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Industrial applications of laser-induced breakdown spectroscopy: a review

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In this review we present a short, although comprehensive, review on the industrial applications of laser-induced breakdown spectroscopy (LIBS). Attention has been devoted to the applications where LIBS can potentially make a difference with respect to other traditional techniques, namely steel and coal industries, and new emerging applications, where the intrinsic features of LIBS are particularly interesting, such as sorting of waste for selective recycling.

1. Introduction

Laser-induced breakdown spectroscopy is an emerging analytical technique, which has attracted the attention of the spectrochemistry community due to the intrinsic simplicity of the experimental apparatus and the possibility of performing remote elemental analysis in a very short time, without the need for pre-treatment of samples.¹

Many authors while describing the characteristics of LIBS start, in the introduction of their papers, with the description of the many different fields of application of laser-induced breakdown spectroscopy. Among them, a very generic term 'Industrial Applications' is always present, accompanied by a few references, often quoting the studies of the same authors or, in the best cases, some of the excellent reviews or book chapters that have been published in recent past.^{2–5}

A search on the Scopus® database with keywords ((“Laser-Induced Plasma Spectroscopy” OR “Laser-Induced Breakdown Spectroscopy”) AND (“industry” OR “industrial”)) reports about 500 papers in 35 years, starting with the manuscript published by Hartford *et al.*⁶ in 1983 about possible industrial applications of the then newborn LIBS technique and ending with the 65 papers published on the same topic in 2019.

Important recent developments in LIBS analysis, related both to the improvements of the experimental setups, with the introduction of mobile double-pulse systems,^{7–9} for example, and to the development of efficient machine learning techniques^{10–14} that allow acquisition of informative spectra and the analysis of large quantities of data in real time, have boosted the interest in out-of-the-lab applications of LIBS, among which

industrial applications appear to have benefitted from most of these technological advances.

As for the general literature in LIBS, the studies related to industrial applications have also increased exponentially in time (see Fig. 1).

However, as discussed in ref. 15, most of the results presented in the literature as industrial applications of LIBS should be considered, more realistically, as 'proofs of principle' often paid for by public research organizations and somewhat forgotten at the end of the project, after the publication of a couple of papers on the results obtained. On the other hand, it is also fair to consider that the important results obtained using LIBS in the industrial fields are probably not disclosed, for preserving the value of the research investment of the industrial partner.

Maintaining our discussion on what is available in the literature, beyond the plethora of generic references, in a few

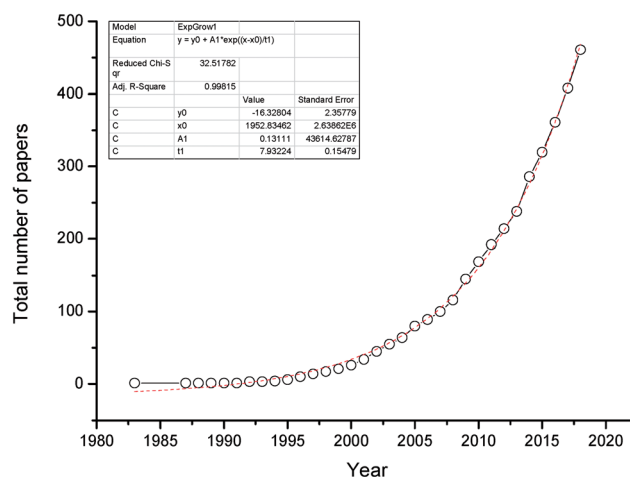


Fig. 1 Total number of papers published since 1987 referring to industrial application of LIBS. The red dashed line is the best exponential fit of the data (black circles).

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applications the LIBS technique seems to be mature enough for substituting or, at least, being complementary to other consolidated techniques. These applications will be discussed in the next sections.

2. Applications of LIBS in industry

The potential of laser-induced breakdown spectroscopy for on-line measurements in the energy production industry was immediately clear to the fathers of modern LIBS. The work of Hartford *et al.*⁶ was published only two years after the publication of the two fundamental papers of Loree and Radziemski,^{16,17} where the acronym LIBS was officially introduced (the first 'LIBS' paper is commonly credited to Brech and Cross,¹⁸ in 1962). The energy industry, in fact, is considered one of the major fields in which LIBS could become the election technique.

