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Laser-induced breakdown spectroscopy in Asia

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is an analytical detection technique based on atomic emission spectroscopy to measure the elemental composition. LIBS has been extensively studied and developed due to the non-contact, fast response, high sensitivity, real-time and multi-elemental detection features. The development and applications of LIBS technique in Asia are summarized and discussed in this review paper. The researchers in Asia work on different aspects of the LIBS study in fundamentals, data processing and modeling, applications and instrumentations. According to the current research status, the challenges, opportunities and further development of LIBS technique in Asia are also evaluated to promote LIBS research and its applications.

1. Introduction

LIBS is short for "laser-induced breakdown spectroscopy" and it is also called laser-induced plasma spectroscopy (LIPS), laser spark spectroscopy (LSS) and other related names [1]. LIBS as an analytical detection technique based on atomic emission spectroscopy to measure the elemental composition was introduced only two years after the invention of laser. In 1962, Brech and Cross [2, 3] studied the optical micro-emission stimulated by a ruby laser. A laser beam is focused in or on a sample, such as gas, liquid, aerosol or solid phase, to produce the hot plasma. The emitted spectra from micro-plasma corresponding to a unique wavelength for each element can be employed to determine the elemental components of measured samples qualitatively and quantitatively. With the development of LIBS devices and analytical methods, LIBS has attracted great attention in various fields as a qualitative and quantitative analytical detection technique due to its non-contact, fast response, high sensitivity and multi-elemental detection features. The successful first international LIBS symposium in 2000 in Pisa, Italy, represented the forming of the international LIBS community. Detailed description of LIBS and its applications has been given in a number of published review papers and text books [4-10].

Due to the great attraction and potential of LIBS technique, more and more researchers in Asia joined LIBS research for a dozen years. As a symbolic event for LIBS research, especially for Asian researchers, in September of 2014, Tsinghua University in China hosted the 8th international symposium on LIBS. After that, the first Asian Symposium on LIBS (ASLIBS 2015) was successfully organized by Wuhan National Laboratory for Optoelectronics (WNLO) of Huazhong University of Science and Technology in China. The next Asian Symposium on LIBS (ASLIBS 2017 in Tokushima) will be hosted by Japanese LIBS group. These symbolic events indicate the rapid development of LIBS research in Asia to catch up with the Euro-Mediterranean Society (EMSLIBS) and the North American Society (NASLIBS) of LIBS. Fig. 1 shows the statistics of LIBS publications in each year in different territories searched from Web of Science. LIBS publications from about 15 Asian countries were counted, such as China, Japan, Korea and so on. More than 30 European countries were refined, such as Italy, France, Germany and so on. USA and Canada were counted together. The search topics are laser-induced breakdown spectroscopy and laser-induced plasma spectroscopy. There may be some missed papers about LIBS in this search condition. However, the growing trend can be evaluated from this statistics. Fig. 1(a) shows the LIBS publications in each year in Asia. LIBS research in Asia is expanding very fast even if this trend started relatively late compared with that of European countries and USA and Canada, as shown in Fig. 1(b) and Fig. 1(c). Parts of the research fields and their representative publications in Asia are listed in Table 1. The wide researches from fundamentals to instrumentations have been studied, especially in China, Japan and Korea. For example, the Chinese Society for LIBS (CSLIBS) has become the most dynamically developing society. The total number of LIBS related papers from all over the world increased continuously after 1995, while it increased much faster from CSLIBS expanded only after 2009. It would be very convincing that CSLIBS has become a new indispensable

force for the development of LIBS world-wide [11]. Several review papers about LIBS in China have been published [12-14]. However, there has not been an overall understanding of the LIBS development status in Asia. It is the time to review LIBS in Asia to acquire a clear image about the strength and the weakness of our current researches to indicate the further development.
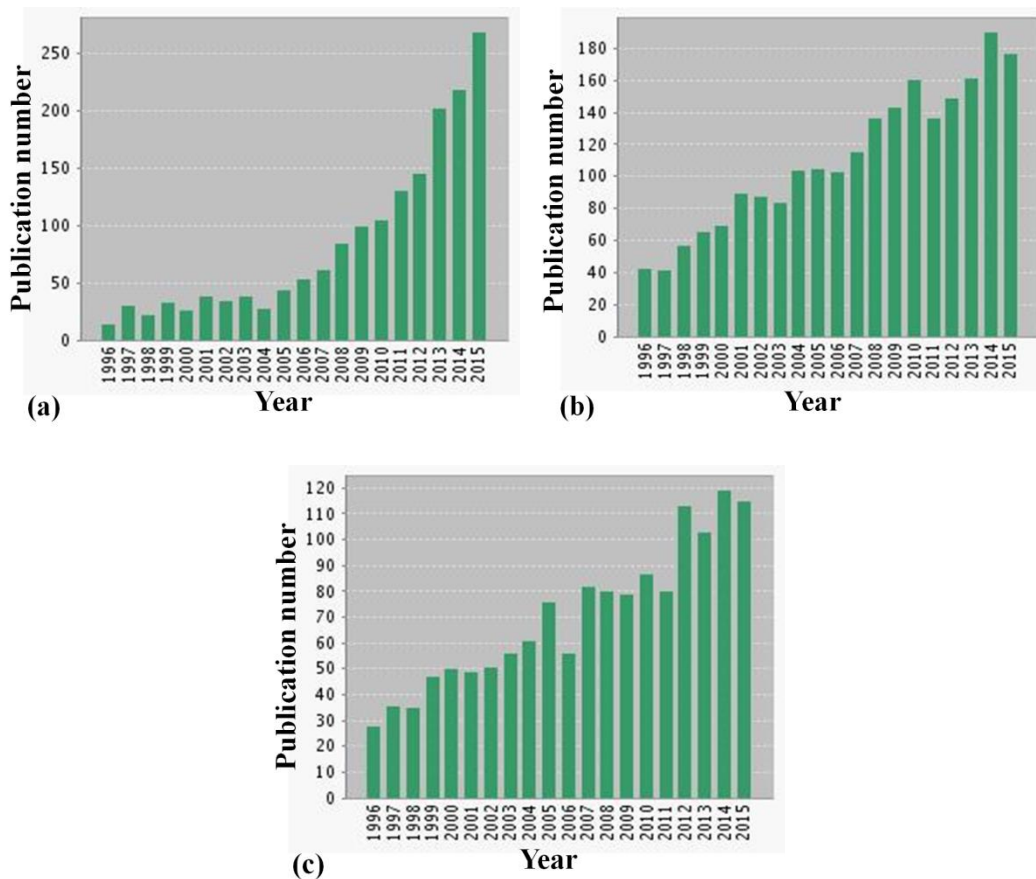

Fig. 1 Statistics of LIBS publications in each year in different territories searched from Web of Science from 1996. (a) Asian countries. (b) European countries. (c) USA and Canada.

Table 1 Parts of research fields and their representative publications in Asia

Country	Research fields	References
China	Plasma physics(fundamentals)	(16)-(18), (23)-(27), (31)-(32)
	Detection limit(fundamentals)	(47), (56)-(59), (61)-(68)
	Data processing and modeling	(70)-(87), (90)-(91), (93)-(97)
	Power plant(applications)	(98)-(100), (108)-(111)
	Iron and steel making processes (applications)	(112), (114), (116), (119)-(123)
	Environment(applications)	(124)-(126), (128), (131)-(132), (139)-(148), (153)
	Human and food safety(applications)	(160)-(161)
	Metallurgy(instrumentations)	(174)-(176)
	Coal fired power plant(instrumentations)	(179)-(181)
	Marine researches(instrumentations)	(186)
Japan	Plasma physics(fundamentals)	(28)-(29)
	Detection limit(fundamentals)	(43)-(46), (60), (69)
	Data processing and modeling	(92)
	Power plant(applications)	(101)-(106)
	Iron and steel making processes (applications)	(117)-(118)
	Environment(applications)	(133)-(137), (149)-(152)
	Coal fired power plant(instrumentations)	(177)-(178)
	Nuclear power plant(instrumentations)	(182)-(183)
	Marine researches(instrumentations)	(185)
Korea	Plasma physics(fundamentals)	(33)
	Iron and steel making processes (applications)	(115)
	Human and food safety(applications)	(159), (162)-(163)
	Nuclear power plant(instrumentations)	(184)
India	Plasma physics(fundamentals)	(37)-(38)
	Data processing and modeling	(88)
Indonesia	Detection limit(fundamentals)	(48)-(53), (55)
	Environment(applications)	(138)
Iran	Plasma physics(fundamentals)	(34)-(36)
	Human and food safety(applications)	(154)-(157)
Pakistan	Plasma physics(fundamentals)	(19)-(22), (30)
	Detection limit(fundamentals)	(54)
	Iron and steel making processes (applications)	(113)
Saudi Arabia	Environment(applications)	(127)

The fundamentals and applications have been extensively studied to improve LIBS technique. This review paper focuses on the work done in Asia from the following aspects: fundamentals, data processing and modeling, applications, instrumentations and challenges.

2. Fundamentals

LIBS fundamental studies are the foundation of clear understanding and successful application of the technique. Fundamental researches focus on the material ablation, species excitation, plasma evolution and characterization, plasma-environment interaction, signal enhancement, etc.

