBS for coal analysis. The paper mainly focuses on the progress of the past few years in the fundamentals, data pretreatment, calibration model, and experimental issues of LIBS and its application to coal analysis. Many important domestic studies focusing on coal quality analysis have been conducted. For example, a proposed novel hybrid quantification model can provide more reproducible quantitative analytical results; the model obtained the average absolute errors (AREs) of 0.42%, 0.05%, 0.07%, and 0.17% for carbon, hydrogen, volatiles, and ash, respectively, and a heat value of 0.07 MJ/kg. Atomic/ionic emission lines and molecular bands, such as CN and C_2, have been employed to generate more accurate analysis results, achieving an ARE of 0.26% and a 0.16% limit of detection (LOD) for the prediction of unburned carbon in fly ashes. Both laboratory and on-line LIBS apparatuses have been developed for field application in coal-fired power plants. We consider that both the accuracy and the repeatability of the elemental and proximate analysis of coal have increased significantly and further efforts will be devoted to realizing large-scale commercialization of coal quality analyzer in China.

Keywords Laser-induced breakdown spectroscopy (LIBS), coal quality, elemental analysis, proximate analysis, calibration model

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Contents

1 Introduction

Coal is the predominant (about 75%) primary energy source in China. With the development of the national economy and increase of the electricity demand, the construction of coal-fired power plants is also increasing. Coal quality directly impacts the boiler performance of coal-fired power plants, the generation efficiency of the generating set, and even safety indicators. Therefore, the comprehensive and systematic understanding of coal quality is very important for coal-fired power plants.

The development of a convenient and reliable coal quality analysis technology is urgently needed in China. Considering the large amount of coal utilized by most coal users (for example, several thousand tons of coal per day are required for a 300 MW power plant), a fast or on-line coal quality analysis technology is a pressing necessity for coal pricing and combustion/utilization optimization in the power industry, coal chemical processing industry, and coal mining industry. Current standard coal quality analysis technologies are usually lengthy and unable to realize fast or on-line analysis. Under the urgent political demands for CO_2 reduction, a fast or on-line coal quality analysis technology has become even more important.

The traditional techniques employed for coal quality analysis can be classified into chemical analysis and physical analysis methods. One technique of the former category is acid extraction, which is widely used but requires multi-reagents and complicated processes (lasting 2–3 h); another technique is thermal sorption analysis, which involves shorter analysis times (8–15 min) but requires the consumption of oxygen and nitrogen gas. The physical analysis methods include X-ray fluorescence (XRF), prompt-gamma neutron activation analysis (PGNAA), inductively coupled plasma-atomic emission spectroscopy, atomic absorption spectroscopy, and near-infrared absorption spectroscopy. Among these analytical techniques, XRF and PGNAA are the most preferable ones for possible application in power plants and are already commercially available. However, both of these methods have difficulties in analyzing low-atomic-number elements, such as C and O. It is thus necessary to develop new techniques suitable for field monitoring. LIBS is an emerging analytical spectroscopy technique that can determine the elemental composition of sample from the line emission of laser-generated plasma using elemental and molecular emission intensities. In comparison with existing online analyzers based on XRF and PGNAA, its main advantages are the absence of any radioactive source and the ability to detect all elements with superior sensitivity and selectivity. This technology demonstrates numerous appealing features that distinguish it from conventional analytical spectrochemical techniques and is considered as an effective analysis tool for coal quality analysis. However, the application of LIBS in coal quality analysis involves some difficulties. Coal is a complicated organic-inorganic hybrid compound. The diversity of the type and the difference of the quality of coal could lead to seriously matrix effects and large measurement errors. To perform accurate coal quality measurements, significant improvements in data analysis, modeling, and equipment stability are required.

Over the past few decades, considerable studies have been reported on LIBS applications for the coal industry, such as coal composition analysis. Specifically, many crucial works focusing on coal quality analysis have been conducted in China. Wang *et al.* [1] improved the sample-to-sample reproducibility, which is the most critical obstacle to the wide commercialization of the technology. This reproducibility has already met the national standard by using special data analysis methods. Lu *et al.* [2] established that the molecular CN band could be employed for fast measurements of the unburned carbon content in fly ash. Zhang *et al.* [3–6] developed both off-line and on-line LIBS apparatuses for possible application in coal-fired power plants; these devices were capable of removing dust generated during the plasma formation process and multiplex sampling. Table 1 shows the contributions of the Chinese LIBS community to coal quality analysis and a comparison with similar foreign technology.

This paper aims to briefly review the recent research progress achieved by the Chinese LIBS community in the development of LIBS specifically for coal quality analysis, with an emphasis on experimental results and calibration methods.

