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Applications of Laser-Induced Breakdown Spectroscopy to Cultural Heritage and Archaeology: a critical review

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Abstract

In this paper, we present a critical review on the applications of the Laser-Induced Breakdown Spectroscopy (LIBS) technique to Cultural Heritage and Archaeology. The strategies used by the groups involved in this kind of research for the analysis of the typical materials of interest (metals, pigments, pottery, glasses, etc.) are discussed in detail, as well as the use of LIBS in combination with other techniques (LIBS and Raman, LIBS and XRF, LIBS and MS). Specific applications of LIBS as a support for Cultural Heritage restoration and the application of the technique for the analysis of underwater objects are treated in separated sessions. In conclusion, new trends of LIBS for Cultural Heritage and Archaeology (micro-LIBS analysis, 3D elemental imaging, Surface- and Nanoparticle-Enhanced LIBS) are introduced and discussed.

Keywords: LIBS, Cultural Heritage, Archaeology

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1 - Introduction

The Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique based on the use of a pulsed power laser which, focused on the sample surface, produce the ablation of a small amount of material and its excitation [1]. The ablated material, in the state of plasma, emits a characteristic spectrum, which give qualitative and quantitative information about the sample composition. Since its introduction, in the late '80 of the last century [2], LIBS has been successfully applied to the analysis of materials of interest in many different fields, ranging from Industrial diagnostics [3–5], Environmental protection [6,7], Bio-medicine [8,9], Forensic Analysis [10,11], etc. The characteristics of speed, portability, capability of in situ remote analysis without sample treatment and ease to use of the equipment, have made LIBS one of the fastest growing analytical techniques in the last century, with the number of LIBS-related papers published per year nearly doubling from 2010 (225 papers) to 2017 (433)[1]. These very same characteristics have made the LIBS technique interesting for Cultural Heritage (CH) and Archaeology applications. However, contrarily to other kinds of applications, the intrinsic micro-destructive nature of the LIBS technique has somewhat limited its diffusion in these fields; up to date, only about 2% of the LIBS papers (slightly more than 100 papers on a total of more than 4000) deals with LIBS applications in Cultural Heritage. Since Cultural Heritage and Archaeological objects are, normally, valuable and delicate, in some cases unique, the use of a destructive (although minimally) technique must be carefully considered. Alternative techniques exist, such as X-Ray Fluorescence, Laser-Induced Fluorescence, Multispectral Imaging, Raman Spectroscopy, etc.. [12], which are portable, non-destructive and may also provide structural information on the nature of the materials under study. From case to case, the importance of the potential results that can be obtained by LIBS, and not with other techniques, has to be considered by Art conservators and Archaeologists against the possible damages to the object of the study. It is evident that, when a non-destructive option exists, it should be preferred to a destructive approach; however, in our opinion, the main obstacle to the application of LIBS in CH and Archaeology is more related to a difficulty in the communication between LIBS researchers and Art historians, conservators and archaeologists, than to real limitations of the technique itself. It has already been discussed [13] how the undoubtable advantages of LIBS have been largely over-boosted in the past against its equally undoubtable drawbacks, creating great expectations, especially in multi-cultural disciplines as CH and Archaeology, that in most of the cases were not actually met. On the other hand, excellent results have been demonstrated when a fruitful dialog between scientists and humanists has been established and the LIBS technique has been applied in response to a real demand of the operators in the field.

This review presents the most outstanding case-studies, which have demonstrated, in the last decades, the effectiveness of the application of LIBS in Cultural Heritage and Archaeology. In some cases, LIBS has been used in conjunction with other analytical techniques, and these applications will be discussed separately. We

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have organized our work according to the main materials analyzed by LIBS (metals, stones, ceramics, pigments, glass, bones, etc.). In a few cases, multi-material objects or collections have been studied. In that case, the works will be quoted in all the relevant chapters. Specific applications, such as LIBS in restoration and in underwater archaeology, will be treated separately, because of their peculiarities.

Several reviews have been published in the past dealing with LIBS applications in CH and Archaeology [14–21]; our review will thus mostly focus on the most recent applications, not covered by the previous works.

2 - Case studies

2.1 LIBS Analysis of metals

The LIBS technique is particularly suited for the analysis of metallic objects [22] and, therefore, the applications of the technique in CH and Archaeology for this kind of studies are also numerous. It should be considered, however, that most of the advantages of LIBS are shared, in these applications, with the Energy Dispersive X-Ray Fluorescence (ED-XRF) technique [23,24]. ED-XRF is a fast and portable technique, which is capable of precise quantitative analysis without pre-treatment of the samples, in a fully non-destructive way. In most archaeometric applications, thus, ED-XRF should be preferred to LIBS. The intrinsic quickness and non-destructive character of ED-XRF allow for extensive sampling of objects in collections (for authentication and provenience studies [25–28], for example) and/or different points of measurements on single objects, improving the statistical significance of the measurements. There are, however, specific situations in which the LIBS technique might give more information with respect to ED-XRF. Since ED-XRF is, intrinsically, a bulk technique, it is very difficult, if not impossible to discriminate the contributions to the XRF spectra coming from different depths under the surface. Moreover, due to the differences in X-Ray absorption by the elements, the XRF spectra are often a complex combination of fluorescence emitted by the elements at depths of several tens of microns under the surface. This is not a problem for the analysis of homogeneous materials; however, metallic artifacts, especially the archaeological ones, may present surface corrosion layers, which would make the ED-XRF quantitative analysis unreliable. On the other hand, the LIBS analysis is limited to the depth of the crater produced on the sample surface (typically less than one micron in metals); this feature, combined with the micro-destructivity of the technique, allows the use of the laser as a 'drill' for sampling the object at different depths. Although the interpretation of the stratigraphic compositional changes is not completely straightforward, because of the possibility of contamination from the border of the crater and the reduction of the signal due to the defocusing of the laser beam, in the analysis of metals for Cultural Heritage and Archaeology the possibility of making a stratigraphic analysis in most of the cases is the only real analytical advantage of the use of LIBS vs. ED-XRF. From a practical point of view, it should also be mentioned the use of safer optical (LIBS) instead of X-Ray excitation (XRF), which should not be neglected, and the possibility of LIBS of making remote analysis using optical fibers or articulated arms (one meter or less) [29] or up to several meters in open path configuration [30]. On the other hand, ED-XRF analysis must

