Frontiers of Physics
https://doi.org/10.1007/s11467-020-1007-z

Front. Phys.
16(2), 22500 (2021)

TOPICAL REVIEW

Development in the application of laser-induced breakdown spectroscopy in recent years: A review

Lian-Bo Guo (郭连波)[1], Deng Zhang (张登)[1], Lan-Xiang Sun (孙兰香)[2], Shun-Chun Yao (姚顺春)[3], Lei Zhang (张雷)[4], Zhen-Zhen Wang (王珍珍)[5], Qian-Qian Wang (王茜蒨)[6], Hong-Bin Ding (丁洪斌)[7], Yuan Lu (卢渊)[8], Zong-Yu Hou (侯宗余)[9], Zhe Wang (王哲)[9,†]

[1] *Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, Wuhan 430074, China*
[2] *State Key Laboratory of Robotics, Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, China*
[3] *School of Electric Power, South China University of Technology, Guangzhou 510640, China*
[4] *State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*
[5] *State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China*
[6] *Key Laboratory of Photonic Information Technology, School of Optics and Photonics, Beijing Institute of Technology, Beijing 100081, China*
[7] *School of Physics, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian 116024, China*
[8] *Optics and Optoelectronics Laboratory, Ocean University of China, Qingdao 266100, China*
[9] *State Key Lab of Power Systems, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China*
Corresponding author. E-mail: † zhewang@tsinghua.edu.cn
Received July 22, 2020; accepted September 7, 2020

Laser-induced breakdown spectroscopy (LIBS) has been widely studied due to its unique advantages such as remote sensing, real-time multi-elemental detection and none-to-little damage. With the efforts of researchers around the world, LIBS has been developed by leaps and bounds. Moreover, in recent years, more and more Chinese LIBS researchers have put tremendous energy in promoting LIBS applications. It is worth mentioning that the application of LIBS in a specific field has its special application background and technical difficulties, therefore it may develop in different stages. A review summarizing the current development status of LIBS in various fields would be helpful for the development of LIBS technology as well as its applications especially for Chinese LIBS community since most of the researchers in this field work in application. In the present work, we summarized the research status and latest progress of main research groups in coal, metallurgy, and water, etc. Based on the current research status, the challenges and opportunities of LIBS were evaluated, and suggestions were made to further promote LIBS applications.

Keywords laser-induced breakdown spectroscopy, application

Contents

*This article can also be found at http://journal.hep.com.cn/fop/EN/10.1007/s11467-020-1007-z.

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is an atomic spectroscopy technique firstly proposed by Breech and Cross in 1962. It has been praised as the "future super star" in analytical chemistry [1, 2]. LIBS is based on the ablative mechanism between the laser and the material. As shown in Fig. 1, a high-energy pulsed laser is focused on the surface of sample which can be in solid, liquid, or even in gas phase, instantly ablating the surface material to form the high temperature plasma. When high energy level atoms and ions in the plasma return to their lower energy levels by releasing photons [3], the elemental infor-

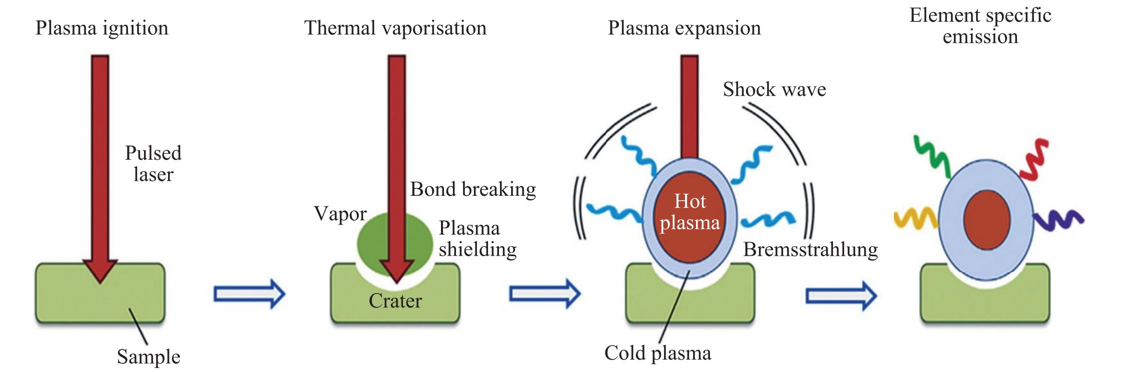

Fig. 1 Schematic of the laser-induced breakdown process. Reproduced with permission from Ref. [4].

mation is conveyed into spectrum.

Figure 2 compares the performance of LIBS and ICP-MS, a traditional element analysis technology [5]. We can see that ICP-MS overtakes LIBS in analytical capability features such as detection power, LDR, and selectivity. However, LIBS has far more practical operational features than ICP-MS, such as portability, remote analysis, fast analysis speed, simple preparation and automation. Compared with XRF [6] and EDX [7], LIBS also shows advantages in real-time *in-situ*/online applications. Therefore, LIBS has been widely considered in the field of industrial application. In 2012, Curiosity rover carried the LIBS device to detect Martian materials, which pushed the LIBS to a climax [8, 9]. During the past decade, LIBS has shown great potential in various applications including food detection [10, 11], environmental monitoring [12], energy [13], biomedicine [14, 15], space exploration [16] and other fields [17].

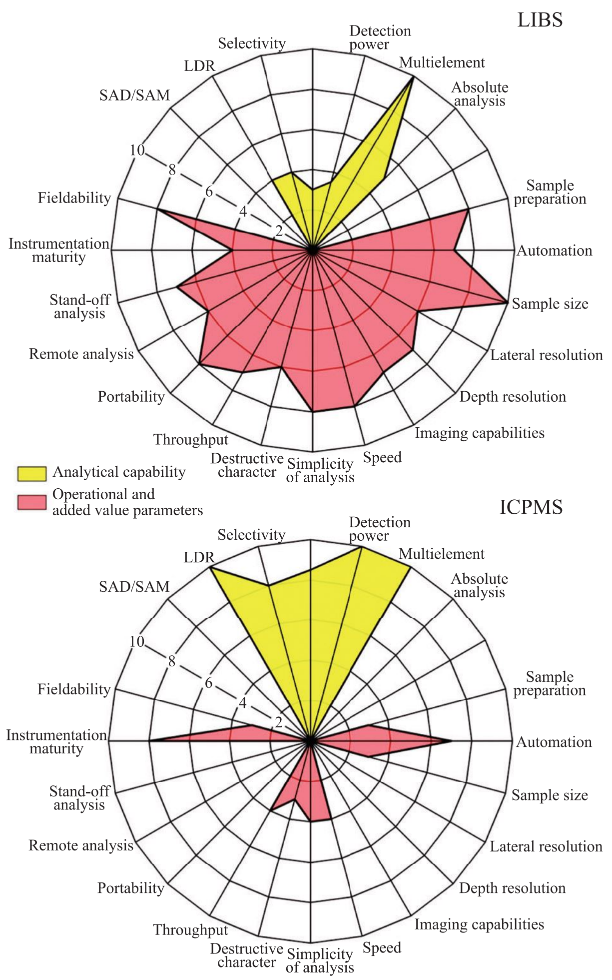

Fig. 2 Spider charts comparing LIBS versus solution ICP-MS. Reproduced with permission from Ref. [5].

At present, LIBS has incomparable advantages in qualitative analysis. But in terms of quantification, LIBS still lags behind other detection technologies due to the common problems such as matrix effect and spectral uncertainty. Meanwhile, LIBS also has its own technical problems in real application, as demonstrated by Fu *et al.*, the inevitable morphological fluctuation caused in plasma evolution severely affected the final LIBS quantitative performance [18]. Till now, LIBS researchers have conducted lots of studies to solve the common and individual problems. As shown in Fig. 3, from 2001 to 2019, the number of LIBS articles published each year grew rapidly, reaching 7336. The number of articles in various application areas is also growing rapidly, which means that LIBS pays more attention to application and commercialization. With the continuous development of Chinese LIBS community, we are able to play a more promoting role in the development of LIBS in the world. Therefore, to fully understand the application status of LIBS in various fields, this review summarizes the research status and latest progress of main research groups at home and abroad in the field of coal, metallurgy, water, soil, food, biomedicines, deep-sea and nuclear. Finally, based on the review, the application status and prospect of LIBS in various fields were discussed as well.

2 Coal analysis

Coal is the major primary energy resource in China with a proportion of more than 60% till now. Moreover, coal is the necessary raw materials in many industries, such as

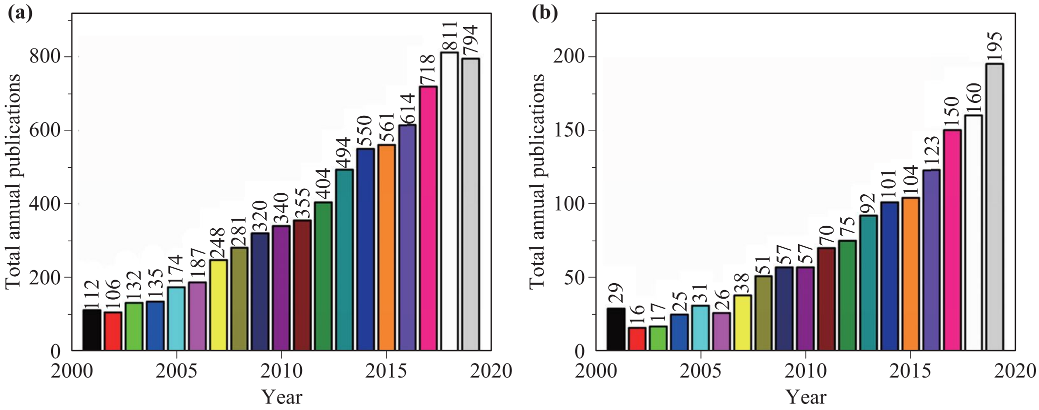

Fig. 3 **(a)** Total number of LIBS articles and **(b)** the number of LIBS articles in coal, metallurgy, water, soil, food, biomedicine, deep-sea and nuclear searched from Web of Science from 2001 to 2019.

cement production, and metallurgical. It currently provides 40% of the world's electricity [19–21]. The properties of coal, including heat value, moisture content, and ash content seriously affect its combustion efficiency and emissions [22, 23]. Therefore, real-time coal analysis technology is urgently needed for coal washing and blending, combustion optimization, pollution reduction and pricing. LIBS has become a promising candidate for coal quality detection due to its advantages of realtime on-line/*in-situ*, full-element measurement [24, 25].

In China, there are several research groups using LIBS for coal analysis, but each research group has their own focus. Wang's group from Tsinghua University [25–34] focused on quantitative coal property analysis using pressed coal powder samples in order to avoid the impact of inhomogeneity and to improve the representativeness of coal sample. Moreover, as the main challenge of LIBS quantitative analysis, repeatability has been specially investigated by Wang's group. They proposed effective methods such as spatial confinement [32], beam-shaping [33], and models like spectral standardization [34], dominant factor based PLS [35] to improve the repeatability as well as the accuracy. A hybrid quantification model was thereafter proposed based on self-adaptive spectral database and combining all these methods mentioned above together [27]. The model applied spectral standardization method to reduce the uncertainty of all the spectral lines, and then identified whether the sample was from the self-adaptive spectral database. If the sample was in the database, the predicted values were directly read. If the sample was not in the database, the values were predicted by a dominant factor based PLS model and the database was updated. This hybrid model achieved full sample-to-sample repeatability. The average measurement errors for carbon, hydrogen, volatiles, ash and heat values are 0.42%, 0.05%, 0.07%, 0.17%, and 0.07 MJ/kg, respectively. All of these measurement accuracies fully meet the requirements of the national standard for coal analysis using traditional chemical processing methods. In addition, they also developed off-line system (cooperated with TSI) and on-line system (with a domestic company) for coal analysis, as Fig. 4 showed. The performance of the off-line system has been certified by authoritative third party. The on-line system has been successfully demonstrated in a real power plant integrated with an automatic sampling unit and with he whole process, including sample preparation and LIBS analysis, taking about 6 minutes for each sample. In addition, the performance of the on-line system is similar to the off-line system since they choose to automatically press the coal powder into pellet samples with the system. The group of South China University of Technology [36–43] mainly studied the dynamic behavior of coal combustion process, and also carried out the research of algorithm model and equipment development. They [41] applied LIBS to analyze the temporal and spatial measurement of flame temperature and the component emissions for coal particle combustion. The results showed that the residual energy could represent the flame temperature, and the emission of H and CN could be the evidence for combustion stage discrimination (devolatilization, secondary reaction, and char combustion). A rapid coal analyzer based on LIBS was developed by them [39] for rapid quality analysis of pulverized coal. This rapid coal analyzer is capable of performing reliable and accurate analysis of coal quality. The group of Shanxi University [44–47] mainly engaged in the development of instruments while conducting basic research on coal quality analysis. They

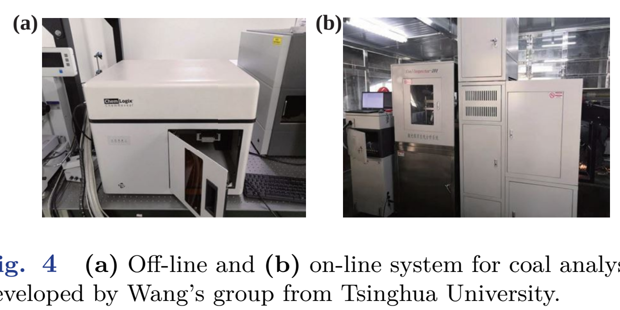

Fig. 4 **(a)** Off-line and **(b)** on-line system for coal analysis developed by Wang's group from Tsinghua University.

have developed a series of coal quality testing equipment, including a LIBS system for on-line quality analysis of pulverized coal in power plants [45]. This system contains the high-pressure gas cleaning device and the sampling equipment. By using the "Bode Rule/DC Level" normalization and the proposed data conversion methods, both elemental (C, Ca, Mg, Ti, Si, H, Al, Fe, etc.) and proximate analysis (fixed carbon, ash, and calorific value) of pulverized coal can be accomplished. The relative errors presented here for elemental analysis were within 10%, while those of ash were in the range of 2.29%–13.47%. They [46] also developed an apparatus comprising an isokinetic sampler, a sample-preparation module, and a LIBS module for on-line analysis of unburned carbon in fly ash. It has been demonstrated that the system can be used for on-line characterization of unburned carbon content in fly ash. Wan's group at Zhejiang University [48, 49] conducted a detailed study of the combustion process of Zhundong coal. They [48] firstly investigated the retention performance of 5 different sorbent additives, including 2 pure additives and 3 typical natural mineral additives on the release of sodium during the combustion of Zhundong coal via a combination of on-line multipoint LIBS technique and off-line measurements including ICP-AES, XRD, and AFTs. The results indicated that all the five sorbent additives showed a significant sodium retention effect, while alumina and kaolin were better additives considering the effects on AFTs. Then they [49] studied the temporal release characteristics of different chemical forms of sodium during the combustion of Zhundong coal and the catalytic effects of sodium on the combustion process via target-sodium removal and enrichment approaches. Li's group at Northwest University [50–52] mainly studied the application of various algorithms in coal quality detection. They applied ICA-WNN for the classification analysis of coal ash [50], K-ELM method for analysis of coal properties [51, 52]. They [53] also proposed a hybrid variable selection method based on WT and MIV to extract useful information from LIBS spectra for calorific value determination of coal.

Deguchi's group at Tokushima University in Japan is mainly engaged in LIBS coal research. They [54–57] focus on the detection of fly ash sample content, together with Wang's team at Xi'an Jiaotong University in China. In a recent study, they [56] used the two-stage cyclone measurement system and LIBS system to carry out real-time quantitative measurement of fly ash content. To improve the quantitative analysis ability, the plasma temperature correction method was used. The feasibility and improved detection ability for the real-time measurement of fly ash contents in power plants have been demonstrated.