Table 1 The special contribution made by Chinese LIBS community for coal quality analysis and a comparison with the similar foreign technology.[a]

Group			**Target**					
			A	**B**	**C**	**D**	**E**	**F**
Organic elements	**C**	MAE	0.42%[1]	N/A	< 10%[4]	N/A	N/A	N/A
		RMSEP	1.35%[42]		N/A			
		RSD	N/A	4.10%[38]	2%[4]			
		ARE	1.66%[42]	N/A	N/A			
	H	MAE	0.05%[1]	N/A	< 10%[4]	N/A		
		RMSEP	0.24%[8]		N/A			
		RSD	N/A	4.45%[38]		3.17%[44]		
		ARE	2.78%[8]	N/A		N/A		
	O	RSD	N/A	4.48%[38]	N/A	2.75%[44]		
		ARE		N/A	19.39%[21]	N/A		
Inorganic elements	**Si, Al, Ca, Fe, Mg, etc.**	N/A	N/A	R>0.97 (Mg and Ca)[38]	MAE:<10% (Si, Na, Mg, Fe, Al, and Ti)[4]	N/A	RSD: ∼10% ARE: ∼10% (Al, Ca, Fe, K, Mg, Si, Na, and Ti)[45] R: 0.91-0.99 (Na, Mg, Al, Si, Fe, and Ca)[47]	RSD≤6% (Fe, Mg, Si, Al, and Ca)[46] R^2 >0.7 (Na and Si)[48] R^2 >0.84 (Ba, Mg, Ti, Fe, and Si)[49]
Proximate analysis results	**Volatiles matter content**	MAE	0.07%[1]	N/A	N/A	N/A	N/A	N/A
		RMSEP	1.41%[26]					
		RSD	N/A	3.89%[28]				
		ARE	5.47%[26]	4.54%[28]	4.42%[3]			
	Ash content	MAE	0.17%[1]	N/A	N/A			
		RMSEP	3.49%[26]		1.82%[3]			
		RSD	N/A	8.50%[28]	N/A			
		ARE	12%[26]	N/A	5.48%[3]			
	Heat value	MAE	0.07%[1]	N/A	N/A			
		RMSEP	1.33%[26]		0.85%[3]			
	Moisture content	RMSEP	0.87%[26]	N/A	N/A			
		ARE	26.2%[26]					

([a]Note: A-Tsinghua University, B-South China University of Technology, C-Shanxi University, D-Mississippi State University, E-Cooperative Research Centre for Clean Power From Lignite, F-Universidad de A Coruña, MAE: mean absolute error, RMSEP: root mean square error of prediction, RSD: relative standard deviation)

2 Fundamentals

Zhang *et al.* [7] established a criterion to evaluate whether the plasma is in local thermodynamic equilibrium (LTE) or not based on the Mc-writer. This calculation method can be used to estimate the plasma temperature and electron density and to determine the LTE condition.

Wang *et al.* [8] studied the effects of the plasma-surrounding gases. LIBS was used to measure three major elements, carbon, hydrogen, and nitrogen, in twenty-four bituminous coal samples. Argon and helium were selected as the optimal ambient gases to enhance the signals and eliminate the interference of nitrogen from the surrounding air. The RSD of the related emission lines and the performance of partial least-squares (PLS) modeling were compared for different ambient environments.

The results showed that argon not only improved the intensity of the signal but also reduced its fluctuation. Additionally, the PLS model exhibited optimal performance in multi-element analysis using argon as the ambient gas. The RMSEP of the carbon concentration decreased from 4.25% in air to 3.49% in argon while the average relative error was reduced from 4.96% to 2.98%. The hydrogen line demonstrated a similar improvement. The nitrogen lines were too weak to be detected even in an argon environment, which suggested that the measured nitrogen signal might originate from the breakdown of nitrogen molecules in the atmosphere.

It is well known that the same element can form different chemical bonds and molecular structures in different materials. The use of molecular CN has been proposed as a means to overcome the interference between the Fe 247.98 nm and C 247.86 nm lines and the strong reduction of the C 193.09 nm line intensity in air. Lu *et al.* [9, 10] focused on the characteristics of the sample structure and the surrounding environment, which are two important factors that affect the LIBS spectrum. Solid materials with different structures containing C and N were analyzed. By comparing the emission of the molecular species in different atmospheres (air and argon), it can be determined whether the molecular species are directly vaporized from the sample or generated through dissociation or interaction between the plasma and air molecules. The results showed that the characteristics of the emission of C_2 bands were similar with those of neutral atomic carbon emission in different atmospheres (air and argon). Although the features of CN band emission are more complicated, they exhibit a close relationship with the presence of CN radicals, the interaction between plasma and air ambient, and the recombination of excited partials.

Lu *et al.* [11] studied time-resolved laser-induced coal plasmas in different gas environments (air, argon, and helium). A comparison of the emission spectra of atomic carbon and molecular CN and C_2 measured during coal ablation in air, argon, and helium is shown in Fig. 1. The spectral characteristics of the atomic and molecular carbon emission depend on the gas environment owing to differences in the physical and chemical properties of the plasma. Coal ablation allowed the researchers to simultaneously measure elemental and molecular emission in order to understand the temporal changes of the plasma properties (electron density, number density, and temperature). Ambient gas has a significant influence on atomic and molecular emission and the plasma excitation temperature is a primary factor driving atomic carbon emission in every gas environment. However, for molecular carbon emission, the atomic number resulting from recombination processes contributes to the creation of a significant difference between excitation and rotational temperatures. The CN molecular band emission, which was measured not only in air but also in Ar and He, originated from the nitrogen in the coal sample. Owing to the presence of a single form of nitrogen in coal, the CN emission intensity can be used to represent the quantity of nitrogen in the coal. The influence of the laser energy on the C_2 rotational temperature was measured and the correlation of the rotational plasma temperature, which was derived from the molecular C_2 band emission, was observed to be a stable parameter that can be used to improve LIBS chemical analysis.