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be performed at close distance; moreover, most of the portable ED-XRF systems have measurement spots of the order of 1 mm^2, while the laser beam in LIBS analysis can be focused up to a few microns in diameter, allowing for a much higher spatial resolution. Even in the presence of thick corroded surface layers (in archaeological samples, the thickness of corroded layer can exceed hundred of microns), the lateral dimensions of the LIBS crater may be kept lower than the typical dimensions of the XRF spot (around 1 mm in diameter).

We will discuss in the following section the combined use of LIBS and ED-XRF, which has been proved, in many cases, to be very effective for maximizing the information and reducing at the minimum the impact on the objects under study.

Among the applications of LIBS to the analysis of metallic object in CH and Archaeology, it is worth mentioning the following works: Corsi et al. [31], who in 2005 made the analysis and classification of copper age weapons (see figure 1).

Figure 1 - One of the copper-age weapons studied in ref. [31].

Fortes et al. [32], who made, in the same year, a chronocultural classification of bronze and iron-age objects; Burgio et al. [33], for the quantitative analysis of fragments for a bronze statue of Le Seur in 2006; Foresta et al. [34], for the quantitative study and classification of 12 bronze statues at the Museum of Crotona in 2012 (figure 2) using Modì [29], a mobile dual pulse LIBS instrument realized by the Pisa group in collaboration with Marwan Scientific Instruments (Pisa).

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Figure 2 - One of the bronze statues studied in Crotona by LIBS (ref. [28])

In all these cases, the samples presented an extended surface corrosion, which made necessary the use of LIBS for the quantitative determination of the alloy composition [35]. Similarly, in 2010 Abdelhamid et al. applied LIBS for the stratigraphic analysis of a gold-coated archaeological decorative copper object [36].

Agresti et al. [37] also realized a mobile LIBS instrument for the analysis of CH and archaeological samples and in 2016, following a previous study by Siano et al. [38], studied the optimization of LIBS depth-profiling for bronze analysis using 3D digital microscopy [39]. The same authors also applied LIBS in conjunction with other techniques, for the analysis of archaeological samples (THz imaging and LIBS in [40], neutron tomography and diffraction, XRF, X-Ray Diffraction and LIBS in [41,42]). Further applications involved the analysis of a Donatello bronze statue [43] and the LIBS authentication study, combined with micro-structural analysis, of Roman copper-alloy coins [44].

Gaudiuso et al. in 2008 worked on copper-based alloy samples from the archaeological site of Minervino Murge (around VII B.C.) using, besides traditional ns LIBS, also fs LIBS, finding that in both cases the LIBS spectra obtained could be used for the quantitative determination of the alloy composition using suitable calibration curves [45].

The complexity of the analysis of CH and archaeological metallic alloys often triggered the need for sophisticated methods for quantitative analysis and classification. In 2001, Corsi et al. [46] published a paper on standard-less quantitative analysis of gold objects, using the Calibration-Free LIBS method [47]. Fornarini et al. developed in 2009 a theoretical model for the quantitative analysis of quaternary bronzes using ns and

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fs LIBS [48,49]. In 2012, Gaudiuso et al. [50] published a paper on the application of LIBS for the analysis of copper-based alloys objects from archeological sites in Southern Italy (from VII century B.C. to VII A.D.), introducing a standard-less quantitative approach named Inverse Calibration-Free method [51]. In 2014, D'Andrea et al. [52–54] introduced an Artificial Neural Network approach for the quantitative analysis of bronze samples. The same technique was used by Lorenzetti et al. [55] for the analysis of the alloy of the Pisa Griffin, a Medieval Islamic statue conserved at Museo dell'Opera del Duomo, in Pisa, Italy (see figure 3).

Figure 3 - LIBS measurements on the Pisa Griffin (ref. [55]).

Pagnotta et al. in 2015 used the Self-Organizing Maps method for the analysis and comparison of two archaeological bronze samples [56]. In the same year, Agresti et al. [57] developed a depth dependent calibration method for the quantitative analysis of bronzes in stratigraphic LIBS studies.

2.2 LIBS analysis of pigments

The first attempt to determine the paintings elemental nature using a spark of few milligram mass fraction is dated back to 1924: in the *Comptes Rendus des Séances de l'Académie des Science* Edmond Bayle and Henry George briefly presented for the first time the idea of use an elemental spectroscopic technique to analyse pigments. This approach should have been considered very challenging, because until 1971 it is hard to find other examples. In fact, thanks to the invention of laser microprobe in the early 1960s and the following technological developments, a significant advance in the spectrochemical analysis of microscopic specimen

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was brought. In 1971, Petrakiev, Samov and Dimitrov identified pigments in old multilayer wall paintings applying the LMAl Zeiss laser microspectral analyser [58]; 8 years later, Roy published in the National Gallery Technical Bulletin the promising results of a versatile and sensitive analytical tool for the qualitative detection of the characteristic and trace elements found in pigment materials [59]. It may be considered as the first case of LIBS for painting diagnostic: a synthetic ruby resonator rod created laser light pulses with power density up to 100MW/cm^2 producing 95 μm diameter laser crater. Multiple spectra were stacked on the photographic plate, covering the spectral range 200-850 nm (see figure 4).

