



## Review

## The development of fieldable laser-induced breakdown spectrometer: No limits on the horizon

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## ABSTRACT

In this review, new trends in the development of fieldable instrumentation based on laser-induced breakdown spectroscopy (LIBS) and its recent applications is presented. Depending on the LIBS configuration we will distinguish between *portable*, *remote* and *stand-off* instruments. Moreover, the development of portable systems gives greater flexibility and also increases the range of LIBS applications. In general, portable instruments are employed in close-contact applications like immovable artworks, contaminated soils and environmental diagnostic, while remote and stand-off instruments are normally used in analytical applications at distances where access to the sample is difficult or hazardous. Although remote and stand-off instruments are both used for chemical analysis at distances, the instrumental configurations are completely different. In remote analysis, an optical fiber is employed to deliver the laser energy a certain distance. This approach has been usually restricted to industrial applications, bulk analysis in water, geological measurements and chemical analysis on nuclear stations. In the case of stand-off applications, the laser beam and the returning plasma light are transmitted in an open-path configuration. In this article we also discuss the instrumental requirements in the design of remote and stand-off instruments.

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## 1. Introduction

Field analytical instrumentation is an appealing choice for fast chemical response (security and military applications), on site measurement capability (environmental monitoring and geological exploration) and those cases where the object cannot be transferred to the

laboratory (cultural heritage applications). In addition, in situ analyses are necessary in such applications where access to the sample is difficult or represents a hazard for the analyst. As a result of this demand, several techniques have been transported from the laboratory to the field. Nowadays, a variety of techniques including X-ray fluorescence spectroscopy (XRF) [1], Raman spectroscopy (Raman) [2], Laser-induced fluorescence (LIF) [3] and Ion mobility spectrometry (IMS) [4] have been successfully used for field measurements with high accuracy and precision in the results. One of the techniques now

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receiving more attention is Laser-induced breakdown spectroscopy (LIBS), as it combines many of the required features in a field portable instrument and has been successfully tested under field conditions [5,6]. Attributes of LIBS such as rapid and *in situ* analysis with no sample preparation make the technique a suitable alternative for field measurements. Portability of the technique is the general characteristic of being readily transportable from one location to another. Also, the term fieldability (capability of portable instruments to work in the field) is directly related to the portability of the analytical method. Analytical capabilities (selectivity, detection power and capability for absolute analysis) and operational featuring (e.g. sample preparation, depth resolution, speed of analysis, scalability and solid sampling capability) of an analytical technique may influence the design of a portable instrument for field applications. For the sake of comparison, the most important features of the above-mentioned analytical techniques in the design of a fieldable instrument are summarized in Table 1. As observed, no single technique offers all the analytical capabilities and operational features needed for the development of an ideal fieldable instrument. Taken into consideration the potential of LIBS for solid sampling with high depth resolution and offering atomic information, the technique could be considered as a good alternative for field instruments. In addition, Raman spectroscopy provides molecular information and presents similar features when compared with LIBS. Also, both techniques share an excitation source of similar characteristics. Nowadays, the combination of several techniques (sensor fusion) offers complementary information about the sample under investigation and also increases the range of field applications. LIBS/Raman and LIBS/LIF are only some examples of hyphenated techniques. Nevertheless, commercial portable instruments such as Raman, XRF and IMS are successfully used for real-world field applications. However, the analytical capabilities of these techniques do not reach the detection power of methods based on mass spectrometry.

In this review, we focus our attention on LIBS as a versatile methodology which possesses the ability of field measurements. New trends in the development of fieldable LIBS instruments and recent applications are reported in this article. Firstly, the fundamentals and applications of laser-induced breakdown spectroscopy are briefly overviewed. Secondly, we categorize the fieldable LIBS instrumentation in portable, remote and stand-off configurations. Details on its instrumental development and recent applications of each configuration are also discussed. Furthermore, available commercial LIBS systems and the impact of LIBS on the scientific community are also presented. Recently, a number of instruments have been introduced in the LIBS2010 International Conference held in Memphis. Unfortu-

nately, the technical information concerning these instruments is not available at present and will not appear in this review.

## 2. Laser-induced breakdown spectroscopy

Since the invention of the laser in the 60s [7] and the later development of its technology during the 80s, laser-induced breakdown spectroscopy (LIBS) has been recognized as an appropriate analytical method for the direct spectrochemical analysis of solids [8,9], liquids [10–12], gases [13], aerosols [14–16] and also environmental, archaeological [17] and geological materials, even in extreme environments.

Briefly, the method is based on *laser-matter* interaction: namely, on the irradiation of a solid surface with a high power density (on the order of a few  $\text{GW cm}^{-2}$  or more), leading to the formation of a plasma containing the analytical information about the constituent elements of the sample [18,19]. The light emitted by the plasma is collected into a spectrograph and resolved both spectrally and in time in order to obtain the analytical information present in the sample. Identification of the spectral lines and measurement of their peak intensity provides qualitative and quantitative information, respectively. Moreover, the peak intensity is determined not only by the concentration of the element in the sample, but also by the properties of the plasma itself. In this sense, quantitative analysis by LIBS is not a trivial task [20]. Along the years, a broad variety of experimental approaches have been proposed to solve different analytical problems. This fact makes difficult the comparison between results obtained in different laboratories. In addition, LIBS strongly depends on matrix effects, pulse to pulse fluctuations, plasma–solid interactions, etc. To overcome these problems, a new procedure for a calibration-free quantitative analysis (CF-LIBS) has been proposed by Palleschi and coworkers [21]. The method, based on the calculation of the plasma temperature and the electron density in the plasma avoids the use of standard reference materials. To apply this methodology, authors assumed that the plasma is in local thermal equilibrium (LTE) and the radiation source is optically thin. In order to improve the accuracy of CF-LIBS results, authors also implemented in the algorithm a correction factor for self-absorbed lines.

LIBS applications are tied to the analytical capabilities of the technique, namely multi-elemental detection in a wide variety of matrices, fast analytical response, remote sensing capabilities and analytical figures of acceptable value for most applications [22,23]. Establishment of LIBS in a wide range of applications involves specific instrumentation. In essence, the laser beam can be focused into the sample surface with a simple lens and then, collect the plasma light with an optical fiber. Depending on the LIBS application, experimental requirements would benefit from advances on optical configurations. In particular, for field applications, LIBS instruments require small and compact lasers (with portable power supply) and miniaturized broadband spectrometers. Development of spectral libraries and data processing algorithms also improve the capability of LIBS for field measurements.

During the past few years, LIBS has experienced a growth in interest as a surface analytical method, as revealed by the wide number of LIBS applications found in the Bibliography [24]. Fig. 1 illustrates the growth in the number of articles published in LIBS in the last 15 years. From 2000, a biannual international meeting focused on the fundamentals and applications of LIBS is organized in order to present the results and developments on the technique. Thanks to the international conferences held in 2000 (Pisa, Italy), 2002 (Orlando, USA), 2004 (Malaga, Spain), 2006 (Montreal, Canada), 2008 (Berlin, Germany) and 2010 (Memphis, USA), publications on LIBS have considerably increased. Furthermore, regional meetings including Euro-Mediterranean Symposium on LIBS (EMSLIBS) and North American Symposium on LIBS (NASLIBS) are on the alternating years with the major international conference.

**Table 1**  
Most important features of different analytical techniques in the design of a fieldable instrument.

	Analytical techniques				
	GC-MS	LIBS	Raman	IMS	XRF
<i>Analytical capabilities</i>					
Selectivity	****	***	****	**	***
Detection power	****	**	***	**	***
Absolute analysis	****	**	****	**	**
Analytical information	Molecular	Atomic	Molecular	Molecular	Atomic
<i>Operational featuring</i>					
Sample preparation	****	****	****	****	****
Sample size	****	****	****	****	****
Lateral resolution	–	****	***	–	**
Depth resolution	–	****	–	–	–
Speed	****	****	****	***	***
Simplicity of analysis	****	****	****	****	****
Solid sampling capability	–	****	****	–	****
Instrumentation maturity	****	**	***	***	***
Scalability	**	****	****	***	****

\*\*\*\* excellent; \*\*\*\* very good; \*\*\* good; \*\* medium; \* poor.

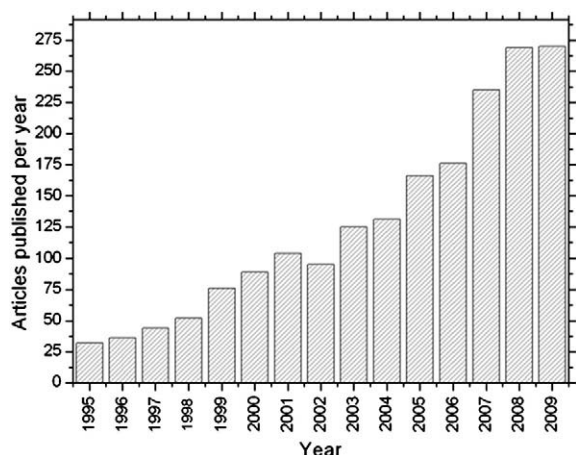


Fig. 1. Articles published per year in LIBS since 1995.

Laser-induced plasmas have been applied to the direct analysis of stainless steel, photovoltaic cells, auto catalytic converters, glass, biological and medical samples, organic and hazardous materials, etc. Furthermore, LIBS is a promising technique for the study and inspection of a broad variety of artworks and cultural heritage objects [25] such as metallic alloys, ceramic, stone pieces, paintings and sculptures. The use of the multipulse mode in LIBS has allowed the improvement of the analytical capabilities of the technique in terms of

the detection limit and the reproducibility of the measurements. Typically, the double pulse technique (DP) was associated with the LIBS analysis of liquids, but it has shown a number of advantages also when applied to solids, making possible the development of the technology (collinear DP, orthogonal DP and crossed beam DP) in a broad variety of analyses [26,27].

