

# Laser-induced breakdown spectroscopy in China

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Laser-induced breakdown spectroscopy (LIBS) has been regarded as a future superstar for chemical analysis for years due to its unique features such as little or no sample preparation, remote sensing, and fast and multi-element analysis. Chinese LIBS community is one of the most dynamically developing communities in the World. The aim of the work is to inspect what have been done in China for LIBS development and, based on the understanding of the overall status, to identify the challenges and opportunities for the future development. In this paper, the scientific contributions from Chinese LIBS community are reviewed for the following four aspects: fundamentals, instrumentation, data processing and modeling, and applications; and the driving force of LIBS development in China is analyzed, the critical issues for successful LIBS application are discussed, and in our opinion, the potential direction to improve the technology and to realize large scale commercialization in China is proposed.

**Keywords** laser-induced breakdown spectroscopy, laser-induced breakdown spectroscopy (LIBS), quantitative analysis, signal enhancement, application, coal, metal, environment, energy

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			Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy (AES) technique and currently is under through a critical time before successful commercialization. The successful application in Mars project greatly draws the technology with much more attention [1]. It was believed that the current status for LIBS is similar to that of twenty years ago for Inductively Charged Plasma (ICP): once the critical issues are successfully addressed, an age of large scale applications for the technology would then arrive. For China, it is even a more critical timing to seize the opportunity to catch up frontiers of the research, to fulfill large scale application	

demands such as online coal property analysis, polluted water monitoring, and steel quality monitoring etc., and to scientifically contribute more to the development of the technology.

In early 1990s, China started to work on LIBS [2, 3] but with very limited work. After 2007, more and more Chinese researchers joined LIBS research incited by the development of its quantitative analysis capability. In 2011, the first Chinese Symposium on LIBS (CSLIBS) was successfully held in Qingdao hosted by the Ocean University of China, which symbolized the starting of the Chinese LIBS community. Since then, the Chinese LIBS community grew up exceptionally fast as listed in Table 1.

At the end of 2012, the first special issue of CSLIBS was published in the journal “Frontiers of Physics” [4]. As another symbolic event, Tsinghua University will host the 8<sup>th</sup> international conference on LIBS in September of 2014. All these facts show the dynamic development of Chinese LIBS society and LIBS research activities. Currently, there were more than 20 research groups working on LIBS and the related fields. Parts of the groups were listed in Table 2 with their research fields and representative publications. It is the time to have an overall understanding of the LIBS development status in China to facilitate the development of Chinese LIBS by identifying the strength and the weakness of our current researches and to further integrate Chinese LIBS community to the

international family by providing a clear picture.

In the following, the paper reviews the work done in China from four aspects: fundamentals, instrumentations, data process and modeling, and applications. Based on the review, the strength and the weakness of LIBS research and the potential direction for LIBS development in China are also discussed.

## 2 Fundamentals

Fundamental study is of great importance since it is the foundation of successful application of the technology. Mainly, the fundamental researches of LIBS study the mechanism of laser-material interaction including laser energy absorption, material ablation, species excitation, plasma evolution and characterization (spatial and temporal resolved plasma distribution and evolution), plasma-environment interaction (interaction among the plasma plume, plasma expansion resulted shockwave, and the plasma surrounding gases), local thermodynamic equilibrium (LTE), and signal enhancement. The main purpose of fundamental research should be to either improve limit of detection (LOD), or measurement reproducibility, or measurement accuracy in addition to understanding of the basic plasma physics.

Overall speaking, there is not much work done on the fundamentals in China. Most of the fundamental studies

**Table 1** Scales and hosts of CSLIBS.

Conference	Hosted by	Number of participants
1 <sup>st</sup> CSLIBS (2011)	Ocean University of China (Qingdao)	~ 40
2 <sup>nd</sup> CSLIBS (2012)	Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences (Hefei)	~ 140
3 <sup>rd</sup> CSLIBS (2013)	South University of Science and Technology of China (Guangzhou)	~ 240

**Table 2** Parts of research groups and their representative publications in China.

Research group	Research fields	References
Anhui Normal University	Fundamental	[5]
Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences	Application (metal)	[6–8]
Beijing Institute of Technology	Application (explosive)	[9–13]
Dalian University of Technology	Fundamental; Application (nuclear)	[14–16]
Huazhong University of Science & Technology	Fundamental; Instrumentation	[17–20]
Hong Kong Baptist University	Fundamental; Instrumentation	[21–35]
Jiangxi Agricultural University	Application (agricultural)	[36–38]
Northwest Normal University	Fundamental; Application (soil, aqueous solution and agricultural)	[39–43]
Ocean University of China	Fundamental; Application (aqueous solution)	[44–50]
Shanxi University	Instrumentation; Application	[51–53]
Shenyang Institute of Automation, Chinese Academy of Sciences	Data processing and modeling; Application (metal)	[54–59]
South China University of Technology	Application (coal and metal)	[60–67]
Tsinghua University	Fundamental; Data processing and modeling; Application (coal)	[68–85]
Zhejiang Normal University	Fundamental; Instrumentation; Application (soil)	[86–93]

were driven by application requirements for improving the LOD, which is critical for trace element detection.

Cheung *et al.* [21–31], Zhou *et al.* [86–89, 92], Wang *et al.* [74, 78], Guo *et al.* [17–20], and Sun *et al.* [39, 40] studied the signal enhancement mechanism/phenomenon using either dual-pulse technology, fast-discharge, spatial or magnetic confinement. In addition to signal enhancement, Wang *et al.* [74, 78] also demonstrated that the interaction between the laser-induced plasma and the moderate cylindrical confinements reflected shockwave is able to stabilize the plasma morphology, therefore improved the pulse-to-pulse measurement repeatability; Guo *et al.* [17] also showed that the measurement accuracy would be improved using spatial confinement thanks to reduced measurement noise. These works were explained more in detail below.

Cheung *et al.* [21–27] studied the laser-excited atomic fluorescence of species in dense plumes (PLEAF). Unlike conventional photon-induced fluorescence, which is handicapped by the one-wavelength-one-transition selectivity therefore being not possible for simultaneous multi-element analysis, Cheung *et al.* showed that multi-element fluorescence is possible if the analytes are embedded in dense plumes and when the excitation wavelength is in the vacuum ultra-violet. The likely mechanism was hypothesized to be photo excited to levels near the ionization limit by regarding these levels were dense and were probably broadened by the extreme plume density to allow efficient absorption of 193 nm photons. Using pulsed ultra-violet laser under the breakdown fluence of the sample, the plasma temperature was much lower than that obtained using a 532 nm laser at similar fluence, but with a comparable electron density. Using pulsed ultra-violet laser under the breakdown fluence, the continuum emission was relatively weak, and the signal-to-background ratio was a thousand times better.

Chan *et al.* [28] and Lui *et al.* [29] improved the LIBS sensitivity using resonance-enhanced LIBS (ReLIBS) scheme using a second laser pulse for photoresonant excitation, in which the host species in a laser ablation plume were excited resonantly by a pulsed dye laser. Time-resolved studies showed that the enhancement was not due to resonance photoionization. Instead efficient and controlled rekindling of a larger plume volume was the key mechanism. The enhancement was shown to be dependent critically on the profile of the first laser pulse as well as the spatial overlap of the two laser pulses. Using this double-pulse scheme, the mass detection limit for sodium was estimated to be about 200 pg, which was five times better than that obtained by single laser pulse configuration [28, 29]. The plasma-environment interaction was also investigated for Re-

LIBS: by choosing a heavier ambient gas and a lower pressure, the expanding plume could be confined as well as thermally insulated to maximize the signal; for instance, an ambient of 13 mbar xenon yielded a signal-to-noise ratio of 110 while the ratio was 53 when the pellet was ablated in air, and decreased further to 5 if the dye laser was tuned off resonance [30]. The effect of the laser beam was also investigated for ReLIBS: for the ablation step, Gaussian beams gave 2 to 3 times better signal-to-noise ratio (SNR) than non-uniform beams. For the rekindling step, if no further sample destruction was allowed, dye laser pulses that intercepted the Plume transversely gave 6 to 12 times higher SNR than the longitudinal case. By combining Gaussian beams and transverse rekindling, the mass limit-of-detection for Mg was about 100 amol while non-resonant analysis was 10x more destructive [31]. In summary, ReLIBS and PLEAF are useful for low concentration trace element detection while more work is still required for clear understanding to the underneath mechanism, such as the different mechanisms of ReLIBS, PLEAF, and normal used dual-pulse LIBS.