2.1 Plasma physics

The study of plasma physics is not only benefit to understand the fundamental of plasma generation and emission, but also to optimize LIBS specific applications. Lei Zhang et al. [15] investigated the emission characteristic of copper ionic lines from the $3d^95s$-$3d^94p$ transition using low pressure LIBS in argon. The emission intensity of the copper emission lines was extremely dependent on the kind of copper lines and the upper level energy. Wei Hang group [16] studied the ion emissions from laser-induced plasmas to provide insights into the hydrodynamic expansion of the plume. The diagnostic methods for the kinetic energy distributions of ionized species were roughly classified. Their interesting features and the angular distributions were summarized, as well as the dependence on laser beam properties, ambient surroundings and target properties. The fundamental theories and calculation methods of laser-induced plasma temperature were also reviewed using the spectroscopic approaches [17]. Its temporal and spatial evolutions together with several influencing factors were discussed, such as laser parameters, ambient surrounding and physical and chemical properties of the sample. The matrix effect in laser ablation and ionization of metal samples were evaluated by the chemometrics and theoretical approaches to understand and control laser ablation process [18].

M. Aslam Baig group [19-22] reported the behavior of the electron temperature and electron number density as a function of laser irradiance and ambient gas pressure. Several samples were studied under different conditions. For example, the zinc plasma, mercury plasma, calcium plasma and aluminum plasma were studied using the fundamental, second and third harmonics of a Nd : YAG laser. The excitation temperature was determined from the Boltzmann plots, whereas the electron number density was estimated from the Stark broaden profile of the spectral lines. Jian Wu group [23-27] studied the plasmas dynamics at the early stage of laser-induced target plasma including the influences of the multi-components of the air particles on the plasmas dynamics. Fig. 2 illustrated the electron number density n_e distributions above the target surface in different delay time with typical spectral images inset. Furthermore, the dominant mechanism for the excitation and ionization of the air particles were also discussed.
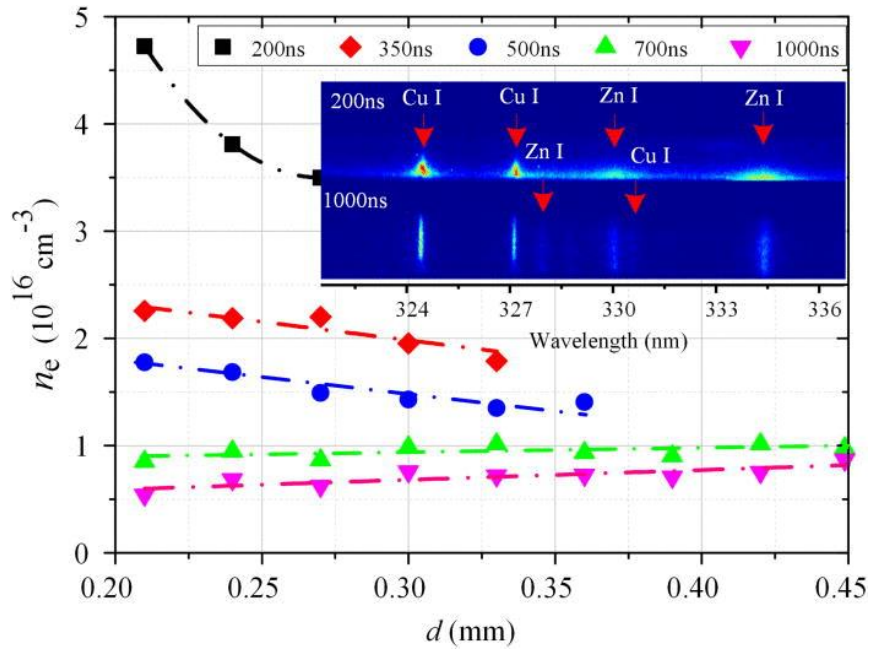
Fig. 2 Electron number density n_e at different distances from the surface of the target with typical spectral images inset [25] (W. F. Wei, J. Wu, X. W. Li, S. L. Jia, and A. C. Qiu, Study of nanosecond laser-produced plasmas in atmosphere by spatially resolved optical emission spectroscopy. Journal of Applied Physics, 2013, 114, 113304.)

Yasuo Iida [28, 29] investigated the effects of atmosphere on the laser vaporization and excitation processes with the spectral measurements and the direct measurement of vaporized weight of samples. The emission spectra, excitation temperatures, and electron densities were shown to be appreciably influenced by the ambient atmosphere. Nazar Farid et al. [30] investigated the effect of different gases and their pressures on the intensity of spectral emission, electron temperature and density of laser-induced plasma by the measurement of Cu targets to understand the ablation mechanisms and plasma parameters under various ambient conditions. Huaming Hou et al. [31, 32] investigated the plasma-ambient pressure interaction mechanism in a liquid environment. The effects of pressure and laser energy on the plasma temperature and electron density were discussed. The time-resolved LIBS emission results demonstrated that the plasma emission was weakly dependent on the ambient pressure during the early stage of plasma and the pressure showed a significant influence on the plasma form during plasma evaluation at a later stage of plasma.

Yong-Ill Lee et al. [33] carried out the plasma emission characteristics, self-absorption, line broadening, emission intensity, and metal ion formation by using two different laser systems on copper atomic and ionic lines under various atmospheric gas and pressure conditions. The degree of self-absorption and line-broadening strongly depended on the surrounding atmosphere and irradiation wavelength, which can be explained by the shock wave excitation of atoms in the outer-sphere plasma. Seyed Hassan Tavassoli group [34] studied the evolution of micro-plasma produced on

aluminum alloy surface in air by ns laser operated at 266 nm with different laser energies. A simplified model of plume expansion with two stages was compared with the experimental results. A one-dimensional model was also introduced to investigate the laser-induced plasma spectra of an aluminum sample in He ambient gas at 1 atm and different laser energies. In this model several coupled stages including laser ablation, plume expansion, plasma formation, laser absorption by plasma and plasma radiation were taken into account [35]. They [36] also investigated the influences of He ambient gas at different pressures on aluminum emissions to study the amount of spectral self-absorption of LIBS spectra by applying the calibration curve and the curve of growth approaches. Both techniques showed the growth of spectral self-absorption by increasing the gas pressure.

Sunku Sreedhar et al. [37, 38] presented the measurement results of high energy materials, such as NTO, RDX, HMX and TNT, obtained using ns and fs LIBS in different atmospheres, which can explicate the decay mechanisms with respect to the molecular species formation dynamics. Koo Hendrik Kurniawan and Kiichiro Kagawa group [39-41] proposed a new LIPS method to realize the high-sensitivity elemental analysis of metal samples using metastable He atoms induced by transversely excited atmospheric-pressure (TEA) CO_2 laser in He ambient gas at 1 atm. The excitation mechanism of hydrogen in TEA CO_2 laser-induced helium gas plasma, atomic emission characteristics of H, C and F was clarified. They [42] also reported the dynamical characteristics of the excitation mechanisms in various stages of the plasma formation by 1 mJ ps laser in N_2 and He ambient gases using space-resolved imaging and time-resolved measurement of the copper sample, which demonstrated the promising application to depth profiling of impurity distribution in the sample.

2.2 Detection limit

Most fundamental researches also focused on the signal enhancement to improve the accuracy and detection limit of LIBS measurement, as well as understanding of the basic plasma physics. Yoshihiro Deguchi group [43-45] compared the detection features of LIBS and laser breakdown time-of-flight mass spectrometry (LB-TOFMS) by measuring different trace species to discuss the laser-induced plasma processes including multi-photon ionization and electron impact ionization under different conditions, such as pressure, laser energy, wavelength, pulse width, etc. The detection limit of gas phase trace species can be enhanced by low pressure and short pulse LIBS. The generation process of laser induced weakly ionized helium plasma was also simulated using the lattice Boltzmann method (LBM) including multi-photon ionization, electron impact ionization and three-body recombination [46]. Yong Zhang et al. [47] investigated the influence of experimental parameters, such as lens-to-sample distances, delay time, atmospheric condition, laser energy, etc. on the spectral emission intensity of LIBS. Under optimum parameters condition, concentration relative standard deviation of C, Si, Mn, P, S, Ni and Cr for low-alloyed steel was 2.37%, 2.18%, 2.23%, 7.8%, 9.34%, 1.92% and 2.13%. The detection limit of C, Si, Mn, P, S, Ni and Cr for pure steel was 0.0045%, 0.0072%, 0.0069%, 0.0027%, 0.0024%, 0.0047% and 0.0024%, respectively. Koo Hendrik Kurniawan group [48-53] analyzed deuterium and

hydrogen in metal samples using LIBS to improve the detection ability and quantitative analysis under different pulse width, buffer gas and pressure conditions, which paved the further technical development of a three-dimensional quantitative micro-analysis of detrimental hydrogen impurity in zircaloy vessels used in nuclear power plants.

The methods mentioned above have improved the detection sensitivity of LIBS though the optimal experimental conditions. Some improvement approaches of LIBS sensitivity have also developed, such as double-pulse LIBS (DP-LIBS), laser ablation fast pulse discharge plasma spectroscopy (LA-FPDPS) and other combination methods. Rizwan Ahmed and M. Aslam Baig [54] compared the single and double-pulse LIBS by aluminum sheet measurement using the fundamental and the second harmonics of Nd:YAG lasers. The double pulse collinear configuration yields more than three hundred times signal enhancement. Zener Sukra Lie et al. [55] developed a time-resolved orthogonal DP-LIBS with helium surrounding gas for the explicit demonstration of time mismatch between the passage of fast moving impurity hydrogen atoms and the formation of thermal shock wave plasma generated by the relatively slow moving major host atoms of much greater masses ablated from the same sample. Lianbo Guo group [56-59] studied the enhancement effects of optical emission by spatial confinement, magnetic confinement, DP-LIBS and their combination. The optical emission enhancement was achieved by combining the spatial confinement and DP-LIBS. The enhancement mechanisms based on shock wave theory and reheating in DP-LIBS were discussed. These results provided a new pathway to improve LIBS sensitivity. Masaki Oba et al. [60] studied the emission characteristics of gadolinium oxide using ns and fs pulse lasers for ablation in DP-LIBS. A function of the laser pulse timing varying from pre-pulse range to reheating range with parameters of the air spark pulses distance from the sample surface and focus position of ablation pulses was discussed to enhance the detection ability. Duixiong Sun et al. [61] investigated the enhancement of emission signal using collinear DP-LIBS. Temporal and spatial evolution of the plasma temperature and electron number density was investigated. A relation between the increases in intensity and excitation energy level was established.