### 3. Fieldable laser-induced breakdown spectroscopy instruments

Advances in optical configurations (such as fiber optics, beam optics and telescopes) for guiding and collecting the plasma light have resulted in instrument design differing from those normally used in laboratory. In addition, continuous advances in reducing the size and weight while increasing the capabilities of lasers, spectrographs and detectors make possible the development of compact and rugged instrumentation. Portable systems give greater flexibility and also increase the range of LIBS applications. Fig. 2 shows a schematic diagram of the most common LIBS instruments employed for field applications. In Fig. 2A, this means a *portable system*, the head laser and the optical arrangements as well as the focusing and collection optics are included in a hand-held probe. In this case, the emission of the plasma is directly collected by a fiber optic cable and guided to the entrance slit of a spectrograph. The development of new materials has allowed the design of fiber optics capable of transmitting laser radiation in the range of  $\text{MW cm}^{-2}$  without any damage to the fiber. In this sense, when the laser emission and the plasma light are transmitted by the same or different fiber optics, the scheme is named

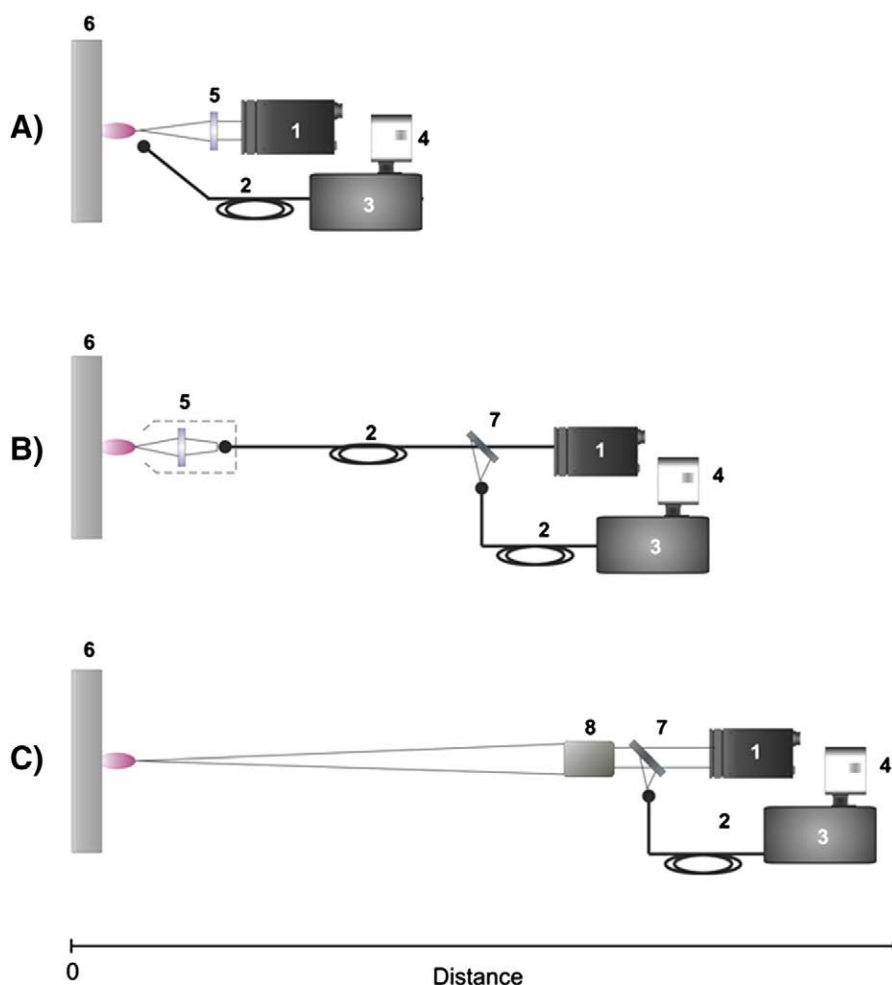


Fig. 2. Alternative configurations for an experimental set-up based on LIBS: A) Portable system, B) Remote system and C) Stand-off system. 1. Laser head, 2. Optical fiber, 3. Spectrometer, 4. Detector, 5. Focusing lens, 6. Sample, 7. Dichroic mirror and 8. Telescope.

a remote system (Fig. 2B). Finally, the schematic diagram in Fig. 2C shows what is widely known as *stand-off detection*. In this approach, the distance at which the laser radiation is focused by a telescope depends on several parameters such as the pulse energy, the laser beam divergence and the optical system employed. Light emitted by the plasma is collected by the same telescope and finally, guided to the spectrograph and the detection system.

The aim of this review is to present an overview of the portable LIBS technology. In this section, we will discuss recent advances and applications on portable, remote and stand-off instruments.

### 3.1. Portable LIBS systems

In the last few years, the number of portable LIBS instruments designed by different research laboratories has considerably increased. Table 2 gives an overview of the different instruments built in the LIBS community. In the majority of works reported in the literature, the laser is a Nd:YAG working at 1064 nm due to the proven reliability and ruggedness of solid-state lasers (which is of paramount consideration for a field instrument) and also for size requirements. Nowadays, the types of field applications (environmental, industrial, geological, cultural heritage and security, among others) make necessary the use of detectors with an analytical response in the entire spectral range. This point requires a compromise between the spectral resolution of the detector and the requirements for a miniature instrument. The first portable LIBS system was developed at Los Alamos National Research Laboratory by Cremers et al. [28]. The instrument was based on a sampling probe, containing the laser head and the fiber cable used to collect the plasma light, and a main unit (containing the laser power supply, the spectrograph, the detector and the personal computer). A photo of the instrument is shown in Fig. 3. The instrument was evaluated for the analysis of Pb in paint, Ba, Be, Pb and Sr in soils and Be and Pb particles in filters. The precision was in the range 23%–47% while the limit of detection (LOD) estimated for the analysis of Pb in paint was 8000 ppm. For the LIBS

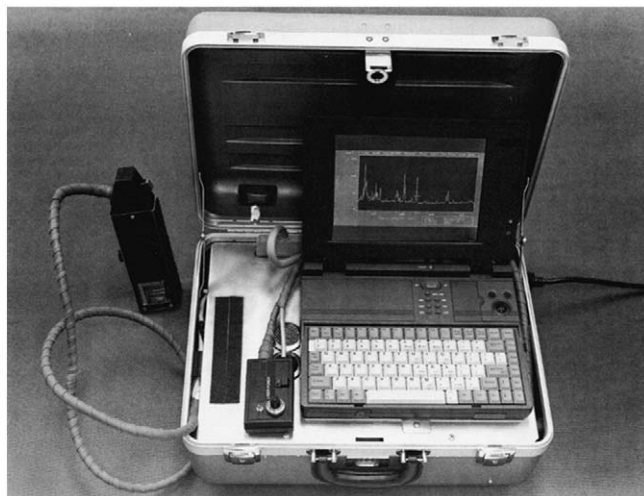


Fig. 3. Photographic detail of the first portable LIBS analyzer designed by Cremers et al. [28]. Published with the permission of the Society for Applied Spectroscopy.

analysis of soils, the LOD was 265 ppm, 9.3 ppm, 298 ppm and 42 ppm for Ba, Be, Pb and Sr, respectively. The LOD calculated for Pb in paint was higher in comparison with that obtained in soils analysis. This was mostly attributed to the use of the Pb (II) 220.35 nm emission line instead of the stronger Pb (I) at 405.78 nm used for soils. Moreover, the results were similar to those obtained by a conventional LIBS apparatus and by XRF.

In 1998, Winefordner et al. [29] designed a portable instrument, very similar to that of Los Alamos, mentioned above. The main difference with respect that published by Cremers was the use of a battery, which increased the autonomy of the system. For this prototype, authors selected a miniature Ocean Optics spectrometer (model S2000). In order to improve the signal to background (SBR)

Table 2  
Operational featuring and main applications by portables LIBS instruments.

References	$\lambda$ (nm)	E (mJ/pulse)	Weight (kg)	Instrumentation	Application	Samples	Limit of detection (LOD)
[28]	1064	20	Suitcase — 14.6 kg	Fiber optic bundle — 2 m  Spectrograph Oriel 1/8 m (2400 l/mm) CCD Oriel (256 × 1024 pixels)	Environmental	Soils  Paint  Particles on filters	Ba (265) <sup>a</sup> , Be (9.3) <sup>a</sup> , Pb (298) <sup>a</sup> and Sr (42) <sup>a</sup> ppm Pb (8000 ppm) <sup>a</sup>  Be (21–63 ng/cm <sup>2</sup> ) <sup>a</sup> , Pb (5.6 µg/cm <sup>2</sup> ) <sup>a</sup>
[29]	1064	21	Suitcase — 13.8 kg	Fiber optic — 2 m Spectrometer Ocean Optics S2000	Industrial	Paint Steel Organic	Pb (0.12%) <sup>a</sup> Mn (0.016%) <sup>a</sup> Ca (0.13%) <sup>a</sup>
[30]	1064	15	Aluminum case	Fiber optic Spectrograph 1/6 m (2400 l/mm) CCD detector	Environmental	Soil	Pb (100 ppm) <sup>a</sup>
[31,32]	1064	50	Backpack — man portable sensor	Fiber optic Spectrometer Ocean Optics LIBS3000	Security	Hazardous material	N/C <sup>b</sup>
[33]	1064	50	Aluminum case	Fiber optic — 2 m Spectrograph 1/8 m (3600 l/mm) ICCD detector	Mineralogical Industrial	Minerals Stainless steel	N/C <sup>b</sup> Cr (0.79%) <sup>c</sup> , Ni (0.18%) <sup>c</sup> , Mn (0.02%) <sup>c</sup> , Ti (0.01%) <sup>c</sup> and Mo (0.1%) <sup>c</sup>
[34]	1064	50	Aluminum case	Fiber optic — 2 m Spectrometer Ocean Optics HR2000	Geological	Speleothems	N/C <sup>b</sup>
[35]	1064 DP-LIBS (Collinear)	50–120	Aluminum case	Fiber optic Echelle spectrometer ICCD detector	Cultural heritage Environmental	Bronze Soils	N/C <sup>b</sup> N/C <sup>b</sup>
[37–39]	1064	50	Backpack — Man portable sensor	Fiber optic — 2 m Spectrometer Ocean Optics 2000	Geological Cultural heritage Environmental	Speleothems Cathedral Road sediments	N/C <sup>b</sup> N/C <sup>b</sup> Pb (190 µg/g — 1) <sup>a</sup>
[40]	1064	45	Control box — 3 kg	Fiber optic — 2 m Spectrometer Ocean Optics HR2000	Cultural heritage	Pigments, Metals, ceramic	N/C <sup>b</sup>

<sup>a</sup> LOD calculated from the calibration curves.