Zhou *et al.* [86, 93] developed laser ablation fast pulse discharge enhanced plasma spectroscopy (LA-FPDPS), which uses a microsecond pulse discharge circuit to enhance the laser-induced plasma emission. Scanning electron microscope (SEM) images of the ablation craters in either silicon crystal samples [86] or in soil samples [92] indicated that the plasma reheating by the discharge spark was the main mechanism for signal enhancement. An even greater enhancement could be obtained if the second-pulse discharge was replaced with a nano-second discharge [87, 93]. Using a discharge voltage of 11 kV, the peak intensities of Pb I 283.31 nm was enhanced about 38.5 times and RSD was reduced to 2.7% from 19%, while SNR was also increased from 3 to 8.9 compared to the traditional single pulse (SP) LIBS system. For the As I 286.04 nm line, the SNR was about 7.2 and RSD was 2.4% for LA-FPDPS even if it could not be observed in SP LIBS system. For Fe, Si, Mg, Ti, Ca, Al etc., the intensity was enhanced by dozens of times while RSD and SNR were improved by 2–3 times [92].

Considerable temperature and electron number density increases of the discharge-enhanced laser plasma generated from soil samples have been observed, and slightly incremented with the rise of discharge voltage [88]. With the discharge voltage of 11 kV, the plasma temperature increased from  $\sim 14\,000$  K to  $\sim 16\,500$  K while the electron number density increased from  $0.8 \times 10^{18} \text{ cm}^{-3}$  to  $1.2 \times 10^{18} \text{ cm}^{-3}$ . When changing the sample to Si crystal, although the temperature of the discharge enhanced plasma increased as well, the electron

number density in the discharge plasma was roughly the same as that in laser plasma, it is likely that the relative high ionization energy of the silicon atom might make it difficult for the ionization process to occur in the discharge process [89].

Wang *et al.* [78] used moderate cylindrical cavity to regularize the laser-induced plasma for signal enhancement and precision improvement. The spectral intensity, plasma temperature and electron density were all enhanced when the cavity was added. The mechanism of enhancement was attributed to the energy brought by the reflected shockwave through compressing the plasma. Unlike the previously reported results where the repeatability of the signal was worse with cavity, Wang *et al.* [78] demonstrated that the cavity can improve the signal repeatability when the cavity was axial symmetric and with appropriate size. The mechanism of repeatability improvement was attributed to plasma morphology regularization by the reflected shockwave in addition to the change of plasma temperature and electron density. Hou *et al.* [74] further investigated the effects of the laser-cavity alignment and the laser ablated aerosols on signal repeatability. By avoiding the variation of the laser-cavity alignment and blowing away the laser ablated aerosols, the signal repeatability was further improved.

Guo *et al.* [17–20] combined magnetic and spatial confinement using a pair of permanent magnets and an aluminum hemispherical cavity (diameter of about 11 mm) for signal enhancement. Enhancement factors of about 22 and 24 in the emission intensity of Co and Cr lines were acquired using the combined confinement, while enhancement factors were about 11 and 12 with only the cavity. Further study showed that the enhancement would also be effective when combined with dual pulse technology: The enhancement factor was 168.6 for the emission intensity of the Cr lines using the combined spatial confinement and dual pulse LIBS (DP-LIBS), while an enhancement factor was 106.1 with only DP-LIBS. In addition, they also demonstrated that when the plasma from steel targets was confined by a hemispherical cavity, the accuracy of quantitative analysis in LIBS could be improved [20].

Sun *et al.* [39, 40] investigated the mechanisms of the emission signal enhancement in collinear double-pulse LIBS. A relation between the signal enhancement and inter-pulse delay time was established. That is, before inter-pulse delay time of 1  $\mu$ s, reheating of the plasmas is the dominant mechanism, but later, new plasmas production becomes more important.

Besides signal enhancement, there were also some other fundamental studies worth mentioning.

Hou *et al.* [44] investigated the self-absorption in laser-induced plasma from nickel sample. It was found that the self-absorption effect was reduced with the increase of laser pulse energy. The results suggested that the self-absorption effect could be alleviated by suitable atomic line selection, operating at higher pulse energy and detecting with longer delay. Hou *et al.* [50] also investigated the pressure effect on the plasma emission from 0.1 to 40 MPa in bulk seawater, and a significant influence was found at the later stage of the plasma comparing with the earlier stage.

Cong *et al.* [5] investigated the spatial and temporal distribution of electron temperature and electron density. The distribution of the plasma electron density along the direction of laser beam was quite symmetry. The electron density at the height of 1.8 mm above the target surface is 3–4 times of that near the target surface. The electron temperature of fs-LIP is lower than that of ns-LIP.

As shown above, most fundamental studies from Chinese researchers focused on signal enhancement to improve LOD. Results showed that spatial confinement and fast discharge would be able to enhance the signal from several times to dozens of times, while dual pulse is able to enhance signal 100 to 1000 times. The reason is quite understandable: A secondary laser pulse is able to inject much more energy to excite the sample species. The emission noise would not be increased too much using the enhancement technologies; therefore, the LOD of LIBS measurement would be improved. Normally, as the LOD of single pulse is about a few ppm for metal elements and hundreds of ppm for non-metal elements. With these enhancement technologies, single pulse LIBS would have potential to obtain a LOD in the order of sub-ppm, while dual pulse LIBS would have the potential to detect trace element in the order of ppb.

Currently, a much deeper understanding to LIBS fundamental physics is the key to break the two bottlenecks for wide commercialization of LIBS: relative low measurement repeatability due to plasma property and morphology fluctuations and relative low accuracy suffered from matrix effects. Yet, the plasma generation and evolution process is such a complicated process that much work is still required to improve the ability of LIBS quantitative analysis. It is a tough challenge but a great opportunity for all researchers including Chinese researchers to contribute more on fundamental studies of LIBS.

### 3 Instrumentations

A typical LIBS system is mainly consisted of laser, spec-

trometer, and coupled charge device (CCD) or intensified coupled charge device (ICCD) as shown in Fig. 1. To build a LIBS setup, the following considerations should be included: the choice of laser (wavelength, pulse duration, and energy), sampling environment (pressure, surrounding gas), emission collection (fiber, collimator), and detector (spectrometer, CCD or ICCD) [94].

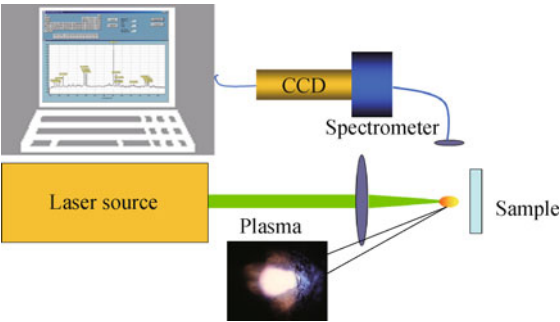


Fig. 1 A schematic configuration of a typical LIBS system.