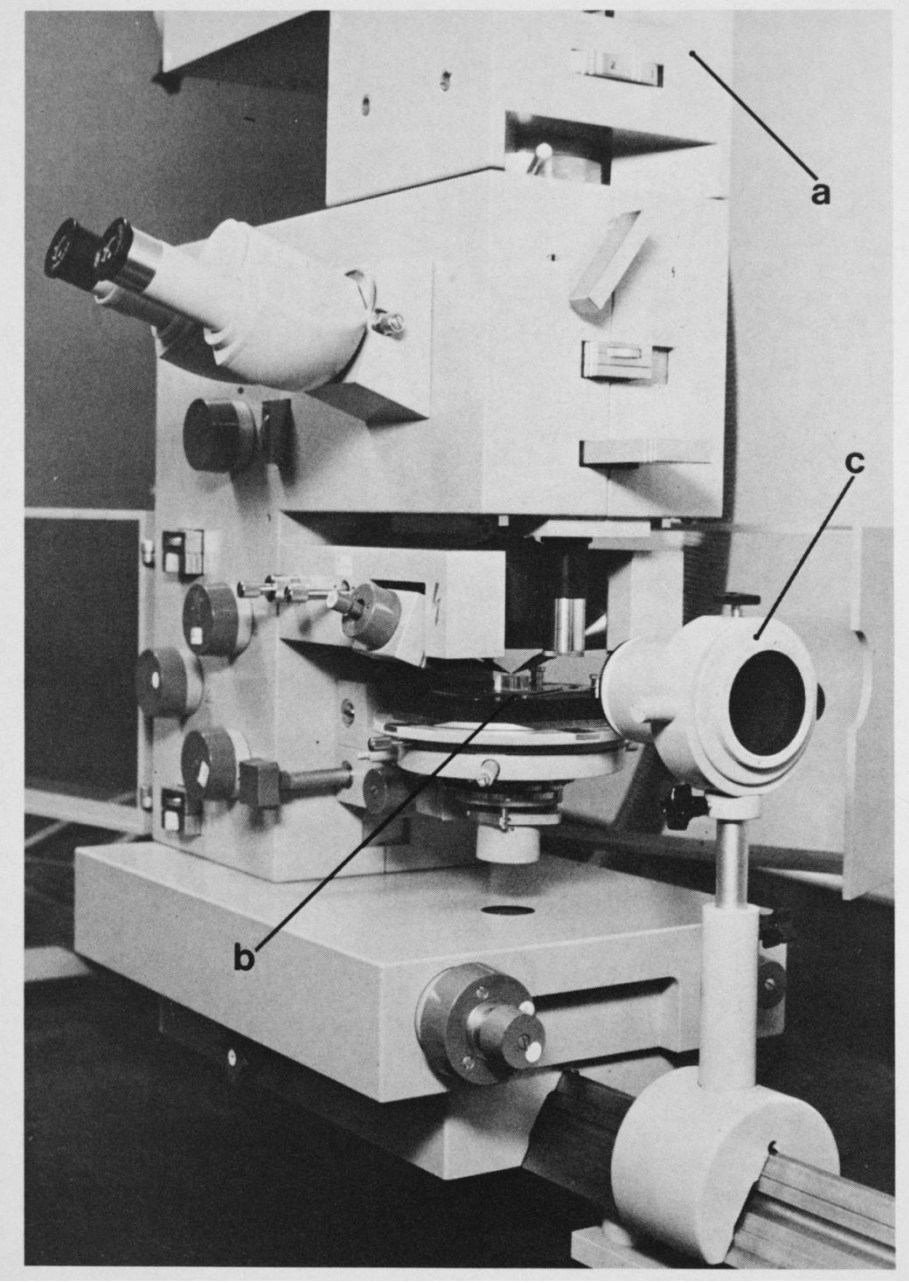

Figure 4 - LMAl Zeiss laser microspectral analyser: (a) optical adaptor, (b) sample stage and spark-gap, (c) imaging quarz lens (ref. [60], courtesy of National Gallery, London, UK).

However, the first paper where the LIBS technique is explicitly mentioned for this purpose, is the work by Anlgos et al. in 1997 [61]. The authors collected LIBS spectra from a wide variety of pigments in powder form and in oil color test samples. Appropriate emission lines for the identification of the metallic elements in the pigments were examined and proposed. Optimal experimental parameters were discussed, demonstrating the analytical capabilities of the technique in the field of pigment analysis of painted artworks. Corsi et al. [60] in year 2000 performed the first LIBS 2D elemental mapping on a II century A.D. Roman fresco from St. Albans, UK (see figure 5).