<sup>b</sup> N/C refers to LOD not calculated.

<sup>c</sup> LOD calculated as background equivalent concentration (BEC-%).



and signal to noise ratio (SNR), the authors moved the fiber optic off axis to view the outer edge of the plasma. With this configuration, the precision and SNR of the measurements was improved 2 and 25 times, respectively. Despite the low pulse energy laser and the use of a poor resolution spectrometer, useful quantitative results on paint, steel, ores, and organic samples were achieved. The LOD ranged from 0.016% for Mn in steel to 0.13% for Ca in organic samples, with acceptable precision (0.4%–4.9%), while the detection of Pb in paint was not satisfactory due to the poor homogeneity of the samples.

Wainner et al. [30] developed a compact and robust chemical LIBS sensor for the rapid and non-destructive detection of Pb in paint and soils. This apparatus is also based on the first instrument design of Los Alamos. The system is contained within an aluminum case and can be operated from both a standard 12-V battery and 115-V AC current. In order to evaluate the portable system, the results were compared with a laboratory LIBS system. In spite of the spectrograph used in the portable instrument is less sophisticated and the resolution is poorer than the lab system, the authors observed that both systems exhibited similar performance in the detection of Pb in both soils and in paint, 0.05%–1% concentration levels. The main problem associated to this analysis is the use of the Pb (I) 405.8 nm which could be self-absorbed but at lower Pb concentrations this effect should not be significant. Although the precision exhibited by the portable instrument was 45%, the limit of detection (LOD) of Pb in soils was estimated at 100 ppm. Finally, the apparatus was successfully tested in a field measurement campaign at sites of documented Pb contamination where the concentrations in soils were higher than 100 ppm. Nevertheless, due to the matrix effects and the presence of interfering lines in the 405.8 nm region, the instrument performed better for soil samples than for paint samples.

In 2004, Ocean Optics Inc. under contract to the Army Research Laboratory, designed a man-portable LIBS sensor, an integrated, lightweight field-deployable sensor technology for the identification and detection of hazardous material [31,32]. The instrument (Fig. 4) was based on a sampling probe and a specially adapted backpack which contains the laser power supply, the computer, the battery (2 h

autonomy) and the spectrometer (seven Ocean Optics spectrometers). The use of a broadband spectrometer is an important advantage since it offers the possibility of recording the full LIBS spectra of organic and hazardous materials, allowing the creation of a spectral library. Fig. 5 shows comparative LIBS spectra of *bacillus globigii* taken in laboratory and with the man-portable instrument. As shown, in spite of the experimental differences (collection optics, laser type and laser power) between instruments, the spectra obtained were similar in both cases. This fact demonstrated the capability to detect hazardous materials in extreme sceneries.

In the last few years, the laser laboratory of the University of Malaga has designed and constructed different portable systems for *stand-off* and *in-situ* applications. In 2003, Laserna et al. [33] described the development of a fully-automated portable LIBS instrument for the quantitative analysis of Ni, Cr and Mn on steel scrap samples provided by Acerinox, S.A. The instrument was composed of a main unit and a hand-held probe. The RSD values obtained during the field analysis were 2.36% for Cr, 5.42% for Ni and 3.40% for Mn. Analytical figures of merit show valuable numbers not only for a portable instrument but comparable to laboratory instruments such as an XRF analyzer. Furthermore, the applicability of the instrument was not restricted to ferrous materials and the same authors tested the portable system's capabilities in the determination of thickness and semi-quantitative composition of alteration layers on the surface of speleothems [34]. For this purpose, the instrument was evaluated in the interior of the Nerja Cave (Spain) over soils, rocks and speleothems. Laser-induced plasma analysis revealed the remarkable presence of several Fe, Si, Al or Mn in the surface of the speleothems, which were absent in the bedrock. From a geological point of view the interest of this research was to evaluate alteration processes and the geochemical degradation of these materials. During the field experiments, the thickness of the alteration layer (no more than 300  $\mu\text{m}$ ) was estimated at nine locations along the tourist galleries. At least one alteration layer was detected at each of the analyzed locations. This data was of crucial interest to preserve the state of conservation in the cave.

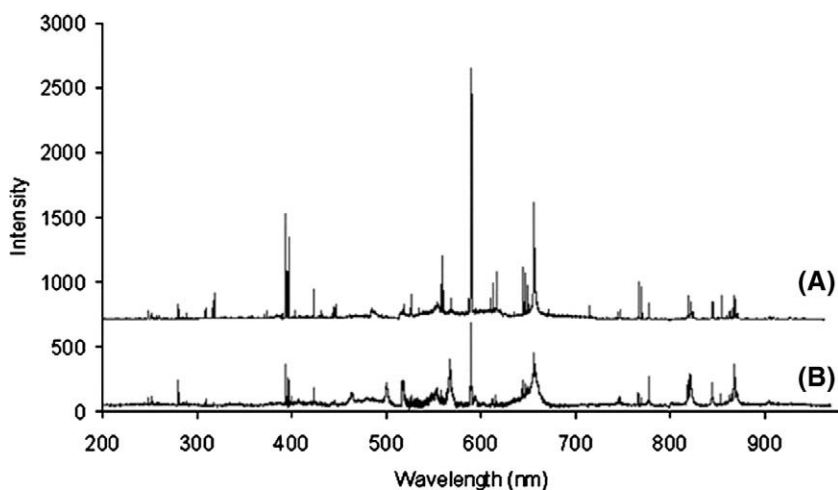
In 2006 the Applied Laser Spectroscopy Laboratory in Pisa and Marwan Technology s.r.l. developed Modi, a new mobile instrument for *in-situ* DP-LIBS analysis [35]. Moreover, Modi is the first instrument integrating the double pulse technology and incorporates a dual-pulse laser which emits two laser pulses in a collinear configuration. It is important to have into account that although Modi is a portable system, is not specially designed for field analysis. Fig. 6 shows a schematic diagram of the set-up used and also a picture of the system. One of the main advantages is that Modi also incorporates the calibration-free method [36] (CF-LBS) for qualitative and quantitative analysis. The system has been satisfactory tested in a broad variety of LIBS applications including cultural heritage analysis, environmental diagnostics and LIBS analysis of precious alloys. The improvement of the DP-LIBS signal in a precious alloy with respect the SP-LIBS spectrum is clearly shown in Fig. 6C.

Recently, Laserna et al. [37] designed a man-portable laser system (Fig. 7). This prototype involves a technological evolution compared to the original instrument [33,34]. The main difference is that both the spectrometer and the computer components are enclosed in a specially adapted backpack. Authors evaluated the functionality of the instrument inside the Nerja Cave. In this research, authors used the spatial capability of LIBS for minor/trace detection to calculate the Sr/Ca intensity ratio in 20 sampling areas of geological interest. Depth profiles analysis of Sr, Mg and Ca were used for Sr/Ca and Mg/Ca calculation, useful for paleoclimate applications.

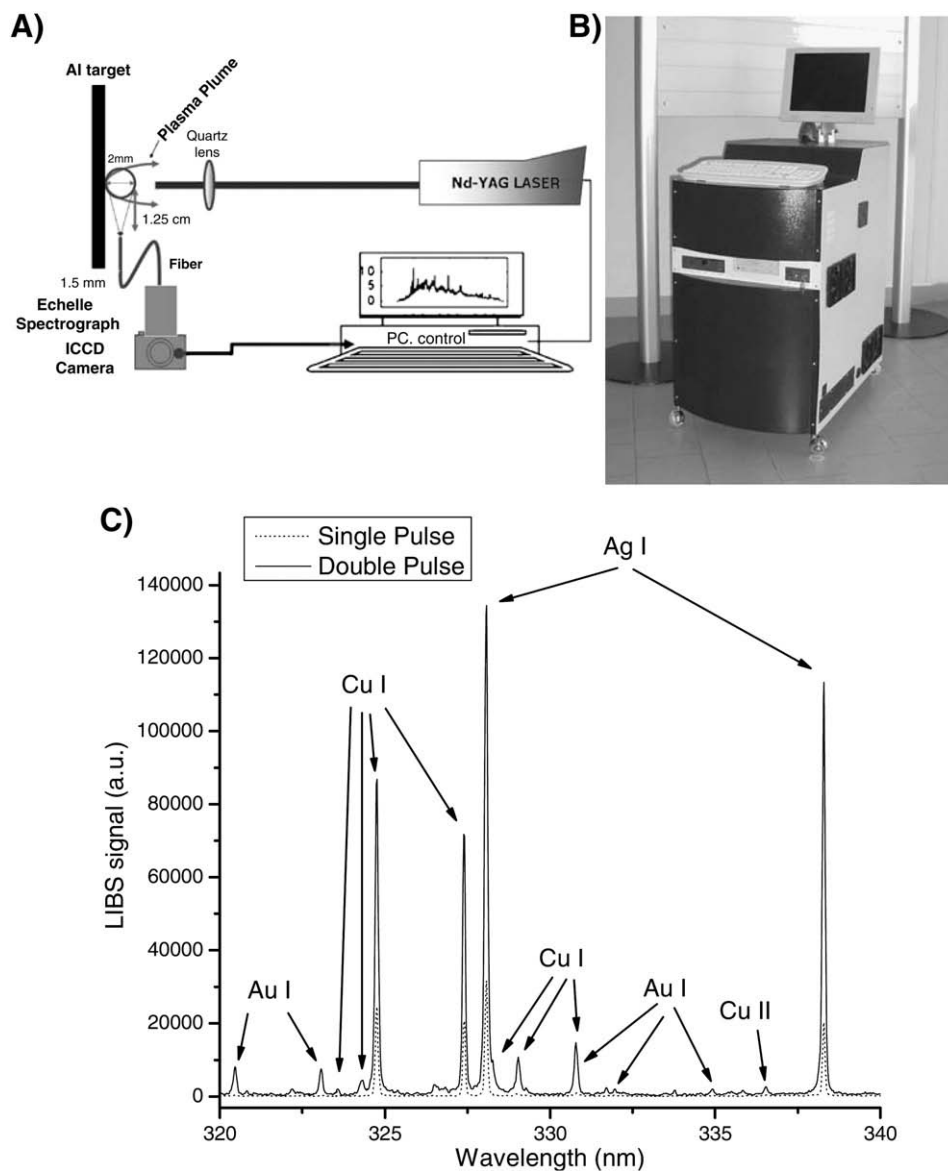
The same authors demonstrated the capability of the man-portable LIBS analyzer for the *in-situ* analytical assessment and chemical imaging of Malaga's Cathedral [38]. It should be noted that authors analyzed a total area of 900  $\text{m}^2$  with this system. In this work, different materials (sandstone, limestone, marble, and cement