Essentially, the instrumental study should be based on the understanding of the plasma physics and its purpose is to provide an optimized LIBS system with stable and informative spectra for specific applications. In China, except for some nano-second laser products, all other high quality devices for LIBS were imported from other countries for most of the researchers. Limited by the industrial background and understanding of the LIBS Physics, there was even less work done on instrumentations than on fundamentals from the Chinese LIBS community. Till now, there was very little publication on

the LIBS components (laser, ICCD, spectrometer) originated from the Chinese LIBS community.

However, in recognition to the potential capability of LIBS, Chinese government launched several projects related to LIBS instrumentation development recently. With the support from the National Natural Science Foundation Committee (NSFC) or Ministry of Science & Technology (MS&T), Sun *et al.* developed a set of equipment for on-line analysis of molten steel, which can semi-quantify the elements of Cr, Mn, Ni, and Si [6]. Zhang *et al.* [52, 53] developed a fully software-controlled LIBS system for on-line quality analysis of pulverized coal. The LIBS module can analyze unburned carbon in fly ash without being affected by the type of coal burned. Guo *et al.* [19, 20] used an aluminum hemispherical cavity to confine plasmas generated from a steel target in LIBS to enhance the sensitivity and stability of the element compositions by LIBS. These projects were listed in Table 3.

In addition to these ongoing government supported projects, there were also some researches on either LIBS system integration or sampling method improvement for special purposes. Cheung *et al.* [21, 32] introduced an acoustic monitor to detect the mass removed in pulsed laser ablation and develop a normalization method. They also designed a vertical sample jet downstream structure for liquid material measurement [21, 22, 33], and based on this technique, they also designed a cytometric LIBS scheme for human blood analysis [34, 35]. Wang *et al.* [74, 78] designed a symmetric cylindrical confinement to

Table 3 The LIBS instrumentation related projects in China.

Project	Supporting program/Sponsor	Objective
Development and application of an innovative multifunction Laser Spectrum Analyzer (Sichuan University)	National Major Scientific Instruments and Equipment Development Special Funds (MS&T)	To develop a hybrid instrument to record both Raman and LIBS spectra To improve the analytical performance, environmental adaptation, and reliability of the sampling method
Development of an on-line analyzer of alloy compositions based on LIBS (Shenyang Institute of Automation, Chinese Academy of Sciences)	National High-Tech Research and Development Program of China (MS&T)	To study and develop an online alloy composition analyzer based on LIBS
Research on on-line coal quality analysis instrument based on laser-induced breakdown spectroscopy (Shanxi University)	Special Fund for Basic Research on Scientific Instruments (NSFC)	To develop a LIBS system for online coal measurement, including ultimate and proximate analysis
Development and demonstration projects of on-line monitoring system in coal & power industry for energy saving and emission reduction (Shanxi University)	National Key Technology Research and Development Program (MS&T)	To develop an on-line coal and gas quality monitoring equipment for an energy-saving demonstration project in coal-fired power plant
Development of high precision LIBS instrument based on resonant excitation and spatial confinement (Huazhong University of Science & Technology)	National Special Fund for the Development of Major Research Equipment and Instruments (MS&T)	To develop LIBS instrument based on resonant excitation and spatial confinement
Development and deployment of a LIBS-sea system (Ocean University of China)	National High-Tech Research and Development Program of China (MS&T)	To develop a LIBS system for in-situ detection of metal ion in deep sea



enhance signal and improve measurement repeatability.

As mentioned above, the researches on instrumentation were not fully developed in China. However, the Chinese government and LIBS community has already showed great interests to integrate our own LIBS system with most on specific purpose (such as coal analysis [52, 53, 74, 78] and metal detection [17]).

## 4 Data processing and modeling

Data processing and modeling plays an important role to LIBS as it bridges the spectra to analytical results. An ideal data processing method should be based on a deep understanding to the plasma physics and capable of minimizing the noise affects, compensating for the signal fluctuations, and reducing the matrix effects. In the present work, only quantitative model were reviewed. The works related to the qualitative analysis can be found elsewhere [11–13, 59].

### 4.1 Data pretreatment

It was known that the LIBS signal was usually suffered from the continuous background, different source of noises such as environmental noise, and spectral interference. Besides, due to fluctuations of laser energy, laser-material interaction, and other experimental parameters, the LIBS signal was also affected by the measurement uncertainties. Therefore, a data pretreatment step was usually taken to reduce the influence of noise (signal denoising process) for LOD improvement and measurement uncertainties reduction (normally using normalization process) for better measurement accuracy; a calibration model would be thereafter built-up to compensate for the matrix effects and predict the elemental concentrations.

#### 4.1.1 De-noising

Optimization of the detection delay in LIBS system would be effective to reduce the continuous background noise, but it will be very hard and cost to further remove the signal noise by hardware improvement. Denoising using data processing method would be a very necessary and helpful approach for signal-to-noise ratio (SNR) improvement or LOD reduction.

Recently, wavelet analysis method was firstly applied for LIBS spectrum denoising by Chinese researchers. Zhang *et al.* [54] applied the wavelet transform method for noise suppression. They proposed a double threshold optimization model for the wavelet-transform denoising

process. The results showed that the LOD was reduced by more than 50% and the SNR was improved by a factor of two. Yuan *et al.* [85] proposed a hybrid model by combining the wavelet transform method and partial least squares (PLS) method. The hybrid model applied wavelet transform method to remove the background and environmental noise. The results showed that only with environmental denoising process using wavelet-transform method, the SNR was improved more than twice for LIBS measurement of carbon in coal in different gases (air, helium, and argon). Due to the noise reduction, the final results of the hybrid model were greatly improved. For example, the root mean square error of prediction (RMSEP) was decreased to 1.94% from 4.18% (using traditional PLS model without denoising) in helium.

There was also some work aimed to pretreat the spectral data for noise reduction in addition to wavelet-transform de-noising. For example, Sun *et al.* [55] designed a threshold for filtering the needless minima of spectral data, applied a polynomial model to estimate the continuum background for the remaining spectral data, and based on these two steps, reduced the noise contained in the spectra. Overlapped peak resolving [49, 57] may be regarded as another de-noising process. Zhang *et al.* [57] proposed a curve fitting method for overlapped Lorentzian peak resolving, the initial values of the peaks were estimated and the interference of noises were reduced. Bi *et al.* [49] applied the algorithm of symmetric zero-area conversion for the peak recognition of LIBS spectra. This method is free from spectrum background and base-line trend influence, applicable to wide range of SNR levels, close to or even better than artificial recognition for weak peak.

#### 4.1.2 Uncertainty reduction

Normalization was the most frequently applied method for uncertainty reduction. Conventional normalization normalized the characteristic line either with internal standard [53, 72] or reference signal such as spectral area [73, 82, 95], acoustic emission intensity [21], and background emission [96].

In general, these reference signal methods, taking advantage of the correlation between the LIBS signal (normally the characteristic line intensity) and the reference signal due to the fluctuations of laser energy and the ablated mass etc., can only indirectly and partly reduce the LIBS signal fluctuations. A better method should be applying the plasma characteristic parameters to directly compensate for the spectral signal fluctuations.