At present, the researches of coal analysis using LIBS are quite prosperous. However, the road to commercialization and industrialization of LIBS coal analysis is still very long. Some challenges are greatly needed to be overcome as summarized by Wang *et al.* and Saha *et al.* [19, 58, 59]. Firstly, quantitative analysis performance of LIBS, particularly long-term repeatability and reproducibility performance under real industrial harsh environments, should be further enhanced. Deeper researches on fundamental are needed to further understand the mechanism of interaction between the laser, coal, plasma, and ambient conditions so as to reveal the origination of uncertainty and matrix effect. Modern algorithms based on large database and artificial intelligence should be integrated with the physical background of LIBS to further improve the measurement precision. Secondly, matrix effect in coal analysis should be further studied to make them applicable to different types of coal, especially considering the marix effect led by volatile matter, ash content and moisture content. Therefore, more experiments should be carried out in the actual detection environment to verify the feasibility of various methods. Meanwhile, LIBS coal analysis system needs to increase sample representativeness, simplify the sample pretreatment process, and integrate with combustion optimization or coal blending systems to benefit the end-user. Different stakeholders need to cooperate to establish the standards of LIBS coal analyzer for different application scenarios.

3 Metallurgy

The development of mining industry and the expansion of the full exploitation and utilization of mineral resources have played a huge and irreplaceable role in promoting the development and progress of human society [60, 61]. Traditional mining includes three steps: mining, beneficiation and metallurgy. Among them, metallurgy is related to whether mineral resources can be fully utilized, and the rapid detection of elemental composition in the process of metallurgical analysis can greatly improve product quality and energy efficiency. However, the traditional analysis methods such as Spark-OES, XRF and EDX are off-line, and require complex sample preparation and cumbersome operations. LIBS can compensate the shortcomings of these traditional detection methods, lots of researchers employed LIBS to the metallurgy process analysis [62–64].

China is a big country in mineral resources, there are many researchers majoring in the metallurgical field application and have made their own contributions. In the analysis of molten metal, the easiest approach is to focus the laser beam directly on the surface of the liquid metal. Via the direct measurement of the molten metal, the effect on the element composition caused by the segregation gradient in the solid sample can be basically eliminated [65, 66]. Wang's group [67] monitored the dissolution mechanism of Fe in 304 stainless steel crucibles in molten aluminum, and found that the concentration of Fe in the molten aluminum alloy can reach saturation. They [68] also developed a system including the LIBS system and the near-infrared spectrometer, which can accurately detect both temperature and element content of molten metal. Although the above methods can measure the melt composition and are relatively straightforward, they also have some disadvantages. Since the molten metal surface usually has oxide slag, molten salt, etc., it is impossible to accurately measure the composition of the molten bulk. Secondly, aerosols and spray particles that exist on the surface of the melt will affect the power density of the laser focused on the surface of the sample, thereby degrading the quality of the spectral data. On the contrary, the usage of immersion probes will improve the performance of LIBS equipment for melt composition analysis. Therefore, Sun's group at Chinese Academy of Sciences [69] employed an immersed LIBS device to realize the *in-situ* measurements of the molten aluminum and electrolyte in industrial aluminum induction cells. The structural diagram of the aluminum induction cell and the LIBS equipment are shown in Fig. 5. In this study, it was found that after pressing the electrolyte powder into a wafer having a diameter of 30 mm at a pressure of 30 MPa for 15 seconds, the obtained electrolyte spectrum was consistent with that of the molten electrolyte.

Researchers in other countries have also done a lot of work in the field of metallurgical analysis. In the on-line inspection of material quality, Laserna's group [70] applied a remote portable stand LIBS system to identify the grade of steel at a distance of 3.6 m from the billet production line. Furthermore, they [71] also employed discriminant function analysis and DP-LIBS to monitor the continuous casting sequence of steel on-line with LIBS equipment at 7.6 meters from a hot–hot plate (900°C). In addition, Sturm's group [72] adopted a LIBS instrument which had been installed temporarily on-site in a rolling mill and its performance was tested in measurement series at 481 steel blooms during routine production. In the analysis of molten metal, Gudmundsson's group [73] reported that LIBS could directly measure trace elements (Cu, Cr, Mn, Sn) in molten aluminum as low as ppm-level. Recently, Herbert's group [74] conducted a successful on-line testing of the OnSpec system at various aluminum facilities by adopting an immersed probe.

The development of intelligence has an unprecedented urgent need for on-line analysis in the metallurgy field. The LIBS research groups in many countries have continued to work hard in this field for many years, especially in China. Some on-line monitoring equipments have been developed and used in metallurgy industry. Due to the harsh environment of the industrial site, LIBS equipment is often subject to metal dust, strong electric fields, and mechanical vibration. These factors could make the laser energy drop, laser light path deflection, optical lens pollution, spectrometer wavelength drift, and unstable trigger board control timing, etc., making LIBS measurement and detection difficult. And it is troublesome to achieve accurate quantitative analysis of metal components in metallurgical processes. Despite so many destructive factors, more stable and accurate equipment will solve these problems in few years with the efforts of researchers.

4 Water monitoring

Water pollution seriously destroys the ecological balance and human health. A series of diseases have been induced by drinking water with excessive heavy metals for a long time. For example, drinking water with excessive Pb can cause diseases of the nervous system and digestive system [75, 76]. Therefore, the monitoring of water pollution is urgent and crucial. In recent years, LIBS, as an elemental detection technology, has been widely applied in water detection [77, 78]. In the following part, we will introduce the recent development of LIBS in water detection.

Due to the problems of liquid splash and plasma quenching, poor detection sensitivity and stability were obtained during the direct liquid detection using LIBS. Therefore, various pretreatment methods have been proposed to improve the detection sensitivity and spectral stability, including liquid flow, liquid–solid conversion, liquid enrichment, and so on. Accordingly, we will introduce the research status of each pretreatment method at home and abroad.

Liquid flow mainly refers to the conversion of static liquid into flowing liquid for detection. Liquid flow detection includes liquid jet detection, drop detection, laminar

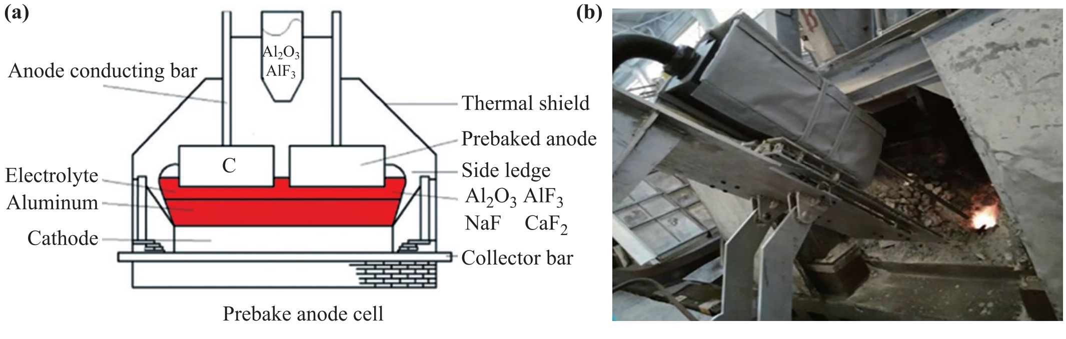

Fig. 5 **(a)** Structural diagram of the aluminum induction cell and **(b)** LIBS equipment for in situ measurement of molten aluminum and electrolyte. Reproduced with permission from Ref. [69].

flow detection, and liquid atomization detection. Many researches have been done about liquid jet detection. For example, Cui's group [79] detected Pb in water using LIBS combined with liquid jet, and LoD of 60 ppm was obtained. For drop detection, Lin's group [80] used electrospray ionization needles to generate uniform drops. The droplets interacted with the laser about 2 mm below the needles tip, and finally achieved the detection of Na, K, and Al. Furthermore, the sensitivities between three methods of static liquid level detection, liquid jet, and laminar flow detection were compared, and the results indicated that optimal sensitivity could be obtained by laminar flow detection [81]. Zheng's group [82] did a series of researches on elements of Mn, Zn, Cu, Pb, Fe, Mg, and Na in liquid sample using LIBS combined with ultrasonic atomization, and investigated the spectral stability and repeatability. Finally, the LoD of 2.93 ppm for Pb was obtained and the relative error did not exceed 7.1%. It is worth mentioning that a new method, namely capillary mode, was proposed to quantify the concentration of elements in water using LIBS, and the problems of liquid splash was effectively prevented [83].

The pretreatment method of liquid–solid conversion was considered to be the most effective method to prevent the liquid splash and plasma quenching in liquid detection. Chemisorption and extraction are currently the most commonly used liquid–solid conversion methods. Commonly used adsorbents and extractants include heavy metal chelates, bamboo charcoal, nano-graphite, nano-graphene, montmorillonite clay, resin, and molten paraffin, etc. In Sichuan University, Duan'group [84] applied dispersive solid-phase microextraction technology to LIBS liquid detection. The nano-graphene was used as adsorbent to enrich and extract Ag, Mn, and Cr in water, and then fixing the nano-graphene powder with epoxy adhesive. The results indicated that a good linearity and LoD could be obtained. Later, they proposed a pretreatment method for LIBS based on metal precipitation and membrane separation for simultaneous elemental analysis in liquid samples. The results showed that the LoDs of Ag, Mn, Cr, and Cu were 0.957–2.59 ng/mL [85]. The group of Huazhong University of Science and Technology simultaneously has done a lot of works about the elemental detection in water using SENLIBS. For example, they detected elements of La, Ce, Pr, and Nd in water using SENLIBS, and the LoDs were 0.85–10.98 mg/L [86]. Further, the heavy metal elements of Cu, Pb, Cd, and Cr were detected by proposing a new method of chemical replacement combined with SENLIBS, and the LoDs of 0.016–0.386 mg/L were obtained [87]. Besides, the improvement effect of stability and accuracy of spreading a water droplet through filter paper on the metal substrate for element detection was investigated [88]. They also investigated the effect of the different substrates of Zn, Mg, Ni, and Si and the pH of solution for detection sensitivity of heavy metals in water. The results indicated that the optimal sensitivity could be obtained using Zn substrate and the detection sensitivity was positively correlated with the boiling point of the substrate [89]. The presence of acids in water inhibited the spectral enhancement of LIBS with phase transformation [90]. Further, they proposed an indirect LIBS method for detecting Cl and S in water, and the LoDs of 2 mg/L for Cl and 5 mg/L for S were obtained. The detection sensitivity was improved by three orders of magnitude compared to direct LIBS [91]. Besides, a large number of research groups were engaged in water pollution detection using liquid–solid conversion. For example, the researchers used graphene oxide for solid-phase extraction, and compared the extraction effects of graphene oxide and activated carbon on heavy metal elements Zn, Cd, Mn, Ni, Cr and Pb [92]. Furthermore, LIBS combined with electrical-deposition, as a liquid–solid conversion method, also could improve the sensitivity of elemental detection in water. A method based on the underwater LIBS combined with electrodeposition for preconcentration was proposed to detect Zn in solution, and the detection sensitivity could be improved about four orders of magnitude [93]. Ripoll's group [94] used LIBS combined with electrospray deposition technology to detect Zn, Cd, Cr, and Ni, and the LoDs of 9–57 ug/kg were obtained. In recent years, LIBS combined with dried-droplet on the substrate surface has developed rapidly. Some substrates were used in liquid pretreatment, such as wood chips, filter papers, absorbent papers, silicon wafers, plant fibers and metal substrate of Al, Zn, and Cu. For example, Pasquini's group [95] used LIBS combined with ring-oven based on preconcentration technique for microanalysis of Na, Fe, and Cu in fuel ethanol. Besides, the scholars have done a lot of researches about LIBS combined with dried-droplet on the substrate surface on Si substrates, including laser pre-ablation of Si substrates [96], and comparsion of three Si substrates [97]. On the basis of dried-droplet analysis, a method named NELIBS was proposed to improve the detection sensitivity. Giacomo's group [98] used NELIBS to analyze the microdrops of solutions with analyte concentration at sub-ppm level and the spectral signal could be enhanced more than 1 order of magnitude. To further improve the sensitivity of solution analysis, some instrument-assisted detection methods were proposed for solution analysis, such as DPLIBS [99, 100], LIBS-LIF [101] and MW-LIBS [102]. For example, LIBS-LIF was applied to realized sensitive analysis of Cu in water, and the LoD of 3.6 ppb was obtained, which was 4–5 orders better than that obtaned in direct analysis of aqueous solutions [101].

At present, the research on LIBS water quality monitoring at home and abroad mainly focuses on sample preparation methods to improve detection performance. However, some of these pretreatment methods are only suitable for laboratory water quality research and cannot be applied to on-line monitoring. Therefore, more pretreatment methods suitable for on-line water quality monitoring should be proposed. Meanwhile, real-time on-line monitoring equipment for water quality should be further developed.

5 Soil monitoring

Soil is the foundation of plant growth, its quality not only affects the growth of plants and animals, but also affects human health. Therefore, the detection of soil is very important, especially the detection of heavy metal elements. The traditional method of soil analysis is time-consuming and complicated, so a fast and real-time analysis technique is urgently needed. LIBS has incomparable advantages over other technologies in soil analysis, and has been widely used in soil detection in recent years [103, 104].

In Huazhong Univerity of Science and Technology, the group [105] proposed a simple and low-cost sample pretreatment method named solid–liquid–solid transformation method. In this method, available heavy metals were extracted from soil through ultrasonic vibration and centrifuging, and then deposited on a glass slide. The LoDs could reach to 0.067 ppm and 0.94 ppm for available Cd and Pb elements in soil, respectively, which were much better than those obtained by conventional LIBS. Besides, Qiu's group [106] successfully demonstrated the multi-element analysis of four heavy metal (Cu, Ni, Cr and Pb) contents using LIBS system based on over 160 agricultural soil samples. Further, the researchers used DP-LIBS to detect elements in soil. For example, Gao's group [107] demonstrated that femtosecond-nanosecond DP-LIBS can be applied as an efficient spectroscopic tool to improve the quantitative analysis of Pb heavy metal in soil. Ding's group [108] used LIBS combined with IPLS to accurately quantify heavy metals (Cu, Zn, Cr and Ni) in oily soil samples. To achieve *in-situ* portable measurement of heavy metals in soil, Zhao's group [109] developed a mobile LIBS system for *in-situ* analysis of heavy metals in soil samples, as shown in Fig. 6. The experimental results showed that the device had good performance, the LoDs for Cu, Pb, and Zn were all below 10 mg/kg, which satisfied the need of heavy metal detection in soil.

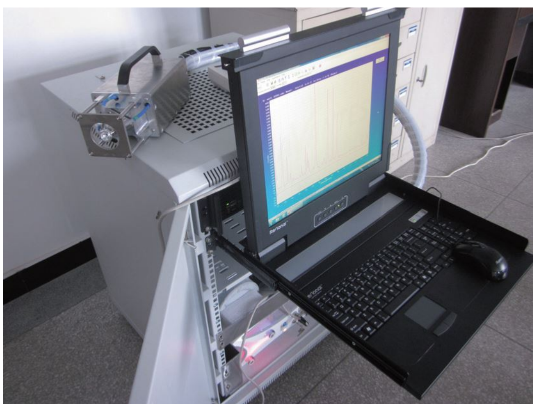

Fig. 6 Overall view of a mobile LIBS system for *in-situ* analysis of heavy metals in soil samples. Reproduced with permission from Ref. [109].

Baig's group at Quaid-i-Azam University has done a lot of researches about detection of heavy metals in soil using magnetic field enhanced LIBS. The effect of magnetic field for detection sensitivity was investigated and the results showed that the emission intensity enhancement factor up to about 8 has been observed. The LoD of Cr could be improved to 7.7 mg/kg in the presence of magnetic field [110]. Further, they used magnetic field assisted CF-LIBS and LA-TOF-MS to analyze the soil samples [111], and analyzed Pb and Cu in soil by LIBS under external magnetic field [112]. The results indicated that good qualitative and quantitative analysis could be obtained in the presence of magnetic field.

Most of the researches on soil detection at home and abroad are to improve the various performance factors of LIBS technique through pretreatment. Significant advances have been made in improving LoD of various elements, reducing matrix effects, increasing signal strength, optimizing S/N ratios, and applying powerful modern stoichiometric methods. However, these results are derived from laboratory, so the on-line and *in-situ* soil detection is still a technical difficulty that needs to be broken through.

6 Food detection

Food is an essential nutrient for human survival, so the quality of food is related to human health. Excessive heavy metal substances in food will increase the risk of cancer and other diseases. China is a country with a large population, and the consumption of food is countless every day, so food safety detection is very important [113, 114]. Traditional food detection technologies are limited to the laboratory and the operation is complex, time-consuming, which can not meet the demand of real-time food quality and safety supervision control. With its technical advantages, LIBS has been widely used in food detection [115–118]. The development of LIBS in the field of food detection at home and abroad in recent years will be introduced accordingly.