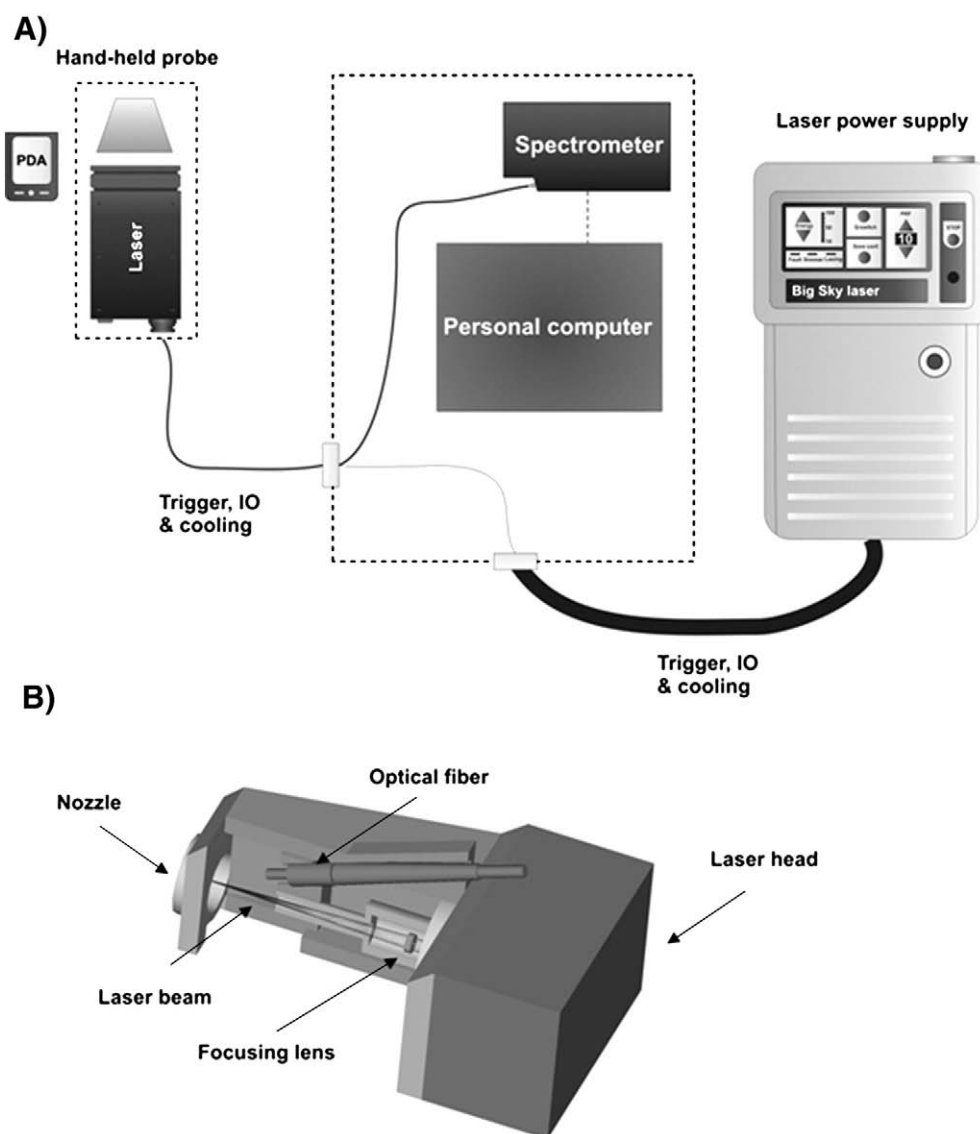
Fig. 4. Photo of a man-portable LIBS sensor in use. Figure takes from reference [31]. © [2005] IEEE.



**Fig. 5.** Comparison of bacillus globigii LIBS spectra from a A) laboratory LIBS setup (140 mJ, 10 ns pulse, single shot) and B) Man-portable LIBS system. Figure takes from reference [31]. © [2005] IEEE.



**Fig. 6.** Dual pulse instrument for LIBS applications, [35]; A) outline of the set-up, B) Photographic detail of Modi instrument and C) LIBS spectra of a precious alloy in SP and DP configuration. Published with the permission of Springer-Verlag.



**Fig. 7.** Schematic diagram of the man-portable LIBS system design by the University of Malaga showing A) the hand-held probe, the main unit, and the laser power supply, and B) detail of a cross-section of the laser head showing the ablation chamber and optical arrangement.

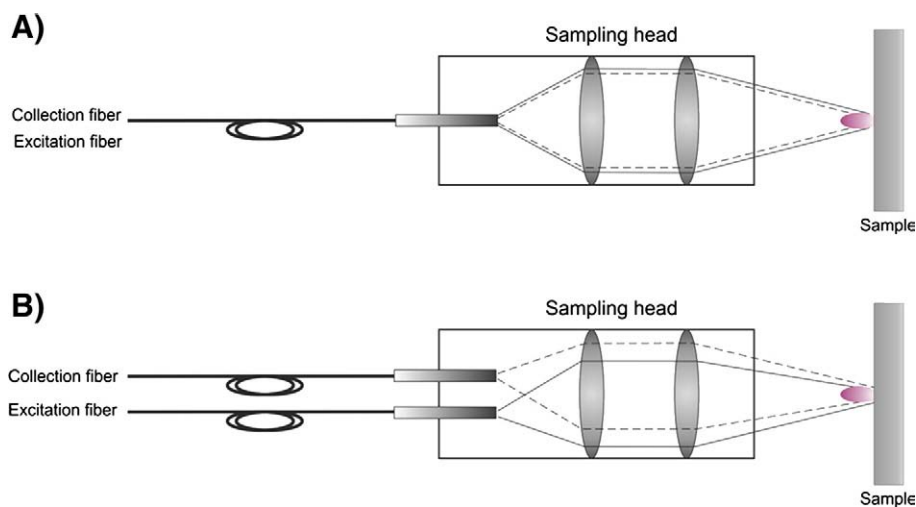
mortar) were discriminated on the basis of different ratios of intensities. In order to obtain an overall view of the distribution of these materials along the facade, the authors generated composition maps for Si/Ca and Ca/Mg. Although the results obtained were quite satisfactory from a restoration point of view, the field experiment was carried out with the help of a scaffolding installed in the facade of the monument and perhaps similar studies could be achieved with a stand-off instrument. Most recently, the same instrument was evaluated for the real time measurement of lead in road sediments [39]. The intense emission line of Pb (I) at 405.78 nm was used for the quantitative determination of low-level concentrations. During the field experiment three sections of a tunnel were analyzed, resulting in an average Pb concentration of  $620 \mu\text{g g}^{-1}$ ,  $480 \mu\text{g g}^{-1}$  and  $660 \mu\text{g g}^{-1}$  in the entrance, the center and the exit of the tunnel, respectively. The accuracy of the LIBS measurements were confirmed by flame-AAS. Finally, the limit of detection achieved by the instrument ( $190 \mu\text{g g}^{-1}$ ) was found to be lower than those demanded by most environmental organizations.

In recent times, a novel compact and portable pulsed laser system was developed for *in situ* LIBS diagnostic and applications [40] in the Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, (IESL-FORTH). In this prototype, authors

evaluated a novel compact and portable laser in order to meet the size, weight and performance requirements for a portable laser-induced breakdown spectrometer. It should be noted that among the results obtained, the new laser source exhibited high performance in terms of laser pulse repeatability, autonomy and interface. Moreover, its ability to work also in DP-LIBS configuration provided versatility in the analytical measurements. This LIB spectrometer has allowed chemical identification within a broad variety of materials, such as pigments in paintings and icons, metals, ceramics, etc....

### 3.2. LIBS measurements at a distance

Laser technology and fiber optics play an increasingly important role in the design and construction of sensors and LIBS measuring systems. The integration of fiber optic cables inside a LIBS system in order to perform remote analysis of materials has been investigated by several laboratory research and private companies. Several possibilities exist when a LIBS measurement at a certain distance is needed: remote analysis (the laser and/or the signal are transmitted through a fiber optic cable) or stand-off analysis (both the laser and the signal are transmitted along an open path configuration). The ability to analyze samples located in certain environments such as



**Fig. 8.** Remote LIBS configuration with A) a unique fiber optic cable for plasma formation (excitation fiber) and collection of the plasma light (collection fiber) and B) individual fiber optic cable for plasma formation and collection of the plasma light.

areas of contamination by toxic or radioactive material, or the application to fast analysis at a distance, are the main advantages of these LIBS configurations.