Wang *et al.* [68–71] developed a “standardization” method by assuming the existence of a “standard state”,

where the standard plasma of specific sample has a standard plasma temperature, electron number density, and total number density of the interested species. In addition, the total number density of the measured species is proportional to its concentration in the sample. By assuming that the fluctuation of total number density of the measured species is proportional to the fluctuations of some reference signal (such as the sum of all line intensity of the interested species) converted to a value the fixed plasma temperature and electron density, the measured the line intensity can finally converted to its standard state value by the following equation [68]:

$$I(n_{s0}, T_0, r_0) = A_1 I(T_0, r_0) + A_2 I_T(T_0, r_0) + A_3 \quad (1)$$

where  $n_{s0}$ ,  $T_0$ ,  $r_0$  indicate the standard total number density of the measured species, standard plasma temperature, and the standard ratio of the singly ionized and neutral species of the interested element, respectively;  $I(n_{s0}, T_0, r_0)$  is the calculated characteristic line intensity at the standard state, while  $I_T(T_0, r_0)$  is the sum of the all line intensity of the measured element converted to the standard plasma temperature and standard electron density using Saha-Boltzman equations. In application to 29 copper alloy samples, the average relative standard deviation (RSD) was decreased to 5.29% from 8.61% using the whole spectrum area normalization, showing a very good improvement for uncertainty reduction.

However, the primary standardization method required a large amount of work in plasma temperature, electron density, and intensity conversion to standard state using Saha-Boltzman equations. A simplified spectrum standardization method was thereafter developed [69]. Taylor expansion was applied to compensate for the intensity fluctuation due to plasma property to its standard state value. The temperature variation was regarded to be proportional to the variation of the logarithm of the ratio of two spectral line intensities of the interested element, the variation of electron number density was regarded to be proportional to the variation of the full width at half maximum (FWHM), and the variation of total number density was regarded to be proportional to the variation of the sum of the multiple spectral line intensities of the measured element. Results showed an even better RSD was achieved for the same set of copper alloys: the average RSD was further decreased to 2.92% from 5.29% in its original version. The improvement was explained as the inaccuracy in plasma temperature and electron density calculations in the previous version. A multi-variate normalization method combining the standardization concept and PLS approach was further proposed by Li *et al.* [71]. Results showed that for the pulse-to-pulse RSD was decreased to

1.8%. Considering the RSD of laser energy being about 3%, the results should be totally acceptable for LIBS measurements. In addition to RSD reduction using the standardization method, it was suggested that the main source of uncertainty was the fluctuation of total number density (or plasma morphology) [68, 69] while the measurement uncertainty actually contributed most errors to LIBS measurement since the measurement accuracy was improved greatly automatically as the measurement uncertainty was reduced in all these work [68–71].

## 4.2 Calibration model

In the present work, only quantitative calibration model was referred since there was very little work with the calibration-free LIBS from China except for some minor work [56]. Currently, there were two kinds of general applied quantitative model available in the World: i) traditional uni-variate model based on the physical principle that the characteristic line intensity of an element is proportional to its concentration in the sample; ii) multi-variate model based on statistical correlation calculation between the full spectral information and the concentration of an element of interest in the sample. Due to its physical background, the traditional calibration model is generally robust for a wider range of sample matrix while since it only applied a few line intensities, the model results in terms of  $R^2$  and RMSEP were generally not as good as the multi-variate model. Wang *et al.* [77, 80–82] proposed a dominant factor based multi-variate model. The dominant factor was essentially the same as traditional uni-variate model, which was able to model the nonlinear and linear relationship based on physical background, while a statistical based PLS method was thereafter to correct the residue errors using full spectral information. Compared with traditional model, the dominant factor based PLS model was able to reduce influence of plasma property fluctuation; while compared with traditional PLS method, the dominant factor endowed the dominant factor based PLS model with physical background, therefore being more robust over a wider range. In the new model, the dominant factor is essentially the first principle component of as for traditional PLS model and the explicitly extracted first principle component (dominant factor) was able to describe nonlinear effects. In application to elemental concentration measurement for different samples such as copper alloys and coal samples, the dominant factor based PLS models was always able to achieved 15% to 50% better in regard to RMSEP while keeping the same  $R^2$  compared with traditional PLS method [75, 77, 80–82]. In addition, the new model remains potential for further improvement

not as the traditional PLS method, and any improvement in plasma physics understanding will improve the dominant factor model as well as the overall model performance.

Lu *et al.* also studied the multivariate calibration model for different application. They developed a set of multivariate calibration models to extract the content information of coal property from LIBS spectra rather than from elements concentration. The results showed that the multivariate method combined LIBS technique provide an alternative accurate and reliable proximate analysis of coal [60, 61]. In addition, the multivariate analysis methods were also employed to improve the measurement accuracy for unburned carbon in fly ash [62] and the K and P in fertilizer [63].

Currently, multivariate calibration model plays an important role for LIBS quantitative analysis in China and worldwide. However, the traditional multivariate model is lack of physical background. The combination of traditional univariate model and multivariate model such as dominant factor based PLS model would be a potential approach in give better performance for LIBS measurements.

For data processing, emphasis should be given that the processing should be established on the basis of plasma physics understanding. For examples, in resolving overlapped peaks, de-convolution calculation may be involved since the overlap process contains the convolution process; in denoising process, the bremsstrahlung radiation and the function of electron density may need to be considered, and the wavelet transform analysis method should be more wavelength specific to reduce more background and environmental noises; while in calibration procedure, explicitly modelling of the interference, self-absorption, plasma property fluctuations, and plasma inhomogeneity and transition would be very important and necessary for potentially improving the measurement precision and accuracy and realizing successful commercialization.

## 5 Applications

For the fast developing China, energy and resource exploration and utilization, environment protection, health care, and building construction are always among the main themes of the society. LIBS, due to its advantages of fast and multi-elemental analyses, less or no sample preparation, was regarded as a potential leading chemical analysis technology for solving many critical application with online, in-situ, or fast analysis requirements in these important areas. Driven by these urgent demands with a

large domestic market, LIBS research in China expanded very fast recently as described above. The applications of LIBS in different fields were presented in detail below.

### 5.1 Coal analysis

Coal is the dominant primary energy source (about 75%) and there is a huge demand for on-line coal analysis technologies in China. As there is a large amount of coal utilized for most coal users (for example, there are about several thousand tons of coal per day needed for a 300 MW power plant), a fast or online coal analysis technology is of a thirsty necessity in coal pricing and combustion/utilization optimization for power industry, coal chemical processing industry, and coal mine industry. Currently available traditional coal analysis technology usually takes a long time and is not applicable for fast or online analysis. Under the urgent political demands for CO<sub>2</sub> reduction, a fast or online coal analysis technology becomes even more important.

Normally, coal analysis includes approximate analysis (fixed carbon content, calorific value, volatile matter content, ash content, and moisture content) and ultimate analysis (including major elements such as C, H, O, N, and S). LIBS has already shown great potential for online or fast coal analysis.

A number of studies on elemental measurements of coal or fly ash by LIBS have been performed. The measurement repeatability of raw coal blocks using LIBS is very poor due to the heterogeneity and irregular shape of coal. Therefore, coal is usually milled into powder and pressed into pellet samples to obtain more stable LIBS signals. In addition, even using coal pellets, the coal analysis still suffers from low measurement precision and accuracy due to multiple factors, such as variations in experimental conditions and matrix effects.

As carbon is the most abundant element in coal and its content can reflect coal quality, determination of carbon content in coal is very important. Feng *et al.* [77, 82] applied a PLS model base on dominant factor for measuring carbon content in bituminous coal samples. Results showed that RMSEP in the proposed PLS model decreased to 3.77% from 5.52% compared to the conventional PLS model.