The researches in China mainly focuse on adulteration, nutrition, elemental analysis of plant origin and the quality detection of food contaminants. Yao's group at Jiangxi Agricultural University started early in the field of food detection, mainly focusing on the analysis of heavy metals (Cr, Cd, Pb and Cu) in various vegetables [119–121], fruits [122–124], cereals [125–127] and meats [128]. They [129] also applied LIBS to the identification of HLB navel oranges. RF models based on CWT and PCA were analyzed to identify the navel orange of HLB. The average accuracies obtained from the CWT-RF and PCA-RF were 96.86%, 97.64% in the training set and 97.45%, 97.89% in the test set, respectively. Their researches fully demonstrated the feasibility of LIBS in the field of food detection. In recent years, Liu's group has developed rapidly in this field. They successfully applied LIBS to the detection of rice leaves [130, 131], maize [132], lettuce [133], tobacco root [134], honey [135, 136] and oilseed rape [137], mainly including the qualitative and quantitative analysis of metal elements (Cr, Cd), the identification of transgenic and infected samples. Since most plant materials contain high moisture content, they [138] investigated the effect of moisture content on signal intensity, stability and plasma parameters, as shown in Fig. 7. Two strategies were further used to reduce the effect of moisture content and shot-to-shot fluctuation. An exponential model based on the intensity of background was used to correct the actual element concentration in analyte. Also, the ratios of signal-to-background for univariable calibration and PLSR for multivariable calibration were used to compensate for the prediction deviations. The PLSR calibration model obtained the best result, with the correlation coefficient of 0.9669 and root-mean-square error of 4.75 mg/kg in the prediction set. The Huazhong University of Science and Technology group [14, 139] has also done some researches. The effects of different pretreatment methods on rice classification were mainly studied. They [139] first compared four different sample preparation methods, like rice powder pellet with boric acid, rice powder pellet, rice grain pellet and rice grain. The rice grain method was found to be simpler and more efficient. Then they [140] proposed a simple and low-cost sample pretreatment method named solid–liquid–solid transformation method. Compare with conventional pellet method, the spectral intensities of Cd and Pb were enhanced significantly using LIBS. The LoDs of Cd and Pb were 2.8 and 43.7 μg/kg, respectively. The LoQs were 9.3 and 145.7 μg/kg, respectively. Wang's group [141] successfully applied LIBS to identify three hazardous bacteria as common food contaminants, Staphylococcus aureus, Bacillus cereus, and Escherichia coli. They proposed the PCA–GA–SVM method to classify six kinds of measured hazardous bacteria, in which the PCA was used to select the feature lines and the GA algorithm was used to optimize feature selection process. The correct classification rate achieved 100%. They also used LIBS to evaluate velvet antler products qualitatively [142]. PCA was used to select the feature lines of LIBS spectra of velvet antler, and two PLS-DA classification models were built to distinguish inferior quality velvet antler from good ones. The quality evaluating accuracy of the velvet antler achieved 100%, and the robustness could be improved by using the intensities of feature lines as inputs.

Compared with China, there are more research groups and a wider range of researches in other countries. Rai's group [143] studied LIBS as a simple and fast method to analyze nutrients in the seeds of cucurbit seeds. The calibration curve method was adopted for quantitative analysis of elements (Mg, Ca, Na and K), and the lin-

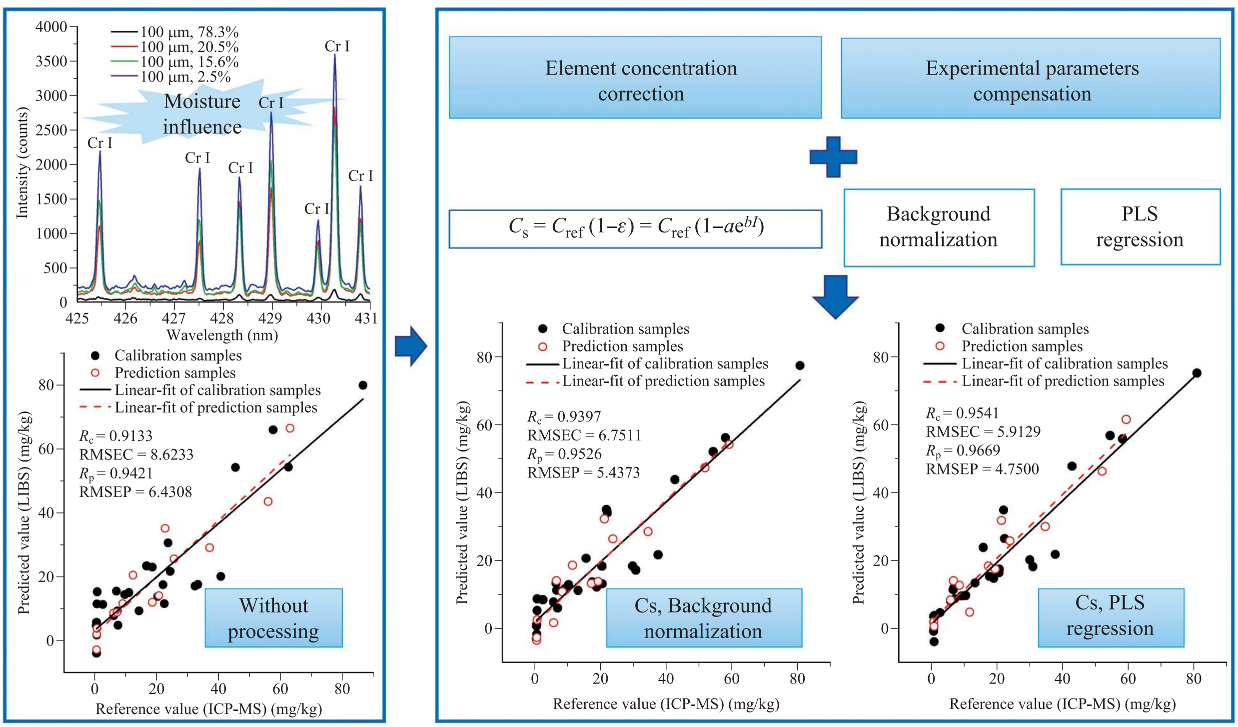

Fig. 7 Overall view of moisture influence reducing method for heavy metals detection in plant materials. Reproduced with permission from Ref. [138].

earity of the calibration curve was good. The results obtained by LIBS were basically consistent with those obtained by AAS. Boyaci's group [144] studied the origin of milk species (bovine, caprine and ovine milk) by LIBS. PCA was used to evaluate LIBS spectra, and PLSR was used to determine the adulteration rate. In these analyses, milk samples were converted into gels to improve the analytical performance of LIBS by eliminating the spatter and low radiation intensity encountered during liquid measurements. Ferreira's group [145] reported an evaluation of LIBS to distinguish good beans and *Blacks*, *Greens* and *Sors* (BGS) defects. Emission lines of elements and emission bands of diatomic molecules derived from organic compounds have good discriminant power. LIBS emissions of N, CN, C, and C_2 were highly correlated with near-infrared spectral absorption bands of proteins, lipids, sugars, and carboxylic acids.

Most current LIBS experiments on food are conducted in laboratories, which have verified the feasibility of LIBS in food detection. However, due to the complex organic matrix of food, the sensitivity of LIBS to the element with low concentration is extremely poor, which makes it difficult to apply in practice. In addition, the non-homogeneity of food determines the preparation of samples is very important. Therefore, more real-time on-line experiments should be carried out so that LIBS can be applied to practical food testing.

7 Biomedicine

There are many metal elements in living organisms, which play an important role in the growth and development of living organisms [146, 147]. The redox-inactive alkali and alkali earth metals, notably Na, K, Mg and Ca, are dynamic entities that transmit signals through rapid and coordinated movement and exchange of metal ion pools. Redox-active transition metals such as Zn, Cu and Fe are known as cofactors involved in the maintenance of structural or catalytic roles. Some elements present in the organism can cause toxicity and harm [3]. Therefore, the analysis of the elemental distribution in tissues is very important for pathological study. Meanwhile, LIBS has the function of element two-dimensional (2D) mapping to reveal the distribution of elements [148]. Therefore, plentiful researchers began to study the identification and element distribution of diseased tissue by LIBS [149–153].

The application of LIBS in biomedicine is an emerging hot spot, and there are mainly three domestic groups to conduct related research. The group of Huazhong University of Science and Technology [14, 15] mainly focused on the application of LIBS to serum detection. They used LIBS to identify NPC serums with an ELM and RF method. The accuracy rate, sensitivity, and specificity of NPC serum and healthy controls reached 98.330%, 99.0222% and 97.751%, respectively. In a recent study, they [154] applied LIBS technology to the study of the biological half-life of inorganic or inorganic-organic composite nanomaterials in vivo. They investigated an efficient way to quantify the metabolic rate using LIBS. Nanoparticle platforms, such as manganese dioxide-bovine serum albumin (MnO_2-BSA) or boehmite-bovine serum albumin (AlO(OH)-BSA) were injected into mice through intravenous administration for LIBS spectrum acquisition. First, the spectral background was corrected using the polynomial fitting method; The spectral interference was eliminated by Lorentz fitting for each LIBS spectrum simultaneously. The SVR was then used for LIBS quantitative analyses. Finally, the LIBS results were compared with the ICP-MS ones. The half-lives of MnO_2-BSA calculated by LIBS and ICP-MS were 2.49 h and 2.42 h, respectively. For AlO(OH)-BSA, the half-lives detected by LIBS and ICP-MS were 3.46 h and 3.57 h, respectively. Li's group at Harbin Institute of Technology [155, 156] realized the identification of malignant tumors by applying LIBS to serum detection. They [157–159] also achieved the classification of different soft tissues (pork fat, skin, ham, loin and tenderloin muscle tissues). To study the distribution of elements in normal and diseased tissues, the histological picture of the HES-stained biopsy of the breast cancer tissue and the corresponding elemental distribution images for Ca, K and Mg were obtained and analyzed. Results showed that different elements have different distribution patterns. For Ca, higher concentrations were generally obtained in the tumour regions. Meanwhile, gradient of the intensities can be observed in the tumour cell regions which look homogeneous in the histological picture. For K and Ca, high concentrations are generally observed in the tumour cell regions, but they have quite different patterns from that of Ca. Meanwhile, a hot spot can be observed for K in the lower region. Wang's group from Beijing Institute of Technology [160] introduced LIBS as a possible solution for the discrimination of infiltrative glioma boundary. They verified that even the tumors collected from different patients showed different colors and morphologies, the tissue composition was similar and the LIBS signals were stable. They analyzed the differences in elements of glioma and infiltrative boundary tissue. Then they used RF to select feature lines and built SVM model based on feature lines to identify fresh glioma tissue with boundary tissue. The accuracy achieved 95%. They also dedicated to clinical microbiology diagnosis [161] and proposed methods to evaluate the contribution of each spectral line to the classification result. They proposed IW-PCA to evaluate the importance weights of lines and compared them with RF. The two methods mutually verified the importance of selected lines and the important lines evaluated both by IW-PCA and RF contributed more to the correct classification rate. According to the evaluated importance weights, appropriate feature lines can be extracted by using these two algorithms.

Abroad, more research groups engaged in biomedical research. Jeong's group [162, 163] mainly analyzed melanocytes with LIBS. They [162] used LIBS to distinguish melanoma from dermis. They took spectra of melanoma cells and surrounding tissue from mice and found that there was little difference in carbon content between melanoma cells and surrounding tissue, but melanoma cells had significantly higher levels of magnesium than surrounding tissue. The elemental map of melanoma cells and surrounding tissues were presented in their study. Motto-Ros's group [164, 165] applied LIBS to the analysis of element distribution in paraffin-embedded samples. The distribution of P, Ca, Mg Zn, Na, Fe in healthy skin tissue and different skin cancer types (melanoma metastasis, Merkel-cell carcinoma and squamous cell carcinoma), Al, Na in cutaneous granulomas and skin pseudolymphoma, Ti, P in pigmentation lymph nodes, and P, Ti, Cu, W and Cr elements in cutaneous scar were successfully realized through LIBS. Part of their results is shown in Fig. 8.

In the field of biomedicine, current research mainly focuses on blood detection and tissue classification, while there are few studies on pathological tissue element distribution and pathology. Meanwhile, plentiful in vitro experiments have been conducted to verify the feasibility of LIBS, but in vivo experiments and related equipment are rarely studied. Therefore, the development of pathology research, *in vivo* experiments and devices will be the future of LIBS in biomedicine.

8 Deep-sea exploration

The ocean, covering about 71% of the earth's surface and averaging about 3792 meters in depth, is one of the most challenging and inaccessible places on earth. Extreme conditions such as high pressure and hypoxia prevent many detection techniques from being applied to deep-sea detection [166]. LIBS has become a new star in ocean exploration with the advantages of LIBS. Numerous publi-

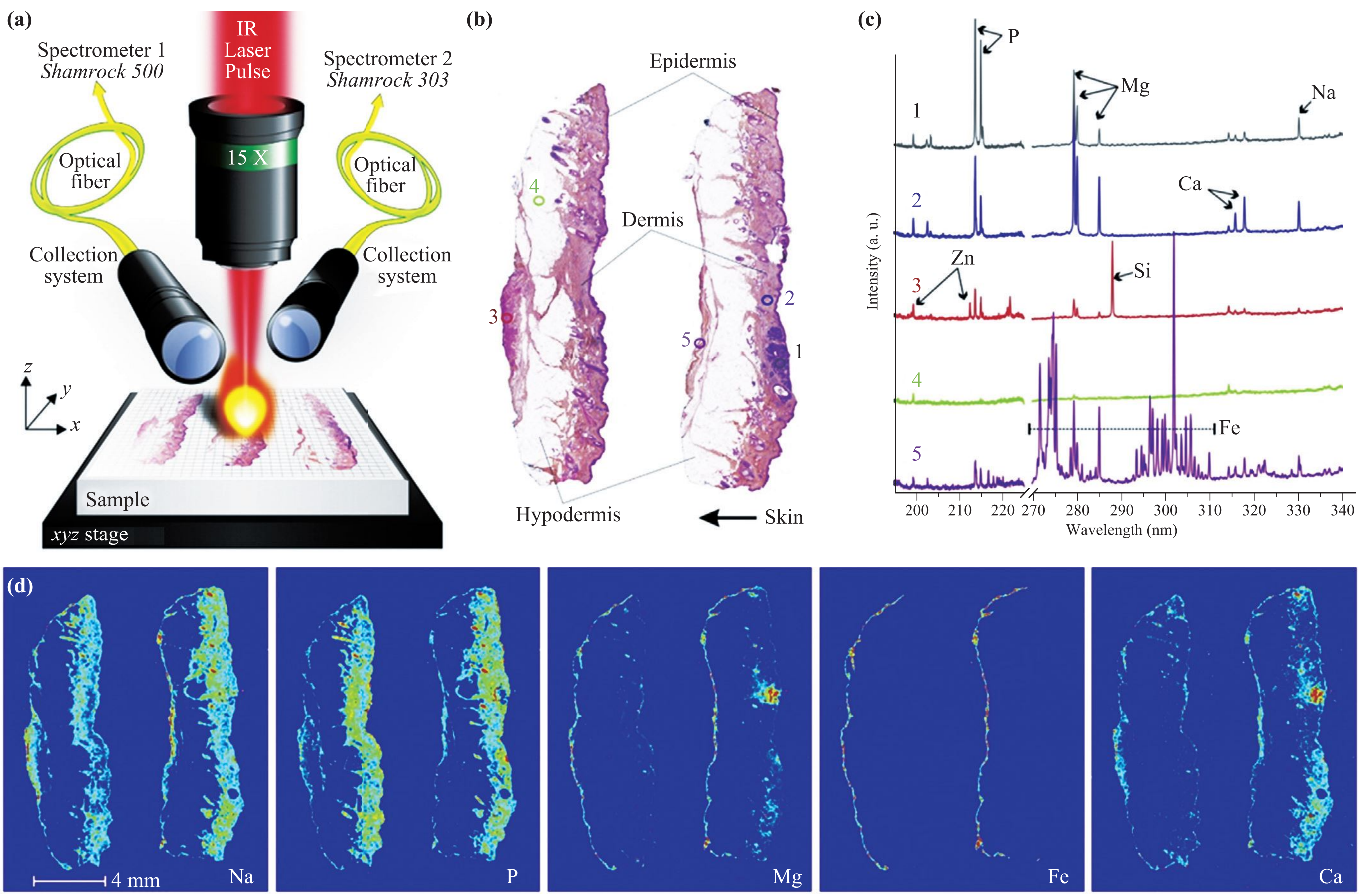

Fig. 8 **(a)** Schematic representation of the main components of the LIBS imaging instrument: a microscope objective to focus the laser pulse, a motorized sample stage and two optical detection systems coupled with two Czerny–Turner spectrometers. **(b)** High-resolution HES histological images of a healthy skin sample before LIBS analysis. **(c)** Typical single shot tissue spectrum covering the 270–340 nm for detecting Mg, Si, Fe, Cu, Al and Na, and the 190–230 nm detecting P and Zn on different areas of the tissue biopsy. **(d)** Na, P, Mg, Fe, and Ca LIBS images for paraffin-embedded skin tissue. Reproduced with permission from Ref. [164].