3 Data pretreatment

3.1 Denoising

The optimization of the detection delay in a LIBS system is an effective way to reduce the continuous background noise; however, the further removal of signal noise by hardware improvement is difficult and costly. The use of a data processing method for denoising seems to be a

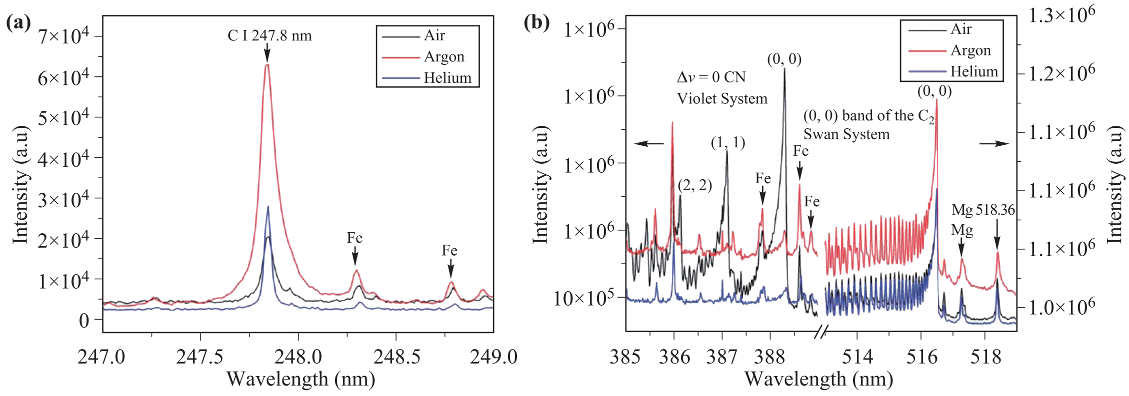

Fig. 1 Emission spectra of **(a)** atomic carbon and **(b)** molecular CN and C_2 observed during coal ablation in air, argon and helium. The gate delay and width were 400 ns and 300 ns, respectively.

necessary and helpful approach to improving the signal-to-noise ratio (SNR) or reducing the LOD.

The wavelet transform, which has undergone rapid development, is a type of multi-resolution analysis method with good time and space frequency local character that is used to investigate the peak information of a spectrum. The technique is considered as a useful tool for spectrum denoising. Given the local character of the wavelet transform, the local position of a peak and its frequency content can be distinguished. Moreover, the signal representation in the wavelet domain is sparse, which allows signal compression and denoising.

3.2 Uncertainty reduction

An relatively high uncertainty is one of the main obstacles to the wide application of LIBS for quantitative measurements. The commonly employed normalization method is not sufficiently effective for uncertainty reduction because of the change of the plasma temperature and electron number density from pulse to pulse weakens the correlation between the ablation mass and the (total or part of the) spectral area for the same sample. A more efficient approach would be to apply the plasma characteristic parameters to directly compensate for the spectral signal fluctuations.

Wang *et al.* [12–15] developed a spectrum standardization method by assuming the existence of a standard state for samples with similar matrices; this state is defined by a standard plasma temperature, electron number density, and total number density of the element of interest. Therefore, a Taylor expansion can be applied near the standard plasma condition to obtain the standard state value of the characteristic line intensity from the theory. The temperature variation was regarded to be proportional to the variation of the logarithm of the ratio of two spectral line intensities of the examined element; the electron number density variation was considered to be proportional to the variation of the full width at half maximum (FWHM); finally, the variation of the total number density was regarded to be proportional to that of the sum of the multiple spectral line intensities of the measured element. Based on these assumptions, a calibration model was established. As a result of the proposed normalization method, the measurement precision and accuracy have been greatly improved and the average RSD, the coefficient of determination (R^2), the RMSEP, and the average value of the maximum relative error have decreased.

3.3 Peak searching and spectral identification

Currently, a large part of LIBS research focuses on quantitative analysis, including the calibration of matrix effects and the improvement of the detection limit. In contrast, automatic qualitative analysis software has attracted little attention. Zhang *et al.* [16] introduced software that can identify spectral lines based on LabVIEW, which is a development platform for virtual instruments. This software can achieve spectrum denoising and peak searching by using a second-derivative calculation and a threshold determination. Fig. 2 displays the spectral processing of the spectrum for qualitative analysis. By comparing with the National Institute of Standards and Technology (NIST) atomic spectra database, the characteristic wavelengths of common elements were determined. The software automatically identified the spectral lines of specific elements and performed qualitative elemental analysis. The proposed method is simple, convenient, feasible, and has a large application potential.

Lu *et al.* [17] implemented spectral identification schemes to acquire spectra containing all the emission lines of the important elements in coal. The obtained spectra were designated as representative spectra. The threshold value was selected to be the background of the line emission plus three times the standard deviation of the background of the representative spectra. A method using a single line and one using combined multiple lines (C 247.8 nm, N 746.8 nm, Si 288.2 nm, and Ca 396.8 nm) were compared to obtain the best results for the spectral identification of coal particle flow.