Li *et al.* [84] proposed a spectrum standardization method to achieve both reproducible and accurate results for measurements of carbon content in bituminous coal by LIBS. The application of the proposed method to measurements of the carbon contents in 24 bituminous coal samples demonstrated that the proposed method had superior performance over the generally applied normalization methods. The RSD and RMSEP for the pro-



posed model were 3.44% and 2.71%, respectively. In addition, it was possible to combine the spectrum standardization and dominant factor based PLS method to further improve the measurement accuracy as well as precision [83]. The proposed model utilized the standard state carbon line intensities, which were obtained from the spectrum standardization method, as the dominant factor to explain the major part of elemental concentration. The residual between the real elemental concentration and the value calculated by the dominant factor were further minimized by the entire spectrum information with PLS algorithm. The RMSEP and ARE for the combination model were further reduced to 1.75% and 2.39%, respectively.

Yuan *et al.* [72] studied the measurement of carbon content in anthracite. They utilized binder to improve the adhesiveness of the pellet surface and chose a major element from binder as the internal calibration element to improve the measurement repeatability. Results showed that by employing the optimized binder  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  with Si from the binder as the internal calibration element the overall best measurement precision and accuracy can be achieved. Wang *et al.* [73] measured three major elements (C, H, and N) in bituminous coal samples. Argon and Helium as ambient gas were utilized to enhance the signals and eliminate the interference of nitrogen from surrounding air. Results showed that argon not only improved the intensity, but also improved the quantitative results of carbon and hydrogen in coal, showing a satisfied accuracy for application. The ARE of carbon content reduced from 4.96% in air to 2.98% in argon, while that of for Hydrogen content was 2.78%. Yet, the nitrogen lines were too weak to be detected even in an argon environment.

Li *et al.* [64] focused on improving the measurement precision of non-metallic elements (C, H, O, and N) and metallic elements (Ca, Mg, Fe, Al, Si, Ti, Na, and K) by the optimizing experimental parameters such as the particle size of the coal powder, the pressing force, lens-to-sample distance, number of laser pulses on one spot, and ambient gas. Results showed that the measurement precision strongly depends on the experimental conditions, and the RSD of LIBS measurement for coal sample can be improved by the optimization of experimental parameters.

Although LIBS is essentially an element measurement technology, coal property analysis by LIBS has also been investigated based on the correlations between elemental composition and coal properties. There were also a few works on coal properties analysis [60, 61, 75]. Yao *et al.* [60] analyzed the ash content in coal using PLS. Thirteen coal samples were used for calibration, and ARE of ash

content in four validation samples was 6.94%. Dong *et al.* [61] measured the volatile matter content of coal with a multivariate analysis model, which utilized the most related factors based on partial correlation and principal component analysis. Seventeen samples were used for establishing the calibration model and three samples were used for validation. The ARE of the volatile matter content in the validation samples was 4.5%, showing an acceptable results for on-line analysis.

Yuan *et al.* [75] utilized a non-linearized multivariate dominant factor based PLS mode to analyze coal properties, such as ash content, volatile content, and calorific value. The direct correlation between coal property and spectral line intensities was modeled by the dominant factor explicitly, whereas residual errors were corrected by PLS method with full spectral information. Forty samples were used for calibration and thirteen samples were used for validation. Results showed that although LIBS was not able to provide results as accurate as those of using traditional chemical processing method, it was fully capable of providing useful information for coal combustion optimization and reliable references for coal pricing. For examples, the AREs of both of ash content and volatile matter are smaller than 20% for all 53 coal samples; the ARE of caloric value is smaller than 4% for most samples, indicating that LIBS should be very applicable in coal quality monitoring and combustion regulations.

Although there has not been any work on raw coal blocks in China, efforts were also taken to measure the elemental concentration directly from coal powder without pressing into pellet. Yu *et al.* [65] studied the effect of particle size on the analysis of major elements (C, H, O, N and S) in pulverized coal, and found the smaller particle size lead to higher plasma temperature which could due to the sufficient thermal diffusion. Yao *et al.* [62] established a multivariate calibration method to measure the unburned carbon in fly ash. Results showed that the multivariate calibration method had a better performance than the univariate calibration method. Yin *et al.* [51] developed LIBS system composed of a LIBS apparatus and sampling equipment to achieve the in situ analysis of pulverized coal. Results showed that the LIBS system was able to realize multipoint sampling and sample-preparation operation. The relative errors of elemental measurements (C, Ca, Mg, Ti, Si, H, Al, Fe, etc.) were within 10%, while those of ash content were in the range of 2.29%–13.47%, showing that the designed LIBS system can provide some reliable information on coal quality. As organic oxygen content in coal is important for optimizing oxygen/coal mixing ratios, Zhang *et al.* [53] proposed a data processing method to calculate organic

oxygen content in anthracite coal under atmospheric conditions. The organic oxygen content was determined by the difference between the total oxygen content and the inorganic oxygen content. The internal normalization of O line intensity with the N line intensity and temperature correction were employed to improve the measurement accuracy of total oxygen content. The Si line intensity and Al line intensity were utilized to calculate the inorganic oxygen content by assuming that the inorganic oxygen of the anthracite coal totally exists in the oxides of silicon and aluminum. Results showed that the absolute error of calculated organic oxygen contents are in the range of 1.15%–1.37%, and the average absolute relative error is 19.39%.

The results of quantitative analysis of coal by Chinese researchers were summarized in Table 4.

As shown above, the results of current coal analysis by LIBS have been very useful and informative already for coal industry. With more efforts on this field, it is very possible to realize successful industrial application for coal pricing or combustion optimization with the help

of a fast coal sampling machine.

## 5.2 Metal analysis

Elemental analysis was very important for assessment of the quality of metal alloys. For example, the measurement of carbon composition was able to indicate the strength and corrosion resistance of steel. With the rapid development of China, tremendous metal materials were utilized for building construction. A fast or real time metal analysis technology draw great interest to Chinese metallurgic industry. At present, spark discharge-atomic emission spectroscopy (SD-AES) and X-ray fluorescence (XRF) were two commercialized technologies for metal analysis, but with certain disadvantages such as the narrow wavelength range, limited kinds of analyzed elements. LIBS was considered to be a potential alternative for metal analysis.

Different calibration models had been studied in the quantitative analysis of metal. Wang *et al.* [97] studied the trace element molybdenum (Mo) detection in

**Table 4** LIBS analysis results of coal by Chinese researchers.

Analyte	Sample conditions	Results	References
C	Bituminous coal pellet, 19 for calibration, 14 for validation	RMSEP = 3.77 % (Averaging 40 pulses for each sample)	[77, 82]
	Anthracite coal pellet, 15 for calibration, 7 for validation	RSD = 12.1% (pulse-to-pulse), RMSEP = 6.25%, ARE = 10.14% (Averaging 40 pulses for each sample)	[72]
	Bituminous coal pellet, 17 for calibration, 7 for validation	RSD = 8.50% (pulse-to-pulse), RMSEP = 3.49%, ARE = 2.98% (Averaging 40 pulses for each sample)	[73]
	Bituminous coal pellet, 16 for calibration, 8 for validation	RSD = 3.44 % (pulse-to-pulse), RMSEP = 1.75%, ARE = 2.39% (Averaging 25 pulses for each sample)	[84] [83]
	Bituminous coal pellet, 4 samples	RSD = 6.17% (Averaging 50 pulses for each measurement, 5 repeated measurements)	[64]
	Bituminous coal powder, 8 for calibration, 3 for validation	RSD = 1.95%, ARE = 2.09% (100 spectra were filtered and the left were averaged for each measurement, 5 repeated measurements)	[51]
H	Bituminous coal pellet, 17 for calibration, 7 for validation	RSD = 6.19% (pulse-to-pulse), RMSEP = 0.24%, ARE = 2.78% (Averaging 40 pulses for each sample)	[73]
	Bituminous coal pellet, 4 samples	RSD = 5.29% (Averaging 50 pulses for each measurement, 5 repeated measurements)	[64]
O	Bituminous coal powder, 8 for calibration, 6 for validation	ARE = 19.39% (Averaging 300 pulses for each measurement, 5 repeated measurements)	[53]
Calorific value	Bituminous coal pellet, 40 for calibration, 13 for validation	ARE = 2.71% (Averaging 36 pulses for each sample)	[75]
Ash	Bituminous coal pellet, 40 for calibration, 13 for validation	ARE = 12% (Averaging 36 pulses for each sample)	[75]
	Coal pellet, 13 for calibration, 4 for validation	RSD = 8.50% (Averaging 50 pulses for each measurement, 3 repeated measurements for RSD calculation) ARE = 6.94% (Averaging 150 pulses for each points)	[60]
Volatile	Bituminous coal pellet, 40 for calibration, 13 for validation	ARE = 5.47% (Averaging 36 pulses for each sample)	[75]
	Coal pellet, 17 for calibration, 3 for validation	RSD = 3.89% (Averaging 50 pulses for each measurement, 3 repeated measurements for RSD calculation) ARE = 4.54% (Averaging 150 pulses)	[61]
Moisture	Bituminous coal pellet, 40 for calibration, 13 for validation	ARE = 26.2% (Averaging 36 pulses for each sample)	[75]