2.1 Energy industry

2.1.1 Fossil fueled power plants. The paper by Hartford *et al.*⁶ proposed LIBS as a diagnostic tool for quality control of the process of gasification of fossil fuels. The authors exploited the peculiarities of the LIBS technique for the diagnosis of trace impurities (Na, K and S) on a coal gasifier, to monitor fossil energy processes. Coal has been, since then, one of the major

lines of research for LIBS, especially in China, where coal power plants are the main sources of energy of the country.¹⁹ Bauer and Buckley²⁰ in a recent paper mentioned coal analysis among the most promising industrial applications of LIBS. In their reviews on LIBS research on coal in China, Zhao *et al.*¹⁹ and Sheta *et al.*²¹ presented several results obtained by Chinese researchers for the coal industry. Most of the papers available in the literature, however, are either very generic and do not give essential information about the practical application of LIBS at power plants, or report the results of laboratory analysis under highly simplified experimental conditions (*i.e.* homogeneous samples obtained by pressing powdered coal in the form of pellets^{22–27}) which can hardly be transferred to the real industrial application.

LIBS systems have been, in fact, proposed for on-line analysis of coal in power plants (see, for example, ref. 28 or 29). However, only a few real tests of LIBS in the coal industry were actually performed.

One of these was done in 2002 by Chadwick and Body³⁰ for the determination of ash content in low-ash lignite. Ash content is one of the most important parameters in coal combustion, since an excessive content of ashes could produce fouling of the burner. It should be noted, however, that the authors determined the ash content starting from the elemental composition of the samples, using carbon as the internal standard. This is acceptable when similar types of coal are burnt in the power

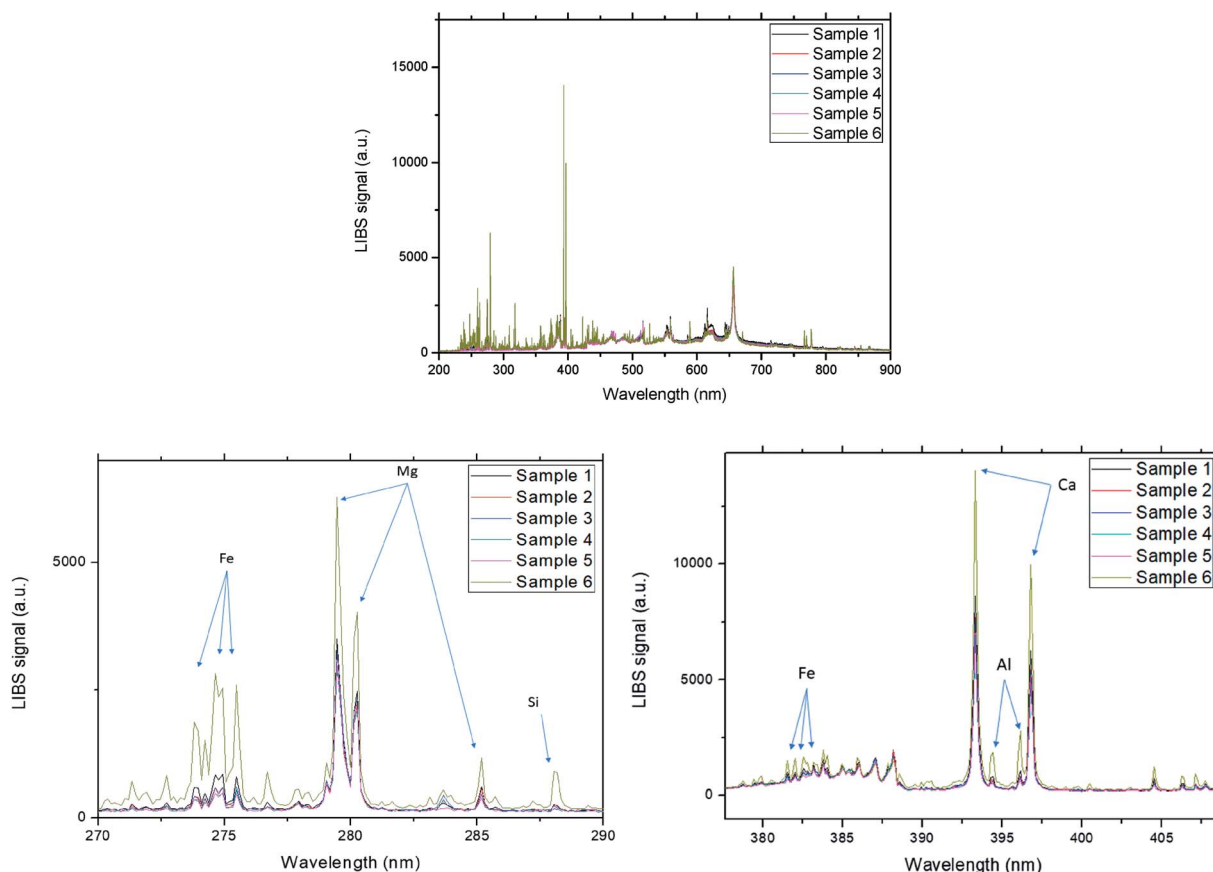


Fig. 2 Comparison of LIBS spectra from the same batch of coal. Top: full LIBS spectrum; bottom: details of the main elements' emission lines.