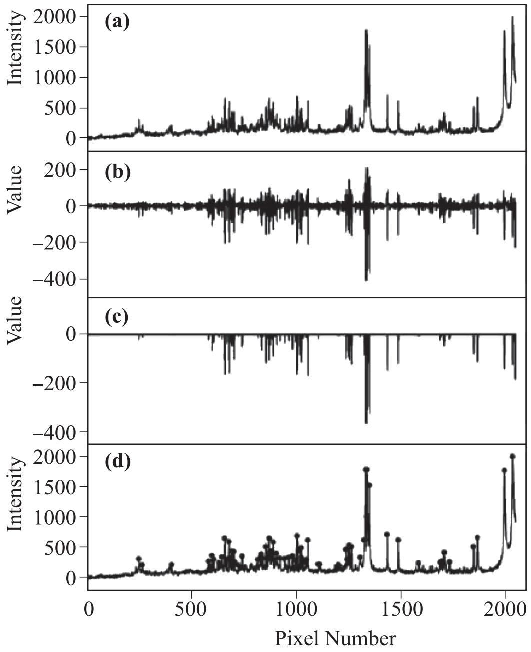

Fig. 2 Spectral processing of the spectrum for qualitative analysis. **(a)** LIBS spectrum, **(b)** second order derivative, **(c)** minus the threshold, **(d)** peak searching results.

4 Calibration model

Various models are applied for the prediction of coal properties; among these, the univariate calibration model is the most commonly used approach owing to its simplicity. However, this conventional model considers only one specific line and cannot accurately predict coal properties owing to the lack of a solid physical background. A better method to achieve precise quantitative analysis is to utilize multivariate analysis to extract more quantitative information from the entire spectrum or from a group of spectral lines of the sample. Lu *et al.* [18, 19] applied both the univariate calibration and the multivariate calibration methods to LIBS data to determine the calibration curve of the unburned carbon in the measured samples. They observed that the traditionally used univariate calibration of LIBS was unsuccessful in the quantitative analysis of fly ashes from different types of coal because of the presence of matrix effects. In contrast, multivariate calibration had a better performance, as it considered the matrix effects as well as the influence on the specific line intensity of the spectroscopic signals of other components of fly ash.

4.1 Internal normalization

Zhang *et al.* [4] measured the organic oxygen content in pulverized anthracite coal under atmospheric conditions. The researchers proposed special spectral processing that included optimal O(I) emission line selection by comparing the spectral correlation coefficients with the N(I) line, internal normalization with the N(I) line, and temperature correction. The method was employed to enhance the multiline analysis method and yielded the most accurate quantitative results. The calibration method used to determine the organic oxygen content of coal exhibited an accuracy of 1.15–1.37% and an average relative error of 19.39%.

Lu *et al.* [20] proposed an internal standardization scheme, named changed internal standardization, and compared it with the traditional internal standardization and with no internal standardization for the analysis of inorganic elements. The proposed internal standardization scheme employed the atomic line of carbon at 247.86 nm, the molecular band of CN at 388.34 nm, and the C_2 line at 516.32 nm to normalize the lines of inorganic elements distributed in the same spectral channel. The evaluation of multivariate calibration models coupled with the changed internal standardization showed a significant improvement in both measurement accuracy and reproducibility compared with the results obtained using fixed internal standardization and no internal standardization.

4.2 Calibration-free

An alternative method to perform quantitative analysis without the need of calibration samples is the calibration-free LIBS. Lu *et al.* [18] established a calibration-free model without self-absorption effects to analyze coal samples. They observed that the slope of the calibration curve was nearly 1 when the concentration of the analyzed element was relatively low and approximately 0.5 when the concentration of C was higher than that of other elements.

4.3 Second-order polynomial multivariate inverse regression

Owing to the poor spectral resolution of the spectrometer and the significant spectral interference, it is difficult to distinguish the C lines from those of Fe. Zhang *et al.* [21] used a simple method to calculate the exact C line intensity without any influence from the adjacent Fe line. A second-order polynomial multivariate inverse regression was suggested as an effective calibration model to minimize matrix effects and ensure more reliable measurement results. The accuracy achieved for unburned carbon analysis was estimated to be 0.26%, while the average relative error was 3.81%. Additionally, Lu *et al.* [22] proposed a method using a Fe spectrum correction to extract the integral intensity of C in the overlapping peak.

4.4 PLS method based on dominant factor

The multivariate PLS technique is a promising method applied for LIBS quantitative measurement. The classical PLS model focuses purely on mathematical data correlation and neglects any underlying physical principle that can lead to large prediction errors. A number of hybrid models for LIBS analysis have been established based on the classical PLS model.

Wang *et al.* [23–27] proposed a PLS method based on the dominant factor. The dominant factor is essentially the same as that used in the traditional univariate model, which can model non-linear and linear relationships based on the physical background. A statistics-based PLS method is subsequently applied to correct the residual errors using the full spectral information. Compared with the traditional PLS model, the dominant factor makes the combination model more robust over a wide concentration range and the PLS application improves the model accuracy for samples with matrices within the calibration sample set. In the model, the dominant factor is essentially the first principal component of the traditional PLS model, which can describe non-linear effects. When applied to elemental concentration measurements for different samples, such as copper alloys and coal samples, the dominant factor-based PLS model can consistently achieve 15–50% better RMSEP than the traditional PLS method while maintaining the same R^2. Additionally, the model has potential for further improvement, in contrast to the traditional PLS method, and any progress in our understanding of plasma physics is expected to improve the dominant factor model and its overall performance.