Nai-Ho Cheung group [62-65] studied the resonance-enhanced LIBS (RE-LIBS) for the sensitive elemental analysis using a second laser for photo-resonant excitation, in which the host species in a laser ablation plume were excited resonantly by a pulsed dye laser. The ambient gas effects and enhancement mechanisms were investigated. By combining the advantages of Gaussian beams for ablation and transverse interception for rekindling, the signal to noise ratio typically improved by more than an order of magnitude over the case of non-Gaussian beams and longitudinal interception. Weidong Zhou group [66-68] developed a LA-FPDPS technique with a nanosecond discharge circuit to enhance the optical emission, the signal to noise ratio and the stability. The local thermodynamic equilibrium (LTE) condition was fulfilled in the soil spark plasma generated by LA-FPDPS. The electron temperature and electron number density of the spark plasma determined by Saha-Boltzmann plot and Stark broadening were larger than that of the simple LIBS laser-induced plasma, in consistency with the intensity of spark spectral lines. The electron temperature and electron number density

have been slightly incremented with the rise of discharge voltage. Ali Khumaeni et al. [69] provided a new technique of microwave-assisted LIBS (MA-LIBS) coupled by a loop antenna for the enhancement of LIBS emission. The microwave was injected through the antenna to expand the LIBS plasma. The calibration curves were obtained from the Gd_2O_3 sample containing different concentrations of Ca by using MA-LIBS method and conventional LIBS. The detection limit of Ca in the Gd_2O_3 sample was enhanced approximately 24 times using MA-LIBS method.

3. Data processing and modeling

According to the emission lines located at specific wavelengths and the intensity of emission lines in LIBS plasma spectra, the qualitative and quantitative information of target elements in the measurement samples can be determined. Therefore, data processing and modeling play the important roles in the analyses of LIBS plasma spectra. Lanxiang Sun group [70] presented a method that can automatically estimate and correct the varying continuum background emission over a very wide spectrum range. Five aluminum alloy samples were measured to compare the elemental calibration cures between original spectra and background-corrected spectra, which demonstrated the credibility of the proposed background correction method. The wavelet threshold denoising method was also employed for noisy laser-induced breakdown spectroscopy spectrum [71]. A method for amending the double thresholds for semi-soft thresholding function was proposed. The detection limits were reduced by more than 50%. The signal to noise ratios were improved by a factor of two by using the proposed method. Spectral peak overlapping is a basic problem in analytical data processing of LIBS. A method that can be used to determine the appropriate initial values of the curve-fitting method by using fractional differential theory was studied to effectively resolve the overlapped peaks in LIBS data processing [72].

Zhe Wang group [73-75] proposed a spectrum standardization method based on the hypothetical existence of an ideal plasma "standard state", which was employed to compensate for the intensity fluctuations of characteristic copper lines due to the variation in plasma characteristic parameters, such as the plasma temperature, the electron density, etc. This model showed the significant improvement in both measurement precision and accuracy. In order to improve the model, a partial least squares (PLS) based on normalization method was proposed to improve the pulse-to-pulse measurement precision for LIBS [76]. A dominant factor based multivariate model was proposed [77-79]. The dominant factor was essentially the same as traditional univariate model, which was able to model the non-linear and linear relationship based on physical background, while a statistical method based on PLS was thereafter employed to correct the residue errors using full spectral information. Based on the characteristics of atomic and ionic lines under various plasma conditions, an algorithm was proposed to improve the data quality for accurate quantitative analysis [80]. According to these studies, the spectrum standardization method and dominant factor based PLS method were combined to improve the measurement accuracy of element content in coal [81-87]. Fig. 3 shows the calibration and validation results of the combination model for carbon content measurement in coal. Table 2 lists the

summary of the analytical results of different models. The results of the proposed model indicate that LIBS has great potential to be applied for the on-line or fast measurement of elemental contents in coal.
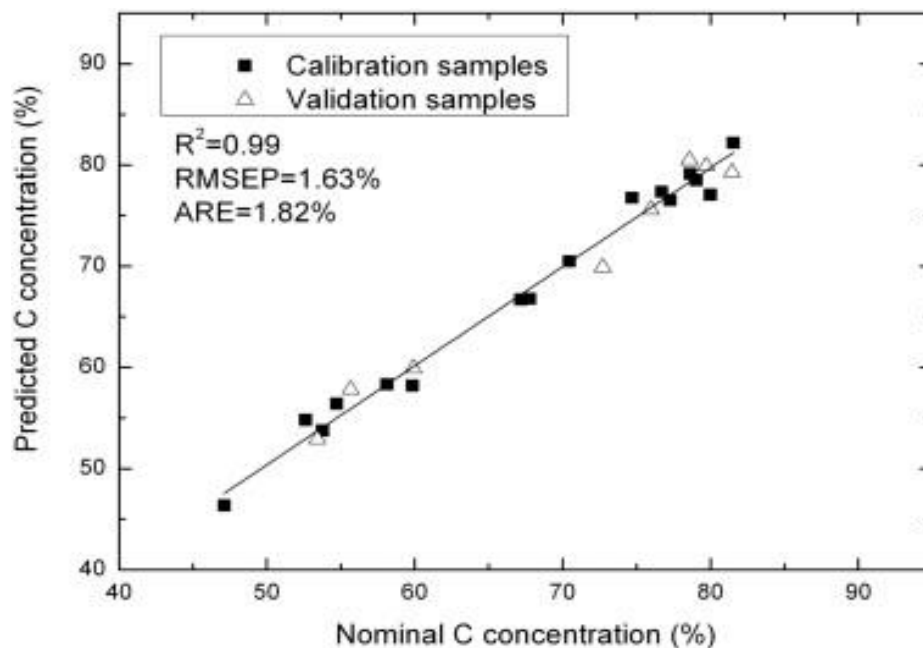

Fig. 3 Calibration and validation results of the combination model of spectrum standardization and dominant factor based PLS method for carbon analysis in coal [81] (X. W. Li, Z. Wang, Y. T. Fu, Z. Li, and W. D. Ni, A model combining spectrum standardization and dominant factor based partial least square method for carbon analysis in coal using laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 2014, 99, 82-86.)

Table 2 Performance summary of different models [81] (X. W. Li, Z. Wang, Y. T. Fu, Z. Li, and W. D. Ni, A model combining spectrum standardization and dominant factor based partial least square method for carbon analysis in coal using laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 2014, 99, 82-86.)

Models	R^2	RMSEP/%	ARE/%
Segmental spectral area normalization	0.75	3.77	4.10
Spectrum standardization	0.90	2.24	2.75
PLS model with the normalized spectral line intensity as the dominant factor	0.99	2.66	3.64
PLS model with the standardized carbon line intensity as the dominant factor	0.99	1.63	1.82

Arnab Sarkar et al. [88] employed LIBS for elemental characterization of high alloy steel using PLS approach to evaluate the analytical performance of the multivariate approach. The effect of different pre-treatment procedures on the raw spectral data before PLS analysis was evaluated based on several statistical (standard error of

prediction, percentage relative error of prediction etc.) parameters. Ye Tian et al. [89] built the optimal partial least squares discriminant analysis (PLS-DA) model and support vector machines (SVM) model by the leave-one-out cross-validation (LOOCV) approach with the calibration LIBS spectra. The coupling of LIBS with the non-linear SVM method showed the great potential to be used for on-line classification of the geological cutting samples. A new classification approach by the joint analysis of PLS-DA and SVM models was also designed to further improve the classification accuracy to enable the cuttings identification with an excellent performance. Jianhong Yang et al. [90] proposed a new LIBS quantitative analysis method based on the analytical line adaptive selection and relevance vector machine (RVM) regression model. The multiple correlation coefficient of the prediction was up to 98.85%, and the average relative error of the prediction was 4.01% by the chromium concentration analysis experiments of 23 certified standard high-alloy steel samples. The proposed method showed the advantages of self-adaptively, high robustness, improved accuracy and probabilistic prediction.