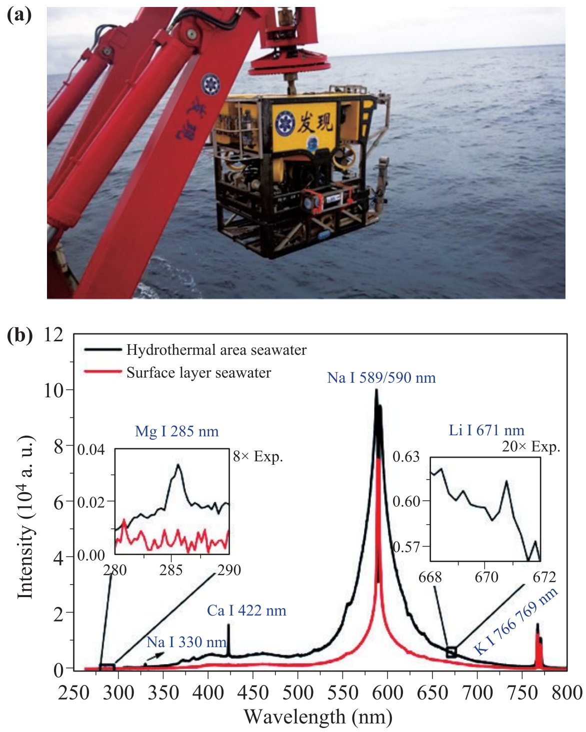

Fig. 9 **(a)** "LIBSea" mounting on the ROV Faxian to be deployed in the Manus area in 2015. **(b)** Comparison between typical sea trial LIBS spectra from the hydrothermal area and LIBS spectra of seawater from the surface layer. Reproduced with permission from Ref. [179].

cations have reported on the research of LIBS in ocean exploration, which mainly include instrument developments and basic researches [167–169].

In China, Zheng's group at Ocean University of China mainly engaged in deep-sea LIBS inspection and exploration. They [170–178] did a lot of basic experimental research and systematically analyzed the influence of laser focus to sample distance, laser wavelength, different focusing arrangements, pressure, salinity, ambient temperature and other factors on the LIBS in sea water. Simultaneously, a LIBS compact system was built by them, which was named as "LIBSea", as shown in Fig. 9. That prototype system was developed as a sensor, which was deployed on ROV to implement *in-situ* seawater analysis [179]. In 2015, LIBS-sea was employed to do the investigation down to 2000 m deep-sea, and the elemental profiling from sea surface to seafloor was firstly reported. The pressure and the temperature were found as main influences for LIBS detection, and the intensified LIBS signal of calcium could be hints for tracking hydrothermal vents which were also confirmed by the colored dissolved organic matter detection [180]. Currently, another compact LIBS system is developing for undersea solids detection, and it will be operated by HOV in the near future.

Compared with China, research groups in other countries started earlier in the field of LIBS deep-sea exploration. As early as 2012, LIBS was used for undersea detection [181], and that was an on-deck instrument of LIBS, named "AQUALAS". The LIBS detection was conducted by a diver who held the LIBS probe to touch alloy samples, and the main body of AQUALAS was placed on board which delivered laser pulses/LIBS signal via an umbilical cable. In 2015, the AQUALAS system was successfully applied for undersea investigation of archeological materials [182]. The dive depth was 30 meters in 2012 and 50 meters in 2015 respectively. However, the pressured air was employed to produce a gas environment for the plasma generation, and the cable length limited the further application in deeper sea. In 2013, a submersible LIBS system developed by Thornton's group, named as "I-SEA", which was applied for the detection of seawater and solids. The whole system was deployed on ROV to carry out the detection at the depth of 200 meters [183]. Based on that, the system was upgraded in 2015 with a new name "ChemiCam", and it was applied for the investigation of hydrothermal vents by a ROV [184]. This time the dive depth was successfully increased to 1000 meters. Actually, the investigation was achieved by 2 separated system. One was used for the seawater detection which put all the components into a chamber. The other one was optical probe system, in which the LIBS probe was connected to the main chamber via an umbilical fiber. During the detection, the ROV manipulator held the LIBS probe to approach the surface of seafloor minerals to implement the element analysis. The obtained results of seawater and sediments were found to be useful in discriminating hydrothermal vents. Recently, the group is attempting to establish LIBS quantitation of hydrothermal minerals during the *in-situ* detection [185].

Although a lot of basic research has been carried out in deep-sea exploration. There is still a long way for LIBS to play a role in ocean applications. The issues to improve the stability of the instrument and to overcome the complexity of the seawater environment are still the focus of future research. Furthermore, it is not easy to compose LIBS system as an ideal sensor with small volume and low-power consumption.

9 Nuclear material detection

Nuclear energy is the energy released from the nucleus through nuclear reactions and is one of the most promising future energy sources [186]. There are two ways to develop nuclear energy, fision of heavy elements and fusion of light elements. Material composition of the reactor components in fusion and fission needs to be examined to determine the state of the equipment [187]. However, the traditional laboratory testing method is cumbersome, time-consuming and dangerous. To overcome these drawbacks, the LIBS technology with advantages of remote, on-line and multi-element detection abilities [188, 189] is becoming increasingly popular in nuclear material analyses [190, 191].

There are two main groups engaged in nuclear contamination detection in China, Wu's group of Xi'an Jiaotong University and Ding's group of Dalian University of Technology. Wu's group mainly focused on examining Z3CN20-09M steel in nuclear fision. They [192] developed a single-lens laser probe of the fiber-optic LIBS system to analyze the elements in the Z3CN20-09M steel, which was used for the main pipelines in nuclear power plants, in ambient air. This system can successfully detect all other elements, except C and P. They [193] also investigated the laser produced plasma and LIBS spectra of Z3CN20-09M steel used for main reactor coolant pipes, and the 16MND5 steel used for nuclear reactor pressure vessels. Ding's group [194–202] dedicated to studying the application of LIBS on nuclear fusion area. They have proved the excellent performance of LIBS in laboratory and fusion devices (Experimental Advanced Superconducting Tokamak, EAST). They also successfully investigated fuel retention and impurity deposition on the first wall [195, 197, 200] and the composition of the PFCs [196] using a LIBS system. Recently, they [194] developed an *in-situ* LIBS system for mapping the deposition distribution (IMap) on a wide area of PFCs for HL-2M (Huan Liu Qi-2 Modification, an advanced new Tokamak in China), as shown in Fig. 10. IMap's design, manufacturing, integration and lab test have been completed. The system can be remotely controlled, and its optical lenses, mirrors, and fibers can be adjusted automatically when scanning over the PFCs. All elements with the emission lines in the range of 380–850 nm can be analyzed, and the isotope species H and D can also be identified clearly with this diagnostic *in-situ*. They [202] proposed a novel DP-LIBS method using the combination of circular and annular nanosecond laser pulses with the aim of overcoming the sensitivity and depth resolution shortcomings of the SP-LIBS approach. This could help us to develop a more effective *in-situ* and minimally destructive LIBS system for the trace impurity deposition and fuel retention on the first wall in the fusion device.

In other countries, many groups studied the application of LIBS in nuclear area as well. In fission area, the detection of U is significant. Harilal's group at Pacific Northwest National Laboratory used LIBS and laser-induced fluorescence to detect U and its isotope in ore, they also studied the plasma dynamic of U [203–206]. Chan's group at Lawrence Berkeley National Laboratory [207] used LIBS to investigate the characteristics of U isotopic by analyzing a series of U_3O_8–$Li_2B_4O_7$ fused glassy disks. They [208] also compared the theoretical accuracy of uranium isotope analysis using LAMIS, LIBS and LAMIS-LIBS using computer simulation. Other groups studied the performance of LIBS in nuclear area. Maji's group at Indira Gandhi Centre for Atomic Research [209] proved the universality of LIBS as an analysis method by measuring the concentrations of lanthanide elements Pr, Nd, Ce, La and Sm in the LiF–KCl matrix. The accuracy of the determination of individual lanthanides from synthetic mixtures has been less than 10%. The LoDs were ranged from 0.04 to 0.1%. In fusion area, Brezinsek's group from Forschungszentrum Juelich studied the application of LIBS, their research mainly relied on Wendelstein 7-X (W7-X, an advanced stellarator in Germany), by studying the plasma facing material in W7-X, the erosion of plasma facing materials and retention of fusion fuel were studied [210, 211].

Research groups at home and abroad have conducted comprehensive studies on nuclear material detection. While doing a lot of basic research, relevant equipment has been developed and applied to practical application testing. However, in order to bring *in-situ* testing ability into effect, the measurement accuracy of fuel and impurities, the isotope detection ability, spectral intensity enhancement method and remote LIBS technique will be the main problems for LIBS nuclear research in the future.

10 Conclusions

As noted at the beginning of this review, LIBS is an atomic emission spectroscopy technique with many advantages, which has attracted lots of researchers. During the past years, the application of LIBS in various fields has developed rapidly, especially in China. This review summarizes the latest research in these eight main LIBS applications, as listed in Table 1.

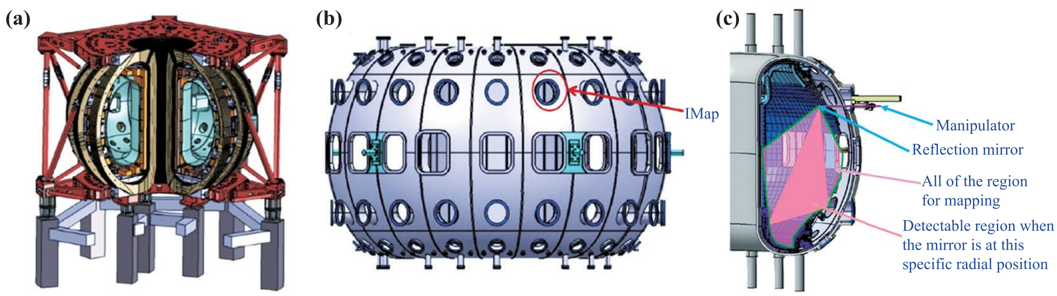

Fig. 10 **(a)** The schematic of the HL-2M tokamak. **(b)** The port for the IMap system on HL-2M, and region available for IMap on HL-2M. Reproduced with permission from Ref. [194].

Table 1 Summary of the main research status in various fields in recent years.

Field	Research group	Analytical objective	Processing method	Results	Ref.
Coal analysis	Tsinghua University	Carbon, hydrogen, volatiles, ash and heat values analysis	Spectrum standardization method-dominant factor based PLS model-self-adaptive database identification	All samples error = 0.42%, 0.05%, 0.07%, 0.17% and 0.07 MJ/kg, respectively.	[27]
	South China University of Technology	Analysis of coal particle combustion behavior	—	The emission of H and CN could be the evidence for combustion stage.	[41]
	Shanxi University	Development of on-line pulverized coal quality analysis equipment	Subtract the background; normalize; discard; and other steps	The relative errors for elemental analysis were within 10%, while those of ash were in the range of 2.29%–13.47%.	[45]
	Zhejiang University	The sodium retention performance of five sorbent additives	—	All the five sorbent additives show a significant sodium retention effect.	[48]
	Northwest University	Calorific value determination of coal	A hybrid variable selection method based on WT and MIV	RMSEP was reduced from 1.2584 MJ/kg to 0.6151 MJ/kg, R^2 was improved from 0.9802 to 0.9879.	[53]
	Tokushima University	The real-time and quantitative measurement of the contents in fly ash	The plasma temperature correction method	The results of LIBS were consistent with the chemical analysis results with $R^2 = 0.9052$ and RMSEP= 3.9%.	[56]
Metallurgy	University of Science and Technology of China	Composition and temperature monitoring of molten metal	—	The relative RMSE of temperature is 0.95%; the relative standard errors of Cr and Mn composition detection were lower than 10%.	[68]
	Chinese Academy of Sciences	Monitoring the molten aluminum and electrolyte components	A new molecular ratio calculation method	The average RSD of the molecular ratio measurement was 0.39%, and the average RMSE was 0.0236.	[69]
	University of Malaga	At-line monitoring of steel continuous casting sequences	DFA	The LIBS system was installed at a safe distance of 7.6 meters from the hot slab.	[71]
	Fraunhofer Institute for Laser Technology ILT	Fast identification of steel bloom composition at a rolling mill	—	The RMSE of prediction was in the range of 0.01–0.2 m.-%.	[72]
	ALTEK Group	Monitoring the chemical composition and cleanliness of molten metal	—	The OnSpec system has been successfully field tested at various aluminum plants.	[74]
Water monitoring	National Taiwan University	Detecting trace metals contained in liquids	Correlation treatment	The LODs were determined to be 0.63 ± 0.02, 1.2 ± 0.1, and 43 ± 5 mg/L for Na, K, and Al.	[80]
	Sichuan University	Ultrasensitive metal detection in aqueous samples	Metal precipitation and membrane separation	The LODs of Cu, Ag, Mn, and Cr obtained were 2.59, 0.957, 0.958 and 1.29 ng·mL^{-1}.	[85]
	Huazhong University of Science and Technology	Chlorine and sulfur determination in water	Indirect laser-induced breakdown spectroscopy	The R^2 of 0.999 and 0.997 were obtained for Cl and S. The LOQs were 2 and 5 mg/L for Cl and S.	[91]
	University of Alicante	Quantification of Zn, Cd, Cr and Ni at trace levels in aqueous samples	External calibration, conventional standard addition calibration and on-line standard addition calibration	The obtained LODs ranged from 9 ug·kg^{-1} to 57 ug·kg^{-1}.	[94]

(*continued*)

Field	Research group	Analytical objective	Processing method	Results	Ref.
	UNICAMP	Simultaneous determination of Na, Fe, and Cu in fuel ethanol	Ring-oven based preconcentration technique	Detection limits of 0.7, 0.4, and 0.3 ug·mL^{-1} and mean recoveries of 109±13%, 92±18%, and 98±12% for Na, Fe, and Cu.	[95]
	University of Bari	Elemental chemical analysis of micro-drops of solutions	NELIBS	The LODs of 2 pg for Pb and 0.2 pg for Ag.	[98]
Soil monitoring	Huazhong University of Science and Technology	Determination of trace available heavy metals in soil	Solid–liquid–solid transformation method	The LODs could reach to 0.067 and 0.94 ppm for available Cd and Pb in soil.	[105]
	Zhejiang University	Rapid quantification of 4 (Cu, Ni, Cr, Pb) heavy metal elements in soils	Several univariate and multivariate methods	The normalized RMSE were 6.84%, 8.87%, 9,71%, 10.76% for Cu, Ni, Cr and Pb.	[106]
	Nanjing University of Information Science and Technology	Accurate quantitative determination of Cu, Zn, Cr and Ni in oily soil	IPLS	The R^2 was improved from 0.96 to 0.99, and the RMSE was reduced from 0.03 to 0.01.	[108]
	Chinese Academy of Sciences	Application of a mobile LIBS system to detect Cu, Pb, Zn in soil	PCA	The measurement errors were less than 12%.	[109]
	Quaid-i-Azam University	Detection of Cr in soil	Magnetic field enhancement	The LOD of Cr was improved from 18.2 mg/kg to 7.7 mg/kg.	[110]
Food detection	Jiangxi Agricultural University	Identification of HLB navel oranges	CWT-RF and PCA-RF	The average accuracies obtained from the CWT-RF and PCA-RF were 96.86%, 97.64% in the training set and 97.45%, 97.89% in the test set.	
	Zhejiang University	Fast detection of Cr in plant materials	Moisture influence reducing method	The R^2 was 0.9669, and the RMSE was 4.75 mg/kg.	[138]
	Huazhong University of Science and Technology	High-sensitivity determination of Ca and Pb in rice	Solid–liquid–solid transformation method	The LODs were 2.8 and 43.7 ug/kg. The LOQs were 9.3 and 145.7 ug/kg, respectively.	[140]
	Beijing Institute of Technology	Detection of the common food contaminants like hazardous bacteria	PCA, GA, ANN and SVM	The correct classification rate of Staphylococcus aureus, Bacillus cereus, and Escherichia coli achieved 100% by the proposed PCA-GA-SVM.	[141]
		Qualitative evaluation of velvet antler products	PLS-DA	The evaluating accuracy of the quality of velvet antler achieved 100%, and the robustness could be improved by using the intensities of feature lines as inputs.	[142]
	University of Allahabad	Identification and quantification of minerals in cucurbit seeds	Calibration curve method and PCA	All calibration curves showed good linearity with R^2 more than 0.95.	[143]
	Hacettepe University	Classification of pure and adulterated milk samples	PCA and PLSR	The R^2 and LOD for caprine milk adulteration with bovine milk were 0.995 and 1.39%. The corresponding values for ovine milk adulteration with bovine milk with were 0.996 and 1.29%.	[144]
	University of Sao Paulo	Quality analysis of unroasted and ground coffee	PCA	It has great potential for discriminating good beans from those with BGS defects by using emission lines of C, CN, C_2 and N.	[145]