Lu *et al.* [28] also employed PLS for the quantitative analysis of the ash content of coal. Moreover, they investigated the influence of the selection of the spectral range used in the PLS model. The experimental results showed that the most rigorous PLS model could be constructed using the spectral data range 290–397 nm. Furthermore, the performance of the PLS model in predicting the ash content in unknown samples was discussed. The ARE, RSD, and LOD were 6.94%, 8.50%, and 1.73%, respectively.

4.5 PLS combined with wavelet transform

Wang *et al.* [29] utilized a PLS and wavelet transform hybrid model to analyze the carbon content of coal using LIBS. The hybrid model comprised two wavelet analysis procedures to pretreat the LIBS spectrum, including environmental denoising and background noise reduction. The processed wavelet coefficients, which contained the discrete line information of the spectra, were used as inputs to the PLS model for the calibration and the prediction of the carbon content. A higher SNR was obtained for the carbon line after environmental denoising and the best decomposition level was determined after the background noise reduction. A comparison between the measurement results of the conventional PLS model and those of the hybrid model is shown in Fig. 3. The prediction ARE decreases from 2.74% to 1.67% in helium, which indicates a significantly improved accuracy in the measurement of carbon in coal.

4.6 Spectrum standardization combined with dominant factor-based PLS method

Wang *et al.* [30] combined the spectrum standardization method and the dominant factor-based PLS method to improve the LIBS accuracy for the measurement of the carbon content in coal. The combination model utilized the spectrum standardization method to accurately calculate the dominant carbon concentration, which was used as the dominant factor. Then, the PLS model with the full spectrum information was employed to correct the residual errors. The combination model was applied to measure the carbon content in 24 bituminous coal samples. The results demonstrated that the combination model could further improve the measurement accuracy compared with the spectrum standardization model and the dominant factor-based PLS model, in which the dominant factor was calculated using the traditional univariate method. The R^2, RMSEP, and RSD for the combination model were 0.99, 1.63%, and 1.82%, respectively. The corresponding values for the spectrum standardization model were 0.90, 2.24%, and 2.75%, whereas those for the dominant factor-based PLS model were 0.99, 2.66%, and 3.64%.

4.7 Principal component analysis

The principal component analysis (PCA) is a linear regression model that can be employed to better describe the chemical variations in samples and to extract a deeper understanding of their chemical structures than the univariate calibration model based on a LIBS spectrum. The model is a data reduction technique that removes redundancy from a large LIBS spectra data set and transforms these data into a small set of principal

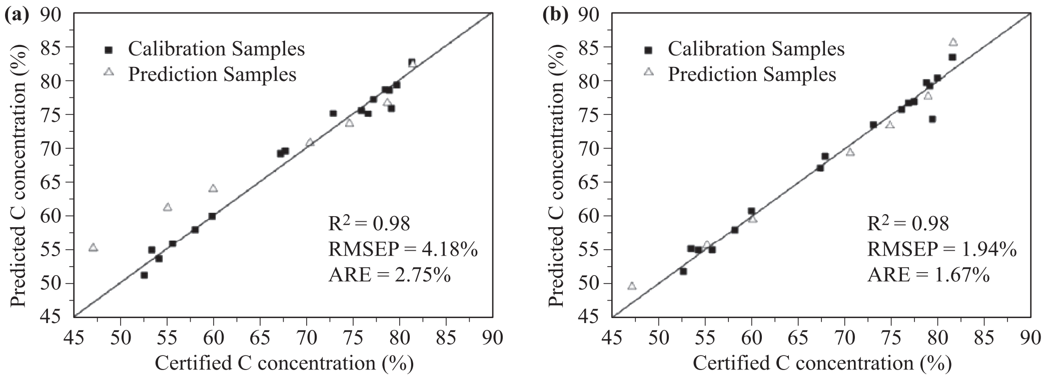

Fig. 3 Calibration and prediction results under ambient helium environment. **(a)** the conventional PLS model, **(b)** the hybrid model.

information extracted from the original variables. Lu *et al.* [31] employed the partial correlation analysis and PCA methods to extract the required spectrum information and established an effective calibration model to quantitatively analyze the volatile matter content in coal.

4.8 Support vector regression combined with PCA

To determine the complex relationship between the concentrations of the analyte of interest and the corresponding plasma spectra, Zhang *et al.* [3] proposed a multivariate non-linear calibration method based on support vector regression (SVR) combined with PCA. This method was shown to enable a significant improvement in cross-validation accuracy by using a calibration set of coal samples. To comprehensively investigate the complicated chemical composition and structure of coal, useful information related to its ash content, volatile matter content, and calorific value were selected by the PCA. The extracted principal components were used as the input data for the SVR model. The combination model exhibited better overall performance than the SVR model, the RMSEP of the ash content and volatile matter content and the calorific value of coal decreased from 2.74% to 1.82%, 1.69% to 1.22%, and 1.23 MJ/kg to 0.85 MJ/kg, respectively. Additionally, the corresponding AREs of the examined samples were reduced from 8.3% to 5.48%, 5.83% to 4.42%, and 5.4% to 3.68%, respectively. The enhanced level of accuracy obtained using SVR combined with PCA-based calibration models opened up avenues for the potential prediction of coal properties.