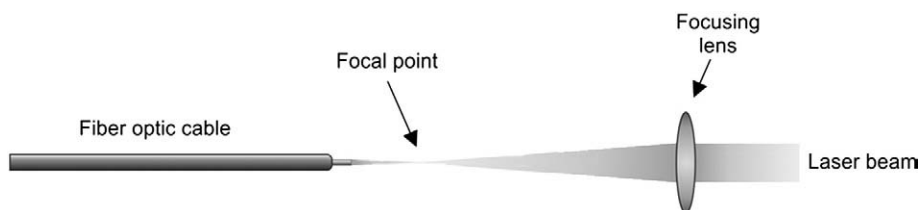
### 3.2.1. Remote LIBS systems

The development of fiber optical materials for long distance sensing provides an opportunity to avoid significant limitations in conventional stand-off analysis. When fiber-optics are used with LIBS instrumentation, two or more optical fibers can be used (Fig. 8). This provides new methods for plasma light collection and it is also capable of transmitting the laser energy through the fiber. At the end of the fiber, the laser beam is focused onto the sample surface by an appropriate optical configuration. Furthermore, there exists the possibility to collect the plasma using the same fiber used to transmit the laser beam. The main goal of this approach is the possibility of a LIBS analysis in situations where the sample of interest is not directly accessible, i.e. industrial and geological applications, hazardous environments and in general, areas of contamination by toxic or radioactive material. Useful technical information for those interested in getting started with fiber delivery of pulses for LIBS was reported by Neuhauser et al. [41]. In this work, the authors explained the design of a robust fiber optic probe for remote sensing by LIBS as well as the basic geometry of a high energy laser pulse in a fiber optic. Basically, it consists of focusing the laser beam into an optical fiber mounted on a xyz stage (Fig. 9). It's important to take into account that the fiber should be placed behind the focus to avoid irreversible damage. The authors also reported the different possibilities of damage of the fiber, which can occur at: a) the fiber input/output end-face due to transgression of the damage threshold, b) the first focal point in the fiber and c) by core/cladding breakdown. Table 3 summarizes the different instruments that use a fiber optic cable for laser delivery in LIBS applications. The maximum distance reached for the instrument as well as the LIBS configuration and the optical system for laser focusing at the output end of the fiber have been also detailed in Table 3.

An early investigation regarding the use of a fiber optic to deliver the laser beam onto the target was proposed by Davies et al. [42]. The system was designed for the analysis of ferrous materials for distances up to 100 m at standard conditions. In this work the authors used a separate fiber to collect the plasma light. A quantitative analysis of Cr, Cu, Mn, Mo, Ni, Si and V was achieved. The limit of detection (LOD) was down to a few hundreds of ppm.

In 1996, Cremers et al. [43] used the same fiber optic described in [42] for the remote LIBS measurements of Cr and Ba in soil. The optical lay-out of the apparatus used in this application can be observed in Fig. 10. As shown, the same fiber was employed to both deliver the laser beam for LIBS analysis and to collect the plasma light. With this configuration, the laser-induced plasmas were generated reproducibly and sufficient light was collected to quantify the emitting species. Moreover, the analytical figures of merit were comparable to those for conventional LIBS measurements. The LOD for Ba and Cr in soil were 26 ppm and 50 ppm, respectively. Most recently, Bousquet et al. [44] designed a mobile LIBS system for the *in situ* analysis of polluted soils. The mobile LIBS system was composed of a mobile trolley gathering the laser and the spectrometer connected to a handpiece (the focusing head) by a 10 m length of optical fibers (Fig. 11). In this prototype, a single lens focuses the laser beam onto the sample surface. A similar configuration was previously chosen by Whitehouse and coworkers [45]. The authors developed a novel design 75 m long umbilical fiber optic probe for remote LIBS (FOLIBS) analysis of copper content in 316 H austenitic stainless steel in a nuclear power station. The limit of detection and the accuracy were calculated to be 360 ppm and 4%, respectively.

Marquardt et al. [46] used a simple fiber optic probe for quantitative LIBS analysis of lead in paint. In this case, an optical fiber of length 4 m transported the laser pulse to the sample and the emission signal to the spectrometer. With this configuration, the LOD was 0.014% for Pb in paint with relative sample standard deviations of 5%–10%. In 1998, the same authors designed and constructed a fiber-optic imaging probe for remote LIBS, remote Raman point analysis and remote Raman imaging



**Fig. 9.** Basic LIBS geometry to focus a laser pulse into an optical fiber.



**Table 3**

LIBS instruments that uses a fiber optic cable for laser delivery.

References	$\lambda$ (nm)	Distance	Fiber diameter	Fiber material	Configuration	Optical system for laser focusing at the output end of the fiber	Energy at the target	Application	Samples
[42]	1064	100 m	550 $\mu\text{m}$	Fused silica	#2 fiber	A pair of lenses, each with $f=25$ mm	12–15 mJ	Nuclear reactor	Ferrous material
[43]	1064	5 m	1500 $\mu\text{m}$	BK7	#1 fiber	A pair of lenses, each with $f=50$ mm	84 mJ	Environmental	Ba and Cr in Soil
[44]	1064	10 m	550 $\mu\text{m}$	Fused silica	#2 fiber	A single lens to focuses the laser beam	60 mJ	Environmental	Soil
[45]	1064	75 m	550 $\mu\text{m}$	Fused silica	#1 fiber	A pair of lenses with $f=41$ mm (L1) and $f=25$ mm (L2)	5.5 mJ	Nuclear reactor	Cu in 316 H austenitic stainless steel
[46]	532	4 m	600 $\mu\text{m}$ 1000 $\mu\text{m}$	Fused silica	#2 fiber	A pair of lenses, a plano convex (L1, $f/2$ , 0.25 NA) and aspheric (L2, $f/0.56$ , 0.9 NA)	4–19 mJ	Industrial	Pb in paint
[48]	1064	30 m	–	Fused silica	#1 fiber	A low $f/\#$ optical system	–	Environmental	Heavy metals in soils
[49]	1064	5 m	600 $\mu\text{m}$	Fused silica	#2 fiber	A pair of lenses with $f=50$ mm (L1) and $f=30$ mm (L2)	30–40 mJ	Industrial	Stainless steel
[50]	532	3 m	1000 $\mu\text{m}$	Fused silica	#1 fiber	A pair of lenses with $f=100$ mm (L1) and $f=38$ mm (L2)	12 mJ	Industrial	Al Alloy
[51]	1064	20 m	550 $\mu\text{m}$	–	#1 fiber	No optical system	9–10 mJ	Industrial	Stainless steel in water

L1. Collimating lens.

L2. Focusing lens.

and demonstrated its use for remote measurement of the atomic and molecular spectra of solid samples [47].

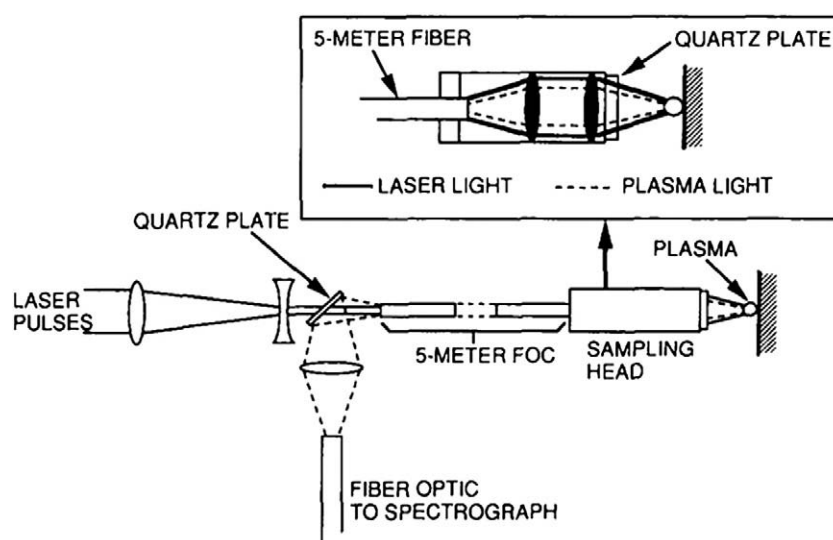
Thierault and coworkers [48] designed a LIBS based instrument for the real time and in situ determination of heavy metals (Pb, Cd and Cr) in soils. The excitation/emission arrangement was housed in a cone penetrometer system. In this work, plasma light was also collected by the same fiber optic cable. Authors also evaluated the sensibility of the instrument as a function of the grain size and moisture content with Pb, Cd and Cr contaminated soils. It should be noted that the instrument exhibited a higher sensibility in dry soil and at particle sizes between 600–800  $\mu\text{m}$ . Nevertheless, the limit of detection calculated under these conditions was below the EPA's site screening levels (SSLs) for Pb, Cd, and Cr in sand.

A few years ago, the University of Malaga designed a laser-induced breakdown spectrometer for quality assessment in the steel industry [49]. The instrument, integrating a robotic arm for sample handling, compares the composition of the finished samples with that of their corresponding heat samples and checks for the occurrence of a possible “mix-up” between consecutive series. Seeking robustness, the laser and the plasma emissions are guided via two different fiber optics, making use of specifically developed optical arrangements. Although the system has been applied to stainless-steel analysis the

instrument can be used for the analysis of many types of materials, offering a wide range of potential applications such as in mining extraction or classification of solid wastes for recycling.

In 2001, Rai et al. [50] used a fiber-optic LIBS system to produce a spark as well as to collect the resulting radiation in an aluminum alloy sample. Several experimental parameters, such as laser energy, temporal conditions, lenses-to-sample distance and sample surface, were tested in order to improve the signal-to-background ratio (SBR). The results were compared with that obtained in a conventional LIBS system that does not use a fiber to transmit the laser beam. For some elements in the sample analyzed, the analytical figures of merit were comparable to those for conventional LIBS measurements and for some elements it was even better. A calibration curve of Cr, Zn, Fe, Ni, Mn, Mg and Cu was also obtained.