Lanxiang Sun and Haibin Yu [91] proposed a simplified procedure to correct the self-absorption effect in calibration-free LIBS (CF-LIBS) by an internal reference method, named internal reference for self-absorption correction (IRSAC). Through the IRSAC method, the points on the Boltzmann plot became more regular, and the evaluations of the plasma temperature and material composition were more accurate than the basic CF-LIBS. Tomoko Takahashi et al. [92] investigated the quantitative analysis of brass targets submerged in pure water using two calibration-free based methods, including CF-LIBS and corrected CF-LIBS (CCF-LIBS) methods. Fig. 4 shows the results of CF-LIBS and CCF-LIBS of different brass targets. CF-LIBS method can be potentially applied for in situ quantification of water-immersed brass alloys measured using a single long pulse. Alternative methods should be investigated to improve the estimates of minor element mass fractions.
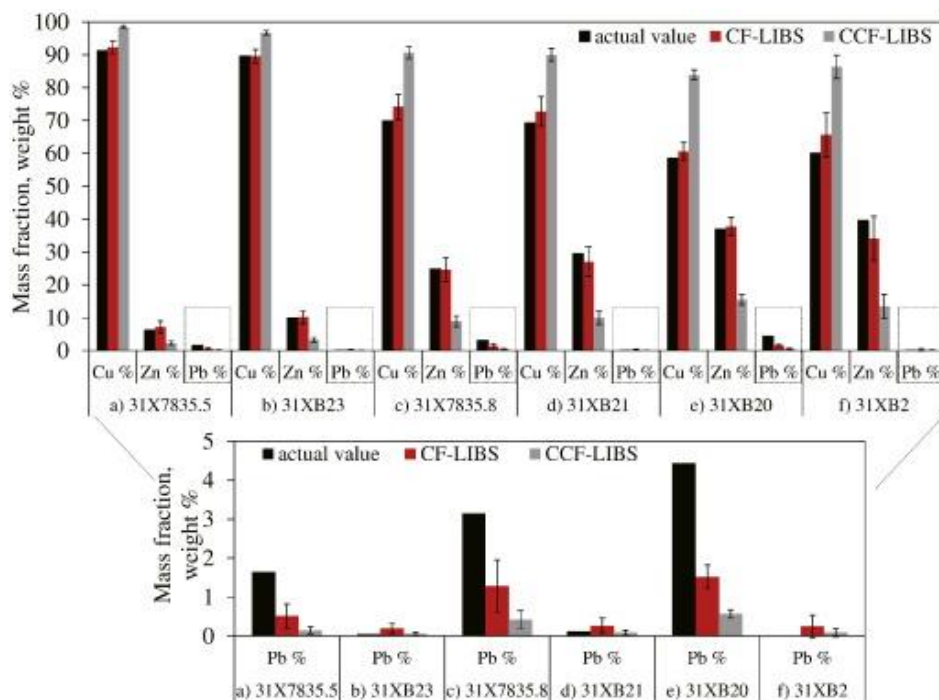
Fig. 4 Results of calculation using the CF-LIBS and CCF-LIBS methods. The subfigure at the bottom shows the enlargement of the Pb mass fraction [92] (T. Takahashi, B. Thornton, K. Ohki and T. Sakka, Calibration-free analysis of immersed brass alloys using long-ns-duration pulse laser-induced breakdown spectroscopy with and without correction for nonstoichiometric ablation. Spectrochimica Acta Part B: Atomic Spectroscopy, 2015, 111, 8-14.)

Jidong Lu group [93, 94] studied the multivariate calibration model to evaluate LIBS potential for directly determining the volatile matter content in coal and extract coal ash content information from LIBS spectra. The results showed that the multivariate method combined LIBS technique provide an alternative accurate and reliable proximate analysis of coal. The multivariate analysis methods were also employed to improve the measurement accuracy for unburned carbon in fly ash and the K and P in fertilizer [95, 96]. Jer-Shing Huang and King-Chuen Lin [97] developed a current normalization method for LIBS to analyze the liquid droplets generated by an electrospray ionization needle. The normalization methods of LIB/current and LIB/background as a function of the laser energy were characterized. According to the Boltzmann equation, the plasma temperature as a function of delay time relating to the onset of continuum background was determined to gain insight into the temperature effect on the LIB/background method.

4. Applications

LIBS technique has been employed in the fields of industrial process, environmental protection, human and food, and other applications, because of its fast response, high sensitivity, simultaneous multi-elemental analysis and non-contact features.

4.1 Power plants

4.1.1 Coal fired power plant

The applications of LIBS technique, recently, have been applied to coal combustion and other power plants. Tingbi Yuan et al. [98] studied the feasibility of using the binder for quantitative carbon measurement in anthracite to improve the measurement repeatability by LIBS. Jie Li et al. [99] studied the effects of experimental parameters on simultaneous elemental analysis of coal by LIBS, including the sample preparation parameters, lens-to-sample distance, sample operation mode, and ambient gas. Lei Zhang et al. [100] developed LIBS technique based on equipment for on-line monitoring of pulverized coal and unburned carbon in fly ash. Zhenzhen Wang et al. [101, 102] employed LIBS to detect the contents of size-segregated particles, such as coal and fly ash. Fig. 5 shows the real-time measurement results of fly ash in different stages, that is, different diameter of the particles. The plasma temperature was corrected by the emission intensity ratio from the same atom to obtain quantitative information. With temperature correction, signal stability has been significantly improved. Trace species were measured using LIBS under different conditions [103]. The interferences of continuum emission and coexisting molecular and atomic emissions decreased using low pressure laser-induced plasma to enhance the detection ability for trace species. The feasible of this method in real applications was demonstrated by measuring Hg in combustion gas which performed preferable results. Ryo Yoshiie et al. [104] also developed a simple and rapid analytical method of heavy metals in sub-micron particulates in flue gas using LIBS. The dust samples were segregated in advance according to particle size using an electrical low pressure impactor (ELPI).
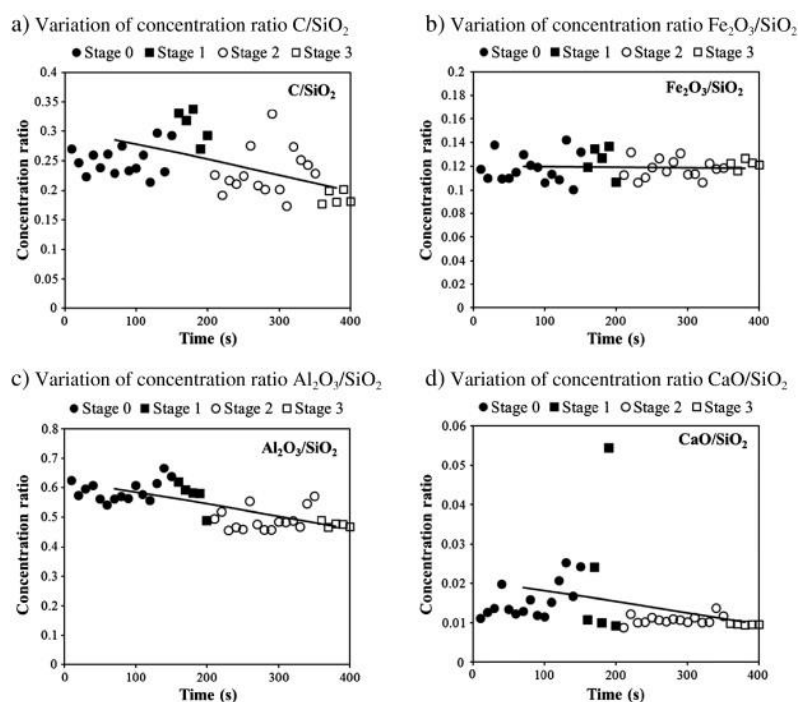

Fig. 5 Real-time LIBS measurement results of fly ash in different stages [102] (Z. Z. Wang, Y. Deguchi, M. Kuwahara, T. Taira, X. B. Zhang, J. J. Yan, J. P. Liu, H. Watanabe and R. Kurose, Quantitative elemental detection of size-segregated particles using laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 2013, 87, 130-138.)

4.1.2 Nuclear power plant

Nuclear power plant is a proven means to supply the growing demand for clean energy. The operation for nuclear power plant is obviously depending on the basis of safe and rational utilization. LIBS technique has been applied for nuclear power plant concerning the leakage detection, in situ materials analysis for inspection and contamination detection, which are significant in the nuclear area. Ali Khumaeni et al. [105] employed a transversely excited atmospheric (TEA) CO_2 laser to analyze the sodium aerosol using laser-induced gas plasma spectroscopy (LIGPS) method. A semi-quantitative analysis of sodium aerosol was made and the detection limit of sodium was approximately 200 ppb. This technique can be applied to the on-line analysis of sodium in fast reactor and the remote in situ monitoring of the leaked sodium. Hironori Ohba et al. [106] investigated the optimal jet thickness using micrometer-thick liquid jets with the slit-type jet nozzle for single-pulse LIBS (SP-LIBS) measurements by high-sensitivity elemental analysis of a liquid sample. Time-resolved observation of the hydrodynamics and plasma emission suggested that the dependence of the signal-to-background ratio on the liquid-sheet thickness was correlated with the volume of flowing liquid that interacted with the pulsed laser beams. Shuzo Eto et al. [107] employed SP-LIBS and DP-LIBS to measure the concentration of chlorine attached to stainless-steel in a dry interim storage facility using a concrete cask. The double-pulse configuration was effective to determine the calibration curve of chlorine. The orthogonal DP-LIBS was useful for a high concentration measurement of chlorine (>0.4 g/m^2). The collinear DP-LIBS was benefit for a low chlorine concentration (<0.4 g/m^2).

The Experimental Advanced Superconducting Tokamak (EAST) is a fully superconducting tokamak, which can realize the control for fusion reaction in the future nuclear power technology. EAST is now in the stage of laboratory research. Some researchers have indicated the application potential of LIBS in EAST. Hongbin Ding group [108-111] studied the chemical analysis of impurity deposition on the plasma facing component (PFC) samples of EAST and HL-2A Tokamak. In-depth and 2D analysis of multilayered PFC samples in a vacuum environment was studied 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, which demonstrated that LIBS can provide a in situ method to discriminate the co-deposited layer from the substrate. An orthogonal DP-LIBS configuration in a reheating scheme has been investigated for the on-line control technique for the laser cleaning process of the polluted first mirror of the HL-2A tokamak to accurately remove the ultrathin co-deposition layer of 0.8 µm.