(*continued*)

Field	Research group	Analytical objective	Processing method	Results	Ref.
Biomedicine	Huazhong University of Science and Technology	Meat species identification	MSC	The identification rate improved from 94.17% to 100% and the coefficient of variation decreased from 5.16% to 0.56%.	[14]
		Discrimination of nasopharyngeal carcinoma serum	RF and ELM	The accuracy rate, sensitivity, and specificity of NPC serum and healthy controls reached 98.330, 99.0222 and 97.751%.	[15]
	Harbin Institute of Technology	Quick and robust diagnosis and discrimination of lymphoma and multiple myeloma	PCA, LDA, QDA, and KNN	The KNN model exhibits the best performances with overall discrimination accuracy of 96.0%.	[155, 156]
	Beijing Institute of Technology	Discrimination of infiltrative glioma boundary	PCA, RF, SVM and KNN	The SVM model built with features selected by RF performs best and the discriminative accuracy achieved 95.0%.	[160]
		Importance evaluation of spectral lines in classification of pathogenic bacteria	IW-PCA, RF and SVM	The lines evaluated important by both IW-PCA and RF contributed more to the correct classification rate (achieved 98.0%).	[161]
	Gwangju Institute of Science and Technology	Mapping of cutaneous melanoma	—	The map showed a close match to the optically observed morphological and histological features near the cancer region.	[162]
	University of Lyon	Analysis of element distribution in paraffin-embedded samples	—	The distributions of elements in various organizations were successfully realized.	[164, 165]
Deep-sea exploration	Ocean University of China	A newly developed compact 4000 m rated LIBS system	—	A fine detection ability was proved with 45 ppm for Ca and 9 ppm for K and less than 10% stability.	[179]
	University of Malaga	Recognition and identification of archeological assets in the wreck	—	Compared to single-pulse, an intensity enhancement factor of 15 was observed.	[182]
	The University of Tokyo	Developing a deep-sea laser-induced breakdown spectrometer	—	Reliable detection of elements with concentrations >1.0 wt% can be achieved.	[184]
Nuclear material detection	Xi'an Jiaotong University	Elemental analysis of Z3CN20-09M steel from nuclear power plants using FO-LIBS	—	It is possible for a single-lens laser probe to realize an accurate calibration and control of the focused spot size.	[192]
	Dalian University of Technology	In situ measurements of fuels and impurities on plasma facing components of EAST and HL-2A/M tokamaks	LIBS combined Laser induced TDS and TOF-MS	A new in situ diagnostic system for mapping the deposition and retention has been designed, fabricated, and tested for EAST and HL-2M.	[194]
	Lawrence Berkeley National Laboratory	Uranium isotopic analysis		The LAMIS-LIBS combined approach improved the precision to 0.42%.	[208]
	Indira Gandhi Centre for Atomic Research	Quantitative analysis of Pr, Nd, Ce, La and Sm	Internal standard method	Both the emission lines showed good regression coefficient ranging from 0.9953 to 0.9996.	[209]
	Forschungszentrum Juelich	Judging the erosion and deposition balance at the passively cooled graphite divertor	LIBS combined with laser-induced ablation-quadrupole mass spectrometry	The combination technique can be used to identify erosion and redeposition areas and determine implantation of H on divertor tiles with marker efficiently.	[210, 211]

The most attractive advantage of LIBS is its capability in realizing on-line or *in-situ* real-time measurement. Therefore, LIBS would be able to demonstrate more and more important to processing industry as the quantification performance of this technology being gradually improved. LIBS has also shown great potential in initial screening analysis for cases that an initial rough test is thirsty needed such as geographic material analysis, nuclear layer detection and deep-sea exploration. Although LIBS has been widely applied in various fields, it still needs time to be widely commercialized. It was believed that LIBS would not be the best option for high-accuracy concentration determination, but with the coming of big-data age, LIBS should play an even more determinative role in chemical analysis since of its *in-situ*/online real-time measurement capability to provide big-data. Also with the generation of large-scale data from LIBS application, the modern artificial intelligence shall play a more important roll in improving LIBS quantification performance. We believe that with the efforts of researchers around the world, LIBS will flourish in various fields.

Appendix: Glossary of terms

AAS	Atomic absorption spectrometry
AFTs	Ash fusion temperatures
ANN	Artificial neural network
CF-LIBS	Calibration free laser-induced breakdown spectroscopy
CWT	Continuous wavelet transform
DFA	Discriminant function analysis
DP-LIBS	Dual-pulse laser-induced breakdown spectroscopy
EAST	Experimental Advanced Superconducting Tokamak
EDX	Energy-dispersive X-ray spectroscopy
ELM	Extreme learning machine
GA	Genetic algorithm
HLB	Huanglongbing-infected
HOV	Human occupied vehicle
ICA-WNN	Independent component analysis-wavelet neural network
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IPLS	Interval partial least squares
IW-PCA	Importance weights based on principal components analysis
K-ELM	Kernel extreme learning machine
KNN	K-nearest neighbor
LAMIS	Laser ablation molecular isotopic spectrometry
LA-TOF-MS	Laser ablative time of flight mass spectrometer
LDA	Linear discriminant analysis
LDR	Linear dynamic range
LIBS-LIF	Laser-induced breakdown spectroscopy assisted with laser-induced fluorescence
LOD	Limit of detection
LOQ	Limit of quantitation
MIV	Mean impact value
MSC	Multiple scattering correction
MW-LIBS	Microwave-assisted laser-induced breakdown spectroscopy
NELIBS	Nanoparticle-enhanced laser-induced breakdown spectroscopy
NPC	Nasopharyngeal carcinoma
PCA	Principal component analysis
PFCs	Plasma facing components
PLS	Partial least-squares
PLS-DA	Partial least squares-discriminant analysis
PLSR	Partial least-squares regression
QDA	Quadratic discriminant analysis
R2	Correlation coefficient
RF	Random forest
RMSE	Root mean square error
RMSEP	Root mean square error of prediction
ROV	Remoted operated vehicle
RSD	Relative standard deviation
SENLIBS	Surface-enhanced laser-induced breakdown spectroscopy
Spark-OES	Spark source optical emission spectrometry
SVM	Support vector machine
SVR	Support vector regression
WT	Wavelet transform
XRF	X-ray fluorescence spectrometry

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (Grant No. 61575073) and Huazhong University of Science and Technology (No. 2020kfyXGYJ105).

References

1. Y. M. Guo, L. B. Guo, J. M. Li, H. D. Liu, Z. H. Zhu, X. Y. Li, Y. F. Lu, and X. Y. Zeng, Research progress in Asia on methods of processing laser-induced breakdown spectroscopy data, *Front. Phys.* 11(5), 114212 (2016)
2. J. D. Winefordner, I. B. Gornushkin, T. Correll, E. Gibb, B. W. Smith, and N. Omenetto, Comparing several atomic spectrometric methods to the super stars: Special emphasis on laser induced breakdown spectrometry, LIBS, a future super star, *J. Anal. At. Spectrom.* 19(9), 1061 (2004)
3. B. Busser, S. Moncayo, J. L. Coll, L. Sancey, and V. Motto-Ros, Elemental imaging using laser-induced breakdown spectroscopy: A new and promising approach for

biological and medical applications, *Coord. Chem. Rev.* 358, 70 (2018)

4. M. Markiewicz-Keszycka, X. Cama-Moncunill, M. P. Casado-Gavalda, Y. Dixit, R. Cama-Moncunill, P. J. Cullen, and C. Sullivan, Laser-induced breakdown spectroscopy (LIBS) for food analysis: A review, *Trends Food Sci. Technol.* 65, 80 (2017)
5. J. Laserna, J. M. Vadillo and P. Purohit, Laser-induced breakdown spectroscopy (LIBS): Fast, effective, and agile leading edge analytical technology, *Appl. Spectrosc.* 72(Suppl. 1), 35 (2018)
6. G. G. Arantes de Carvalho, M. B. Bueno Guerra, A. Adame, C. S. Nomura, P. V. Oliveira, H. W. Pereira de Carvalho, D. Santos, L. C. Nunes, and F. J. Krug, Recent advances in LIBS and XRF for the analysis of plants, *J. Anal. At. Spectrom.* 33(6), 919 (2018)
7. M. Scimeca, S. Bischetti, H. K. Lamsira, R. Bonfiglio, and E. Bonanno, Energy dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis, *Eur. J. Histochem.* 62(1), 2841 (2018)
8. C. Fabre, S. Maurice, A. Cousin, R. C. Wiens, O. Forni, V. Sautter, and D. Guillaume, Onboard calibration igneous targets for the Mars Science Laboratory Curiosity Rover and the Chemistry Camera laser induced breakdown spectroscopy instrument, *Spectrochim. Acta B At. Spectrosc.* 66(3–4), 280 (2011)
9. L. Peret, O. Gasnault, R. Dingler, Y. Langevin, S. Bender, D. Blaney, S. Clegg, C. Clewans, D. Delapp, C. M. Donny, S. Johnstone, C. Little, E. Lorigny, R. McInroy, S. Maurice, N. Mittal, B. Pavri, R. Perez, R. C. Wiens and C. Yana, Restoration of the Autofocus capability of the ChemCam instrument onboard the Curiosity rover (2016)
10. S. Moncayo, J. D. Rosales, R. Izquierdo-Hornillos, J. Anzano, and J. O. Caceres, Classification of red wine based on its protected designation of origin (PDO) using Laser-induced Breakdown Spectroscopy (LIBS), *Talanta* 158, 185 (2016)
11. Y. G. Mbesse Kongbonga, H. Ghalila, M. B. Onana, and Z. Ben Lakhdar, Classification of vegetable oils based on their concentration of saturated fatty acids using laser induced breakdown spectroscopy (LIBS), *Food Chem.* 147, 327 (2014)
12. E. C. Ferreira, E. J. Ferreira, P. R. Villas-Boas, G. S. Senesi, C. M. Carvalho, R. A. Romano, L. Martin-Neto, and D. M. B. P. Milori, Novel estimation of the humification degree of soil organic matter by laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 99, 76 (2014)
13. C. K. Kim, J. H. In, S. H. Lee, and S. Jeong, Influence of plasma conditions on the intensity ratio calibration curve during laser induced breakdown spectroscopy analysis, *Opt. Lett.* 39(13), 3818 (2014)
14. Y. W. Chu, S. S. Tang, S. X. Ma, Y. Y. Ma, Z. Q. Hao, Y. M. Guo, L. B. Guo, Y. F. Lu, and X. Y. Zeng, Accuracy and stability improvement for meat species identification using multiplicative scatter correction and laser-induced breakdown spectroscopy, *Opt. Express* 26(8), 10119 (2018)
15. Y. Chu, T. Chen, F. Chen, Y. Tang, S. Tang, H. Jin, L. Guo, Y. Lu, and X. Zeng, Discrimination of nasopharyngeal carcinoma serum using laser-induced breakdown spectroscopy combined with an extreme learning machine and random forest method, *J. Anal. At. Spectrom.* 33(12), 2083 (2018)
16. R. Gaudiuso, M. Dell'Aglio, O. De Pascale, G. S. Senesi, and A. De Giacomo, Laser induced breakdown spectroscopy for elemental analysis in environmental, cultural heritage and space applications: A review of methods and results, *Sensors (Basel)* 10(8), 7434 (2010)
17. J. Peng, F. Liu, F. Zhou, K. Song, C. Zhang, L. Ye, and Y. He, Challenging applications for multi-element analysis by laser-induced breakdown spectroscopy in agriculture: A review, *TrAC Trends in Analytical Chemistry* 85, 260 (2016)
18. Y. T. Fu, W. L. Gu, Z. Y. Hou, S. A. Muhammed, T. Q. Li, Y. Wang, and Z. Wang, Mechanism of signal uncertainty generation for laser-induced breakdown spectroscopy, *Front. Phys.* 16(2), 22502 (2021)
19. S. Sheta, M. S. Afgan, Z. Hou, S. C. Yao, L. Zhang, Z. Li, and Z. Wang, Coal analysis by laser-induced breakdown spectroscopy: A tutorial review, *J. Anal. At. Spectrom.* 34(6), 1047 (2019)
20. T. Ctvrtnickova, M. P. Mateo, A. Yañez, and G. Nicolas, Laser Induced Breakdown Spectroscopy application for ash characterisation for a coal fired power plant, *Spectrochim. Acta B At. Spectrosc.* 65(8), 734 (2010)
21. T. Ctvrtnickova, M. P. Mateo, A. Yañez, and G. Nicolas, Application of LIBS and TMA for the determination of combustion predictive indices of coals and coal blends, *Appl. Surf. Sci.* 257(12), 5447 (2011)
22. M. P. Mateo, G. Nicolas, and A. Yanez, Characterization of inorganic species in coal by laser-induced breakdown spectroscopy using UV and IR radiations, *Appl. Surf. Sci.* 254(4), 868 (2007)
23. D. Redoglio, E. Golinelli, S. Musazzi, U. Perini, and F. Barberis, A large depth of field LIBS measuring system for elemental analysis of moving samples of raw coal, *Spectrochim. Acta B At. Spectrosc.* 116, 46 (2016)
24. L. Zhang, Z. Y. Hu, W. B. Yin, D. Huang, W. G. Ma, L. Dong, H. P. Wu, Z. X. Li, L. T. Xiao, and S. T. Jia, Recent progress on laser-induced breakdown spectroscopy for the monitoring of coal quality and unburned carbon in fly ash, *Front. Phys.* 7(6), 690 (2012)
25. T. Yuan, Z. Wang, S. L. Lui, Y. Fu, Z. Li, J. Liu, and W. Ni, Coal property analysis using laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.* 28(7), 1045 (2013)
26. T. Yuan, Z. Wang, Z. Li, W. Ni, and J. Liu, A partial least squares and wavelet-transform hybrid model to analyze carbon content in coal using laser-induced breakdown spectroscopy, *Anal. Chim. Acta* 807, 29 (2014)
27. Z. Hou, Z. Wang, T. Yuan, J. Liu, Z. Li, and W. Ni, A hybrid quantification model and its application for coal analysis using laser induced breakdown spectroscopy, *J. Anal. At. Spectrom.* 31(3), 722 (2016)

28. J. Feng, Z. Wang, L. Li, Z. Li, and W. Ni, A nonlinearized multivariate dominant factor-based partial least squares (PLS) model for coal analysis by using laser-induced breakdown spectroscopy, *Appl. Spectrosc.* 67(3), 291 (2013)

29. X. Li, H. Yin, Z. Wang, Y. Fu, Z. Li, and W. Ni, Quantitative carbon analysis in coal by combining data processing and spatial confinement in laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 111, 102 (2015)

30. X. Li, Z. Wang, Y. Fu, Z. Li, J. Liu, and W. Ni, Application of a spectrum standardization method for carbon analysis in coal using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 68(9), 955 (2014)

31. X. Li, X. Mao, Z. Wang, and R. E. Russo, Quantitative analysis of carbon content in bituminous coal by laser-induced breakdown spectroscopy using UV laser radiation, *Plasma Sci. Technol.* 17(11), 928 (2015)

32. Z. Wang, Z. Hou, S. Lui, D. Jiang, J. Liu, and Z. Li, Utilization of moderate cylindrical confinement for precision improvement of laser-induced breakdown spectroscopy signal, *Opt. Express* 20(23), A1011 (2012)