This approach has been also applied to the LIBS analysis of materials submerged in water [51]. The measurements were conducted using a fiber optic of 20 m length. The fiber delivered the laser radiation to the target material and also collected the plasma emission for LIBS analysis. In this work, the laser beam was directed onto the sample surface with no optical components. In addition, argon, nitrogen and compressed air were used as buffer gases. Several parameters such as the influence of the buffer gas flow, the



**Fig. 10.** Optical lay out of the remote LIBS configuration designed in [43] for soil analysis. In this configuration the same fiber optic cable was used for plasma formation and collection of the plasma light. Published with the permission of the Society for Applied Spectroscopy.

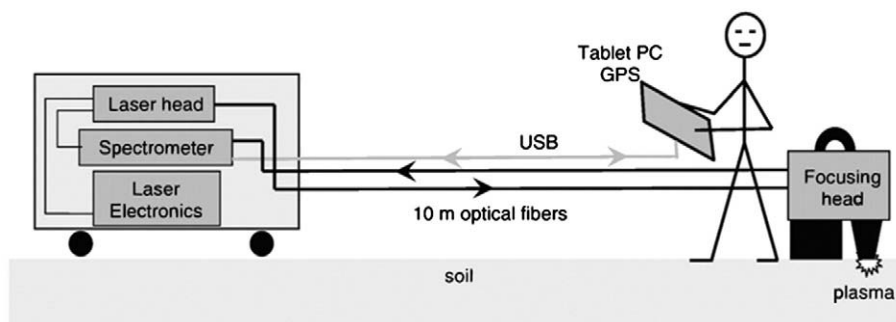


Fig. 11. Schematic display of the mobile LIBS instrument taken from [44]. The laser and the spectrometer are held on a trolley and connected to the focusing head by optical fiber. Published with the permission of Elsevier.

temperature and electron density and the working distance from the sample were conducted in order to optimize the instrument. The LOD for standard steel samples were  $310 \pm 45$  ppm,  $325 \pm 48$  ppm and  $455 \pm 55$  ppm for Cr, Mn and Si, respectively.

### 3.2.2. Stand-off LIBS systems

Because of its simple and direct nature, the LIBS technique is an optimal candidate for use as a sensor, employed in the field (e.g., environmental monitoring), in industrial processes (e.g., quality control in an assembly line), or in settings that are adverse to human health (e.g., nuclear reactors). In cases when a large area must be analyzed, an open-path configuration should be used. In this configuration, namely stand-off LIBS (ST-LIBS), both the laser radiation and the returning light from the plasma are transmitted through a transparent atmosphere. This approach requires a high laser power density in order to generate an useful laser-induced plasma at long distance, and also for collecting the sufficient plasma light for analytical purposes. One of the major problems associated with ST-LIBS is the attenuation of light by the atmosphere. In addition, light propagation and attenuation depend on the distance that the light travels. The attenuation is bidirectional, while the path propagation is horizontal in most of the cases near the surface. A priori, the variables that can affect the behaviour of light are wind, humidity, atmospheric pressure, various sources of thermal radiation and the wavelength of the photons. All these variables affect the behaviour of the propagating light, because variation in these parameters implies a change of the complex refractive index. Also, the presence of particles of variable diameter may affect the atmosphere transmittance. Recently, a theoretical study of atmospheric extinction mechanisms of optical radiation was carried out by Ferrero et al. [52]. Authors evaluated how the propagation of light is affected by the atmosphere and demonstrated that atmospheric extinction of the return plasma light is small when compared with the inverse square law attenuation with target distance. Most recently, Laserna et al. [53] reported the effect of atmospheric turbulence on LIBS experimental measurements at distances up to 120 m. Fig. 12 shows a photographic detail of the ST-LIBS sensor specially designed for distances up to 120 m. Several consequences of atmospheric turbulence, including the spreading of the laser beam, random variation of the position of the laser beam centroid on the target (beam wander), fluctuations in the position of the plasma image at the telescope focal plane, and the irradiance fluctuations, affecting both the laser beam transmission and the atomic emission reception, were discussed. Results were of great interest since beam wander effect increases with range and turbulence and may become the dominant noise source of LIBS measurements at a distance.

Furthermore, the distances feasible in a stand-off LIBS configuration depend on many parameters including the features of the laser (such as pulse energy and power, beam divergence, and spatial profile) and also the optical system used to focus the pulses at a

distance. Most of the LIBS systems designed for stand-off applications use nanosecond laser pulses. Nevertheless, recent studies have reported the used of femtosecond laser pulses for LIBS measurements at distances in the range of kilometres. In a recent review [54] Sallé et al. report the use of an open-path configuration for the LIBS analysis of objects at a distance. In this review, the authors explain in detail the LIBS fundamentals for the design of a stand-off instrument as well as the specifications regarding the laser system, the optical system used for laser focusing and plasma light collection, and the spectrograph and detector system. Previously, Panne [55] classified laser remote sensing into two configurations, *direct* analysis when both the laser radiation and the plasma emission are transmitted in an open-path atmosphere and *indirect* analysis when the laser and the signal are transmitted through a fiber optic cable. The details of different configurations, the instrumentation, and mobile platforms for remote sensing are also explained in this report. In 1987 Cremers demonstrated the capability of LIBS for chemical analyses at distances up to 2.4 m [56]. In this setting, Cremers evaluated the use of a long focal length lens to generate the laser-induced plasma and an optical fiber to collect the emission light, with a high reproducibility. In addition, the author studied a number of field-based and industrial applications by LIBS when a portable laser was built for remote detection. In this



Fig. 12. Photographic detail of the LIBS instrument designed for stand-off analysis at distances up to 200 m.

**Table 4**

Laser focusing system for stand-off analysis of hazardous and energetic materials.

References	$\lambda$ (nm)	Energy	Distance	Optical system for laser focusing	Samples	Instrumentation
[53]	1064	1200 mJ	Up to 120 m	Cassegrain open-truss telescope	Metal samples	Dichroic mirror, Fiber optic
[58]	1064	350 mJ	25–95 m	A pair of lenses with $f=189$ mm (L1) and $f=-62.1$ mm Dichroic mirror	Metal samples	Concave Al mirror, dichroic mirror, fiber optic
[57]	1064	350 mJ	45 m	Same as [58]	Energetic materials	Same as [58]
[60]	1064	$2 \times 275$ mJ	20 m	Schmidt-Cassegrain telescope	Metal samples Biological samples Energetic materials	Fiber optic
[61]	1064	$2 \times 250$ mJ	25 m	Same as [60]	Energetic materials	Same as [60]
[62]	1064	$2 \times 335$ mJ	20 m	Same as [60]	Energetic materials	Same as [60]
[63]	1064	$2 \times 335$ mJ	30 m	Same as [60]	Energetic materials	Same as [60]
[64]	1064	$2 \times 275$ mJ	20 m	Same as [60]	Biological materials	Same as [60]
[66]	1064	800 mJ	30 m	Cassegrain telescope	Metal samples Energetic materials	Fiber optic

work, a qualitative and quantitative analysis of metals in stainless steel samples was performed at a distance, with accuracy and precision of 5% and 10%, respectively.

It is important to take into account that the optical configurations for laser focusing and plasma light collection depend on the analytical application. In this review, we will only discuss the experimental requirements for the *in situ* analytical applications in stand-off LIBS measurements.

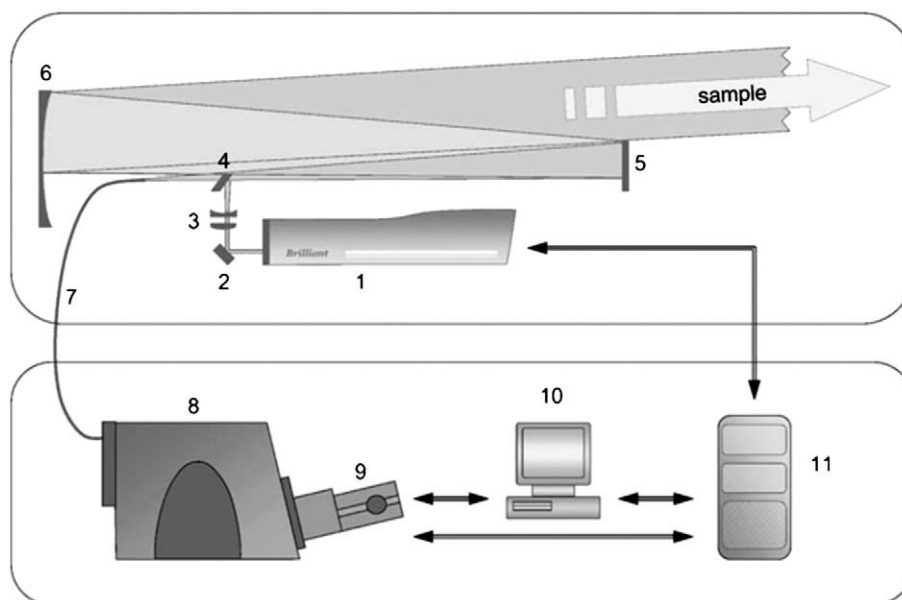
### 3.2.3. Applications of ST-LIBS

**3.2.3.1. Detection of explosives.** Nowadays, the stand-off detection of explosives and hazardous materials by LIBS is one of the applications receiving more attention. As is known, LIBS possess many attractive attributes for a fast field-portable sensor system. The portability and remote capabilities of LIBS make this technique one of the most suitable ones for hazardous materials in the field. Explosive materials are organic compounds mainly consisting of C, H, O and N. It should be noted that the entrainment of atmospheric O and N into the laser-induced plasma complicates the discrimination of energetic and non-energetic materials. Nevertheless, although LIBS is essentially an elemental technique, it has been successfully tested as a powerful method for the chemical detection and identification of these kinds of

materials. The most important laser focusing systems in stand-off analysis of explosives are summarized in Table 4.