4.2 Iron and steel making processes

With the features of excellent temporal and spatial resolutions, LIBS appears to be a very promising analysis method in steel industry. The element distribution measurements of materials at the whole production stages can provide the information of material quality and production processes. Shujun Qiao et al. [112] reviewed the recent development of LIBS in the field of geology, such as the qualitative and

quantitative analyses of geological materials, the analyses of ores, extraterrestrial materials, etc. T. Hussain and M A Gondal [113] discussed the LIBS ability as a rapid tool for the open pit ore analysis. The various trace elements of Cu, Cr, Ca, Mg, Zn, Ti, Si, Fe and Al presented in the ore sample were measured. The estimated concentrations of trace metals using the LIBS setup agreed with that of the well-established standard method of inductively coupled plasma atomic emission spectrometry (ICP-AES). Liwen Sheng et al. [114] developed LIBS integrated with random forest to identify and discriminate the iron ore grades. The classification and recognition of the iron ore grade were completed using their chemical properties and compositions. The study demonstrated that LIBS integrated with random forest showed better predictions of classification compared with that of SVM.

Teasam Kim et al. [115] described a sensitive optical technique for compositional mapping of solid surfaces using LIBS. A standard aluminum alloy was used to select and characterize the compositional distribution and an image of the surface display. The surface contamination of a copper stain around the conductor area has been clearly characterized in the scanning LIBS map. Changmao Li et al. [116] showed a simple LIBS setup that can be used for the accurate quantitative analysis of P in iron and low alloy steel in air. The interference from the iron and copper lines on the P emission line at 214.91 nm using different delay time was studied to reduce the matrix effect. The detection limits of P were 12 ppm and 9 ppm for pig-iron and low-alloy steel samples, respectively.

In iron and steel making processes, the slags are as important as the products. Shunsuke Kashiwakura and Kazuaki Wagatsuma [117, 118] employed LIBS for the rapid determination of compositions of stainless steels in steel scrap. Utilizing the optimal measurement parameters, such as gate width, delay time, laser energy and the number of laser shots, six types of stainless steels were separated by detecting Ni, Cr and Mo in stainless steels. The precise calibration lines were also discussed for practical analyses. Zhibo Ni et al. [119] proposed a normalization method using the integral intensity of plasma image to reduce the influence of experimental parameter fluctuations on quantitative analysis of slag components. Various experiments with slag samples were performed by increasing the set threshold for edge extraction of plasma image. The relativity between spectral line intensity and mass fraction was enhanced efficiently compared with the results without normalization and normalized by whole spectrum area. Tianlong Zhang et al. [120] applied LIBS technique coupled with SVM and PLS methods to perform the quantitative and classified analysis of 20 slag samples.

LIBS is applied not only as an elemental analytical technique but also a new way to determine the microstructure changes of steel samples. Jidong Lu group [121, 122] employed LIBS to analyze the steel samples with different microstructures, such as the discrimination of pearlitic/ferritic from martensitic phases. The plasma parameters of different microstructures, such as line intensity, temperature and ablated crater, have been studied and compared with each other. The metallographic structure and the mechanical properties of the samples can also be analyzed to estimate the aging grade

of metal materials [123]. The peak intensities of the specimens with different aging grades are shown in Fig. 6.
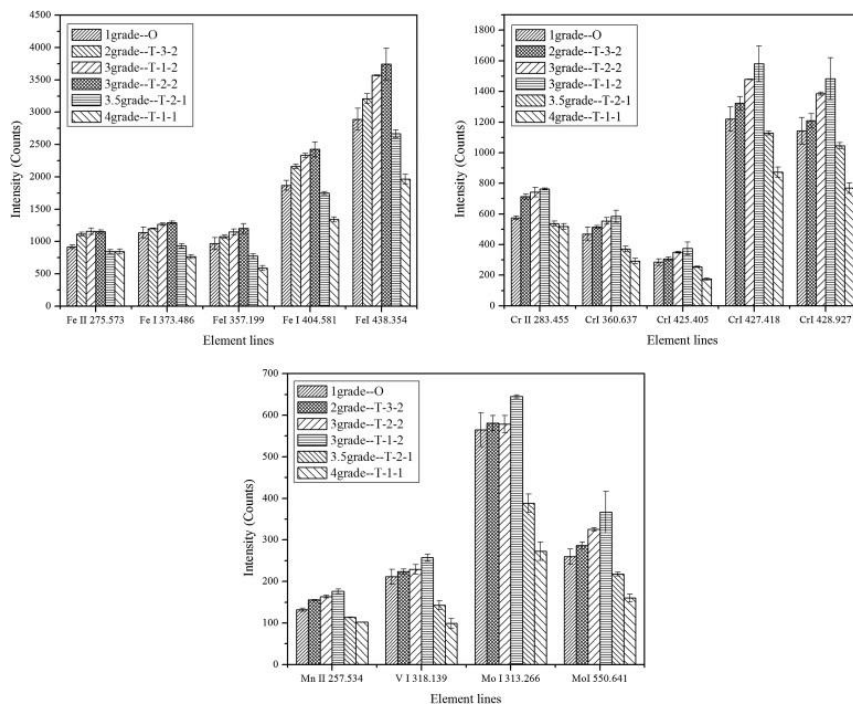

Fig. 6 The peak intensities of the samples [123] (J. Li, J. D. Lu, Y. Dai, M. R. Dong, W. L. Zhong, and S. C. Yao, Correlation between aging grade of T91 steel and spectral characteristics of the laser-induced plasma. Applied Surface Science, 2015, 346, 302-310.)

4.3 Environment

4.3.1 Soil and aerosol measurement

The environmental pollution is becoming increasingly severe with the development of economy. The rapid and precise measurement of trace species with variable compositions is imperative for the soil, atmosphere and water. Weidong Zhou group [124-126] employed the developed LA-FPDPS technique to enhance the atomic emissions of heavy metals in soil, such as Pb, As, Mg, etc. A specifically designed high voltage and rapid discharge circuit was used to reheat the laser plasma and enhance the plasma emission to improve the measurement precision and detection limit. W Aslam Farooq et al. [127] investigated the LIBS spectra of major and trace elemental compositions of collected soil sample from different desert areas of Riyadh city in Saudi Arabia. More than hundreds of spectral lines for many elements, such as Al, Fe, Mg, Si, Mn, Na, Ca and K, were highly resolved for the composition of natural soil samples. The observed results indicated the soil matrix dependence of electron temperature and density. G.C. He et al. [128] used the Boltzmann plot method and Saha-Boltzmann equation to determine the plasma temperature and electron density when applying LIBS for the quantitative analysis of elemental composition of soil. The concentrations of elements in soil, such as Mg, Ca, Si, K, Al, Ti, Cr and Mn, were obtained by the internal standard of iron element and some selected atomic/ionic lines.

Takashi Fujii et al. [129] experimentally demonstrated the remote sensing of the constituents of micro-particles in the atmosphere by LIBS-lidar using femtosecond terawatt laser pulses. Na fluorescence from saltwater aerosols in air was observed remotely at a distance of 16 m using a 318 mm diameter Newtonian telescope, a spectrometer and an ICCD camera The in situ measurement suggested that the laser-induced filaments played a crucial role in the breakdown of the atmospheric particles, such as aerosols, clouds, and toxic materials. M. M. Suliyanti et al. [130] demonstrated that the direct analysis of powder samples is possible when utilizing laser-controlled dust production in a small chamber at a He pressure of one atmosphere employing two laser systems. Furthermore, the method can also be used to analyze liquid samples by placing a drop of liquid onto a small piece of cotton to avoid splashing.

4.3.2 Liquid measurement

The LIBS plasma lifetime of liquid sample is shorter due to the pressure, volatility and quenching effects of liquid compared with that of solid and gas samples. The sensitivity, stability and repeatability of LIBS signal are lower than that of solid samples, leading to the greatly increasing difficulty of LIBS analyses. Numerous papers have reported LIBS measurement of different forms of liquid phase materials. Muhua Liu group [131, 132] developed a LIBS system to determine the toxic metal of Cr in wastewater. Experimental conditions were optimized to improve the sensitivity and repeatability of the LIBS system through a parametric dependence study in potassium bichromate ($K_2Cr_2O_7$) aqueous solutions. Cr element at 357.87, 359.35, 360.53, 425.43, 427.48 and 428.97 nm was measured and discussed. The intensity ratio calibration improved the accuracy of measurement than single line calibration. Tetsuo Sakka group [133-135] studied the effect of pulse width in underwater LIBS from the point of view of the plume formation, spectral profile of atomic emission lines and the behavior of nascent cavitation bubbles. A new experimental method for two-dimensional space-resolved emission spectroscopy of laser-induced plasma in water was developed, which showed the great potential to be used in the detailed investigation of laser ablation plasma in water [136]. They also investigated the expansion dynamics of the cavitation bubble generated by a Q-switched Nd:YAG multi-pulse microchip laser irradiation of a solid target immersed in water [137].