4.9 Multivariate regression combined with properties correction

A linear multivariate regression method combined with the correction of the plasma properties, including temperature and self-absorption, was employed to construct a calibration model for unburned carbon (UC) developed by Lu *et al.* [2]. The intensity ratios $\mathrm{I}_{MgII280.27}/\mathrm{I}_{MgI285.21}$ and $\mathrm{I}_{MgII279.55}/\mathrm{I}_{MgII280.27}$ were considered as the independent variables of the multivariate regression applied for the correction of the plasma temperature and self-absorption, respectively. As shown in Fig. 4, the proposed calibration model yields a near-zero y-intercept, which represents a high sensitivity for the quantification of UC. Obviously, combining the plasma temperature correction with the self-absorption one provides a realistic regression approach for the calibration of fly ashes. It was confirmed that the LIBS measurement of UC in fly ash using molecular CN had comparable accuracy, precision, and LOD than using atomic C and met the requirement of the national power industry standard.

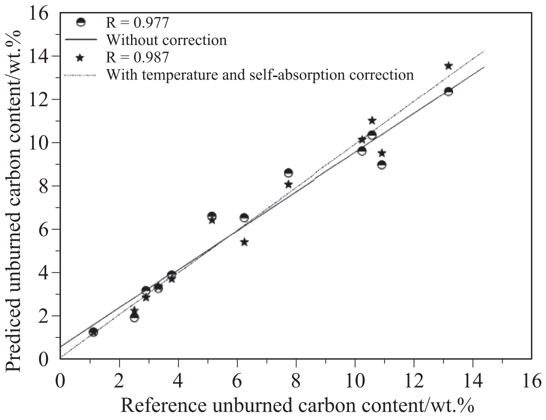

Fig. 4 Regression plots of UC generated by multivariate calibration models.

4.10 A hybrid quantification model

Wang *et al.* [1] proposed several methods to improve both the precision (sample-to-sample reproducibility) and the accuracy of LIBS quantification. Standardized spectra are compared with a large spectral database to establish whether the examined sample is a new sample or is already included in the database and has known composition/property information. If the sample is new, a dominant factor-based PLS model is applied to provide quantitative analytical results. Then, the new standardized spectral information and analytical results are incorporated in the spectral database, making it updatable to future measurements. If the sample is already included in the database, the analytical results are directly obtained from the database. For coal analysis, the results showed that the RSD of carbon for different measurements of the same sample was 0.3%, proving that LIBS can provide high reproducibility, at least for coal analysis applications. The AREs for carbon, hydrogen, volatiles, and ash and the heat values were 0.42%, 0.05%, 0.07%, 0.17% and 0.07 MJ/kg, respectively; all these measurement accuracies fully satisfy the requirements of the national standard for coal analyses that use traditional chemical processing methods. The work was the first quantitative application of LIBS with real industrial requirements and proved the technical feasibility of LIBS for accurate quantification.

5 Experimental issues

Measurement accuracy is affected by a multitude of factors, such as instrument precision, physical/chemical properties of the samples, laser parameters, photoelectric detector parameters, measurement parameters, and environmental conditions.

5.1 Sample properties

5.1.1 Particle size

To analyze the effects of particle size, Lu *et al.* [18] prepared four samples with different particle sizes for a LIBS experiment. The influence of particle size was obvious, as the decrease of the powder particle size led to a remarkable increase of plasma temperature.

5.1.2 Moisture content

The analytical performance of coal can be greatly influenced by its moisture content. It has been observed that large moisture content variations could lead to substantial alterations of LIBS spectra and large errors in coal quality evaluation [32]. Wang *et al.* [12] determined that with the increase of moisture content, most spectral line intensities (even H and O) decreased, and the corresponding RSDs increased. The researchers investigated the plasma morphology and spatially resolved spectra of coal to determine the mechanism of these effects. They observed that under laser radiation, part of the moisture evaporated first and ablated earlier than in other coal materials, leading to a type of laser energy shield that induced surrounding water vapor dissociation, ionization, and splashed particle reflection. The lower laser energy absorption made the ablation of the coal mass less effective and decreased the line intensity. Specifically, the decrease in the H line intensity could be caused by water vapor containing H and O being pushed to the cooler exterior layer of the plasma. The higher RSDs could be attributed to the unpredictable earlier moisture evaporation process and large fluctuations in the plasma morphology and properties. Their results also showed that the SNRs of the line intensities decreased with increasing moisture content, which provided useful information for the quantitative analysis of coal moisture content.