In 2006 Lopez-Moreno et al. [57] demonstrated the capabilities of stand-off LIBS for the chemical detection of energetic materials at distances up to 45 m. Although the energetic materials chosen were of military use, the aim of this research was a preliminary investigation of the capabilities of LIBS for the stand-off detection of explosive residues in the field. The stand-off instrument was previously designed and developed by the University of Malaga [58]. A schematic of the experimental set-up is shown in Fig. 13. In this work, the authors used the C<sub>2</sub> Swan band as well as the H, O and N emission intensity ratios in order to classify the samples into organic explosive, organic non-explosive, and non-organic compounds. The authors also shown satisfactory results for the detection of explosive materials in one fingerprint or 100 ppm solution drop containing about 5  $\mu$ g of explosive.

In recent times, efforts at Army Research Laboratory (ARL) have been focused on improving the selectivity and sensitivity of LIBS for the detection of explosive residues [59]. In 2007 the authors studied for the first time the effect of double-pulse LIBS on explosive materials [60]. In this previous report, the authors used a collinear DP-LIBS configuration to improve the discrimination of explosives by diminishing the contribution of atmospheric oxygen and nitrogen to the LIBS signal. Furthermore, the use of ROC curves and PCA algorithms also improved LIBS detection. Although DP-LIBS is not as effective at displacing the atmosphere with an



**Fig. 13.** Schematic diagram of the LIBS instrument designed for stand-off analysis at distances up to 25 m, (1) laser, (2) folding mirror, (3) lenses, (4) dichroic mirror, (5) focusing mirror, (6) primary mirror, (7) fiber optic cable, (8) spectrograph, (9) detector, (10) personal computer and (11) laser power supply. Reproduced with permission from [58].

inert gas, it does have the advantage of being applicable to a stand-off LIBS system [61]. In this prototype, the combined double-laser pulse was directed along the axis of the telescope by an articulating arm and focused at distance up to 20 m. It is important to take into account that the substrate material for the residue sample was aluminum foil. The authors evaluated the advantages of DP stand-off LIBS over single pulse analysis for explosive detection. Most recently, the same authors extended the discrimination of explosive residues on a simple aluminum substrate to more complex organic and inorganic substrates [62].

It should be noted that the collection of LIBS spectra from an unknown sample is only the first step in explosives detection. The most important feature in this research is the ability for discriminating between explosive and non-explosive materials. At present, the method of relative atomic and molecular LIBS emission intensity prior to the chemometric analysis is widely recognized in this task. Over the years, different statistical tools including flow chart analysis, linear correlation, principal components analysis (PCA), the soft independent method of class analogy, and partial least squares discriminant analysis (PLS-DA) have been used to detect explosive residues [63,64] and chemical and biological warfare agents [65]. Most recently, Ferrero et al. [66] proposed an easy solution for obtaining the relation between a spectrum and a spectrum base. This solution, called method of normalized coordinates (MNC), was based on the algebraic determination of the problem spectrum coordinates with respect to the library base. In addition, this method allows the detection of the presence of several compounds in a mixture and also the improvement of the discrimination capacity compared to the linear correlation method.

Most recently, González et al. [67] demonstrated that ST-LIBS detection of explosives behind a barrier was possible as long as part of the laser beam energy can go through the barrier and at least part of the plasma light can be collected. As expected, the LIBS signal was found to depend on the specific barrier composition. Nevertheless, they found that the position of the barrier between the target and the standoff sensor was irrelevant for explosives detection. Also, in the less favorable case, a decision based on 8 shots was enough to obtain a sensitivity of 100% without false alarms.

**3.2.3.2. Use of ST-LIBS for planetary exploration.** Since the 80 s, the LIBS technique has been under investigation in laboratories around the scientific world. In the 90 s, Los Alamos National Laboratory recognized the potential of LIBS for future planetary exploration and started a complete study of this application. Data relating to planetary geology is the main goal in the use of LIBS for space exploration. This task is of crucial importance since it could answer some questions such as the physical and chemical evolution of the solar system, the geological processes on the Earth and the optimal weather conditions for life. The possibility of LIBS for stand-off analysis and the ease of combination with other spectroscopic methods such as Raman and LIF has increased the possibility of the implementation of LIBS as an instrument in future space missions. The stand-off and fast capabilities of LIBS will greatly increase the number of possible measurements during the limited lifetime of a mission.

At early stages, Blacic et al. [68] demonstrated outdoors the feasibility of remote LIBS for the analysis of geological samples at 24 m by loading laboratory equipment onto a movable cart. Based on this preliminary work, Cremers et al. [69] verified that the technique had sufficient sensitivity to detect the elements of interest to lunar geologists at concentrations in a moon rock simulant. Remote analysis was performed in the laboratory at distances of 10.5 m on an *Apollo 11* rock simulant. These advances were followed by additional research into LIBS for application to Mars exploration [70]. In this work, the same system was used for stand-off analysis of soils at reduced air pressures and in a simulated Martian atmosphere (5–7 Torr of CO<sub>2</sub>). Remote analysis at 20 m showed that LIBS signals increased under Martian conditions but decreased when the pressure was further reduced.

An initial field test of a stand-off LIBS instrument for applications in space missions was accomplished by Wiens et al. [71]. This group started to develop LIBS for future use from a rover or lander on a planetary surface to remotely obtain elemental information on rocks and soils within 20 m of the instrument. The system, a compact sensor head housing the laser head and all the optical arrangements was mounted on a prototype rover. Geological, mineralogical and elemental composition for rock and soil targets was performed by using the prototype rover instrument.

In 2004, the efforts of the LIBS community in the field of planetary exploration were recognized when a new LIBS instrument was selected for the mobile NASA Mars Science Laboratory (MSL) rover. This instrument, called ChemCam, was scheduled for launch in 2010 to investigate Martian geochemistry. The ChemCam package consists of two remote sensing instruments: LIBS and a Remote Micro-Imager (RMI), mounted on a rover body, for elemental analysis at distances from 2 to 9 m. The LIBS provides elemental compositions, while the RMI places the LIBS analyses in their geomorphologic context. The main objective of ChemCam is the fast chemical characterization and identification of soils and rocks [72]. For this reason, the international team entrusted to develop stand-off LIBS technology for space exploration has been working with new data processing methods. Calibration curves as well as multi-matrix calibration curves and a calibration free approach have been applied in the LIBS analysis of rocks at distances between 2 and 6 m [73,74]. Nevertheless, the results obtained by these methodologies were comparable and in good agreement with the requirements of ChemCam.

**3.2.3.3. Stand-off analysis using femtosecond LIBS.** LIBS is a versatile spectroscopy technique based on the emission light of the analytical constituents in a laser-induced plasma, usually that produced by a nanosecond laser pulse system (ns-LIBS). In recent times, femtosecond laser pulses (fs-LIBS) have also been proposed for use in LIBS analysis. Several advantages of using ultra-short laser pulses including a lower ablation energy threshold, low continuum emission, higher sensitivity, and improved detection precision, contributing to make this approach an attractive alternative for the design of new and more sensitive LIBS systems. In fact, the use of femtosecond and picosecond laser pulses for remote LIBS applications has increased considerably in the last few years. The main problems associated with fs-LIBS are its more expensive set-up and also its size, complexity, and the associated requirement for a highly controlled operating environment.

In 2002, *Teramobile*, a new mobile femtosecond multi-terawatt laser and detection system was designed through collaboration between French and German organizations [75]. The experimental set-up consisted of two main parts: the laser system and the detection system, both contained in a standard container of 6 m length and 2.5 m width. The container was transportable and provides a stable environment under various climatic conditions. In this work, the authors report the applications and first results of the *Teramobile* system. Rohwetter et al. [76] demonstrated the capability of ultra short laser pulses for remote LIBS analysis of Cu and Al targets at distances up to 25 m. Furthermore, the laser system used generates pulses in the nanosecond, femtosecond and picosecond regimes which allowed direct comparison between the three laser pulse durations. The femtosecond pulses were found to produce LIB spectra which avoid external interference in the chemical identification of complex and unknown samples. Also, the limit of detection estimated for the Cu sample was 100 ng at a distance of 25 m.

The development of remote filament-induced breakdown spectroscopy (R-LIBS) has allowed LIBS analysis at distances higher than those obtained with typical nanosecond laser pulses. It has been reported that filamentation occurs at a distance as far as a few kilometers in the atmosphere, overcoming the diffraction limit of conventional ns-LIBS to deliver a high laser intensity over a long distance [77]. This approach is based on the use of filaments produced



by ultrashort laser pulses propagating in air. The formation of filaments in the air is a well understood process and can be described by the action of two nonlinear physical effects: the optical Kerr effect and multiphoton absorption. Filaments appear as a result of a dynamic equilibrium between Kerr lens focusing and defocusing on the laser-induced plasma produced by multiphoton/tunnel ionization of the air molecules. The equilibrium limits the laser intensity inside the filament core to about  $5 \cdot 10^{13} \text{ W/cm}^2$  (intensity clamping). A well-described report of femtosecond filamentation in a transparent media (air (gases), transparent solids and liquids) was presented by Couairon and Mysyrowicz [78].