Some methods have been developed to overcome the sensitivity drawbacks of direct measurement, such as electro-deposition process, extraction adsorbent, atomization, etc. Koo Hendrik Kurniawan et al. [138] employed the electro-deposition process for practical and highly sensitive detection of metal impurities in aqueous samples, such as Cu, Ag, Pb, Al, Cr and Sr, using LIBS technique in low-pressure He gas. The detection limit was comparable with that offered by inductively coupled plasma-mass spectrometry (ICP-MS). Zhijiang Chen et al. [139] also developed the ultra-sensitive trace metal analysis of water by LIBS after electrical-deposition of the analytes on an aluminium surface. The detection limits 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 mg/L, respectively. Zhijiang Chen and Dehua Zhu et al. [140, 141] also employed bamboo charcoal and wood slice substrates as a solid-phase extraction adsorbent to overcome the sensitivity drawbacks

in liquid sample analysis. The trace metal elements, such as Cr, Mn, Cu, Cd and Pb, in aqueous solution were detected. It demonstrated the enhanced detection limits than those obtained by directly analyzing liquid samples where the laser was focused on a liquid surface. Qingyu Lin et al. [142] employed the porous electrospun ultrafine fibers as a solid-phase support to quantify Cr and Cu in aqueous solutions by LIBS. With this pre-treated sample technique, the detection limits for Cr and Cu were improved to 1.8 and 1.9 ppm, respectively. Lijuan Zheng et al. [143] analyzed chlorine content brought by salt in a composite powder when the sample was prepared in the forms of pellet or solution to compare the matrix effect. For the solution samples, the mixture powder was first dissolved into solution and then dropped on the surface of a pure metallic target. The surface-assisted LIBS configuration has been demonstrated that no significant matrix effect was observed for solutions prepared with powders. Ronger Zheng group [144] introduced a filter paper as solid substrate to improve the detection sensitivity of Mn in liquids by LIBS. The compact echelle spectrometer with ICCD was used for two field samples of Mn solution simulating industrial wastewater and seawater with the detection limits of 2.87 and 2.73 mg/L to apply this approach to onsite detection. They [145] also developed an ultrasonic nebulizer assisted LIBS (UN-LIBS) system for trace metal elements detection, such as Mn, Zn, Cu, Pb, Fe, Mg and Na, for aqueous samples by transforming the liquid sample into a dense cloud of droplets using an ultrasonic nebulizer to improve the ablation efficiency. The obtained detection limits were comparable or much better than that of the reported signal enhancement approaches when the laser energy was as low as 30 mJ. Zhenzhen Wang et al. [146] introduced the liquid jet of $CsNO_3$ solution to the measurement chamber and detected using LIBS directly at low pressure. The distinct and round plasma can be acquired when reducing the pressure. The defocus mode and measurement area were discussed to improve Cs signal and the signal-to-background ratio. Cs detection limit can reach to 22.8 ppb at pressure of 26 kPa in this study, which can be improved under the optimal experimental conditions with the higher efficient detector.

DP-LIBS has also been applied for liquid measurement to improve the detection ability. Nai-Ho Cheung group [147, 148] demonstrated the trace analysis of aqueous lead colloids by two-pulse LIPS. The first Nd:YAG laser pulse created a vapor plume with the particulates concentrated which then atomized by an ArF laser pulse. The lead emissions were enhanced compared with that achieved by conventional LIBS. Tomoko Takahashi and Blair Thornton et al. [149-152] discussed the hydrostatic pressure effect on analysis of the composition from the bulk liquids at high pressure using DP-LIBS and a long-duration ns laser. The results indicated that DP-LIBS may be suitable for in situ measurement up to 5 MPa of the chemical composition of solids submerged in lakes, rivers and shallow seas, as well as the long-pulse irradiation up to 30 MPa. Youli Yu et al. [153] also performed the DP-LIBS experiments in collinear beam geometry in order to evaluate the technique for the element measurement in solution. Under the optimized experimental condition, calibration curves of atomic lines Cu at 324.7 and 327.4 nm were derived and the optimal detection limit of Cu in solution was found to be 2.0 mg/L, which was better than that using a SP- LIBS.

4.4 Human and food safety

There is also a special attention on the application of LIBS in biological matrix analysis, as well as the food concerning human safety. Seyed Hassan Tavassoli group [154, 155] employed LIBS technique for the analyses of biological samples. The association between identification of diseases and fingernail elements has been studied. Characteristic LIBS spectra of human fingernail samples from a healthy, an osteopenic and an osteoporotic subject are presented in Fig. 7. A statistical multivariate method named discriminant function analysis (DFA) has been used to classify the subjects into healthy and patient groups. Some relation between the elemental composition of nails, gender and age can also be found according to the analyses of human fingernails. The ability of LIBS in discrimination of diabetes mellitus patients and nondiabetic subjects using DFA method according to the elemental composition of fingernails was clarified and investigated [156]. LIBS was also performed for discrimination of the healthy and carious teeth for possible application during some treatment of teeth [157]. A multivariate statistical method called PLS-DA has been utilized for classification of spectra into two groups of healthy and carious parts.
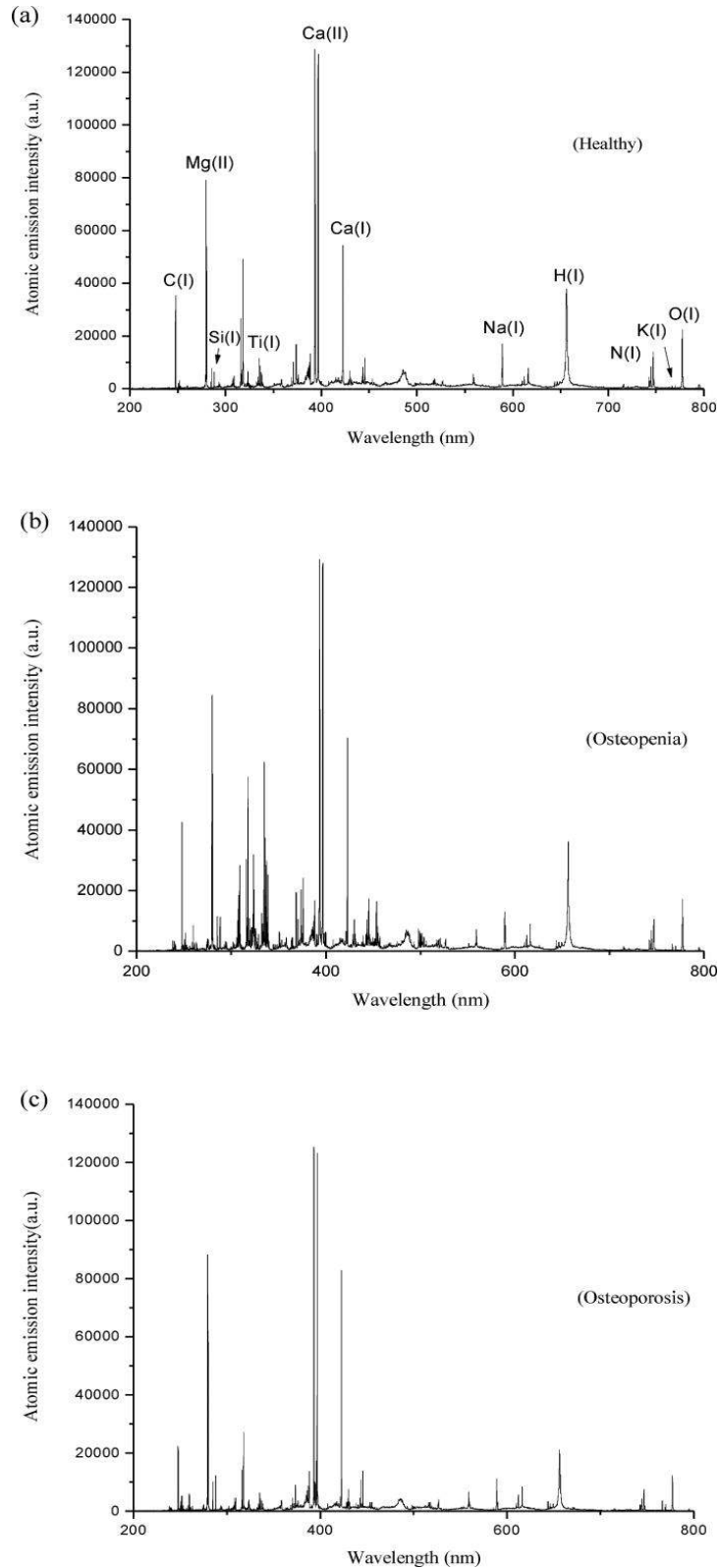
Fig. 7 Characteristic LIBS spectra of human fingernail samples [154]. (a) A healthy with some atomic emissions identified. (b) An osteopenic. (c) An osteoporotic subject. (M. Bahreini, Z. Hosseinimakarem and S. H. Tavassoli, A study of association between fingernail elements and osteoporosis by laser-induced breakdown spectroscopy. Journal of Applied Physics, 2012, 112, 054701.)

W Aslam Farooq et al. [158] analyzed UV irradiated dental nano-composite restorative material qualitatively using LIBS. Trace species of Si, Au, Al, Ti, Ca, Zr, Fe, Mn, Mg and Zn in different abundance ratios were detected in these samples. The elemental composition was found to be quite similar but the relative abundance of Zr and Si was higher in more UV exposed material. Comparing the measurement results with that using energy-dispersive X-ray spectroscopy (EDS), it showed that LIBS analysis was more pronounced than the EDS analysis. Soogeun Kim and Sungho Jeong [159] investigated the effects of temperature-dependent optical properties on the change of fluence rate and temperature distribution within biological tissues during low-level laser therapy (LLLT) by experimental and numerical methods. The predicted fluence rate and temperature by the proposed mathematical model agreed closely with the measured values of porcine skin.

Many researchers have also investigated the applications of LIBS for analysis of food. Jiantong Han et al. [160] employed CF-LIBS to quantitatively analyze the variations of the metallic elemental mass concentrations in the tobacco and tobacco ash samples, such as Fe, Ca, Al, Cu, K, Li, Mg, Mn, Na, Sr, Ti and Zn. The decreased mass of these elements from tobacco to tobacco ash may be present in the cigarette smoke as particulate phase, which may effect on biochemical processes in the human body. Mingyin Yao et al. [161] provided an assessment of the performance of LIBS to investigate the heavy metals in natural organic materials compared with that of atomic absorption spectrometry (AAS), which demonstrated the capacity of LIBS in the determination of the concentrations of Cr in Gannan navel orange. The complex matrix effect in organic samples made the established calibration curve difficult to be used for the accurate quantitative analysis. The LIBS sensitivity for direct analysis of heavy metals in natural agricultural products without contamination treatment should be improved in the future. Yonghoon Lee group [162, 163] investigated the discrimination ability of the elements in edible sea salts using LIBS according to the intensity correlation analysis of the observed emission lines, such as Na at 330.237 and 330.298 nm, Cl at 725.662 nm, K at 766.490 nm, Li at 670.776 and 670.791 nm, Mg at 285.213 nm, etc. Classification models using a few emission lines selected based on the results from intensity correlation analysis and the full broadband LIBS spectra were developed based on principal component analysis (PCA) and PLS-DA provided a dependable model for discriminating the edible sea salts.