5.2 Laser parameters

5.2.1 Wavelength

Wang *et al.* [33, 34] observed that because of the reduced thermal effects of the 266-nm-wavelength laser ablation, it resulted in better crater morphology on the coal pellets. Additionally, it provided better laser-sample coupling and lower plasma shielding, resulting in better signal reproducibility and higher carbon line intensity, as shown in Fig. 5. The carbon content of bituminous coal samples exhibited better linearity with atomic carbon line intensities measured with the 266-nm-wavelength laser than those measured with the 1064-nm-wavelength one. Both the 266-nm- and 1064-nm-wavelength lasers can achieve good performance in the quantitative analysis of the carbon content in coal using the PLS method.

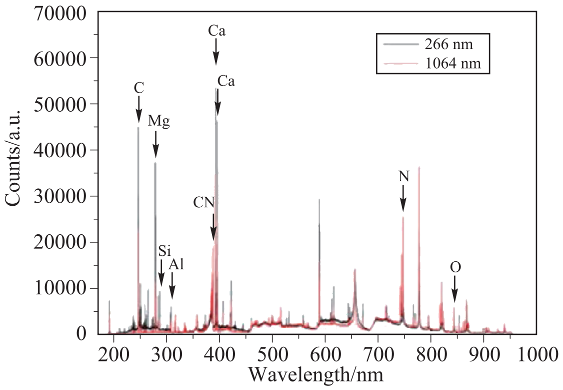

Fig. 5 Comparison of two spectra of coal ablated by 266 nm wavelength and 1064 nm wavelength, respectively.

5.2.2 Laser power stabilization

For practical applications, pulsed-laser power fluctuations can lead to poor measurement stability. Zhang *et al.* [35] developed a pulsed-laser power stabilization device to stabilize the output power of Nd:YAG laser by using a closed-loop negative feedback signal. They observed that different beam split ratios had little impact on the pulsed-laser power stabilization effect. Smaller beam split ratios produced faster the stabilization speeds. After stabilization, the output power of the laser was maintained in a predefined range and the RSD was reduced from 2.4% to 1.1%. This technique ensured the stability of the long-time operation of LIBS and improved its performance.

5.2.3 Reduction of the laser beam divergence angle

The quality of a laser beam is often characterized by a parameter known as the beam divergence, which is the angular spreading of light waves as they propagate through space. Even a perfect laser beam experiences some beam divergence due to diffraction effects. The beam expander (BE) is a telescope used to expand the diameter of a laser beam and it is useful for the reduction of the laser beam divergence angle, which results in a better focusing effect. As shown in Fig. 6, Zhang *et al.* [36] used a BE to expand the laser beam to a suitable diameter. Considering that the BE was likely to affect the experimental parameters, they also investigated the effects of factors such as the tablet machine pressure and the energy, repetition rate, and focus position of the laser. Finally, they modified the BE included in the experimental LIBS setup used for coal quality analysis accordingly and demonstrated the improvement in signal quality and stability achieved by using the BE.

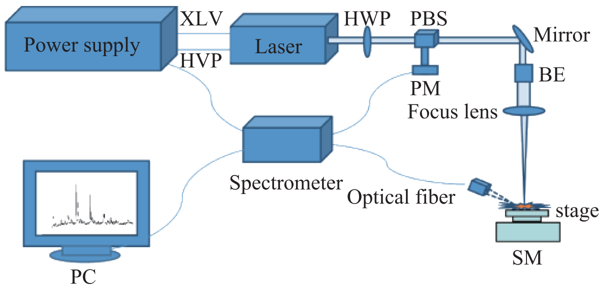

Fig. 6 Schematic diagram of the experimental setup.

5.2.4 *Laser quality improvement*

To decrease the stray light in the laser beam (including pumping light and frequency-doubled light) and improve the SNR of the spectral lines for the measured elements, Zhang *et al.* [37] inserted a narrow-band filter and a diaphragm in the light path; as a result, the baseline decreased by a third compared to the original spectra. Furthermore, additional works were devoted to optimizing other key parameters, including the laser pulse energy, delay time of the spectrometer, laser focus position, rotation speed of the sample stage, and laser beam quality.

Lu *et al.* [38] investigated the effects of the experimental parameters on LIBS, including the sample preparation parameters, lens-to-sample distance, sample operation mode, and the ambient gas.

5.3 Enhanced LIBS

5.3.1 *Cylindrical confinement*

Wang *et al.* [39–41] designed a symmetric cylindrical confinement cavity to enhance the signal and improve measurement repeatability. They demonstrated that the spectral intensity, plasma temperature, and electron density were all enhanced when the cavity was added. The enhancement was attributed to the energy delivered by the reflected shockwave through the compression of the plasma. The repeatability improvement was attributed to the plasma morphology regularization obtained by the reflected shockwave in addition to the change of the plasma temperature and electron density.

To increase the signal repeatability and improve the stability of the plasma morphology under more flexible conditions, Wang *et al.* [42] presented two methods aimed at improving cylindrical confinement. In the first method, the multi-cavities moving with the sample were modified to a single cavity fixed to the sample; in the second one, an air fan was used to remove the aerosols after each laser pulse. In addition to using cylindrical cavity confinement, the dual-pulse excitation technique and spark discharge can also enhance the signal. It was demonstrated that the combination of spark discharge and spatial confinement provided a better signal. Moreover, the pulse-to-pulse signal repeatability, signal intensity, and SNR were all improved compared with those obtained when using only confinement or discharge. The carbon content of coal was measured by using a model that combined the spectrum standardization method and the dominant factor-based PLS model. For the combination model with cylindrical cavity confinement, the coefficient of determination, RMSEP, ARE, and average absolute error were 0.99, 1.35%, 1.66%, and 1.08%, respectively, whereas the corresponding values for the combination model without cylindrical cavity confinement were 0.99, 1.63%, 1.82%, and 1.27%. This was the first LIBS carbon measurement for coal analysis that achieved an average absolute error close to 1.0%.