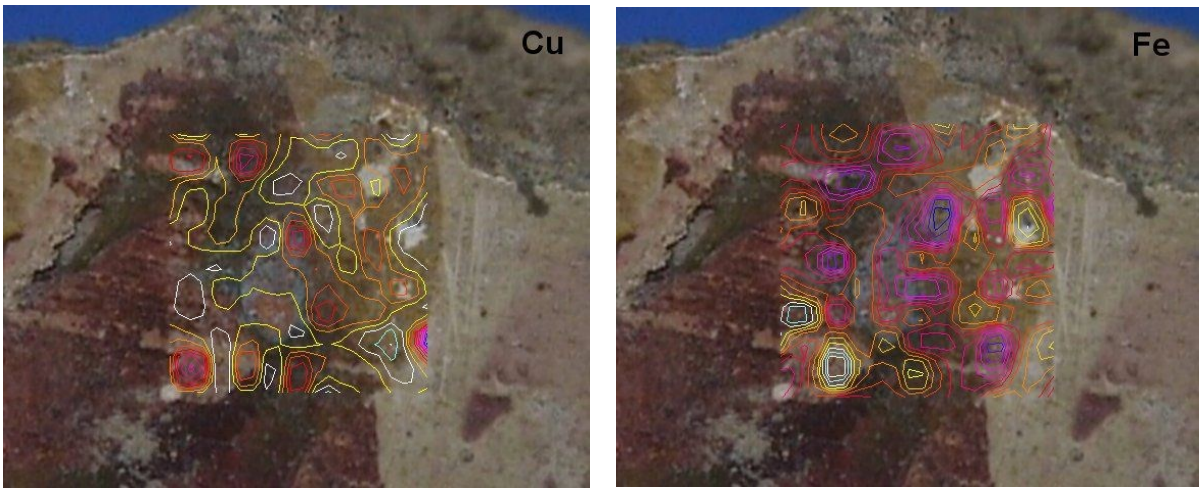

Figure 5 - LIBS elemental mapping (Cu and Fe) on a Roman Fresco (ref. [60]). Red indicates high concentration of the element, blue low concentration.

The same year, Borgia et al. [62] demonstrated the possibility of doing quantitative standardless determination of the composition of the pigments using Calibration-Free LIBS. Later, several examples have been reported in the literature, from the analysis of azurite ($Cu_3(CO_3)_2(OH)_2$) and lapis lazuli, a mixture of minerals with lazurite ($(Na,Ca)_8[(S,Cl,SO_4,OH)_2[(Al_6Si_6O_{24})]$) as the main constituent [63], to byzantine icons [64], Bronze Age painted plaster [65], Roman frescos [66,67], oil paintings [68], grisaille [69], prehistoric rock wall painting [70], Neolithic painted pottery [71] (figure 6) and painted enamel [72].

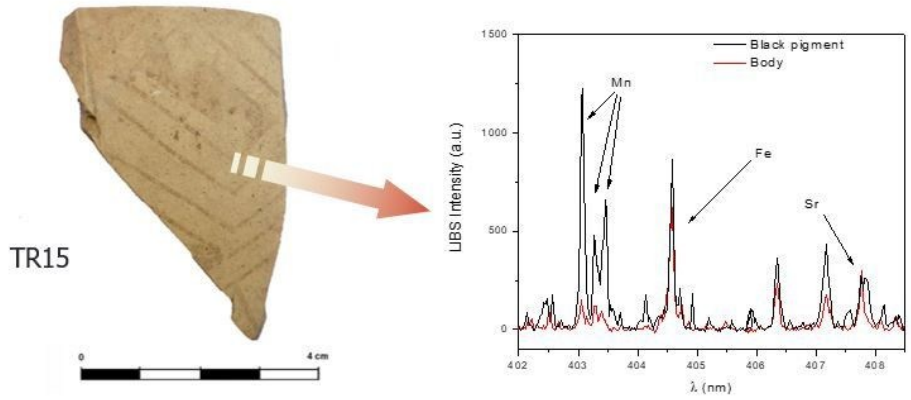

Figure 6 - LIBS analysis on Neolithic pottery, showing the use of Mn oxide as black pigment (ref. [71]).

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Generally, these studies demonstrate that LIBS can be successfully used to identify inorganic, but also organic materials such as the protective polymer or binders [73]. Comparing the emission of CN and C_2 bands in the plasma, in fact, Bai et al. [74] discriminated casein, animal glue, oil and egg yolk in mock-up samples painted with a layer of the pigment cinnabar (HgS). To advance the separation, chemometric method based on the Principal Component Analysis (PCA) was used; the 266 nm radiation allowed for a better performance.

The main drawback of the technique, its micro-destructivity, can be turned into an advantage: each laser pulse can expose a new layer of the artworks, providing a sort of cross-sectional analysis [75]. To better associate the LIBS information to the single layer it is necessary to know the exact depth of the crater after each pulse. For metal alloys [76] it has been already demonstrated that it is possible to estimate the depth of the crater after each pulse with Optical Coherence Tomography (OCT), but only assuming a constant ablation rate throughout the whole experiment. This seems not the case for paint layers, but Kaszewska et al. [77] suggested anyway the use of spectral-domain OCT instrument after each laser pulse as a fast profilometer. In this way, they were able to obtain the precise in-depth scaling of elemental concentration profiles, and the recognition of layer boundaries by estimating the corresponding differences in material ablation rate; the expected statistical errors for the crater-depth determination were about ±4 μm.

Nevertheless, the mass ablation is not the only LIBS weakness; an interesting work by Bruder et al. [78] studied the discoloration phenomenon of lead pigments analysed by LIBS. They found that the pigments faded after a few days exposure under ambient atmosphere. It was established that the mechanism is due to the formation of lead oxide (PbO) through recombination between atomized lead and oxygen in the plume [79]. A threshold for discoloration occurrence was estimated; in particular, if the total amount of energy delivered (fluence-per-shot × number of shots) is less than 35–40 J cm^{-2}, no discoloration is observed. LIBS conditions could then be determined in order not to induce visible discoloration and to ensure a correct preservation of the artwork. In general, for the study of delicate pigments the use of a laser with shorter pulse duration (picosecond or femtosecond lasers) could reduce the photo-thermal effect [80]. Unfortunately, cinnabar even with very low laser energy value tends to darken, irreparably [81].

The elemental content of paint materials was determined in most cases leading to the identification of the pigment used in agreement with da from analyses of the same samples with other established techniques, both elemental as well in terms of different detectable elemental content, such XRF [82] and XRD [83], or molecular for complementary information, mainly Raman, by trying to identify the compounds before and after the laser shot [84], but also FT-IR [85], LIF [18] and HPLC-UV/VIS [86].