33. Z. Hou, M. S. Afgan, S. Sheta, J. Liu, and Z. Wang, Plasma modulation using beam shaping to improve signal quality for laser induced breakdown spectroscopy, *J. Anal. At. Spectrom.* 35(8), 1671 (2020)

34. Z. Wang, L. Z. Li, L. West, Z. Li, and W. D. Ni, A spectrum standardization approach for laser-induced breakdown spectroscopy measurements, *Spectrochim. Acta B At. Spectrosc.* 68, 58 (2012)

35. J. Feng, Z. Wang, L. West, Z. Li, and W. D. Ni, A PLS model based on dominant factor for coal analysis using laser-induced breakdown spectroscopy, *Anal. Bioanal. Chem.* 400(10), 3261 (2011)

36. H. Qin, Z. Lu, S. Yao, Z. Li, and J. Lu, Combining laser-induced breakdown spectroscopy and Fourier-transform infrared spectroscopy for the analysis of coal properties, *J. Anal. At. Spectrom.* 34(2), 347 (2019)

37. S. Yao, J. Zhao, J. Xu, Z. Lu, and J. Lu, Optimizing the binder percentage to reduce matrix effects for the LIBS analysis of carbon in coal, *J. Anal. At. Spectrom.* 32(4), 766 (2017)

38. Z. Lu, J. Mo, S. Yao, J. Zhao, and J. Lu, Rapid determination of the gross calorific value of coal using laser-induced breakdown spectroscopy coupled with artificial neural networks and genetic algorithm, *Energy Fuels* 31(4), 3849 (2017)

39. S. Yao, J. Mo, J. Zhao, Y. Li, X. Zhang, W. Lu, and Z. Lu, Development of a rapid coal analyzer using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 72(8), 1225 (2018)

40. M. Dong, L. Wei, J. Lu, W. Li, S. Lu, S. Li, C. Liu, and J. H. Yoo, A comparative model combining carbon atomic and molecular emissions based on partial least squares and support vector regression correction for carbon analysis in coal using LIBS, *J. Anal. At. Spectrom.* 34(3), 480 (2019)

41. S. Li, M. Dong, F. Luo, W. Li, L. Wei, and J. Lu, Experimental investigation of combustion characteristics and NOx formation of coal particles using laser induced breakdown spectroscopy, *Journal of the Energy Institute* 93(1), 52 (2020)

42. W. Li, M. Dong, S. Lu, S. Li, L. Wei, J. Huang, and J. Lu, Improved measurement of the calorific value of pulverized coal particle flow by laser-induced breakdown spectroscopy (LIBS), *Anal. Methods* 11(35), 4471 (2019)

43. W. Li, J. Lu, M. Dong, S. Lu, J. Yu, S. Li, J. Huang, and J. Liu, Quantitative analysis of calorific value of coal based on spectral preprocessing by laser-induced breakdown spectroscopy (LIBS), *Energy Fuels* 32(1), 24 (2017)

44. L. Zhang, L. Dong, H. Dou, W. Yin, and S. Jia, Laser-induced breakdown spectroscopy for determination of the organic oxygen content in anthracite coal under atmospheric conditions, *Appl. Spectrosc.* 62(4), 458 (2008)

45. W. Yin, L. Zhang, L. Dong, W. Ma, and S. Jia, Design of a laser-induced breakdown spectroscopy system for on-line quality analysis of pulverized coal in power plants, *Appl. Spectrosc.* 63(8), 865 (2009)

46. L. Zhang, W. Ma, L. Dong, X. Yan, Z. Hu, Z. Li, Y. Zhang, L. Wang, W. Yin, and S. Jia, Development of an apparatus for on-line analysis of unburned carbon in fly ash using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 65(7), 790 (2011)

47. L. Zhang, Y. Gong, Y. Li, X. Wang, J. Fan, L. Dong, W. Ma, W. Yin, and S. Jia, Development of a coal quality analyzer for application to power plants based on laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 113, 167 (2015)

48. Y. Z. Liu, Z. H. Wang, Y. Lv, K. D. Wan, Y. He, J. Xia, and K. F. Cen, Inhibition of sodium release from Zhundong coal via the addition of mineral additives: A combination of online multi-point LIBS and offline experimental measurements, *Fuel* 212, 498 (2018)

49. Y. Liu, Z. Wang, K. Wan, Y. Lv, J. Xia, Y. He, and K. Cen, *In situ* measurements of the release characteristics and catalytic effects of different chemical forms of sodium during combustion of Zhundong coal, *Energy Fuels* 32(6), 6595 (2018)

50. T. Zhang, C. Yan, J. Qi, H. Tang, and H. Li, Classification and discrimination of coal ash by laser-induced breakdown spectroscopy (LIBS) coupled with advanced chemometric methods, *J. Anal. At. Spectrom.* 32(10), 1960 (2017)

51. C. Yan, J. Qi, J. Ma, H. Tang, T. Zhang, and H. Li, Determination of carbon and sulfur content in coal by laser induced breakdown spectroscopy combined with kernel-based extreme learning machine, *Chemom. Intell. Lab. Syst.* 167, 226 (2017)

52. C. Yan, J. Qi, J. Liang, T. Zhang, and H. Li, Determination of coal properties using laser-induced breakdown spectroscopy combined with kernel extreme learning machine and variable selection, *J. Anal. At. Spectrom.* 33(12), 2089 (2018)

53. C. Yan, T. Zhang, Y. Sun, H. Tang, and H. Li, A hybrid variable selection method based on wavelet transform and mean impact value for calorific value determination of coal using laser-induced breakdown spectroscopy and kernel extreme learning machine, *Spectrochim. Acta B At. Spectrosc.* 154, 75 (2019)
54. 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, *Spectrochim. Acta B At. Spectrosc.* 87, 130 (2013)
55. Z. Z. Wang, Y. Deguchi, S. Katsumori, A. Ikutomo, J. J. Yan, J. P. Liu, K. Tainaka, K. Tanno, H. Watanabe, and R. Kurose, Improved measurement characteristics of elemental compositions using laser-induced breakdown spectroscopy, *Spectroscopy (Santa Monica)* 31(1), 22 (2016)
56. Z. Wang, R. Liu, Y. Deguchi, S. Tanaka, K. Tainaka, K. Tanno, H. Watanabe, J. Yan, and J. Liu, Detection improvement of unburned carbon content in fly ash flow using libs with a two-stage cyclone measurement system, *Energy Fuels* 33(8), 7805 (2019)
57. R. W. Liu, Y. Deguchi, W. G. Nan, R. M. Hu, Z. Z. Wang, Y. Fujita, S. Tanaka, K. Tainaka, K. Tanno, H. Watanabe,J. P. Liu, and J. J. Yan, Unburned carbon measurement in fly ash using laser-induced breakdown spectroscopy with short nanosecond pulse width laser, *Adv. Powder Technol.* 30(6), 1210 (2019)
58. Z. Wang, T. B. Yuan, Z. Y. Hou, W. D. Zhou, J. D. Lu, H. B. Ding, and X. Y. Zeng, Laser-induced breakdown spectroscopy in China, *Front. Phys.* 9(4), 419 (2014)
59. J. P. Singh and S. N. Thakur, Laser-Induced Breakdown Spectroscopy, Elsevier, 2007
60. W. W. Wu, The concentration of silver from oxidative silver-manganese ore with united technologies of beneficiation and metallurgy, *Nonferrous Metals (Mineral Processing)* 5 (2003)
61. F. Z. Dong, X. L. Chen, Q. Wang, L. X. Sun, H. B. Yu, Y. X. Liang, J. G. Wang, Z. B. Ni, Z. H. Du, Y. W. Ma, and J. D. Lu, Recent progress on the application of LIBS for metallurgical online analysis in China, *Front. Phys.* 7(6), 679 (2012)
62. V. Lakshmanan, A. Ojaghi, and B. Gorain, Beneficiation of Gold and Silver Ores, in: Innovations and Breakthroughs in the Gold and Silver Industries, Springer, 2019
63. M. Gaft, Laser-Induced Breakdown Spectroscopy (LIBS) for On-line Control in Mining Industry, in: Applied Industrial Optics: Spectroscopy, Imaging and Metrology, Optical Society of America, 2011
64. D. H. Diaz Ordonez, Laser-induced breakdown spectroscopy (LIBS) for analysis of precious metals in minerals, 2017
65. S. W. Hudson, J. Craparo, R. De Saro, and D. Apelian, Applications of laser-induced breakdown spectroscopy (LIBS) in molten metal processing, *Metall. Mater. Trans. B* 48(5), 2731 (2017)
66. 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, *Spectrochim. Acta B At. Spectrosc.* 112, 40 (2015)
67. Q. Zeng, C. Pan, C. Li, T. Fei, X. Ding, X. Du, and Q. Wang, Online monitoring of corrosion behavior in molten metal using laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 142, 68 (2018)
68. Z. Qiang, P. Congyuan, F. Teng, D. Xiaokang, W. Shengbo, and W. Qiuping, Composition and temperature monitoring of molten metal by a combined LIBS-IR thermometry system, *J. Appl. Spectrosc.* 85(5), 817 (2018)
69. L. X. Sun, H. B. Yu, Z. B. Cong, H. Lu, B. Cao, P. Zeng, W. Dong, and Y. Li, Applications of laser-induced breakdown spectroscopy in the aluminum electrolysis industry, *Spectrochim. Acta B At. Spectrosc.* 142, 29 (2018)
70. L. M. Cabalin, T. Delgado, J. Ruiz, D. Mier, and J. J. Laserna, Stand-off laser-induced breakdown spectroscopy for steel-grade intermix detection in sequence casting operations, At-line monitoring of temporal evolution versus predicted mathematical model, *Spectrochim. Acta B At. Spectrosc.* 146, 93 (2018)
71. J. Ruiz, T. Delgado, L. M. Cabal´in, and J. J. Laserna, At-line monitoring of continuous casting sequences of steel using discriminant function analysis and dual-pulse laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.* 32(6), 1119 (2017)
72. V. Sturm, C. Meinhardt, R. Fleige, C. Fricke-Begemann, and J. Eisbach, Fast identification of steel bloom composition at a rolling mill by laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 136, 66 (2017)
73. S. H. Gudmundsson, J. Matthiasson, B. M. Bjornsson, H. Gudmundsson, and K. Leosson, Quantitative *in-situ* analysis of impurity elements in primary aluminum processing using laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 158, 105646 (2019)
74. J. Herbert, J. Fernandez, R. D. Saro, and J. Craparo, The Industrial Application of Molten Metal Analysis (LIBS), 2019
75. O. T. Butler, W. R. L. Cairns, J. M. Cook, and C. M. Davidson, Atomic spectrometry update –a review of advances in environmental analysis, *J. Anal. At. Spectrom.* 32(1), 11 (2017)
76. X. Yu, Y. Li, X. Gu, J. Bao, H. Yang, and L. Sun, Laser-induced breakdown spectroscopy application in environmental monitoring of water quality: A review, *Environ. Monit. Assess.* 186(12), 8969 (2014)
77. H. Tian, L. Jiao, and D. Dong, Rapid determination of trace cadmium in drinking water using laser-induced breakdown spectroscopy coupled with chelating resin enrichment, *Sci. Rep.* 9(1), 10443 (2019)
78. J. Kang, R. Li, Y. Wang, Y. Chen, and Y. Yang, Ultrasensitive detection of trace amounts of lead in water by LIBS-LIF using a wood-slice substrate as a water absorber, *J. Anal. At. Spectrom.* 32(11), 2292 (2017)
79. N. K. Rai, A. K. Rai, A. Kumar, and S. N. Thakur, Detection sensitivity of laser-induced breakdown spectroscopy for Cr II in liquid samples, *Appl. Opt.* 47(31), G105 (2008)
80. J. S. Huang, C. B. Ke, L. S. Huang, and K. C. Lin, The correlation between ion production and emission intensity in the laser-induced breakdown spectroscopy of liquid droplets, *Spectrochim. Acta B At. Spectrosc.* 57(1), 35 (2002)

81. F. A. Barreda, F. Trichard, S. Barbier, N. Gilon, and L. Saint-Jalmes, Fast quantitative determination of platinum in liquid samples by laser-induced breakdown spectroscopy, *Anal. Bioanal. Chem.* 403(9), 2601 (2012)

82. Z. Shilei, Z. Ronger, L. Yuan, C. Kai, and X. Junshan, Ultrasonic nebulizer assisted LIBS: A promising metal elements detection method for aqueous sample analysis, *Plasma Sci. Technol.* 17(11), 979 (2015)

83. D. Zhang, Z. Hu, Y. Su, B. Hai, X. Zhu, J. Zhu, and X. Ma, Simple method for liquid analysis by laser-induced breakdown spectroscopy (LIBS), *Opt. Express* 26(14), 18794 (2018)

84. X. Wang, L. Shi, Q. Lin, X. Zhu, and Y. Duan, Simultaneous and sensitive analysis of Ag (I), Mn (II), and Cr (III) in aqueous solution by LIBS combined with dispersive solid phase micro-extraction using nano-graphite as an adsorbent, *J. Anal. At. Spectrom.* 29(6), 1098 (2014)

85. X. Wang, Y. Wei, Q. Lin, J. Zhang, and Y. Duan, Simple, fast matrix conversion and membrane separation method for ultrasensitive metal detection in aqueous samples by laser-induced breakdown spectroscopy, *Anal. Chem.* 87(11), 5577 (2015)

86. X. Yang, Z. Hao, M. shen, R. Yi, J. Li, H. Yu, L. Guo, X. Li, X. Zeng, and Y. Lu, Simultaneous determination of La, Ce, Pr, and Nd elements in aqueous solution using surface-enhanced laser-induced breakdown spectroscopy, *Talanta* 163, 127 (2017)

87. X. Y. Yang, Z. Q. Hao, C. M. Li, J. M. Li, R. X. Yi, M. Shen, K. H. Li, L. B. Guo, X. Y. Li, Y. F. Lu, and X. Y. Zeng, Sensitive determinations of Cu, Pb, Cd, and Cr elements in aqueous solutions using chemical replacement combined with surface-enhanced laser-induced breakdown spectroscopy, *Opt. Express* 24(12), 13410 (2016)

88. X. Yang, R. Yi, X. Li, Z. Cui, Y. Lu, Z. Hao, J. Huang, Z. Zhou, G. Yao, and W. Huang, Spreading a water droplet through filter paper on the metal substrate for surface-enhanced laser-induced breakdown spectroscopy, *Opt. Express* 26(23), 30456 (2018)

89. S. Ma, Y. Tang, Y. Ma, Y. Chu, F. Chen, Z. Hu, Z. Zhu, L. Guo, X. Zeng, and Y. Lu, Determination of trace heavy metal elements in aqueous solution using surface-enhanced laser-induced breakdown spectroscopy, *Opt. Express* 27(10), 15091 (2019)

90. S. Ma, Y. Tang, Y. Ma, D. Dong, L. Guo, H. Zhu, J. Liu, and Y. Lu, The pH effect on the detection of heavy metals in wastewater by laser-induced breakdown spectroscopy coupled with a phase transformation method, *J. Anal. At. Spectrom.* 35(1), 198 (2020)

91. S. Ma, Y. Tang, S. Zhang, Y. Ma, Z. Sheng, Z. Wang, L. Guo, J. Yao, and Y. Lu, Chlorine and sulfur determination in water using indirect laser-induced breakdown spectroscopy, *Talanta* 214, 120849 (2020)

92. F. Ruiz, L. Ripoll, M. Hidalgo, and A. Canals, Dispersive micro solid-phase extraction (DμSPE) with graphene oxide as adsorbent for sensitive elemental analysis of aqueous samples by laser induced breakdown spectroscopy (LIBS), *Talanta* 191, 162 (2019)

93. A. Matsumoto, A. Tamura, R. Koda, K. Fukami, Y. H. Ogata, N. Nishi, B. Thornton, and T. Sakka, On-site quantitative elemental analysis of metal ions in aqueous solutions by underwater laser-induced breakdown spectroscopy combined with electrodeposition under controlled potential, *Anal. Chem.* 87(3), 1655 (2015)

94. L. Ripoll and M. Hidalgo, Electrospray deposition followed by laser-induced breakdown spectroscopy (ESD-LIBS): A new method for trace elemental analysis of aqueous samples, *J. Anal. At. Spectrom.* 34(10), 2016 (2019)

95. J. Cortez and C. Pasquini, Ring-oven based preconcentration technique for microanalysis: Simultaneous determination of Na, Fe, and Cu in fuel ethanol by laser induced breakdown spectroscopy, *Anal. Chem.* 85(3), 1547 (2013)