complex metallic alloys. Using Mo I 550.649 nm line for linear calibration, the relative error was found to be 5.57%. Wang *et al.* [7] studied the trace element Mn and Cr in steel by LIBS, where the major element Fe was taken as the internal reference element. The determination coefficient  $R^2$  of the calibration curve was 0.998 and 0.979 for Mn and Cr respectively. The LOD of Mn and Cr in steel were about 50 ppm and 400 ppm respectively.

Sun *et al.* [58] paid attention to quantitative analysis of Mn and Si in different alloy steels. Considering about the serious matrix effects of different steels and the strong line overlaps of steel spectra, the multivariate quadratic nonlinear function was used for calibration. The root mean square error (RMSE) was 0.732% and 0.0231% for Mn and Si respectively. Chen *et al.* [8] used calibration-free method for quantitative analysis of slag samples. The relative measurement errors of Ca, Si, Al and Mg were 5%, 13%, 14% and 31%, respectively. Sun *et al.* [56] applied calibration-free method combined with self-absorption correction for quantitative analysis of different alloys. The measurement errors were listed in Table 5.

Zhang *et al.* [98, 99] investigated the steel measurement using LIBS. It was found that the spectral line intensity is stronger in argon than in helium, nitrogen and air gas environment, with the detection limits of dozens of ppm for C, Si, Mn, P, S, Ni, and Cr. Dong *et al.* [6] reviewed the application of LIBS for metallurgical analysis in China, where quantitative results of various metal samples with different calibration methods were summarized. The LOD for solid metal was tens to hundreds of ppm, while for molten metal the LOD was hundreds of ppm.

For online monitoring in metallurgical industry, the metal sometimes has to be analyzed in molten state. Chen *et al.* [66] compared the plasma spectra of molten steel in air and in argon. The result demonstrated that the argon atmosphere not only prevents the molten steel from oxidation but also increases the emission intensity of the plasma. Online monitoring equipment for molten steel analysis was also developed. Sun *et al.* [100, 101] developed an experimental equipment to measure the elemental components of molten steels. They found that the steel temperature strongly affects the spectral line intensity, and the detection capability of minor elements in molten steel is higher than in normal steel. Furthermore, they also achieved the on-line and semi-quantitative analysis of Cr, Mn, Si and Ni in molten steels. The RSD is lower than 7.43%, and the RMSE is lower than 0.058%.

Besides analysis of elementary composition of metal and alloy, LIBS also has been used for surface diagnostics. Yao *et al.* [67] proposed to develop a non-destructive diagnostics technology for detecting failure trend of heat transfer surfaces for steel using LIBS, based on the matrix effects caused by the changes of microstructure and mechanical properties of boiler tube. Using PCA, the pearlite/ferrite and martensite can be successfully distinguished to identify microstructures on the target surface. Table 5 briefly summarizes the results of metal analysis with LIBS in China.

As shown in Table 5, although there have been many works done on metal analysis using LIBS, much more quantitative works with sufficient metal samples are still required to prove that LIBS has the capability to realize fast or online metal analysis. In addition, the

**Table 5** Brief results of metal analysis.

Sample conditions	Elements	Method	Results (RE means relative error)	reference
Aluminum alloy, 1 sample	Cu, Mn, Al	Calibration-free	Cu:RE = 20.05%; Mn:RE = 41.98%; Al:RE = 0.51%	[56]
Iron-chromium alloy, 1 sample	Cr, Fe	Calibration-free	Cr:RE = 6.59%; Fe:RE = 2.53%	[56]
Iron-chromium-nickel alloy, 1 sample	Cr, Fe, Ni	Calibration-free	Cr:RE = 5.88%; Fe:RE = 2.56%; Ni:RE = 1.28%	[56]
Alloy steel, 6 for calibration, 1 for validation	Mo	Univariate linear	RE = 5.57%	[97]
Steel, 5 for calibration, no validation	Mn, Cr	Internal standard	Mn: $R^2$ = 0.998, LOD = 50 ppm; Cr: $R^2$ = 0.979, LOD = 406 ppm;	[7]
Steel, 15 for calibration, 5 for validation	Mn, Si	Multivariate quadratic non-linear	Mn:RMSE = 0.732% (calibration samples); Si:RMSE = 0.0231% (calibration samples)	[58]
Slag, 1 sample	Ca, Si, Al, Mg	Calibration-free	Ca:RE = 5%; Si:RE = 13%; Al:RE = 14%; Mg:RE = 31%	[8]
Molten steel, 4 samples for calibration, no validation	Mn, Si, Cr	Univariate linear	Mn: $R^2$ = 0.987, LOD = 75.7 ppm; Si: $R^2$ = 0.956, LOD = 23.8 ppm; Cr: $R^2$ = 0.927, LOD = 724.5 ppm;	[66]
Steel, 1 sample	Metallographic diagnostic	PCA	Pearlite/ferrite and martensite are successfully classified	[67]

quantitative method applied for coal analysis should be very effective in improving the measurement precision and accuracy for metal.

### 5.3 Soil analysis

Soil pollution has attracted people's attention in recent years. In China, soil analysis using LIBS was mainly focused on the metal element analysis.

Chen *et al.* [102] applied LIBS to measure barium and strontium in soil using standard soil samples, the relative error of Ba and Sr were 5.7% and 5.1% respectively. He *et al.* [41] measured the concentrations of eight elements (Mg, Ca, Si, K, Al, Ti, Cr and Mn) using Fe line as the internal reference line. The relative errors for Mg, Ca, Si, K and Al were lower than 10%, while for the heavy elements Ti, Cr and Mn, the relative errors were about 13%, 14% and 18% respectively. The relative low accuracy for heavy metals could mainly come from the fact that the concentrations are very low for them in soil.

In order to improve the LOD for metal elements, LA-FPDPS was applied to the quantitative measurement of Mg, Pb and Sn in soil [91]. A linear calibration model was established for Mg with  $R^2$  of 0.99. Considering the evident self-absorption of Pb and Sn, polynomial calibration models were established for Pb and Sn with  $R^2$  of 0.98 and 0.93, respectively. The LODs based on the linear portions of the calibration curves were 34, 1.5 and 0.16 ppm for Mg, Pb and Sn, respectively.