As for other LIBS applications, the use of chemometric techniques allows for a semi-automatic pigment recognition. Duchêne et al. [87] showed the promising use of Soft Independent Modelling of Class Analogy (SIMCA) and Partial Least-Squares Discriminant Analysis (PLS-DA) for improving the recognition of unknown spectra acquired in laboratory. The first step lied in the direct spectral comparison of the major lines of the reference and those of the unknown pigment, then each pigment is associated with one element of its

composition. Unfortunately, the method didn't allow for on-site identification, due to the difference of signal intensities between the data and the experimental spectra. Thanks to a more robust instrumentation and using a different approach Syvilay et al. [88] reached better results. The Standard Normal Variate (SNV) method was applied to overcome undesired LIBS signal variations for in-situ depth analyses of painting layers from mural painting. The results were very promising but, as highlighted by the same authors, it is worth noting that even if the method allows for a better visualization of wavelength intensities and so a better recognition of the peaks, the SNV transformation depends on the mean and the standard deviation of the all spectrum, so the efficiency will change according to the specific material. Principal Component Analysis (PCA) was also employed to verify the presence of clusters related to the depth profile analysis of prehistoric paintings [89], attributing the distinct layers. In several samples, in fact, a layer of impurities due to geological processes was deposited on the surface, and the PCA score plot enabled to identify unequivocally the spectra belonging only to the pigment layer.

Finally, it is worth mentioning an interesting approach by Syta et al. [90], which combined LIBS and Laser-Ablation ICP Mass Spectrometry (LA-ICP-MS) for elemental mapping of inorganic archaeological samples: using a 266 nm Nd:YAG laser, cross-sections of mediaeval Nubian objects with specific blue painting layers, including either Egyptian blue or lapis lazuli, were analysed. The distribution of selected elements was mapped with a scan rate of 10μm/s.

2.3 LIBS analysis of geological materials

Since the dawn of the LIBS method, the scientific community linked to the study of geological materials and, among them, those used in Cultural Heritage, has seen in LIBS a valuable tool, in particular for field use. Pottery, among the geological materials of interest for CH, plays a major role in the LIBS application in this field. Pottery is an artificial transformation, through cooking, produced starting from a mixture of geological materials (clays and other materials used to improve the technical characteristics). The principal application on these materials is the study of glazes: the capability to obtain a depth profile that shows qualitatively all the elements in sample, also the low-atomic number ones, is well suited to these studies. One of the first works used glass beads for building a calibration curve for the analysis of archaeological glazes on pottery [91]. In the analysis of complex and multi-stratified artificial materials such as glazed ceramics, there is a need to understand the contribution given by each layer of the material analyzed to the plasma emission spectrum. The contribution provided by the Colao et al. [92] and Lazic et al. [93] studies are very interesting in that respect. The part of the first paper regarding the glaze pottery from Urbino and the second paper, deal with two main problems on this kind of analysis: the inhomogeneity of the material and the contribution of each thin layer to the plasma emission spectrum. The first problem is overcome averaging different spectral lines for each analyzed element; the second problem, as bisque and glaze both contain the same elements, is surpassed by separating the single contribution of bisque and glaze in the emission spectra. Other studies deal with the arguments in a qualitative way going to identify the pigments used for pottery decoration

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[94,95], sometimes comparing the results with other techniques such as SEM/EDX for quantitative purposes [96]. The works of Erdem et al. [97] shifts the focus on the determination of the compositional variation of clay. To overcome the problems given by the natural lack of homogeneity of the ceramic body, the authors analyzed potsherds and pellets obtained from grinded potsherds. A further step forward is the use of a chemometric methods (Principal Component Analysis - PCA) for determining similarities and differences between the analyzed fragments. Genc Oztoprak et al. [98] proposed the use of PCA and Partial Least Squares – Discriminant Analysis (PLS-DA) to classify some ceramic fragments, also focusing on the possibility of doing the LIBS analysis in situ. Xenogiannopoulou et al. [99] made a complete study of Attic black pottery by LIBS analysis, comparing the results with consolidated techniques such as AAS, SEM/EDX, XRF and XRD. Lasheras et al. [100] used LIBS with calibration curves on different standards prepared with KBr and zinc as internal standard for the analysis of Roman pottery and compared their results with Atomic Absorption Spectrometry (AAS). Khedr et al. [101,102] introduced a combination of LIBS and ED-XRF that provided good results, underlining the possibility of carrying out in situ measurements on glazes.

An aspect not dealt with in these works was the possibility to carry out analyses of the Rare Earth Elements (REE) that in geological materials might be useful to identify their origin. A single attempt in this direction was been presented by Rai et al. [103] who have qualitatively studied pottery coming from the Indian site of Kausambi, identifying precise sets of REE that have allowed to confirm the common provenance of the raw materials. Remaining in the Indian geographical area, particularly in the north-east of the country, Singh et al. [104] used LIBS and SEM/EDX to determine the chemical composition and the probable firing temperature of eight ceramic fragments (five Neolithic and three belonging to the historical period). They use LIBS for a qualitative characterization of the ceramic body, while the quantitative analysis was entrusted to the SEM micro-probe. In 2013, LIBS was also used by Legnaioli et al. [105] for a multi-technique authentication analysis of an archaeological ceramic vase.

A new approach that in the future could potentially fit into the normal analytical routine is that introduced by Pagnotta et al. [106] in 2018. Starting from slices of potsherds (negatives of thin sections), the authors mapped a portion of surface samples using a scanning μ-LIBS instrument and analyzed it qualitatively, through the use of image-based techniques. In another paper, Pagnotta et al. [107] extended the previous method for segmenting the elemental maps in qualitatively similar areas, through SOM algorithms (see figure 7).