96. D. Bae, S. H. Nam, S. H. Han, J. Yoo, and Y. Lee, Spreading a water droplet on the laser-patterned silicon wafer substrate for surface-enhanced laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 113, 70 (2015)

97. N. Aras, and Ş. Yalçn, Investigating silicon wafer based substrates for dried-droplet analysis by laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 152, 84 (2019)

98. A. De Giacomo, C. Koral, G. Valenza, R. Gaudiuso, and M. Dell'Aglio, Nanoparticle enhanced laser-induced breakdown spectroscopy for microdrop analysis at subppm level, *Anal. Chem.* 88(10), 5251 (2016)

99. V. N. Rai, F. Y. Yueh, and J. P. Singh, Study of laser-induced breakdown emission from liquid under double-pulse excitation, *Appl. Opt.* 42(12), 2094 (2003)

100. K. Rifai, S. Laville, F. Vidal, M. Sabsabi, and M. Chaker, Quantitative analysis of metallic traces in water-based liquids by UV-IR double-pulse laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.* 27(2), 276 (2012)

101. Y. Wang, J. Kang, Y. Chen, and R. Li, Sensitive analysis of copper in water by LIBS–LIF assisted by simple sample pretreatment, *J. Appl. Spectrosc.* 86(2), 353 (2019)

102. M. Wall, Z. Sun, and Z. T. Alwahabi, Quantitative detection of metallic traces in water-based liquids by microwave-assisted laser-induced breakdown spectroscopy, *Opt. Express* 24(2), 1507 (2016)

103. R. Gaudiuso, M. Dell'Aglio, O. D. Pascale, G. S. Senesi, and A. D. Giacomo, Laser induced breakdown spectroscopy for elemental analysis in environmental, cultural heritage and space applications: A review of methods and results, *Sensors (Basel)* 10(8), 7434 (2010)

104. R. Kumar, A. Devanathan, N. Mishra and A. Rai, Quantification of heavy metal contamination in soil and plants near a leather tanning industrial area using Libs and TXRF, *J. Appl. Spectrosc.*, 86(5), 840 (2019)

105. R. Yi, X. Yang, R. Zhou, J. Li, H. Yu, Z. Hao, L. Guo, X. Li, Y. Lu, and X. Zeng, Determination of trace available heavy metals in soil using laser-induced breakdown spectroscopy assisted with phase transformation method, *Anal. Chem.* 90(11), 7080 (2018)

106. T. Wang, M. He, T. Shen, F. Liu, Y. He, X. Liu, and Z. Qiu, Multi-element analysis of heavy metal content in soils using laser-induced breakdown spectroscopy: A case study in eastern China, *Spectrochim. Acta B At. Spectrosc.* 149, 300 (2018)

107. S. Zhao, C. Song, X. Gao, and J. Lin, Quantitative analysis of Pb in soil by femtosecond-nanosecond double-pulse laser-induced breakdown spectroscopy, *Results in Physics* 15, 102736 (2019)

108. Y. Ding, G. Xia, H. Ji, and X. Xiong, Accurate quantitative determination of heavy metals in oily soil by laser induced breakdown spectroscopy (LIBS) combined with interval partial least squares (IPLS), *Anal. Methods* 11(29), 3657 (2019)

109. D. Meng, N. Zhao, M. Ma, L. Fang, Y. Gu, Y. Jia, J. Liu, and W. Liu, Application of a mobile laser-induced breakdown spectroscopy system to detect heavy metal elements in soil, *Appl. Opt.* 56(18), 5204 (2017)

110. M. Akhtar, A. Jabbar, S. Mehmood, N. Ahmed, R. Ahmed, and M. Baig, Magnetic field enhanced detection of heavy metals in soil using laser induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 148, 143 (2018)

111. M. Akhtar, A. Jabbar, S. Mahmood, Z. A. Umar, R. Ahmed, and M. Aslam Baig, Analysis of soil by magnetic field assisted calibration-free laser induced breakdown spectroscopy (CF-LIBS) and laser ablation–time-of-flight mass spectrometry (LA-TOF-MS), *Anal. Lett.* 52(14), 2312 (2019)

112. M. Akhtar, A. Jabbar, N. Ahmed, S. Mahmood, Z. Umar, R. Ahmed, and M. Baig, Analysis of lead and copper in soil samples by laser-induced breakdown spectroscopy under external magnetic field, *Appl. Phys. B* 125(6), 110 (2019)

113. G. Kim, J. Kwak, J. Choi, and K. Park, Detection of nutrient elements and contamination by pesticides in spinach and rice samples using laser-induced breakdown spectroscopy (LIBS), *J. Agric. Food Chem.* 60(3), 718 (2012)

114. R. A. Multari, D. A. Cremers, T. Scott, and P. Kendrick, Detection of pesticides and dioxins in tissue fats and rendering oils using laser-induced breakdown spectroscopy (LIBS), *J. Agric. Food Chem.* 61(10), 2348 (2013)

115. D. Yang and Y. Ying, Applications of Raman spectroscopy in agricultural products and food analysis: A review, *Appl. Spectrosc. Rev.* 46(7), 539 (2011)

116. L. M. Dale, A. Thewis, C. Boudry, I. Rotar, P. Dardenne, V. Baeten, and J. A. F. Pierna, Hyperspectral imaging applications in agriculture and agro-food product quality and safety control: A review, *Appl. Spectrosc. Rev.* 48(2), 142 (2013)

117. G. Nicolodelli, G. S. Senesi, A. C. Ranulfi, B. S. Marangoni, A. Watanabe, V. de Melo Benites, P. P. A. de Oliveira, P. Villas-Boas, and D. M. B. P. Milori, Double-pulse laser induced breakdown spectroscopy in orthogonal beam geometry to enhance line emission intensity from agricultural samples, *Microchem. J.* 133, 272 (2017)

118. S. Pandhija and A. K. Rai, Screening of brick-kiln area soil for determination of heavy metal Pb using LIBS, *Environ. Monit. Assess.* 148(1–4), 437 (2009)

119. C. Wang, L. Huang, M. Liu, P. Yang, T. Chen, H. Hu, W. Li, and M. Yao, Influence of water content on the detection of sensitivity of Pb in potatoes by LIBS, *Acta Agriculturae Universitatis Jiangxiensis* 38(2), 393 (2016)

120. C. Wang, L. Huang, M. Liu, T. Chen, H. Yang, H. Hu, and M. Yao, Enhancement of Pb intensity in potatoes by microwave assisted LIBS, *Chinese Journal of Analysis Laboratory* 35(5), 506 (2016)

121. C. Wang, L. Huang, S. Hu, M. Liu, T. Chen, H. Yang, H. Hu, and M. Yao, Feasibility of predicting the distribution of Cu in Navel orange pulp by LIBS spectra of peel, *Chinese Journal of Analysis Laboratory* 35(3), 253 (2016)

122. W. B. Li, L. T. Yao, M. H. Liu, L. Huang, M. Y. Yao, T. B. Chen, X. W. He, P. Yang, H. Q. Hu, and J. H. Nie, Influence of spectral pre-processing on PLS quantitative model of detecting cu in navel orange by LIBS, *Spectroscopy and Spectral Analysis* 35(5), 1392 (2015)

123. W. B. Li, M. Y. Yao, L. Huang, T. B. Chen, J. H. Zheng, S. Q. Fan, M. H. Liu, X. W. He, J. L. Lin, and J. Y. Ouyang, Effect of characteristic variable extraction on accuracy of Cu in Navel orange peel by LIBS, *Spectroscopy and Spectral Analysis* 35(7), 2021 (2015)

124. C. H. Wang, L. Huang, T. B. Chen, M. H. Liu, H. Yang, H. Q. Hu, and M. Y. Yao, Feasibility of analyzing Cr in rice husk and coarse rice with LIBS, *Spectroscopy and Spectral Analysis* 37(11), 3590 (2017)

125. H. Yang, L. Huang, M. Liu, T. Chen, C. Wang, and M. Yao, Comparison of precision and accuracy in analyzing Cd in rice by LIBS combined with multivariate regression, *Chinese Journal of Analysis Laboratory* 36(4), 399 (2017)

126. C. Wang, L. Huang, M. Liu, T. Chen, H. Yang, and M. Yao, Determination of heavy metal chromium in rice husk by LIBS coupled with SiPLS, *Laser & Optoelectronics Progress* 53(11), 113001 (2016)

127. C. Wang, L. Huang, M. Liu, T. Chen, H. Yang, and M. Yao, Comparison of accuracy in detecting Cr in pork by LIBS coupled with different characteristic lines, *Chinese Journal of Analysis Laboratory* 36(1), 32 (2017)

128. H. Yang, C. H. Wang, M. H. Liu, T. B. Chen, L. Huang, and M. Y. Yao, Improvement of LIBS accuracy in detecting Pb in pork by physical pretreatment of samples, *Spectroscopy and Spectral Analysis* 37(8), 2580 (2017)

129. G. F. Rao, L. Huang, M. H. Liu, T. B. Chen, J. Y. Chen, Z. Y. Luo, F. H. Xu, X. H. Xu, and M. Y. Yao, Identification of Huanglongbing-infected nave oranges based on laser-induced breakdown spectroscopy combined with different chemometric methods, *Appl. Opt.* 57(29), 8738 (2018)

130. J. Peng, Y. He, Z. Zhao, J. Jiang, F. Zhou, F. Liu and T. Shen, Fast visualization of distribution of chromium in rice leaves by re-heating dual-pulse laser-induced breakdown spectroscopy and chemometric methods, *Environ. Pollut.* 252(Pt B), 1125 (2019)

131. J. Peng, Y. He, J. Jiang, Z. Zhao, F. Zhou, and F. Liu, High-accuracy and fast determination of chromium content in rice leaves based on collinear dual-pulse laser-induced breakdown spectroscopy and chemometric methods, *Food Chem.* 295, 327 (2019)
132. X. Liu, X. Feng, F. Liu, J. Peng, and Y. He, Rapid identification of genetically modified maize using laser-induced breakdown spectroscopy, *Food Bioprocess Technol.* 12(2), 347 (2018)
133. T. Shen, W. Kong, F. Liu, Z. Chen, J. Yao, W. Wang, J. Peng, H. Chen, and Y. He, Rapid determination of cadmium contamination in lettuce using laser-induced breakdown spectroscopy, *Molecules* 23(11), 2930 (2018)
134. F. Liu, T. Shen, W. Kong, J. Peng, C. Zhang, K. Song, W. Wang, C. Zhang, and Y. He, Quantitative analysis of cadmium in tobacco roots using laser-induced breakdown spectroscopy with variable index and chemometrics, *Front. Plant Sci.* 9, 1316 (2018)
135. J. Peng, W. Xie, J. Jiang, Z. Zhao, F. Zhou, and F. Liu, Fast quantification of honey adulteration with laser-induced breakdown spectroscopy and chemometric methods, *Foods* 9(3), 341 (2020)
136. Z. Zhao, L. Chen, F. Liu, F. Zhou, J. Peng, and M. Sun, Fast Classification of Geographical Origins of Honey Based on Laser-Induced Breakdown Spectroscopy and Multivariate Analysis, *Sensors (Basel)* 20(7), 1878 (2020)
137. F. Liu, F. Liu, T. Shen, J. Wang, Y. He, C. Zhang, W. Zhou, T. Shen, J. Wang, Y. He, C. Zhang, and W. Zhou, Detection of sclerotinia stem rot on oilseed rape (Brassica napus L.) based on laser-induced breakdown spectroscopy, *Trans. ASABE* 62(1), 123 (2019)
138. J. Peng, Y. He, L. Ye, T. Shen, F. Liu, W. Kong, X. Liu, and Y. Zhao, Moisture influence reducing method for heavy metals detection in plant materials using laser-induced breakdown spectroscopy: A case study for chromium content detection in rice leaves, *Anal. Chem.* 89(14), 7593 (2017)
139. P. Yang, Y. Zhu, X. Yang, J. Li, S. Tang, Z. Hao, L. Guo, X. Li, X. Zeng, and Y. Lu, Evaluation of sample preparation methods for rice geographic origin classification using laser-induced breakdown spectroscopy, *J. Cereal Sci.* 80, 111 (2018)
140. P. Yang, R. Zhou, W. Zhang, R. Yi, S. Tang, L. Guo, Z. Hao, X. Li, Y. Lu, and X. Zeng, High-sensitivity determination of cadmium and lead in rice using laser-induced breakdown spectroscopy, *Food Chem.* 272, 323 (2019)
141. Y. Zhao, Q. Wang, X. Cui, G. Teng, K. Wei, and H. Liu, Discrimination of hazardous bacteria with combination laser-induced breakdown spectroscopy and statistical methods, *Appl. Opt.* 59(5), 1329 (2020)
142. Y. Du, Q. Wang, Y. Zhao, X. Cui, and Z. Peng, Rapid qualitative evaluation of velvet antler using laser-induced breakdown spectroscopy (LIBS), *Laser Phys.* 29(9), 095602 (2019)
143. J. Singh, R. Kumar, S. Awasthi, V. Singh, and A. K. Rai, Laser Induced breakdown spectroscopy: A rapid tool for the identification and quantification of minerals in cucurbit seeds, *Food Chem.* 221, 1778 (2017)
144. B. Sezer, S. Durna, G. Bilge, A. Berkkan, A. Yetisemiyen, and I. H. Boyaci, Identification of milk fraud using laser-induced breakdown spectroscopy (LIBS), *Int. Dairy J.* 81, 1 (2018)
145. T. V. Silva, S. Z. Hubinger, J. A. Gomes Neto, D. M. B. P. Milori, E. J. Ferreira, and E. C. Ferreira, Potential of Laser Induced Breakdown Spectroscopy for analyzing the quality of unroasted and ground coffee, *Spectrochim. Acta B At. Spectrosc.* 135, 29 (2017)
146. B. B. S. Jaswal and V. K. Singh, Analytical assessments of gallstones and urinary stones: A comprehensive review of the development from laser to LIBS, *Appl. Spectrosc. Rev.* 50(6), 473 (2015)
147. G. L. Coté, V. K. Unnikrishnan, R. Nayak, S. Bhat, S. Mathew, V. B. Kartha and C. Santhosh, Biomedical applications of laser-induced breakdown spectroscopy (LIBS), *Proc. SPIE 9332, Optical Diagnostics and Sensing XV: Toward Point-of-Care Diagnostics, 933211* (2015)
148. R. Grassi, E. Grifoni, S. Gufoni, S. Legnaioli, G. Lorenzetti, N. Macro, L. Menichetti, S. Pagnotta, F. Poggialini, C. Schiavo, and V. Palleschi, Three-dimensional compositional mapping using double-pulse micro-laser-induced breakdown spectroscopy technique, *Spectrochim. Acta B At. Spectrosc.* 127, 1 (2017)
149. T. R. Loree, The detection of elements in biomedical fluids by laser-induced breakdown spectroscopy, doi: 10.2351/1.5057553 (1983)
150. V. Singh, V. Kumar, J. Sharma, Y. Khajuria, and K. Kumar, Importance of laser induced breakdown spectroscopy for biomedical applications: A comprehensive review, *Materials Focus* 3(3), 169 (2014)
151. S. J. Rehse, H. Salimnia, and A. W. Miziolek, Laser-induced breakdown spectroscopy (LIBS): An overview of recent progress and future potential for biomedical applications, *J. Med. Eng. Technol.* 36(2), 77 (2012)
152. Y. Markushin, N. Melikechi, A. Marcano O., S. Rock, E. Henderson, and D. Connolly, LIBS-based multi-element coded assay for ovarian cancer application, in: Reporters, Markers, Dyes, Nanoparticles, and Molecular Probes for Biomedical Applications, International Society for Optics and Photonics, 2009, p. 719015
153. Q. Wang, W. Xiangli, G. Teng, X. Cui, and K. Wei, A brief review of laser-induced breakdown spectroscopy for human and animal soft tissues: Pathological diagnosis and physiological detection, *Appl. Spectrosc. Rev.* 1 (2020)
154. Y. Chu, Z. Zhang, Q. He, F. Chen, Z. Sheng, D. Zhang, H. Jin, F. Jiang, and L. Guo, Half-life determination of inorganic-organic hybrid nanomaterials in mice using laser-induced breakdown spectroscopy, *J. Adv. Res.* 24, 353 (2020)
155. X. Chen, X. Li, X. Yu, D. Chen, and A. Liu, Diagnosis of human malignancies using laser-induced breakdown spectroscopy in combination with chemometric methods, *Spectrochim. Acta B At. Spectrosc.* 139, 63 (2018)
156. X. Chen, X. Li, S. Yang, X. Yu, and A. Liu, Discrimination of lymphoma using laser-induced breakdown spectroscopy conducted on whole blood samples, *Biomed. Opt. Express* 9(3), 1057 (2018)