4.5 Other applications

Besides the major applications of LIBS technique discussed above, some other applications were also studied from space exploration to various material analyses in daily life. Zener Sukra Lie et al. [164] demonstrated the possibility and viability of spectrochemical analysis of carbon as well as other elements in solid samples on Mars using LIBS. The validity of shock wave excitation mechanism for the plasma emission generated was verified by ns laser in low pressure CO_2 ambient gas mimicking the Mars atmosphere. Shuzo Eto et al. [165] determined the two-dimensional emission intensity profile of multiple elements in reinforced concrete that used in infrastructure buildings and basements by collinear DP-LIBS without buffer gas or SP-LIBS with helium buffer

gas. These results suggested that the quantitative estimation by LIBS of carbonation depth and chloride penetration can be performed simultaneously, quickly and quantitatively. Lingling Peng et al. [166] used LIBS to investigate the applicability for the rapid analysis of heavy metals in spent Zn-Mn batteries. Besides the major elements of C and Zn, a number of minor and trace elements were identified and determined in the positive and negative electrode materials. Teppei Nishi et al. [167] proposed a LIBS method of in situ elemental analysis of the electrode surface in electrolytic solution. Different data analysis methods were compared to discuss the data analysis effect on the final results. The application of the present method can be extended to various electrochemical systems. Walid Tawfik et al. [168] studied the laser-induced crater depth, mass and emission spectra of laser-ablated high-density polyethylene (HDPE) polymer using LIBS. The comparison between LIBS results and scanning electron microscope (SEM) images showed that LIBS could be used to estimate the crater depth, which was applicable for thin-film lithography measurements, on-line measurements of thickness in film deposition techniques, etc.

LIBS technique have been reported for the analyses of the organic compounds in the measurement of the ratio of the fuel to air, laser ignition of combustible mixtures, detection and spectral identification of organic explosives, flame ignition, as well as combustion diagnostics. Qianqian Wang et al. [169] carried on three aspects of research about LIBS for explosives detection, such as simulating LIBS spectra of explosives, detecting LIBS spectra of explosives, and analyzing LIBS spectra of explosives using chemometric approaches of PCA and PLS. It is demonstrated that LIBS coupled with the chemometric techniques showed the capacity to discriminate organic explosive from plastics. Shigeru Tachibana group [170, 171] studied the combined effect of spatial and temporal variations of equivalence ratio on combustion instability in a low-swirl combustor using LIBS to understand the mixture dynamics inside the combustor. Yiyang Zhang et al. [172] employed the low-intensity LIBS to study the synthesis of TiO_2 nanoparticles in a stagnation swirl flame, which can identify TiO_2 nanoparticle formation and characteristics during flame synthesis in situ. Spontaneous Raman spectroscopy (SRS) was employed to obtain the local non-plasma gas-phase temperatures. By taking into account the above mentioned applications, Hadi Nozari et al. [173] employed LIBS technique to distinguish the organic vapors according to their vapor pressures and the number of constituent moles, such as acetone, ethanol, methanol, cyclohexane and nonane in gaseous state.

According to the above discussion, LIBS as an elemental analysis method is suitable for the composition measurement of solid, liquid and gas materials in various fields, as well as the process monitoring in different plants because of its detection features and simplicity of LIBS apparatus.

5. Instrumentations

LIBS technique can be applied in various fields according to the above mentioned applications, which benefits from the mobile instrumentation to realize the potential capability of LIBS technique. Therefore, the affordable commercial instrumentation,

the standardization of measurement procedures and calibration methods are significant for the reproducible and reliable LIBS analyses in situ quantitatively.

LIBS instrumentations have been applied to the commercial plants, marine researches, human, etc. Xiong Wan and Peng Wang [174] built a remote LIBS system with a compact custom of 15 m focus optical component, combining a six times beam expander using a telescope to measure the elemental compositions of minerals. A multi-spectral line calibration method was proposed for the quantitative analysis of elemental compositions. Its feasibility and superiority over a single-wavelength determination have been confirmed by the comparison with the traditional chemical analysis of the copper content in ore. Qingdong Zeng et al. [175] developed a portable fiber-optic LIBS (FO-LIBS) system to quantitatively analyze the elements of Mn and Ti in pig iron. The time-resolved images of plasma plumes were obtained with lower plasma temperature and electron density, that is, lower self-absorption. The leave-one-out cross-validation method was used to evaluate the detection accuracy. The ablated craters and detection accuracy were better than those obtained by conventional LIBS. Furthermore, the FO-LIBS system was more promising for industrial applications due to the cost effective, more compact and suitable features. Lanxiang Sun et al. [176] developed a DP-LIBS system combining a Cassegrain telescope for the in situ analysis of molten steel. The quantitative analyses of Si, Mn, Cr, Ni and V in molten steel samples were evaluated using a univariate model and a PLS model. The sealed LIBS setup was also transferred to a steel plant for application test. Fig. 8 shows the photos of application test in the steel plant. The measurement accuracy of LIBS system approached the requirements of plant's accuracy.
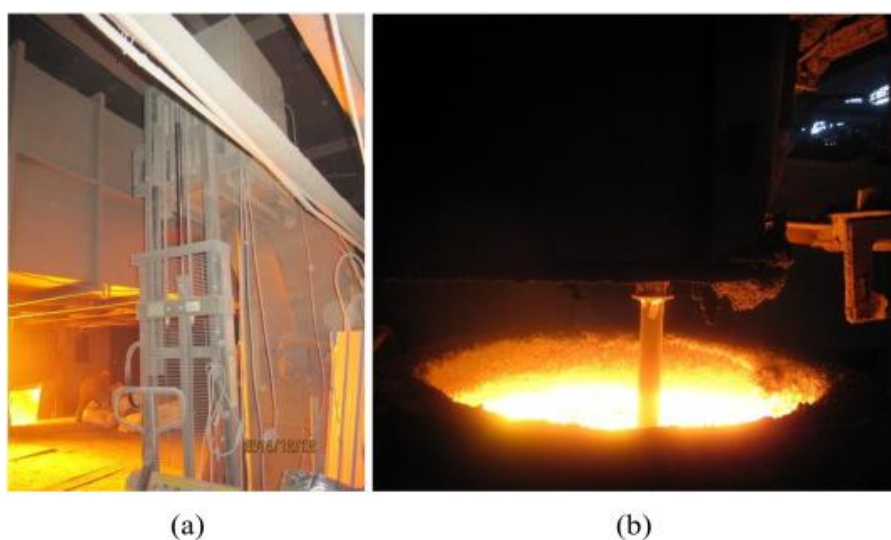

Fig. 8 Application test photos in a steel plant [176]. (a) Sealed LIBS setup installed along the ladle path. (b) The refractory lance tip immersed into the liquid steel in the ladle during measurements. (L. X. Sun, H. B. Yu, Z. B. Cong, Y. Xin, Y. Li, and L. F. Qi, In situ analysis of steel melt by double-pulse laser-induced breakdown spectroscopy with a Cassegrain telescope. Spectrochimica Acta Part B: Atomic Spectroscopy, 2015, 112, 40-48.)

Yoshihiro Deguchi et al. [177, 178] employed LIBS to detect the carbon content in fly ash, char and pulverized coal under high-pressure and high-temperature conditions. An automated LIBS unit has been developed and applied in a 1000 MW pulverized coal-fired power plant for real-time measurement as shown in Fig. 9. The satisfactory agreement of the measurement results was obtained between LIBS method and the conventional method. It has been demonstrated that the boiler control was possible in an optimized manner by utilizing the unburned carbon content in fly ash. Wangbao Yin group [100, 179-181] developed a fully software-controlled LIBS system comprising a self-cleaning device for on-line quality analysis of pulverized coal and unburned carbon in fly ash. The elemental contents of C, Ca, Mg, Ti, Si, H, Al, Fe, S, and organic oxygen and the proximate analyses of Q_{ad} and A_{ad} were realized through the optimal data processing methods, which showed the capability of performing a pre-feedback to obtain the optimal boiler control and to improve the combustion efficiency of the thermal power plant.
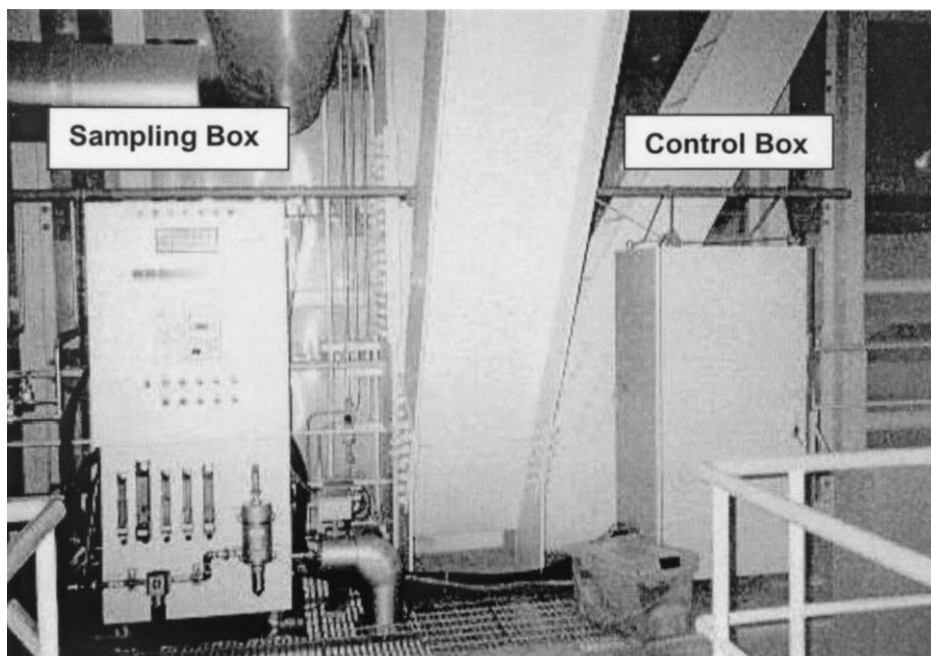

Fig. 9 Photograph of unburned-carbon measurement apparatus [177] (M. Kurihara, K. Ikeda, Y. Izawa, Y. Deguchi and H. Tarui, Optimal boiler control through real-time monitoring of unburned carbon in fly ash by laser-induced breakdown spectroscopy. Applied optics, 2003, 42, 6159-6165.)