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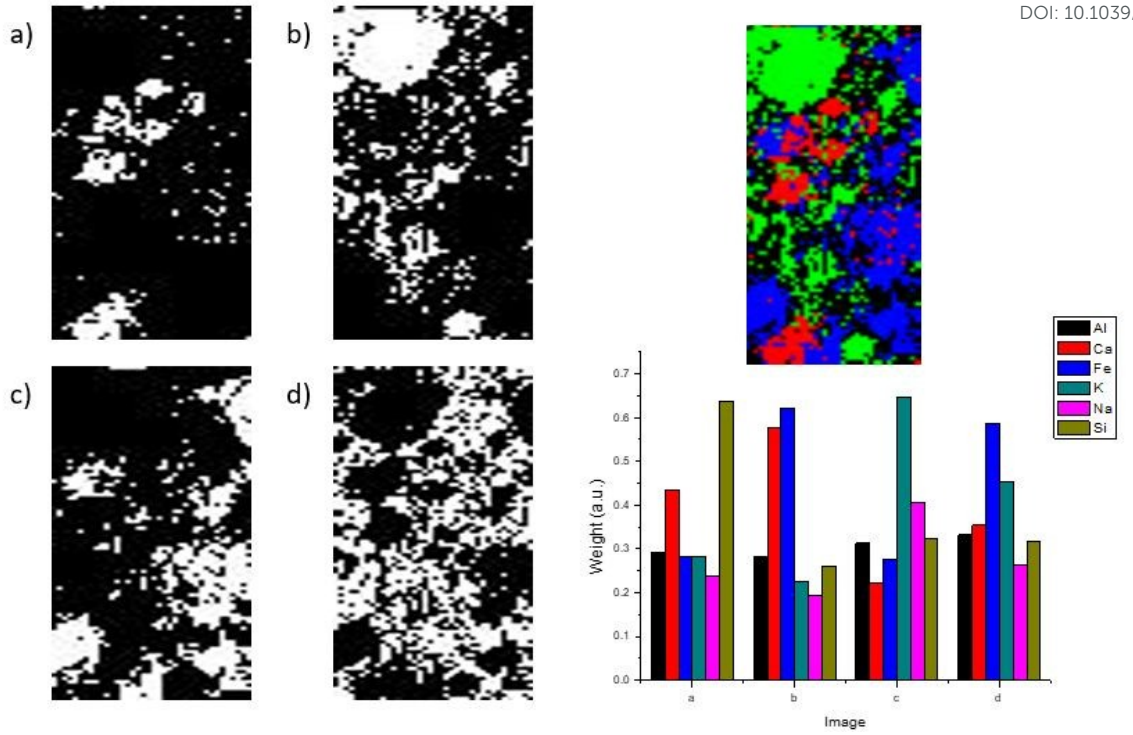

Figure 7 - Reconstruction of the mineralogical composition of a Roman mortar sample from SOM images (ref. [107])

The same authors thus performed standard-less analysis by CF-LIBS, in a fast and semi-automated way, on the prototype spectra provided by the SOM analysis, thus solving the problem of analyzing thousands of spectra to overcome the lack of homogeneity of the material. The work was carried out on mortars coming from the Castle of Adrano (Sicily) [108].

LIBS was also used as a diagnostic tool for the process of laser cleaning of marble, for the first time, by Maravelaki et al. in 1997 and 1999 [109,110]; in 2001, the same authors also characterized the encrustation layer of marble by LIBS [111]. Other works that used LIBS for monitoring the cleaning processes of marble and stones were published in 2001 by Dickman et al. [112] and Klein et al. [113], who studied the discoloration of marble following the laser cleaning, by Hildenhagen and Dickmann in 2003 [114], by Colao et al. [115] in 2004 and by Khedr et al. [116] in 2011. The LIBS analysis of historical marbles for provenience studies was proposed by Lazic et al. in 2004 [117] and then performed in 2007 by Bakry on marbles from Jeddah, Saudi-Arabia [118], Mahmood et al. [119] in 2010, on a variety of marbles extracted from Quetta region of Boluchistan, Pakistan, and by Fahad and Abrar in 2018 [120]. Columbu et al. [121] used LIBS for the analysis of limestone Nuragic statues from Mont'e Prama archaeological site (XI-IX cent. BC) in Sardinia (see figure 8). A blind clustering analysis of the LIBS spectra based on Graph Theory [122] helped in determining the provenance of raw materials employed for the artefacts, indicating the compatibility of all analysed statue samples with geological outcrops from Santa Caterina di Pittinuri area.

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Figure 8 - The 'Giants' of Mont'e Prama, analysed by LIBS in ref. [121] (photo S. Carboni).

The potential of LIBS for underwater analysis of marbles has been demonstrated in 2005 by Lazic et al. [123] and by Guirado et al. in [124].

An interesting work for the mapping of historic buildings was proposed by Fortes et al. [125] in a study performed at the Cathedral of Malaga, in Spain. The authors used a standoff system to reach areas of the building otherwise difficult to access without expensive scaffolding, demonstrating the possibility of remote LIBS characterization and monitoring of stone degradation in historical and modern buildings. In their work, a qualitative characterization of different materials was carried out following a well-defined and structured protocol, in order to reach an accurate description of the construction materials with a good spatial

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resolution. Brai et al. [126], in their study on bricks and mortars sampled in the ancient Greek-Roman Theatre of Taormina, used XRF and LIBS to distinguish chemical characteristics and state of degradation of these building materials. Hemeda [127] combined different techniques (SEM/EDX, MO, XRD, DT-TGA, etc.) focusing on the study of construction materials at the Kom El-dikka site in Alexandria, Egypt.

Raneri et al. [128] studied mortars' LIBS elementary maps with image-processing methods, coupling the qualitative analysis to the data provided by optical and scanning electron microscopy. Senesi et al. [129] in 2018 presented an innovative application of LIBS micro-mapping for the characterization of the surface degradation of the construction materials of the *Castello Svevo* in Bari (Italy). The same author also took advantage in 2018 of the handheld LIBS instrumentation that is now available for the analysis of stone monuments [130], using a Calibration Free (CF-LIBS) approach [131] for obtaining a quantitative determination of the elemental composition of the sample.