157. X. Li, X. An, R. Fan, X. Yu, and D. Chen, Classification of soft tissues using laser-induced breakdown spectroscopy, SPIE Proceedings Novel Biophotonics Techniques and Applications IV, 2017, p. 1041303

158. X. Li, S. Yang, R. Fan, X. Yu, and D. Chen, Discrimination of soft tissues using laser-induced breakdown spectroscopy in combination with k nearest neighbors (kNN) and support vector machine (SVM) classifiers, *Opt. Laser Technol.* 102, 233 (2018)

159. X. Li, S. Yang, X. Chen, G. Yao, A. Liu, and X. Yu, Multi-elemental imaging of breast cancer tissues using laser-induced breakdown spectroscopy. In: 2019 Conference on Lasers and Electro-Optics Europe & European Quantum Electronics Conference (CLEO/Europe-EQEC), IEEE, 2019

160. G. Teng, Q. Wang, H. Zhang, W. Xiangli, H. Yang, X. Qi, X. Cui, B. S. Idrees, K. Wei, and M. N. Khan, Discrimination of infiltrative glioma boundary based on laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 165, 105787 (2020)

161. Q. Wang, G. Teng, X. Qiao, Y. Zhao, J. Kong, L. Dong, and X. Cui, Importance evaluation of spectral lines in Laser-induced breakdown spectroscopy for classification of pathogenic bacteria, *Biomed. Opt. Express* 9(11), 5837 (2018)

162. Y. Moon, J. H. Han, J. H. Choi, S. Shin, Y. C. Kim, and S. Jeong, Mapping of cutaneous melanoma by femtosecond laser-induced breakdown spectroscopy, *J. Biomed. Opt.* 24(3), 1 (2018)

163. J. J. Lee, Y. Moon, J. H. Han, and S. Jeong, Analysis of major elements in pigmented melanocytic chicken skin using laser-induced breakdown spectroscopy, *J. Biophoton.* 10(4), 523 (2017)

164. S. Moncayo, F. Trichard, B. Busser, M. Sabatier-Vincent, F. Pelascini, N. Pinel, I. Templier, J. Charles, L. Sancey, and V. Motto-Ros, Multi-elemental imaging of paraffin-embedded human samples by laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 133, 40 (2017)

165. B. Busser, S. Moncayo, F. Trichard, V. Bonneterre, N. Pinel, F. Pelascini, P. Dugourd, J. L. Coll, M. D'Incan, J. Charles, V. Motto-Ros, and L. Sancey, Characterization of foreign materials in paraffin-embedded pathological specimens using in situ multi-elemental imaging with laser spectroscopy, *Mod. Pathol.* 31(3), 378 (2018)

166. F. J. Fortes, S. Guirado, A. Metzinger, and J. J. Laserna, A study of underwater stand-off laser-induced breakdown spectroscopy for chemical analysis of objects in the deep ocean, *J. Anal. At. Spectrom.* 30(5), 1050 (2015)

167. M. Lawrence-Snyder, J. P. Scaffidi, W. F. Pearman, C. M. Gordon, and S. M. Angel, Issues in deep ocean collinear double-pulse laser induced breakdown spectroscopy: Dependence of emission intensity and inter-pulse delay on solution pressure, *Spectrochim. Acta B At. Spectrosc.* 99, 172 (2014)

168. N. Idris, M. Ramli, R. Hedwig, Z. S. Lie, and K. H. Kurniawan, Preliminary study on detection sediment contamination in soil affected by the Indian Ocean giant tsunami 2004 in Aceh, Indonesia using laser-induced breakdown spectroscopy (LIBS), *AIP Conference Proceedings* 1719, 030051 (2016)

169. P. Pease, and V. Tchakerian, Source provenance of carbonate grains in the Wahiba Sand Sea, Oman, using a new LIBS method, *Aeolian Res.* 15, 203 (2014)

170. J. Song, J. Guo, Y. Tian, Y. Lu, and R. Zheng, Effect of LFTSD on underwater laser induced breakdown spectroscopy with different laser energies, *Proceedings Volume 10461, AOPC 2017: Optical Spectroscopy and Imaging* 78 (2017)

171. Y. Tian, B. Xue, J. Song, Y. Lu, Y. Li, and R. Zheng, Comparative investigation of laser-induced breakdown spectroscopy in bulk water using 532- and 1064-nm lasers, *Appl. Phys. Express* 10(7), 072401 (2017)

172. B. Xue, N. Li, Y. Lu, Y. Li, and R. Zheng, Emission enhancement of underwater collinear dual-pulse laser-induced breakdown spectroscopy with the second pulse defocused, *Appl. Phys. Lett.* 110(10), 101102 (2017)

173. J. Song, J. Guo, Y. Tian, B. Xue, Y. Lu, and R. Zheng, Investigation of laser-induced plasma characteristics in bulk water under different focusing arrangements, *Appl. Opt.* 57(7), 1640 (2018)

174. J. Guo, A. S. Mahmoud, N. Li, J. Song, and R. Zheng, Study of pressure effects on ocean *in-situ* detection using laser-induced breakdown spectroscopy, *Plasma Sci. Technol.* 21(3), 034022 (2019)

175. N. Li, J. Guo, C. Zhang, Y. Zhang, Q. Li, Y. Tian, and R. Zheng, Salinity effects on elemental analysis in bulk water by laser-induced breakdown spectroscopy, *Appl. Opt.* 58(14), 3886 (2019)

176. N. Li, J. Guo, L. Zhu, Y. Lu, Y. Tian, and R. Zheng, Effects of ambient temperature on laser-induced plasma in bulk water, *Appl. Spectrosc.* 73(11), 1277 (2019)

177. B. Xue, Y. Tian, Y. Lu, Y. Li, and R. Zheng, Characteristics of the secondary breakdown of DP-LIBS in bulk water with different axial focusing arrangements and laser energies, *Spectrochim. Acta B At. Spectrosc.* 151, 20 (2019)

178. Q. Li, Y. Tian, B. Xue, N. Li, W. Ye, Y. Lu, and R. Zheng, Improvement in the analytical performance of underwater LIBS signals by exploiting the plasma image information, *J. Anal. At. Spectrom.* 35(2), 366 (2020)

179. J. Guo, Y. Lu, K. Cheng, J. Song, W. Ye, N. Li, and R. Zheng, Development of a compact underwater laser-induced breakdown spectroscopy (LIBS) system and preliminary results in sea trials, *Appl. Opt.* 56(29), 8196 (2017)

180. W. Ye, J. Guo, N. Li, F. Qi, K. Cheng, and R. Zheng, Depth profiling investigation of seawater using combined multi-optical spectrometry, *Appl. Spectrosc.* 74(5), 563 (2020)

181. S. Guirado, F. J. Fortes, V. Lazic, and J. J. Laserna, Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea, *Spectrochim. Acta B At. Spectrosc.* 74–75, 137 (2012)

182. S. Guirado, F. J. Fortes, and J. Javier Laserna, Elemental analysis of materials in an underwater archeological shipwreck using a novel remote laser-induced breakdown spectroscopy system, *Talanta* 137, 182 (2015)

183. B. Thornton, T. Sakka, T. Takahashi, A. Tamura, A. Matsumoto, and T. Ura, Laser-induced breakdown spectroscopy for *in situ* chemical analysis at sea, in: 2013 IEEE International Underwater Technology Symposium, 2013

184. B. Thornton, T. Takahashi, T. Sato, T. Sakka, A. Tamura, A. Matsumoto, T. Nozaki, T. Ohki, and K. Ohki, Development of a deep-sea laser-induced breakdown spectrometer for in situ multi-element chemical analysis, *Deep Sea Res. Part I Oceanogr. Res. Pap.* 95, 20 (2015)

185. T. Takahashi, S. Yoshino, Y. Takaya, T. Nozaki, K. Ohki, T. Ohki, T. Sakka, and B. Thornton, Quantitative in situ mapping of elements in deep-sea hydrothermal vents using laser-induced breakdown spectroscopy and multivariate analysis, *Deep Sea Res. Part I Oceanogr. Res. Pap.* 158, 103232 (2020)

186. F. R. Doucet, G. Lithgow, R. Kosierb, P. Bouchard, and M. Sabsabi, Determination of isotope ratios using Laser-Induced Breakdown Spectroscopy in ambient air at atmospheric pressure for nuclear forensics, *J. Anal. At. Spectrom.* 26(3), 536 (2011)

187. A. Sarkar, V. M. Telmore, D. Alamelu, and S. K. Aggarwal, Laser induced breakdown spectroscopic quantification of platinum group metals in simulated high level nuclear waste, *J. Anal. At. Spectrom.* 24(11), 1545 (2009)

188. B. Bhatt, K. Hudson Angeyo, and A. Dehayem-Kamadjeu, LIBS development methodology for forensic nuclear materials analysis, *Anal. Methods* 10(7), 791 (2018)

189. D. A. Cremers, A. Beddingfield, R. Smithwick, R. C. Chinni, C. R. Jones, B. Beardsley, and L. Karch, Monitoring uranium, hydrogen, and lithium and their isotopes using a compact laser-induced breakdown spectroscopy (LIBS) probe and high-resolution spectrometer, *Appl. Spectrosc.* 66(3), 250 (2012)

190. S. Almaviva, L. Caneve, F. Colao, R. Fantoni, and G. Maddaluno, Remote-LIBS characterization of ITER-like plasma facing materials, *J. Nucl. Mater.* 421(1–3), 73 (2012)

191. C. Li, C. L. Feng, H. Y. Oderji, G. N. Luo, and H. B. Ding, Review of LIBS application in nuclear fusion technology, *Front. Phys.* 11(6), 114214 (2016)

192. Y. Qiu, J. Wu, X. Li, T. Liu, F. Xue, Z. Yang, Z. Zhang, and H. Yu, Parametric study of fiber-optic laser-induced breakdown spectroscopy for elemental analysis of Z3CN20-09M steel from nuclear power plants, *Spectrochim. Acta B At. Spectrosc.* 149, 48 (2018)

193. J. Wu, H. Yu, Y. Qiu, Z. Zhang, T. Liu, F. Xue, W. Yu, X. Li, and A. Qiu, X. Li and A. Qiu: Plasma characteristics and element analysis of steels from a nuclear power plant based on fiber-optic laser-induced breakdown spectroscopy, *J. Phys. D Appl. Phys.* 52(1), 014006 (2019)

194. L. Cai, Z. Wang, C. Li, X. Huang, D. Zhao, and H. Ding, Development of an in situ diagnostic system for mapping the deposition distribution on plasma facing components of the HL-2M tokamak, *Rev. Sci. Instrum.* 90(5), 053503 (2019)

195. Z. Hu, C. Li, Q. Xiao, P. Liu, F. Ding, H. Mao, J. Wu, D. Zhao, H. Ding, and G. N. Luo, Preliminary results ofin situlaser-induced breakdown spectroscopy for the first wall diagnostics on EAST, *Plasma Sci. Technol.* 19(2), 025502 (2017)

196. D. Zhao, C. Li, Z. Hu, C. Feng, Q. Xiao, R. Hai, P. Liu, L. Sun, D. Wu, C. Fu, J. Liu, N. Farid, F. Ding, G. N. Luo, L. Wang, and H. Ding, Remote in situ laser-induced breakdown spectroscopic approach for diagnosis of the plasma facing components on experimental advanced superconducting tokamak, *Rev. Sci. Instrum.* 89(7), 073501 (2018)

197. Z. Hu, N. Gierse, C. Li, J. Oelmann, D. Zhao, M. Tokar, X. Jiang, D. Nicolai, J. Wu, F. Ding, S. Brezinsek, H. Ding, G. N. Luo, and C. Linsmeier, Laser induced ablation spectroscopy for in situ characterization of the first wall on EAST tokamak, *Fusion Eng. Des.* 135, 95 (2018)

198. M. Imran, L. Y. Sun, P. Liu, H. Sattar, D. Zhao, Z. Mu, and H. Ding, Depth profiling of tungsten coating layer on CuCrZr alloy using LIBS approach, *Surf. Interface Anal.* 51(2), 210 (2019)

199. P. Liu, D. Wu, L. Y. Sun, D. Y. Zhao, R. Hai, C. Li, H. Ding, Z. H. Hu, L. Wang, J. S. Hu, J. L. Chen, and G. N. Luo, Laser-induced breakdown spectroscopy to monitor ion cyclotron range of frequency wall cleaning Li/D codeposition in EAST tokamak, *Fusion Eng. Des.* 118, 98 (2017)

200. J. Liu, D. Wu, C. Fu, R. Hai, X. Yu, L. Sun, and H. Ding, Improvement of quantitative analysis of molybdenum element using PLS-based approaches for laser-induced breakdown spectroscopy in various pressure environments, *Plasma Sci. Technol.* 21(3), 034017 (2019)

201. C. Li, N. Gierse, J. Oelmann, S. Brezinsek, M. Rasinski, C. P. Dhard, T. S. Pedersen, R. Konig, Y. F. Liang, H. B. Ding, C. Linsmeier and the W7-X team, Laser-induced breakdown spectroscopy for Wendelstein 7-X stellarator limiter tile analysis, *Phys. Scr. T* 170, 5 (2017)

202. R. Hai, L. Sun, D. Wu, Z. He, H. Sattar, J. Liu, W. Tong, C. Li, C. Feng, and H. Ding, Enhanced laser-induced breakdown spectroscopy using the combination of circular and annular laser pulses, *J. Anal. At. Spectrom.* 34(10), 1982 (2019)

203. S. Harilal, C. Murzyn, M. Phillips, and J. B. Martin, Hyperfine structures and isotopic shifts of uranium transitions using tunable laser spectroscopy of laser ablation plumes, *Spectrochim. Acta B At. Spectrosc.* 169, 105828 (2020)

204. E. J. Kautz, P. J. Skrodzki, M. Burger, B. E. Bernacki, I. Jovanovic, M. C. Phillips, and S. S. Harilal, Time-resolved imaging of atoms and molecules in laser-produced uranium plasmas, *J. Anal. At. Spectrom.* 34(11), 2236 (2019)

205. S. Harilal, P. Diwakar, N. LaHaye, and M. Phillips, Spatio-temporal evolution of uranium emission in laser-produced plasmas, *Spectrochim. Acta B At. Spectrosc.* 111, 1 (2015)

206. M. C. Phillips, B. E. Brumfield, N. LaHaye, S. S. Harilal, K. C. Hartig, and I. Jovanovic, Two-dimensional fluorescence spectroscopy of uranium isotopes in femtosecond laser ablation plumes, *Sci. Rep.* 7(1), 1 (2017)

207. J. Song, G. C. Y. Chan, X. Mao, J. D. Woodward, R. W. III Smithwick, T. G. Schaaff, A. C. Stowe, C. D. Harris, R. Zheng, V. Zorba, and R. E. Russo, Multivariate nonlinear spectral fitting for uranium isotopic analysis with laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 150, 67 (2018)

208. X. Mao, G. C. Y. Chan, I. Choi, V. Zorba, and R. E. Russo, Combination of atomic lines and molecular bands for uranium optical isotopic analysis in laser induced plasma spectrometry, *J. Radioanal. Nucl. Chem.* 312(1), 121 (2017)

209. S. Maji, S. Kumar, K. Sundararajan, and K. Sankaran, Feasibility study for quantification of lanthanides in LiF–KCl salt by laser induced breakdown spectroscopy, *J. Radioanal. Nucl. Chem.* 314(2), 1279 (2017)

210. J. Oelmann, N. Gierse, C. Li, S. Brezinsek, M. Zlobinski, B. Turan, S. Haas, and C. Linsmeier, Depth-resolved sample composition analysis using laser-induced ablation-quadrupole mass spectrometry and laser-induced breakdown spectroscopy, *Spectrochim. Acta B At. Spectrosc.* 144, 38 (2018)

211. D. Zhao, R. Yi, J. Oelmann, S. Brezinsek, M. Rasinski, Y. Gao, M. Mayer, C. Dhard, and M. Krause, Ex situ analysis of W7-X divertor plasma-facing components by picosecond laser diagnostics, *Phys. Scr.* 2020(T171), 014018 (2020)