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plant but might introduce large errors in the general case (carbon content in coal could vary up to 25% depending on the origin and quality of the coal used). The authors also noted that the intrinsic inhomogeneity of the samples is the major obstacle to obtain the precise determination of the elemental composition of the coal, which is needed, according to their approach, for the determination of the ash content. A similar approach was used in coal power plants by Gaft *et al.*³¹ for the on-line determination of ash content in coal. In fact, even for coal samples coming from the same batch, the LIBS spectra show a large variability in the intensity of the lines associated with the main elements that affect the ash content (Al, Si, Fe and Mg), reflecting the large variations in their concentration from sample to sample (see Fig. 2).

Legnaioli *et al.*³² obtained a very good agreement between predicted and nominal values for ash content in coal using an artificial neural network method, preceded by spectral selection for outlier removal (see Fig. 3).

Another key parameter for monitoring and optimizing the efficiency of coal combustion in power plants is the Upper Calorific Value (UCV) of coal.³³ As for the determination of ash content, several papers have been published reporting laboratory results on homogenized coal pellets^{25,34} which demonstrated the practical feasibility of LIBS analysis but, as in the case of ash content determination, do not transfer immediately to the on-line analysis of coal on the conveyor belt at power plants.

A critical point for coal analysis at the conveyor belt is given by the large changes in focus position that occur during the operation of the plant. Gaft *et al.*³¹ used an auto-focusing system of the laser beam on the surface of the samples; the system is very effective, although the use of delicate moving components in the industrial environment can be problematic. De Saro *et al.*³⁵ worked around the problem by picking a measurement point where the coal samples remain at a fixed distance with respect to the laser focusing lens. This approach is hardly

transferrable to different coal plants; therefore, it cannot be considered as a solution of the problem.

A promising method for avoiding sampling and treatment of the coal and managing the variations in the lens-to-sample distance at the conveyor belt has been recently proposed by Redoglio *et al.*³⁶ The method proposed by the authors allows, in principle, the measurement of the main parameters of coal (ash content and calorific value) without sampling by using a large depth of field (more than 10 cm) LIBS system. A similar experimental setup has been realized and successfully tested by the authors of ref. 32 (see Fig. 4).

Also in this case, an artificial neural network can be set-up for calculating the UCP. However, the spectral regions to use as input of the ANN must be chosen carefully, corresponding to the emission lines of the elements actually affecting the output (upper calorific power). Several semi-empirical formulas exist, linking coal characteristics to the UCP. The Dulong formula³³ links the UCV to the carbon, hydrogen, oxygen and sulfur content of coal; Mason–Gandhi formula³⁷ does not use oxygen concentration, substituting this information with the ash content value. More complex, non-linear formulas have also been proposed.³⁸

An alternative formula was obtained by Palleschi, Paganini and Masci (PPM),³⁹ assuming a more general linear relationship

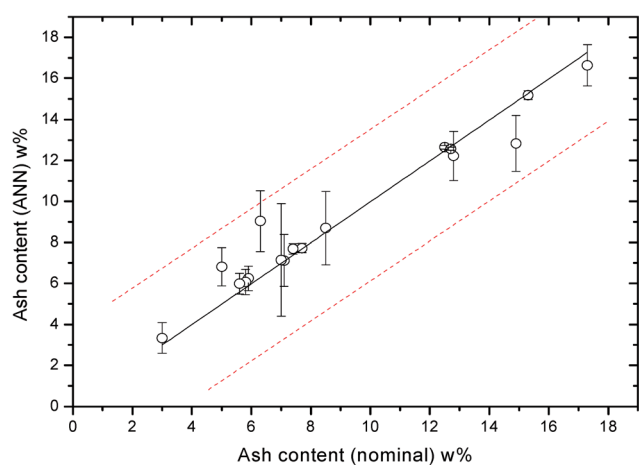


Fig. 3 Predicted values of ash content vs. nominal content for different coal types. The agreement is good (black line represents perfect agreement), with a maximum difference less than 4% (red lines).