The elemental analyses of nuclear materials in the nuclear industry are critical for the waste management, process control and safeguards. The merits of LIBS continue to attract interest for the in situ measurement in nuclear industry. Morihisa Saeki and Chikara Ito et al. [182, 183] developed a transportable FO-LIBS instrument to inspect the post-accident nuclear core reactor of the TEPCO Fukushima Daiichi nuclear power plant (F1-NPP), which was feasible for the material analysis of underwater debris under a high-radiation field by single-pulse breakdown with gas flow or double-pulse breakdown. The optical fiber containing 1000 ppm hydroxyl showed enough radiation resistance for the radiation-induced transmission losses. The infrared imaging was

effective for observation under high radiation doses. The simulated debris, a mixture of CeO_2 (surrogate of UO_2), ZrO_2 and Fe, was employed to demonstrate the feasibility of the developed FO-LIBS system for analyzing the debris materials in the F1-NPP. Yongdeuk Gong et al. [184] investigated the effect of optical transmittance of the shielding window on the analytical performance of the stand-off LIBS for the inaccessible nuclear materials located behind a shielding window. The multivariate calibration using PLS was also successfully applied for the through-window LIBS analysis.

Blair Thornton et al. [185] deployed a deep-sea LIBS instrument to study the chemical composition of seawater and mineral deposits at depths of more than 1000 m. Exemplary measurements of both seawater and mineral deposits were made during deployments of the device at an active hydrothermal vent field in the Okinawa trough. The instrument can be deployed from a remotely operated vehicle (ROV) and revealed the unique ability to perform in situ, multi-element analysis of both liquids and solid deposits at depths of up to 3000 m. There are some techniques with the combination of LIBS and other methods for the material analysis, such as LIBS-LIF, LIBS-Raman, etc. Yuan Lu et al. [186] introduced a LIBS-Raman hybrid system into the seashell research. The compositional distribution of the shell was obtained using LIBS for the element detection and Raman for the molecule recognition, which demonstrated that the micro-chemical diagnostics of LIBS-Raman was a potential way to construct a three-dimensional analysis for the shell research. Fatima Matroodi and Seyed Hassan Tavassoli [187] introduced a combined LIBS and Raman setup by using a single laser and detection system with the advantage that the intensity ratio of LIBS and Raman signals can be controlled by rotating the half-wave plate. The problematic fluorescence signals in detecting Raman signals can be weakened due to the utilization of a pulsed laser as an excitation source. This introduced setup is a good choice for mineral analysis when comparing the measurement results of mineral samples and organic liquid samples.

The improvement of sampling method and LIBS system integration is also important for some special purposes. Zhe Wang group [188, 189] designed a symmetric cylindrical confinement to enhance the signal and to improve the measurement repeatability when utilizing a Spectrolaser 4000 LIBS system (XRF, Australia). The image taken by ICCD verified that the confinement improved the stability of the plasma morphology. Behnam Ashrafkhani et al. [190] developed a point auto-focus system to improve the spectral repeatability of LIBS. Yixiang Duan group [191, 192] designed a miniature digital delay generator to build the time-resolved LIBS. A multi-functional sampling chamber for LIBS was also constructed and developed for elemental analysis in situ, which showed important applications in LIBS instrumentation and multi-elemental analysis. Nai-Ho Cheung group [193, 194] introduced an acoustic monitor to detect the mass removed in pulsed laser ablation with a developed normalization method. They also designed a vertical sample jet downstream structure for spectrochemical analysis of liquid material measurement under different conditions

[195-197]. Based on this technique, a cytometric LIBS scheme was also designed for human blood analyses [198, 199].

As mentioned above, the researches on instrumentation were not fully developed. The LIBS instrumental study essentially should be based on the understanding of the plasma physics, detection features and specific applications. It is significant for LIBS researchers to integrate and develop the optimized LIBS system with the stable and informative spectra for the specific purposes.

6. Conclusions and challenges

6.1 Conclusions

LIBS technique has attracted the comprehensive attention and the increasing researchers in Asia join LIBS research in different research aspects, such as fundamentals, data processing and modeling, applications and instrumentations, as summarized in Table 3. Its development shows the rapid growth to catch up with the international LIBS pace.

Table 3 Parts of research fields and main results

Research	Research fields	Main results	References
Fundamentals	Plasma physics	matrix effect, excitation temperature, electron number density, self-absorption	(15)-(36)
	Detection limit	optimal experimental conditions, DP-LIBS, RE-LIBS, LA-FPDPS, MA-LIBS	(43)-(53), (54)-(61), (62)-(65), (66)-(68), (69)
Data processing and modeling		partial least squares(PLS), calibration-free LIBS (CF-LIBS)	(76)-(89),(91)-(92)
Applications	Power plant	coal, fly ash, trace species; sodium aerosol, impurity deposition	(98)-(104); (105), (108)-(111)
	Iron and steel making processes	raw materials, iron and steel, slag, microstructure	(112)-(114), (115)-(116), (117)-(120), (121)-(123)
	Environment	soil, liquid	(124)-(128), (131)-(153)
	Human and food safety	fingernail, biological tissues, food	(154)-(156), (159), (160)-(163)
Instrumentation	Metallurgy	minerals, pig iron, molten steel	(174)-(176)
	Coal fired power plant	pulverized coal, unburned carbon in fly ash	(177)-(181)
	Nuclear power plant	nuclear core reactor	(182)-(184)
	Marine researches	seawater, mineral deposits, seashell	(185)-(186)

In order to successfully apply LIBS technique, the fundamentals such as plasma physics, detection limit enhancement, have been extensively studied in the technical aspect. The data processing and modeling were studied to improve the accuracy for the qualitative and quantitative measurement of target elements. Numerous papers focus on various LIBS applications, such as power plants, metallurgy, environmental protection, human and food safety, etc., because of its strong signal intensity and simplicity of the apparatus. The availability of LIBS instrumentation has also been studied for the reproducible and reliable quantitative LIBS analyses in situ. However, as presented above, the complex physical processes and characteristics in the laser-induced plasma processes should be studied deeply to understand and enrich LIBS technique. The data

processing and modeling still should be developed to improve the quantitative capability. As for the LIBS instrumentation discussed above, the researches on LIBS technique of instrumentation were not fully studied and developed. The LIBS technique need to be developed to commercialize and realize the online applications in the existing and potential fields. Stimulated by the application potential of LIBS, critical challenges and innovations in Asia, LIBS technique in Asia develops quickly to obtain the unprecedented research scale, commercial opportunity and development orientations. Until now there are several significant and symbolic events for LIBS in Asia, such as the forming of the Asian society of LIBS (ASLIBS), the success of hosting the 8th international LIBS conference in Beijing and ASLIBS2015 in Wuhan, China. ASLIBS is believed to contribute more for the further development of LIBS.

6.2 Challenges

The potential of LIBS research and application is supported by urgent demands in Asia with huge market, such as power plants, metallurgy, environment, etc. Opportunity always is side with challenge. In order to demonstrate its fullest potential, it is necessary for LIBS technique in Asia to overcome several challenges. The improvement of its quantitative capability is one of the important factors to meet industrial requirements. Enhancement of its sensitivity, long-time durability and cost reduction of its system are also the required and important factors for industrial applications.

The most important feature of LIBS is the utilization of direct laser-material interaction, which leads to the exclusive properties of LIBS compared to conventional analytical techniques. Ironically, this feature causes most of the challenges inherent in LIBS because the laser-induced plasma processes differs depending on the sample conditions and input laser parameters such as energy density, pulse width, and laser wavelength. It is inevitable for the improvement of its quantitative capability of LIBS to understand the detailed mechanism of the laser-material interaction and plasma-surrounding gas interaction. These fundamental works have to be driven by international collaboration especially with EMSLIBS and NASLIBS which have wider experience and knowledge of LIBS compared to ASLIBS.

It is worth noting that the development of LIBS will be driven by the utilization and combination with other techniques. There appear several LIBS related techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [200, 201], laser ablation molecular isotopic spectrometry (LAMIS) [202, 203] and so on. The control of laser-sample interaction and plasma conditions is also important to meet LIBS challenges.

ASLIBS community will become an important rising strength and is expected to contribute more for the further LIBS development not only with special applications, but also with fundamental knowledge. Together with the international researchers, LIBS technique will be developed extensively and thoroughly as a significant laser detection, analysis and diagnostics technique.

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