Except for solid soil, LIBS was also applied to soil slurry analysis. With the motivation of developing an in-situ sensor for monitoring heavy metal in soil slurry, Lu *et al.* [48] measured Pb in soil slurry using manganese as the internal reference. The LIBS signals of Pb I 405.78 nm and Mn I 403.07 nm from the slurry samples were investigated. It was found that the intensity ratio of Pb/Mn increased as a linear function of the concentration of Pb with correlation coefficient  $R^2$  of 0.99. Table 6 briefly summarizes the results of soil analysis.

As shown in Table 6, the work for quantitative analysis using LIBS for soil is not sufficient, although LIBS has shown very good potential for this application. To realize high quality quantitative analysis results, much more standard soil samples should be required, which was somehow difficult to obtain.

### 5.4 Aqueous solution analysis

LIBS analysis of aqueous solutions was also investigated by Chinese researchers, which was mainly motivated by ocean exploration, ocean pollution detection, and sewage treatment. Researchers evaluate the potential of LIBS for underwater application [21, 33, 103–106], but it still needs further effort because of the complex interaction process between laser and liquid. Laser-induced breakdown in either bulk or the surface of liquids creates several inherent drawbacks, such as splashing, surface ripples, extinction of emission, and shorter plasma lifetime, all of which adversely affect sensitivity and analytical precision. Yao *et al.* [107, 108] measured the toxic metal Cr in wastewater. With the relative error higher than 10%, they indicate that the application of LIBS aiming the direct analysis of heavy metals in water is a great challenge that still needs efforts for its development and validation. In order to apply LIBS for aqueous solution analysis, design and optimization of the experimental scheme become very important.

To evaluate the potential of LIBS for on-line monitoring toxic metals pollution in ocean. Wu *et al.* [45] directly analyzed sewage by sampling the sewage to liquid jet. The metal ions in  $\text{CuSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$  aqueous solutions were detected and the LOD of lead and copper was found to be 50 ppm and 31 ppm respectively. Feng *et al.* [109] studied Pb in  $\text{Pb}(\text{NO}_3)_2$  aqueous solution by a simple homemade liquid jet device. The LIBS system are optimized to be 57 mJ pulse energy, 135 ns detection delay, and  $20 \text{ mL} \cdot \text{min}^{-1}$  liquid flow rate. Using Pb I 405.781 nm line, the LOD was found to be at the level

**Table 6** Summary of the results of soil analysis.

Sample conditions	Elements	Results	References
Standard soil pellet, 4 for calibration, 1 for validation	Ba, Sr	Ba:RE = 5.7%; Sr:RE = 5.1% (Averaging 50 pulses for each sample)	[102]
Natural soil pellet, 1 sample	Mg, Ca, Si, K, Al, Ti, Cr, Mn	Mg:RE = 2.82%; Ca:RE = 3.10%; Si:RE = 4.06%; K:RE = 4.52%; Al:RE = 9.64%; Ti:RE = 13.48%; Cr:RE = 13.53%; Mn:RE = 17.86%	[41]
Standard soil pellet, 6 for calibration, no validation	Mg, Pb, Sn	Mg:LOD = 34ppm; Pb: LOD = 1.5ppm Sn:LOD = 0.16ppm (Averaging 20 pulses for each sample)	[91]
Artificial prepared soil slurries, 6 for calibration, no validation	Pb	$R^2 = 0.99$	[48]



of 60 ppm.

Another direct analysis method is using ultrasonic nebulizing technology for sampling. As showed by Zhong *et al.* [46], the liquid sample is transformed into dense droplets by ultrasonic nebulizing, and then these dense droplets are analyzed by LIBS. Results showed that even with a low laser pulse energy (30 mJ), the signal of LIBS still has a long lifetime and a high signal to background ratio (SBR). The LOD of Mg could reach as low as 0.242 ppm.

Another sampling method for aqueous solution analysis is indirect method, which transforms liquid to solid. Zhu *et al.* [110] use bamboo charcoal as a solid-phase extraction adsorbent to detect trace metal element (Pb) in aqueous solution. With this method, the liquid analysis was transformed to solid surface analysis which could overcome the drawbacks in liquid sample analysis. The calibration curve was constructed by using standard solutions with variable concentrations, and the LOD of Pb was estimated to be  $8.5 \mu\text{g}\cdot\text{mL}^{-1}$ . This system has also been used for quantitative analysis of wastewater, where the relative error of the concentration of Pb in wastewater was about 6.4%, and the RSD was 7.0%.

Chen *et al.* [111, 112] found that the detection sensitivity of trace heavy metals in water was enhanced 2–3 orders by using wood slice substrates to absorb water

samples or pre-concentration with electrical-deposition technique. Using wood slice substrates for absorption, calibration curves for five metal elements, Cr, Mn, Cu, Cd, and Pb under trace concentrations have been obtained, and the LOD were determined to be in the range of  $0.029\text{--}0.59 \text{ mg}\cdot\text{L}^{-1}$ , 2–3 orders of magnitude better than those obtained by direct analysis of liquid surface. For electrically deposition technology, the analytes were enriched on the surface of a polished high purity aluminum plate. After 10 minutes of deposition in 400 mL of water solution with 36 V deposition voltage, the LOD of Cr, Mn, Cu, Zn, Cd and Pb were determined to be 0.572, 0.374, 0.083, 5.623, 0.528 and  $0.518 \mu\text{g}\cdot\text{L}^{-1}$ , respectively. Similarly, Lu *et al.* [47] converted the cations in water to solid granules on the surface of an immersed metallic sheet through electrically assisted replacement reaction. The LOD of copper cation ( $\text{Cu}^{2+}$ ) was 16 ppb in aqueous solution of  $\text{CuSO}_4$ . Table 7 briefly summarizes the results of aqueous solution analysis.

The LOD, precision and accuracy of direct analysis of aqueous solution were unsatisfactory in practice. Enrichment methods represent useful pretreatment approaches for improving the analytical performance. However, enrichment methods are time-consuming and may be unsuitable for real-time analysis. Efforts still need to be taken for direct aqueous solution analysis required in fast

**Table 7** Brief results of aqueous solution analysis.

Sample conditions	Elements	Results	References
Aqueous solution, 8 for calibration, 1for validation	Cr	RSD of intensity = 7.6%, RSD of concentration = 8.5%, LOD = 39 ppm (accumulation of 15 laser shots for one spectra and 10 such spectra were averaged)	[107]
Aqueous solution, 8 for calibration, 1for validation	Cr	RSD of intensity = 6.5%, LOD = 6 ppm RE = 10.8% (after spectra smoothing) (accumulation of 10 laser shots for one spectra and 5 such spectra were averaged)	[108]
Aqueous solution using liquid jet, 5 for calibration, no validation	Pb	LOD = 60 ppm, $R^2=0.99$ (Averaging 30 pulses for each sample)	[109]
Aqueous solution extracted by bamboo charcoal and pressed into pellet	Pb	LOD = 8.5 ppm, RSD of concentration = 7%, RE = 6% (Averaging 50 pulses for one measurement, five measurement for each sample)	[110]
Aqueous solution absorbed by wood slice, 5 chlorides with different concentrations (5–1500 ppm)	Cr, Mn, Cu, Cd, Pb	Cr:LOD = 0.034 ppm; Mn:LOD = 0.036 ppm; Cu:LOD = 0.029 ppm; Cd:LOD = 0.59 ppm; Pb:LOD = 0.074 ppm	[111]
Element in Aqueous solution electrically deposited on aluminium plate, different concentrations of 6 chlorides	Cr, Mn, Cu, Zn, Cd, Pb	Cr:LOD = 0.572 ppb; Mn:LOD = 0.374 ppb; Cu:LOD = 0.083 ppb; Zn:LOD = 5.623 ppb; Cd:LOD = 0.528; Pb:LOD = 0.518	[112]
Liquid jet, different concentrations with no sample numbers mentioned	Cu, Pb	Cu:LOD =31 ppm; Pb:LOD=50 ppm	[45]
Dense droplets by ultrasonic nebulizing; 8 for calibration, no validation	Mg	Mg:LOD = 0.242 ppm; $R^2=0.99$	[46]
Enrich the element in aqueous solution onto immersed metallic sheet, 7 diluted samples, without calibration	$\text{Cu}^{2+}$	$\text{Cu}^{2+}$ :LOD = 16 ppb	[47]

or online measurements.