The capability of R-LIBS for the analysis of metallic targets at distances up to 90 m and 180 m was demonstrated by the *Teramobile* group. In 2004, Stelmasczyk et al. [79] presented the emission LIB spectra of copper and iron at 90 m. In this experiment, a typical multiple-filamentation pattern, exhibiting around 30 filaments across the beam profile, was observed on the sample. It should be noted that the signal measured by R-FIBS did not depend on the propagation distance (R) when compared with a focused beam. Fig. 14 shows the distance dependence of the range-corrected R-FIBS signal from the 521.8 nm line of copper. As observed, due to the  $1/R^2$  term, the signal-to-noise ratio (SNR) decreased with the detection distance, and its extrapolated value drops to 1 around 150 m. This distance must be seen as a lower limit. Nevertheless, improvement in the detection system could enhance the R-FIBS signal by a factor of 100. In addition, this fact should allow R-LIBS measurements at distances up to the kilometer range. Subsequently, Rohwetter et al. [80] analyzed aluminum samples at a distance of 180 m, obtaining the same results as Stelmasczyk. The main goal of this report was to demonstrate the ability of R-FIBS to generate plasmas at distances exceeding 100 m. The lifetime of the plasma line emission was about 130 ns, a decay time much shorter than that observed in conventional LIBS with focused pulses (femtosecond, picosecond or nanosecond duration) at shorter distances. Finally, a parameter estimation based on the experimental data at 90 m shows that kilometer-range R-FIBS operation would be possible with an improved high-throughput spectrometer coupled to a telescope with a primary mirror of 70 cm diameter and an ICCD camera. Very recently, Xu et al. [81] evaluated the numerous advantages of remote sensing of metallic targets using R-LIBS. The authors calculated the temperature (6794 K) and electron density ( $8 \cdot 10^{17} \text{ cm}^{-3}$ ) in the plasma generated on a lead target by femtosecond laser pulse filamentation in ambient air. These results were acquired at a delay time of 20 ns respect to the laser pulse and as such, leads to a high SNR value. In this report, the authors also concluded that the single-shot detection limit can be extended to the kilometer range.

Nowadays, the remote filament-induced breakdown spectroscopy technique has also been applied in different field such as the

discrimination of samples of geological interest [82], the detection and identification of biological agents in security applications [83], and the analysis of cultural heritage samples [84].

**3.2.3.4. New trends in stand-off LIBS.** In recent times, one of the major advantages of using LIBS is the possibility to combine it with other spectroscopic techniques. This ability is really noticeable when combined with analytical methods that use essentially the same instrumentation and also have stand-off analysis capability. In this sense, the analytical techniques widely used in combination with LIBS for stand-off applications are Raman spectroscopy and laser-induced fluorescence (LIF).

Raman spectroscopy is a light-scattering method that provides vibrational information about the molecule being analyzed. The theory of Raman spectroscopy is beyond the scope of this work; however, additional information may be found in [85]. Nevertheless, the advantages of Raman spectroscopy have allowed the chemical identification of chemical substances over the years. The technique has been widely tested in polymer analysis, environmental monitoring, material processing and cultural heritage applications. Nowadays, significant advances in laser technology offer the possibility of remote and stand-off Raman for field measurements [86]. The combination of Raman and LIBS techniques yields complementary information about the sample under examination [87]. Wiens et al. [71] reported the advantages of combining both techniques in a single instrument for stand-off analysis at distances up to 8 m. In this work, the authors demonstrated the feasibility of and synergy of the Raman/LIBS instrument for the chemical identification of minerals at distances. One of the major fields of application of this combination is the chemical analysis of rock, soils and materials of geological interest for planetary explorations and space missions. In addition, an instrument combining Raman and LIBS has been pre-selected to be on board the next mission to Mars of the *European Space Agency* (ESA) in 2013 [88]. Raman and LIBS will be integrated in a single instrument inside a rover on the Martian surface to perform in situ analysis of soils in searching for signs of past and/or present life on Mars.

Recently, the combination of both techniques has also been applied to the stand-off detection of explosives and related materials [89]. However, the number of published reports in this field is limited. One of the main advantages in the fusion of Raman and LIBS is the complementary information extracted from the same single spot when both sensors work side-by-side. In those cases, only the data were fused. As an example, a new standoff spectrometer based on the fusion of LIBS and Raman spectroscopy was built by Miziolek et al. [90]. The authors demonstrated the capability of both methodologies for the detection and discrimination of explosives residues at distances up to 50 m. Discrimination of these residues was improved by using the LIBS/Raman instrument in comparison with the results obtained when both techniques worked alone. Most recently, Laserna et al. [91] designed a simultaneous Raman-LIBS instrument for stand-off analyses of explosives using a mobile integrated sensor platform. In this report, the authors demonstrated the ability of this sensor to simultaneously acquire, in real time, both molecular and multi-elemental information from the same laser event at distances up to 20 m. Both signals were collected through a bifurcated optical fiber and conducted into two identical detection systems.

Another analytical technique that may have potential for combination with LIBS is laser-induced fluorescence (LIF). LIF is one of the most sensitive approaches available for analytical purposes. It is relatively easy to implement, phenomenological straightforward, well investigated and largely non-invasive. Furthermore, LIF has been widely used in the analysis of vegetation, pollutants and cultural heritage samples. The combination LIBS/LIF yields valuable information since it combines the atomic information provided by LIBS with the molecular data provided by LIF. A mobile LIDAR system was used for LIBS/LIF measurements on cultural heritage samples at distances of

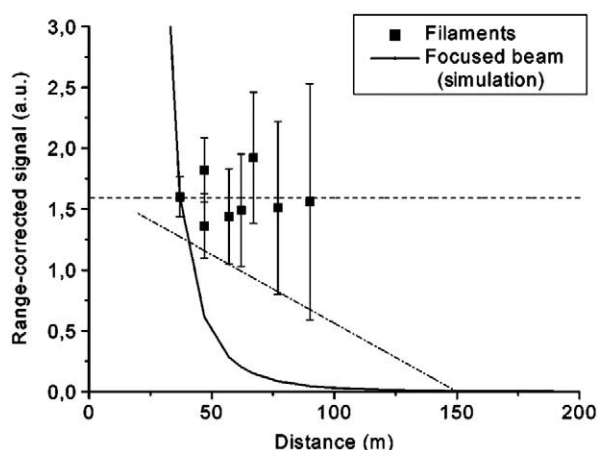


Fig. 14. Distance dependence of the range-corrected R-FIBS signal from the 521.8 nm line of copper. Reproduced with permission from [79].

60 m [92]. In this experiment, elemental imaging was achieved by coaxial transmission and common folding of the transmission and reception optical paths using a large computer-controlled mirror. In this report, the authors also discuss the relative advantages of long- and short-pulse remote LIBS/surface cleaning/LIF.

#### 4. Commercial systems

After the successful development of integrated prototypes in research laboratories, several companies have presented commercial versions of transportable LIBS instruments, usually for specific applications. Nowadays, although several companies are continuously working on the design and development of commercial systems for research laboratories, the industry, and also private and public organizations, the commercialization of LIBS has not grown as much as expected. This is due to a number of limiting factors: (1) current lasers are still too large, heavy and expensive for fieldable systems if full LIBS performance is required, and (2) the inherent problems (i.e., accuracy, matrix effects, difficulties with quantitative analysis and sample inhomogeneity) associated with the technique when a real-world application is needed. Nevertheless, the commercialization of LIBS still needs a lot of effort not only in the improvement of the analytical figures of merit, but also in the portability (size and weight) of the instrument. Furthermore, future and new trends in LIBS could benefit by the combination of LIBS with other analytical methods. Table 5 summarizes some of the commercial systems now available, for example, PharmaLIBS™250 (Pharmalaser), LIBS2500 (Ocean Optics Inc.), LIBSCAN™ 50/100 (Applied Photonics Ltd.), Insight™ (Photon Machines) and ECCO™ (Foster and Freeman), among others. However, most of these examples summarized in Table 5 are benchtop and specific for one application. Currently, there is no guarantee that a rugged, compact, user-friendly in a broad range of applications, battery-powered and not too expensive fieldable LIBS instrument will be commercialized anytime soon.

#### 5. Conclusions

In this review, new trends in the development of fieldable instrumentation based on laser-induced breakdown spectroscopy (LIBS) and its recent applications have been presented. Fieldable systems offer large flexibility and also increase the range of LIBS applications to areas such as environmental monitoring, geological surveillance, cultural heritage, industrial processes and military and homeland security. This report distinguished between close-contact inspection (portable systems) and analysis of distant objects (remote and stand-off instruments). Only those LIBS instruments specially designed for in situ applications on field have been reviewed here. Advances in the development of laser sources (high repetition rate, low power consumption and low cost), the implementation of microchip lasers and fiber based lasers with high power, the design of new optical

configurations for guiding and collecting the light and the use of panoramic detectors with high data transfer rate are nowadays the future of fieldable LIBS instrumentation. Capability of LIBS for field measurements would also benefit from the development of improved data processing algorithms. Also, the maturity of the instrumentation could offer the possibility of a LIBS system to be mounted on a remotely operated vehicle (ROV) specially designed for air, ground or underwater analysis. Analytical performance of fieldable LIBS instrumentation in terms of sensibility and reproducibility are in good agreement with the requirements for field measurements.

The stand-off analysis of solids at distances up to 100 m has been demonstrated with nanosecond pulses. A large number of telescopes has been described in the literature to tightly focus the laser beam at large distances for plasma formation and plasma light collection. Developments of ST-LIBS are closely related to military and security applications and to the analysis of explosives and energetic materials. In the last few years, femtosecond pulses have also been proposed in the design of stand-off LIBS sensors due to its lower ablation energy threshold, low continuum emission, higher sensitivity, and improved detection precision. For long distance analysis in the kilometre range, a new approach based on filaments induced by femtosecond pulses has been also demonstrated. This review also reports recent advances in the combination of LIBS with other analytical techniques such as Raman spectroscopy or LIF spectroscopy as new trends in stand-off instrumentation. These methods improve the analytical capability of a conventional LIBS system since they combine the multi-elemental information of LIBS with the molecular information provided by Raman and LIF. Nevertheless, the future of portable LIBS instrumentations depends on a key ingredient: the imagination of the researcher in designing and assembling the LIBS system and also, in the commercialization of rugged and user-friendly systems.

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**Table 5**  
Commercial LIBS systems.

Company	LIBS system
Ocean Optics	LIBS2500
Thermo-electron	ARL laserspark
Pharmalaser	PharmaLIBS™250
Applied Photonics	ST-LIBS™ FO-LIBS™ LIBSCAN™ 50/100
Laser Analysis Technologies	Spectrolaser system
Applied Spectra	RT-100 series LIBS system
Photon Machines	Insight™ Crossfire™ Tracer2100
BAe System	ECCO™
Foster and Freeman	
StellarNet, Inc.	Porta-LIBS-2000

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