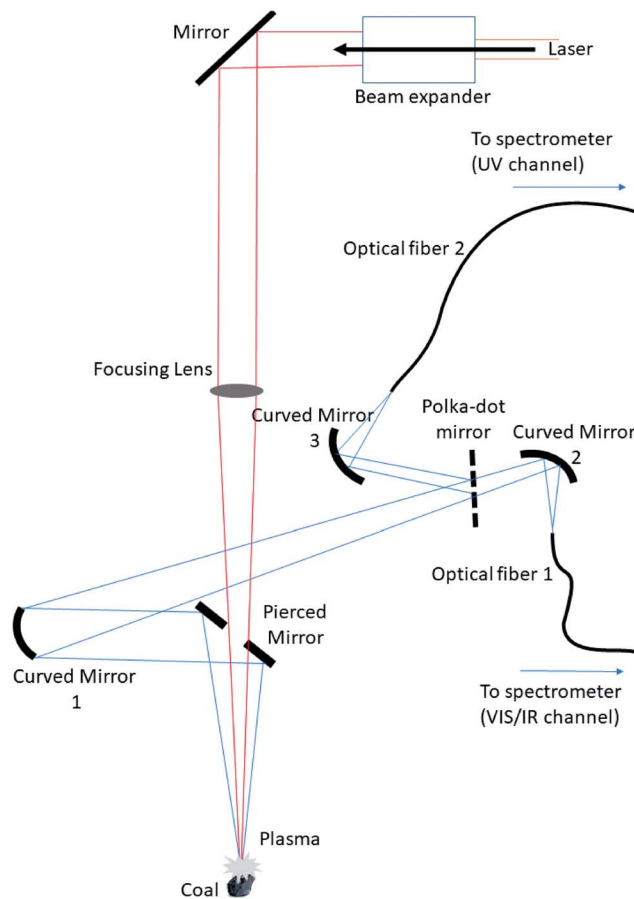


Fig. 4 Large depth of field double-pulse LIBS apparatus realized at the ALS Laboratory in Pisa.³²



between UCP and the concentrations of carbon, hydrogen, sulfur, nitrogen and the ash content. The coefficients of the linear combination were obtained through a partial least squares analysis⁴⁰ applied to all the samples in a large database of over 4000 different types of coal. After that, the model was progressively simplified, removing the elements less correlated to the UCV. Palleschi, Paganini and Masci found that using just carbon and hydrogen concentration the PPM formula

$$\text{UCP}_{\text{PPM}} = 69.45C + 224.3H + 853.3 \quad (1)$$

reproduces well the experimental UCPs of the samples.

Based on this result, Palleschi, Paganini and Masci limited the spectral regions to be used as inputs in the ANN to the carbon and hydrogen lines, obtaining very good agreement between predicted UCP and nominal values, for the samples studied in ref. 32 (Fig. 5).

Recent applications of LIBS to oil shale have been proposed for discrimination from limestone by Paris *et al.*⁴¹ and for determination of the calorific power.⁴²

LIBS was also used for *in situ* diagnosis of the products of combustion of oil-fired power plants in 2002 by Corsi *et al.*,⁴³ who demonstrated the possibility of performing remote LIBS analysis for the control of the emissions of fossil fueled power plants.

2.1.2 Nuclear industry. The possibility of using LIBS for the analysis of materials in the hostile environment of a nuclear power plant was discussed for the first time by Davies *et al.* in 1996.⁴⁴ However, it was the UK firm Applied Photonics which pioneered the studies and application of LIBS to the nuclear industry.^{45,46} Following the same route, several applications of LIBS for the analysis of nuclear materials were reported in the past few years. Harilal *et al.* studied the space and temporal evolution of uranium LIBS spectra.⁴⁷ Lang *et al.*⁴⁸ in 2018 used LIBS for the study of nuclear contaminated steel (304 stainless steel type; this material is often used in nuclear material reprocessing sites). The authors performed stratigraphic

analysis to understand the penetration depth of ⁹⁰Sr and ¹³⁷Cs under the metal surface. They found that only Sr can be detected at realistic concentration; the depth profiles obtained, after optimization of the laser energy, were in very good agreement with glow-discharge-optical emission spectroscopy. LIBS was also used for the analysis of nuclear-grade graphite by Horsfall *et al.*⁴⁹ in 2019. The authors remarked that the discrimination by LIBS of nuclear grade graphite from other C-based materials in nuclear waste can be plagued by errors in classification and proposed more robust statistical methods, along with the use of molecular carbon emission, for the analysis of waste which can be especially useful for decommissioning and waste management. A methodology for LIBS forensic analysis of nuclear materials has been recently proposed by Bhatt *et al.*⁵⁰

A robotic LIBS system has been proposed for detecting the presence of chlorine-bearing salts on the surface of canisters used for dry storage of spent nuclear fuel.⁵¹

Of special interest is the application of a particular kind of LIBS analysis, called LAMIS,⁵² for remote analysis of uranium isotopes using femtosecond lasers.⁵³ In LAMIS, the emissions associated with the transitions of simple molecules are studied, to enhance the isotopic spectral separation, which is typically very difficult to resolve in atomic emission.^{54–56}