### 5.5 Nuclear

LIBS has also a wide range applications in the nuclear area such as leakage detection, in situ materials analysis for inspection and contamination detection. In China, the application research mainly related to the Experimental Advanced Superconducting Tokamak (EAST) and HL-2A Tokamak. LIBS has two potential roles in Tokamak, namely end-point detection to preserve the bulk materials and chemical analysis. In China, only the chemical analysis of impurity deposition on the plasma facing component (PFC) samples of EAST and HL-2A was studied by the group from Dalian University of Technology.

Hai *et al.* [14, 15] have involved in-depth and 2D analysis of multilayered PFC samples in a vacuum environment. The decrease in concentrations of the depositional elements (such as D, Li) was clearly observed in the depth from 0 to 100  $\mu\text{m}$ , but the concentrations of the substrate elements were found to be relatively uniform in the depth after dozens of laser pulses. Moreover, the linear correlation approach has been applied for improving the accuracy of depth profile analysis and identifying the interface boundary between the deposition layer and the substrate. This would help to develop LIBS technique to monitor the impurity deposition and fuel retention on the first wall of EAST.

LIBS has been applied for the analysis of ITER-like deposits consisting of a mixture of W/Al/C and D. It is demonstrated that LIBS can provide an in-situ method to discriminate the co-deposited layer from the substrate. It is found that an energy density about 7 J/cm<sup>2</sup> (1 GW/cm<sup>2</sup>) is needed for the removal of the co-deposited layer with a removal rate about 0.11  $\mu\text{m}$  per laser pulse without remarkable damage to the substrate [16].

Hai *et al.* [113] applied LIBS as an on-line control technique for the laser cleaning process of the polluted first mirror of the HL-2A tokamak. An orthogonal DP-LIBS configuration in a re-heating scheme has been investigated to accurately remove the ultrathin co-deposition layer of 0.8  $\mu\text{m}$ . In this configuration, the first laser is employed for cleaning purpose and the second laser is used for analysis.

### 5.6 Explosive

The traditional explosive detection such as ion-mobility spectrometry (IMS) and gas chromatography rely on vapor detection cannot achieve real-time and remote detection. LIBS has great potential for fast and remote detection of explosives.

Wang *et al.* [9–11] detected LIBS spectra of inorganic explosives, and also analyze LIBS spectra of organic explosives using chemometric approaches. They have investigated the time-resolved LIBS spectra of black powder, NaNO<sub>3</sub> and KNO<sub>3</sub>, indicating that the intensity ratio of O/N could be used for explosive discrimination. Using PCA and PLS-DA, the organic explosives (TNT) was distinguished from seven types of plastics. The results showed that PLS-DA had better reliability than PCA for discriminating TNT from plastics.

### 5.7 Agricultural product analysis

In recent years, the analysis of plants or agricultural products attracted great interest of LIBS researchers in China.

Sun *et al.* [42] used a 1064 nm laser focused onto the surface of folium lycii, and the relative concentration of different elements (Ca, Mg, Al, Si, Ti, Na, K, Li, and Sr) were determined, with errors ranging from 20% to 50%. They also studied the trace elements in tobacco and tobacco ash using calibration-free technique [43], and the difference of metallic elements mass concentration between tobacco and tobacco ash has been observed.

Yao *et al.* [36–38] applied LIBS for quantitative analysis of navel orange. Because of the limit of LIBS sensitivity for trace elements, the experiment was implemented by pre-contamination treatment. After pre-contamination treatment, the LOD of chromium was determined to 11.64 mg/g. Using PLS calibration, the  $R^2$  was found to be 0.9806 and the relative error of 12 samples was 10.94%. The results of their work made contribution to the development of LIBS application to agricultural product analysis which was meaningful for the safety of agricultural products.

### 5.8 Other applications

Besides the major application fields discussed above, some other applications were also studied although lack of systematic report, such as aerosol analysis, wasted battery analysis and the oil drilling particles analysis, which are introduced as below.

Zhang *et al.* [114] reported a phase-selective breakdown phenomenon in the in-situ LIBS diagnostics of TiO<sub>2</sub> nano-aerosols. By setting laser fluence between the breakdown thresholds of gas and particle phases, only particle phase matter in the aerosol system is atomized and excited with Ti atomic spectra detected. No bremsstrahlung background is observed even without any delay for the detector. Since the technique strictly distinguishes particle phase and gas phase, the phase-

selective LIBS can be used to trace the phase transition from gas precursor to particles, which is a basic process in heterogeneous reactive flows e.g. flame synthesis.

Peng *et al.* [115] use LIBS to investigate the applicability for the rapid analysis of heavy metals in spent Zn-Mn batteries. By using calibration-free method, it was found that the concentrations of heavy metals of vanadium, manganese, zinc, iron and copper were high in the mixture of positive electrode, while zinc and lead were with high concentration in the negative electrode. The maximum relative error was about 34% for Mn.

Tian *et al.* [116] used LIBS for identification of four kinds of cutting samples. The cutting samples which were produced in the process of oil drilling were identified by PLS-DA model with an accuracy of 86.7%.

In summary, most of LIBS researches were closely related to the urgent demands of economic development, such as energy and resource exploration and utilization (coal, metal, underwater, nuclear) and environment protection (soil and agricultural products). Therefore, once any one of the main applications (coal, metal, soil, or aqueous water production) was successfully commercialized, there would be plenty of market for LIBS development, which will be a great impetus for international community.

Although LIBS has shown great potential in many fields, the technology has not gained very successfully commercialization in any fields until now. Considering the fact that LIBS spectra were easily to be influenced by multiple factors, such as variations of experimental parameters and matrix effect, it would be very hard for an ordinary industrial operation to deduct accurate quantitative analysis results from a general LIBS system. Besides, for different applications, the optimum system parameters as well as the sampling methods varied greatly. Researchers should serve as the bridge between LIBS manufacturers and end-users by fixing the optimized system including experimental setup parameters, sampling method, and quantitative analysis algorithm for every specific application. A versatile LIBS system would be very attractive for researchers for their experiments, while specialized LIBS analyzers would be the only way-out for the technology. If a specialized LIBS system can be commercialized for a specific field, such as on-line coal analysis, LIBS applications in other fields will be greatly incited and motivated, which thereby facilitates a generalized application of LIBS.

## 6 Conclusions

As a rapidly developing analytical technique, LIBS has

been studied and introduced into different application fields in China. In this paper, the fundamentals, the instrumentation, the data processing and modeling, and the applications of LIBS in China are reviewed.

Through this review, it is found that the main driving force of LIBS research in China is the application demands. The critical issues for successful application of LIBS are the improvements of the precision, the accuracy and the sensitivity for quantitative analysis. Chinese researchers have done many works in signal enhancement, sampling method, denoising method, quantitative calibration models, and demonstration of LIBS in various application fields.

In addition, due to the complexity of LIBS and the different requirements of various fields, the potential direction to mature the technique and to realize its large scale commercialization is to develop specialized LIBS systems for specific fields of application instead of general LIBS systems.

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