2.4 LIBS analysis of bones, teeth and other organic materials

The LIBS technique has been proposed, in the past, for the analysis of biological samples for medical diagnostics [132] and forensic science [133]. The same methods used in that field can be applied to the study of archaeological biological findings (or human or animal origin) such as bones, teeth and other organic materials. Alvira et al. [134] in 2010 applied LIBS to the determination of strontium and magnesium in dentin and enamel of Neolithic, middle age, and modern Homo sapiens teeth. The authors noted that the values of the Mg/Ca and Sr/Ca ratios are higher in dentin than in enamel, but also reported the existence of a considerable heterogeneity in the distribution of these elements within and between dental tissues. They finally considered that this kind of analysis could be useful for evolutionary anthropology studies, since the data acquired can provide information regarding early nutrition, seasonality, and residential mobility.

Galiová et al. [135] in 2010 analyzed by both LIBS and LA-ICP-MS the dentine of a prehistoric bear (*Ursus arctos*) tooth. Using LIBS technique Abdel-Salam et al. [129] in 2007 demonstrated a simple method for the qualitative and quantitative estimation of hardness of calcified tissues (enamel of human teeth, shells and eggshell) based on LIBS plasma ionic-to-atomic line intensity ratios of Mg (or Ca).

Rusak et al. [136] in 2011 studied by LIBS the conservation status of 6000-year-old sheep and cattle archaeological bones, finding that the Ca/F ratio was higher in well preserved bones with respect to degraded one.

Garofano et al. [137] in 2011 studied the archaeological case of the 'Venice vampire lady'. The skull of a female individual was discovered during the excavation of an XVI century mass grave in Venice, with a brick inserted in the mouth for keeping it wide open. The forensic anthropological analysis evidenced that the brick was inserted in the mouth post-mortem, as part of a ritual against vampires believed to survive in the grave eating their own funeral shrouds. The LIBS analysis of the bones for the determination of the paleo-diet of the 'Venice vampire lady', whose age at death was determined by the anthropological analysis to be around

60 years, indicated a dominant vegetarian diet, possibly integrated by fish. The LIBS analysis confirmed the hypothesis of a low social status of the deceased, also suggested by the presence of arthritic deformation of the left shoulder probably due to a fatiguing work.

Kasem, Russo and Harith in 2011 and 2014 determined from the LIBS analysis of archaeological bones and teeth the dietary habits of individuals belonging to four different ancient Egyptian dynasties representing the Middle Kingdom (1980–1630 B.C.), Second Intermediate Period (1630–1539/23 B.C.), the Late Period (664–332 B.C.) and the Roman–Greek Period (30 B.C.–A.D. 395) [7,138]. The authors pointed out that any conclusion about dietary habits must take into account postmortem effects such as biological degradation and diagenetic effects (especially from the surrounding soil).

In a similar work, in 2015 Al-Khafif and El-Banna [139] studied the dietary habits of ancient Egyptians through the LIBS analysis of mandibles excavated from Qubbet el Hawa Cemetery in Aswan (Egypt). The authors in particular focused their attention to three successive eras: First Intermediate Period, Middle Kingdom, and Second Intermediate Period. They found that in the First Intermediate period the Sr/Ca ratio was significantly lower with respect to other periods and interpreted this result as the indication of consumption of imported cereals in years of famine. The increase of this ratio in Middle Kingdom and Second Intermediate Period was interpreted as the result of the improvement of the climatic, social, economic, and political conditions and a reflection of the amelioration of the agriculture conditions in that times.

Also of interest for Cultural Heritage and Archaeological studies is the LIBS analysis of foxing stains in paper and parchment in 2002 by Bicchieri et al. [140] and the analysis of coral and hard wood prayer beads performed by Lie et al. in 2006 [141].

2.5 LIBS analysis of glass and precious stones

Many other materials of interest for Cultural Heritage and Archaeology have been studies using LIBS. Muller and Stege [142] in 2003 evaluated the potential of LIBS for the analysis of historical glasses. In 2005, Carmona et al. [143] analyzed corroded glasses by LIBS, classifying a group of historical glasses based on lead contents. The authors found that the composition of the corroded layer and of the bulk glass could be determined with minimal disruptive analysis. Szelagowska et al. [144] studied medieval stained glasses from St. Mary's Church and Corpus Christi Basilica in Krakow (14^{th} – 16^{th} century) and from Polish historical buildings (18^{th} - 20^{th} century) coupling the LIBS analysis with SEM/EDX, for correlating the glass composition with the morphology of the samples. The authors were able to distinguish between medieval and modern glasses on the basis of their component (soda-lime-silicate for modern glasses and potash-lime-silicate for historic glasses); on this basis, they were able to classify an unknow stained glass sample as a modern glass. Palomar et al. [139] and Oujja et al. [140] between 2013 and 2015 studied the process of degradation of Roman glasses with LIBS stratigraphy, finding that this technique was particularly useful for glasses conserved under burial conditions.

LIBS has also been used for the analysis of precious stones by McMillian et al. [145] in 2006; the findings of this study were used for demonstrating the possibility of determining the provenience of beryl in 2008 [146]. Agrosì et al. used standard-less micro-LIBS for the analysis of emeralds in 2014 [147] and on six samples of a rare red variety of beryl, using Calibration Free-LIBS analysis [47]. The authors demonstrated the capability of LIBS of discriminating between red beryl ($Be_3Al_2(SiO_3)_6$) and pezzottaite (raspberry beryl, $Cs(Be_2Li)Al_2Si_6O_{18}$) by observing the differences in Cs and Li emission lines [148].