2.1.3 Solar energy industry. The first application of LIBS to solar cell analysis was proposed by Hidalgo *et al.* in 1996.⁵⁷ The authors used the capability of the technique for performing in-depth analysis for quality control of the titanium dioxide antireflection coating in solar cells. The same group also proposed the use of LIBS tomographic and surface mapping of carbon impurities in silicon.⁵⁸ An application of LIBS which appears to be very interesting in the field of the solar cell industry is the analysis of thin film CuIn_{1-x}Ga_xSe₂ (CIGS) solar cells. Kowalczyk *et al.*⁵⁹ used LIBS for determining the concentration of sodium in CIGS cells. Similarly, Lee *et al.*^{60–62} studied the absorption layer of CIGS cells, in terms of ablation and spectroscopic characteristics, for a rapid composition analysis of thin film solar cells. Diego-Vallejo *et al.*^{63,64} studied the selective ablation of copper-indium-diselenide solar cells using LIBS coupled with artificial neural networks and classification methods. Choi *et al.*^{65,66} studied the effect of laser spot size and wavelength in LIBS analysis of CIGS. Kim *et al.*^{67,68} compared LIBS thin film and bulk analysis of CuIn_{1-x}Ga_xSe₂, studying the influence of wavelength on LIBS measurement of thin film CIGS. In *et al.*^{69–72} focused their research on the improvement of selenium analysis and reproducibility of LIBS measurements of CIGS cells with the fluctuation of the experimental parameters and applied self-absorption normalization to improve the reliability of the LIBS results; the conclusion of their work is that LIBS can be a viable technique for rapid quantitative analysis and depth profiling of CIGS thin solar cell films.

2.2 Metal industry

Many laboratory studies are reported in the LIBS literature, dealing with the analysis of metals and metallic alloys,^{73–77}

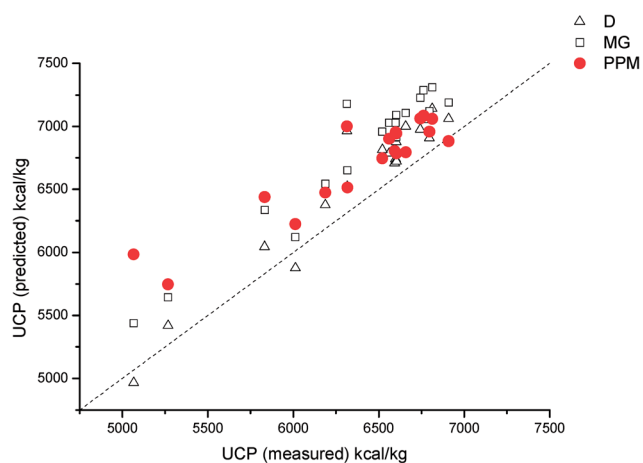


Fig. 5 Comparison between the Dulong (open triangles), Mason–Gandhi (open squares) and Palleschi–Paganini–Masci (red circles) formulas, for the coal samples analysed in the database.



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which can be indirectly referred to industrial applications. Two reviews by Noll *et al.* outlined the major applications up to the date of their publication;^{3,78} new applications of LIBS in the metal industry have been presented and discussed in ref. 79. In the following, attention will be restricted to the applications of LIBS successfully demonstrated in the industrial environment, for process optimization and quality control. It should be considered, however, that the LIBS technique can be a valid alternative to spark OES for off-line analysis of metals, as demonstrated in many recent papers.

2.2.1 Steel industry. The economic importance of the steel industry has motivated many research studies aimed at the optimization of the production processes or quality control of the products. The LIBS technique is particularly suitable for the analysis of metals, and therefore many applications in the metallurgic industry (mainly steel and aluminum) have been proposed and tested in the past few decades. One of the first industrial applications of LIBS steel analysis was the on-line analysis of steel pipes for early detection of surface defects (the LIBSGRAIN project, funded by the European Commission)⁸⁰ (see Fig. 6). Aimoto *et al.* performed (off-line) a similar analysis.⁸¹

In 2003, Kraushaar *et al.* made off-line analysis of slag samples from a steel plant⁸² to simulate the on-line analysis of molten steel.⁸³ Gondal *et al.*⁸⁴ studied by LIBS the possible presence of dangerous elements in waste slag from the steel industry. The authors analyzed the levels of contamination by cadmium, calcium, sulfur, magnesium, chromium, manganese, titanium, barium, phosphorus and silicon in slag samples and found very good agreement with the results of conventional chemical analysis. They concluded that LIBS can be effectively applied to rapid online analysis of iron slag waste.

The LACOMORE (laser-based continuous monitoring and resolution of steel grades in sequence casting machines) project, funded by the European Commission, has demonstrated the possibility of on-line control of the process of continuous steel casting.^{8,85–88} This would provide large potential saving by reducing the steel waste, through a careful control of the intermix region in passing from one steel grade to the other (Fig. 7).

The Canadian firm Tecnar is offering a LIBS system, named GalvaLIBS, for the analysis of molten metals, including steel.⁸⁹

On-line depth profiling of Mg-coated galvanized steel on moving targets has been documented by Ruiz *et al.*⁹⁰ LIBS has also been used for the analysis of surface coating on steel by



Fig. 6 LIBSGRAIN project: mounting of the laser at the plant for pipe analysis (left) and mapping of steel composition (right).