5.3.2 *LIBS combined with laser ablation-inductively coupled plasma-mass spectrometry*

The combination of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) with LIBS can provide isotopic information and enhance the measurement sensitivity and essentially expand the dynamic analysis range of LIBS. LIBS can be employed for the measurement of major and minor elements while LA-ICP-MS can be used simultaneously for trace-element measurements. The analytical benefits of these simultaneous measurements go beyond using one measurement to correct the other. Lu *et al.* [17] employed this tandem approach to simultaneously determine major and minor elements (C, Si, Ca, Al, and Mg) as well as trace elements (such as V, Ba, Pb, and U) in coal samples.

5.4 On-line/off-line LIBS apparatus

5.4.1 *Off-line LIBS apparatus and sample preparation*

For the implementation of off-line LIBS, sample preparation is necessary. The coal samples are generally pressed into pellets so as to achieve repeatable multi-pulse analysis. However, unlike bituminous samples, anthracite samples either cannot form pressed pellets or the surface of the resulting pellet is not sufficiently tenacious to sustain multiple laser shots. Typically, binders must be used to bind the anthracite powder together and make the pressed pellets more suitable for LIBS measurements. To improve measurement repeatability, Wang *et al.* [43] determined that the optimal binder $Na_2SiO_3{\cdot}9H_2O$ can yield the overall best measurement precision and accuracy when the Si from the binder is used as the internal calibration element.

The off-line LIBS-based coal quality analyzer (Fig. 7) is an integrated and fully software-controlled analysis apparatus designed by Zhang *et al.* [3]. The instrument comprises three parts: the optical system, the analysis chamber, and the control module. The apparatus was designed for possible application to power plants and offers fast and precise coal quality analysis results.

5.4.2 On-line LIBS apparatus

Zhang *et al.* [4] designed an on-line LIBS apparatus (shown in Fig. 8) that aims to utilize the fundamental advantages of LIBS in a commercially viable form suitable for in situ quantitative analysis. This fully software-controlled LIBS system comprises a LIBS apparatus and sampling equipment. Special attention was paid to the LIBS apparatus, the data processing methods (especially the normalization with the Bode Rule/DC Level method), and the specific settings (including the software-controlled triggering source, high-pressure gas cleaning device, sample preparation module, and sampling module). The system achieved the best direct measurements for C, H, Si, Na, Mg, Fe, Al, and Ti with measurement errors lower than 10% for pulverized coal. The apparatus was demonstrated to be sufficiently accurate for industrial application for the on-line monitoring of pulverized coal. The proximate analysis method was also introduced in that work [4], and the experimental error of air dried Ash was shown to be in the range 2.29%–13.47%. A programmable logic controller controlled the on-line coal sampling equipment, which was designed based on aerodynamics and could perform multipoint sampling and sample-preparation operations.

Zhang *et al.* [5, 6] developed a LIBS apparatus for application in power plants that comprised an isokinetic sampler, a sample-preparation module, and a LIBS module. They confirmed that this apparatus was suitable for the on-line LIBS characterization of UC content in fly ash.

Fig. 7 Photograph of off-line LIBS apparatus.

Fig. 8 Photograph of on-line LIBS apparatus.

6 Conclusion

This paper briefly reviews the domestic progress in LIBS-based coal quality analysis and mainly focuses on the data pretreatment, calibration model, and experimental issues of LIBS.

The accuracy of coal quality analysis mainly depends on factors such as the emission signal enhancement, denoising method, spectral identification, surrounding gases, experimental parameters, quantitative calibration models, and instrumentation. For example, regarding quantitative calibration models, multivariate analysis is a general method used to perform precise quantitative analysis. Calibration-free LIBS can overcome the matrix effect but involves many difficulties, such as self-absorption and the lack of parameters such as the constitution, the hardness, the surface finish, etc. The dominant factor-based PLS model can reduce the influence of plasma property fluctuations on quantitative analysis accuracy. Finally, PCA can be employed to better describe the chemical variations in samples and to extract a deeper understanding of their chemical structures. Regarding instrumentation, a fully software-controlled LIBS system comprising a LIBS apparatus and sampling equipment has already been implemented in power plants. The symmetric cylindrical confinement approach has been proposed for signal enhancement and the improvement of measurement repeatability.

Undeniably, Chinese researchers have already made important progress in developing and demonstrating practical LIBS-based coal quality analysis technologies and instruments. Nevertheless, there is still room for further improvement regarding automation, laser system design, and system stability. The application of LIBS in on-line coal quality analysis also deserves more attention and further efforts in this field could achieve its successful industrial application for coal pricing or combustion optimization with the help of a fast coal sampling machine.

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