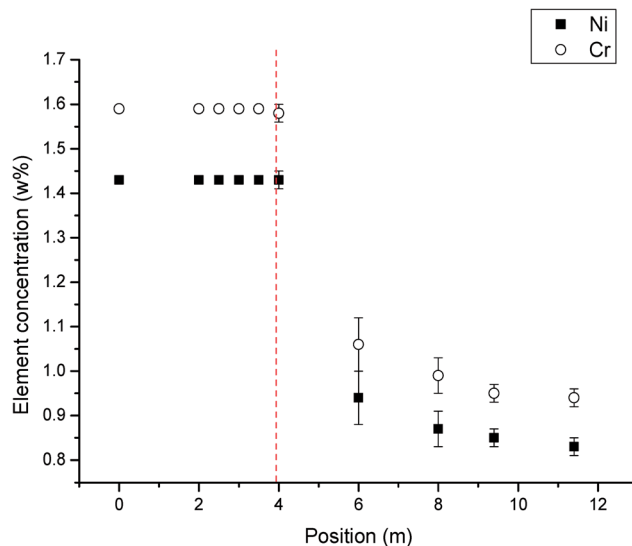


Fig. 7 LACOMORE project: change in Ni and Cr concentration measured by double pulse LIBS in continuous casting of steel (data from ref. 85).

Balzer *et al.* (Al coating⁹¹ and Zn coating⁹²), Nagy *et al.* (Al–Ni coating)⁹³ and Pacher *et al.* (Ni–Co coating).⁹⁴

Elfaham *et al.*⁹⁵ used LIBS for evaluating the surface hardness of steel samples, using the ratio between the calcium ion and neutral lines (Ca II/Ca I) and compared the results with the Vickers mechanical method. The authors found a very good agreement between the two measurements, once self-absorption corrections are applied to the LIBS line intensities. The authors also stressed the importance of self-absorption correction for a precise quantitative analysis of steel composition.

The use of hand-held LIBS instrumentation⁹⁶ as an alternative to laboratory measurements^{97–99} has also been proposed for steel analysis.

Girón *et al.*¹⁰⁰ used LIBS for monitoring and characterizing dangerous particulates in the hostile environment of the steel industry. The authors used a standoff LIBS system deployed at a steel factory during the LACOMORE measurements for the analysis of particulates in the ambient air. The power density of the laser beam at the focus was high enough to produce air breakdown; Girón *et al.* collected the spectra at a fixed repetition rate of the laser, obtaining spectra corresponding to pure air breakdown (only elements from the atmosphere were visible) and other spectra characterized by line emission of elements from the particulates produced in the industrial process (Ca, Al, Ti, and Li from casting powder, Cr from the steel). Using conditional analysis, the authors were able to give an estimate of the concentration of the particulates in the working environment and noted that the concentration of dangerous elements, considering the relatively low sampling rate of the technique, might be considered as significant.

2.2.2 Aluminum industry. Aluminum has been studied by LIBS since the early stages of development of the technique, because of the relative simplicity of its emission spectrum and



the importance of this material in the metal industry.^{101–105} Among the most interesting industrial applications of LIBS is the one involving the on-line analysis of molten aluminum.^{89,106}

A commercial LIBS system for at-the-line and on-line liquid aluminum analysis has been developed by the DTE firm, in Iceland.¹⁰⁷

2.2.3 Other metals. Copper-based alloys have been studied extensively by LIBS,^{108–111} for the same motivation as for aluminum alloys. Moreover, copper-based alloys are often studied in the framework of cultural heritage or archaeological studies,¹¹² a field where the capabilities of LIBS are particularly appreciated. The industrial applications of LIBS on copper-based alloys, in contrast, are not particularly numerous. Among the few, one that is worthy of mention is the use of LIBS for determining the composition of industrial copper concentrates proposed by Łazarek *et al.*¹¹³

Zinc-alloys (Zamac) were analyzed using LIBS by Messaoud *et al.*¹¹⁴

2.3 Pharmaceutical industry

The applications of LIBS for characterization and quality control in the pharmaceutical industry have been the subject of several papers at the beginning of this century.^{115–117} As a matter of fact, one of the first commercial LIBS instruments, called PharmaLIBS 250, was realized for quality control of pharmaceutical tablets by PharmaLaser Inc., a Canadian firm supported by the Industrial Material Institute (IMI) of the National Research Council of Canada (NRCC). Good performances of the instruments for assessing the homogeneity of tablets' coating were reported by Mowery *et al.*¹¹⁵ Other applications of the instruments were discussed by St Onge *et al.* in ref. 116 and 117. PharmaLaser went out of the market in the first decade of this century, but the research on pharmaceutical applications of LIBS continued. LIBS was used for the characterization of film coatings by Madamba *et al.*¹¹⁸ The authors successfully evaluated by LIBS the thickness, homogeneity and composition of pharmaceutical tablet coatings, demonstrating how these parameters can be correlated to the photostability of the coating. Arantes de Carvalho *et al.*¹¹⁹ studied by LIBS the macro and micronutrients in pharmaceutical tablets, arriving at the conclusion that LIBS is a viable technique for the analysis of multielement tablets for the determination of Ca, Cu, Fe, Mg, Mn, P and Zn. Myakalwar *et al.*¹²⁰ explored the effectiveness of multivariate chemometric analysis for the study of pharmaceutical tablets and for their classification, concluding that LIBS can be effectively used for quality control and detection of possible counterfeits. The peculiar characteristics of LIBS for performing in-depth analysis were exploited by Zou *et al.*,¹²¹ which demonstrated the possibility of obtaining 3D chemical images of pharmaceutical tablets, with a depth resolution of about 2.6 μm , which can be usefully exploited for determining coating thickness and uniformity, as well as the presence of contaminants, evidenced by their peculiar elemental composition.

The problem of characterization of pharmaceutical tablet coatings has been recently discussed by Yang *et al.*,¹²² who compared different techniques, including LIBS, for quality control of the products.

An alternative approach to standard LIBS analysis was proposed by Yang *et al.*,¹²³ who characterized the molecular emission signal produced by the laser-induced plasma in the mid- and long wave infrared region (4–12 μm), demonstrating a strong correlation between the LIBS signal and the results of conventional infrared molecular spectroscopy of the organic compounds present in pharmaceutical products.

In recent years, LIBS has been used for analysis and quality control of traditional medicinal products.^{124–126}

2.4 Building industry

The LIBS technique has been proposed in the building industry mainly for quality control of concrete structures. Back in 1996 Pakhomov *et al.*¹²⁷ used LIBS for detecting lead in concrete. Other elements often studied for their importance in concrete structures are carbon,¹²⁸ sulfur^{128–132} and, most of all, chlorine.^{128,132–140} Sulfur and chlorine are elements not easily detectable by conventional LIBS analysis. Gehlen *et al.*¹³³ optimized the laboratory conditions for chlorine analysis on concrete drill cores, finding optimal detection limits with the Cl UV line at 134.72 nm and working at an environmental pressure of 60 mbar. The authors also tried collinear double-pulse LIBS, without obtaining any improvement of the detection limits. One of the most exhaustive reports on the detection of chlorine in concrete was delivered by Omenetto *et al.*¹⁴¹ in the framework of a research grant assigned to the University of Florida, Gainesville, FL, USA, by the Florida Department of Transportation. The authors tested several experimental configurations for Cl analysis in concrete and mortars; the best results were obtained by analyzing the ionic Cl line at 479.454 nm in a He atmosphere. Similar results were obtained using a LAMIS⁵² approach, analyzing the CaCl molecular band at 593.5 nm. As already noted in ref. 133, the use of double pulse (in this case, in the orthogonal configuration) did not improve the detection limits obtained using single pulse LIBS and LAMIS (LOD \cong 0.05 wt%).

Use of LIBS for detection of asbestos in construction materials was also proposed by Caneve *et al.* in 2005.¹⁴²

2.5 Waste management industry

The possibility of LIBS to operate remotely on fast moving objects has led to several applications of the technique in the waste management industry. One of the first proposals of LIBS in the waste and recycling industry was aimed at identification and sorting of plastic substances;^{143–146} more recently, a combination of LIBS and Raman technique has been demonstrated to be very effective for this purpose.¹⁴⁷ Other applications have demonstrated the effectiveness of LIBS for the control of the process of recovering precious metals from electronic wastes.^{148,149} Similarly, the determination by LIBS of the fraction of plastic waste from mobile phone scraps has been discussed by Camara Costa¹⁵⁰ and Aquino.¹⁵¹

Another important application of LIBS is related to the European Commission project SHREDDERSORT, aimed at the efficient sorting of non-ferrous metallic scraps from the automotive industry¹⁵² (see Fig. 8).





Fig. 8 SHREDDERSORT project: non-ferrous metallic scraps from the automotive industry.

Secopta Analytics GMBH, a German firm, has produced a commercial instrument for sorting aluminum scraps.¹⁵³ Based on similar principles, the REFRASORT project, funded by the European Commission, has developed a LIBS sorting procedure for refractory wastes.¹⁵⁴

The feasibility of using LIBS for the analysis of spent batteries has been demonstrated by Peng *et al.*¹⁵⁵

2.6 Mining industry

The LIBS technique has been extensively used for the analysis of mining products for several years.^{156–162} Gaft *et al.*¹⁶³ were among the first to sense the potential of LIBS for on-line geological analysis. An industrial analyser was proposed in 2014;¹⁶⁴ the recent development of LIBS instrumentation for fast elemental imaging has opened the way for 3D elemental analysis of geological materials.^{165–167}

ELEMISSION, a Canadian firm, has developed a commercial instrument for geological analysis¹⁶⁸ which is able to obtain elemental LIBS images at kHz rate.¹⁶⁹

2.7 Food and feed industry

Another important application of LIBS is the quality control and adulteration detection in the food and feed industry. Defects, contamination and adulteration, as well as the micro-nutrient content of several foods have been studied by LIBS. An extensive review of the capabilities and limitations of LIBS in food analysis has been recently published by Sezer *et al.*¹⁷⁰

Silva *et al.* used LIBS for predicting the amount of defective beans in coffee blends.¹⁷¹ Khalil *et al.*¹⁷² applied LIBS for the detection of micro-toxic elements in commercial coffee brands, using double-pulse LIBS. Sezer *et al.* used LIBS for detecting possible adulteration of *Coffea arabica*, by fraudulent addition of wheat, corn and chickpea,¹⁷³ as well as milk adulteration with wheat¹⁷⁴ (see also Bilge *et al.*¹⁷⁵ and Moncayo *et al.*¹⁷⁶). Abdel-Salam *et al.*¹⁷⁷ used LIBS for quality assessment of commercial infant formulas vs. maternal milk. Similarly, Dos Santos *et al.*¹⁷⁸ studied the optimal calibration conditions for the determination of Ca, Mg and K in powdered milk and dietary tablets. Ferreira *et al.*¹⁷⁹ used LIBS for the determination of Ca in breakfast cereals. Gondal *et al.*¹⁸⁰ studied by LIBS the composition of tea samples, finding a good agreement with ICP-MS measurements. Also Zhang *et al.*¹⁸¹ performed LIBS analysis on Chinese tea leaves, with the purpose of optimizing the optimal spectral lines for classification and quality control. Se *et al.*¹⁸² used chemometric analysis for the determination of Ca,

Mg and Na content in honey. The challenges for application of LIBS in agricultural studies were discussed in a recent review by Peng *et al.*¹⁸³ Eum *et al.*¹⁸⁴ discussed the combined use of LIBS and near-infrared spectroscopy for the identification of the geographical origin of vegetable samples. Atta *et al.* used LIBS for the quantification of micro-nutrients (zinc, iron) in wheat,¹⁸⁵ noticing that LIBS analysis can be useful for growers in selecting the wheat genotypes richer in these micronutrients. Sezer *et al.*¹⁸⁶ proposed LIBS as a rapid, reliable, and environmentally friendly alternative to standard protein assay methods; the authors successfully correlated the nitrogen concentration with the protein content in wheat flour and whole meal. Shen *et al.*¹⁸⁷ proposed LIBS for rapid determination of possible cadmium contamination in lettuce.

Sezer *et al.*¹⁸⁸ used LIBS for the identification and quantification of LiNa, a toxic salt substitute in meatballs, demonstrating a limit of detection for Li of about 4.5 ppm. Bilge *et al.*¹⁸⁹ and Chu *et al.*¹⁹⁰ used LIBS for the identification of different meat species; Velioglu *et al.*¹⁹¹ exploited these results for the identification of possible offal adulteration in beef. A similar analysis was done by Casado-Gavalda *et al.*¹⁹² using copper content in beef as a possible indicator of offal adulteration. Dixit *et al.*^{193,194} proposed the use of LIBS elemental imaging for salt diffusion in brining of meat, and demonstrated the possibility of LIBS quantification of rubidium as trace element in beef.

The feasibility of on-line LIBS control in the poultry meat production industry has been discussed by Andersen.¹⁹⁵

3. Conclusion

Several considerations can be derived from the analysis of recent literature on the industrial applications of LIBS: the traditional fields of application of LIBS seem to attract strong interest from the scientific community. Several commercial LIBS instruments have been proposed for on-line analysis of materials in the metallurgic industry, and special attention is given to the possibility of on-line control of the production process (continuous casting of steel, analysis on liquid metals, *etc.*). Also in the field of energy production, the unique advantages of LIBS forecast an imminent transfer of the laboratory prototypes to the real industrial environment, especially for on-line analysis of coal. LIBS is also very promising for its application in recycling (plastic and metallic wastes, mainly) and mining industries. Other industrial applications of LIBS, such as the ones in pharmaceutical and food industries, seem to be less mature, mainly because of the complexity of the products to be analysed, which are probably better dealt with molecular techniques such as infrared spectroscopy, Raman, *etc.* The rapid technological developments in the field of compact laser systems and spectrographs, as well as the drop in the cost of these instruments, are expected to greatly contribute to the implementation of LIBS in the industrial sector.

Conflicts of interest

There are not conflicts to declare.



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