Koral et al. [149] demonstrated the possibility of performing minimally-destructive LIBS analysis on transparent samples and gemstones (glasses, tourmaline, aquamarine and ruby) using Nanoparticle-Enhanced LIBS (NELIBS).

Finally, in 2018 McManus et al. [150] coined the term Quantagenetics® (from *quantum*, referring to the quantum property of light and *genesis*, or origin) for the process of authentication of materials through their LIBS spectra. The method, in spite of its fancy name, is based on a simple correlation analysis between the LIBS spectra, using the Euclidian distance between them; in any case, with their method the authors were able to classify the provenience of 510 emeralds from 18 Colombian mines, with a success rate of 99.4%.

3 - LIBS in combination with other techniques

When analyzing cultural heritage objects, there is the need to obtain as comprehensive as possible information, and it is often reached by using two or more complementary analytical techniques.

Many examples of integrated approaches, based on the use of independent instruments, have been published in the literature, although the realization of hybrid devices sharing common parts represents the most interesting topic in this field. An obvious advantage of this set-up is that objects will not need to be moved from one instrument to the other, reducing analysis time, and more importantly the same spot on the object's surface can be easily probed. In this chapter we will highlight the application where the combination of LIBS with one or more techniques presented evident synergies, giving more information than the ones that might be obtained through the separate application of each technique.

3.1 LIBS and Raman spectroscopy

LIBS can be combined with spectroscopic techniques such as laser-induced fluorescence (LIF) spectroscopy, diffuse reflectance spectroscopy, and hyperspectral imaging, nevertheless the most explored hybridization for the analysis of cultural heritage materials is with Raman spectroscopy [151–153]. The required spectral resolution and optimal spectral region for Raman and LIBS measurements are indeed roughly similar, and both techniques utilize similar equipment for spectra induction and detection.

An important concern encountered in this combination is the protection of the sample from excessive energy loads that might lead to thermal damage or even surface ablation, thus hindering Raman analysis. Moreover, the optimal wavelength to fit both LIBS and Raman is the 2nd harmonic (532 nm) of Nd:YAG laser, which nonetheless may prevent the recording of Raman signal in CH samples rich in organic binding materials, due

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to the emission of unwanted fluorescence.

In the years, several approaches have been suggested to combine Raman and LIBS techniques in a single instrument: two laser sources (CW laser for Raman, pulsed laser for LIBS) [83,154–156], the same laser system adjusting the energy of the laser pulse (low energy for Raman, high energy for LIBS) [157–161]; simultaneous Raman and LIBS measurements in single pulse differentiated in time (leading edge of the nanosecond laser pulse for Raman, laser pulse tail for LIBS) [162] or space (scattering photons from the intact edge for Raman, emitting photons from the inner region for LIBS) [163]; simultaneous double pulse measurements dividing Raman and LIBS signals acquisition using a few microsecond delay (first low energy pulse for Raman, second high energy pulse for LIBS) [164].

The first example of LIBS-Raman instrument applied to the analysis of artworks has been proposed in 2006 by Giakoumaki and coworkers for pigments identification [158]. In their hybrid system, a single nanosecond Q-switched Nd:YAG laser working with the 2nd harmonic (532 nm) is used as excitation source for LIBS and Raman measurements. Raman scattering and atomic emission are collected through the same lens used to focus the laser beam, then a CCD detector is used operating in the continuous mode for recording the Raman signal and in the gated mode for LIBS signal. The Raman or LIBS analysis are performed by simply adjusting the energy of the laser pulse below or above the material's ablation threshold, respectively. Working in single pulse mode and with 2–4 mJ as beam energy (fluence: 6–12 J/cm2), the authors demonstrated that almost four cycles of Raman-LIBS analysis could be performed of the same spot, which allows compositional depth-profiling studies. Later, the same configuration has been applied by Osticioli et al. [159] to the analysis of three different samples of artistic/architectural interest.

Hoehse et al. [155] improved the spatial resolution of the system with a newly designed dual arm Echelle spectrometer for both techniques, also reducing measurement time and increasing robustness because no moving parts (gratings or prisms) are required. The performances of the instrument were demonstrated by the mapping of heterogeneous mineral samples and in-depth analysis of pigments.

As the employment of a single pulsed laser for both methods leads to unfavourable signal-to-noise ratios in Raman spectroscopy due to the low duty cycle, recently Lednev et al. [164] developed a new approach combining Raman and LIBS within a single laser event running the laser in double pulse mode. The possibility of accurately controlling power density during Raman measurement prevents the thermal alteration of the sample. Moreover, the independent gating (Raman camera is gated during first laser pulse interaction, LIBS camera is triggered after short delay with the second laser pulse) enables the acquisition of high-quality Raman/LIBS spectra.

3.2 LIBS and X-Ray Fluorescence

In 2007, Ferretti et al. [165], in the framework of an experimental campaign on the so-called "Porticello Bronzes", at the Museo of the Magna Grecia in Reggio Calabria (figure 9), proposed the use of LIBS and XRF,

with the purpose of reducing the impact on the samples caused by the application of the micro-destructive LIBS technique through a preliminary screening performed using the non-destructive XRF.

Figure 9 - The “Philosopher Head” of Porticello (ref. [165])

The intuition of the authors was confirmed by the finding that, from a qualitative point of view, the elemental composition determined by XRF was equivalent to what determined by LIBS, thus allowing the use of XRF for general classification, reducing the LIBS measurements at the minimum necessary for the precise quantitative determination of the sample composition. The effectiveness of this approach was confirmed in following studies on the “Magnificent Crater” of Trebeništa, Macedonia [166] (figure 10), where LIBS was used for the precise determination of the composition of the ternary bronze alloy on the basis of which some applications were reproduced according to the ancient manufacturing techniques.

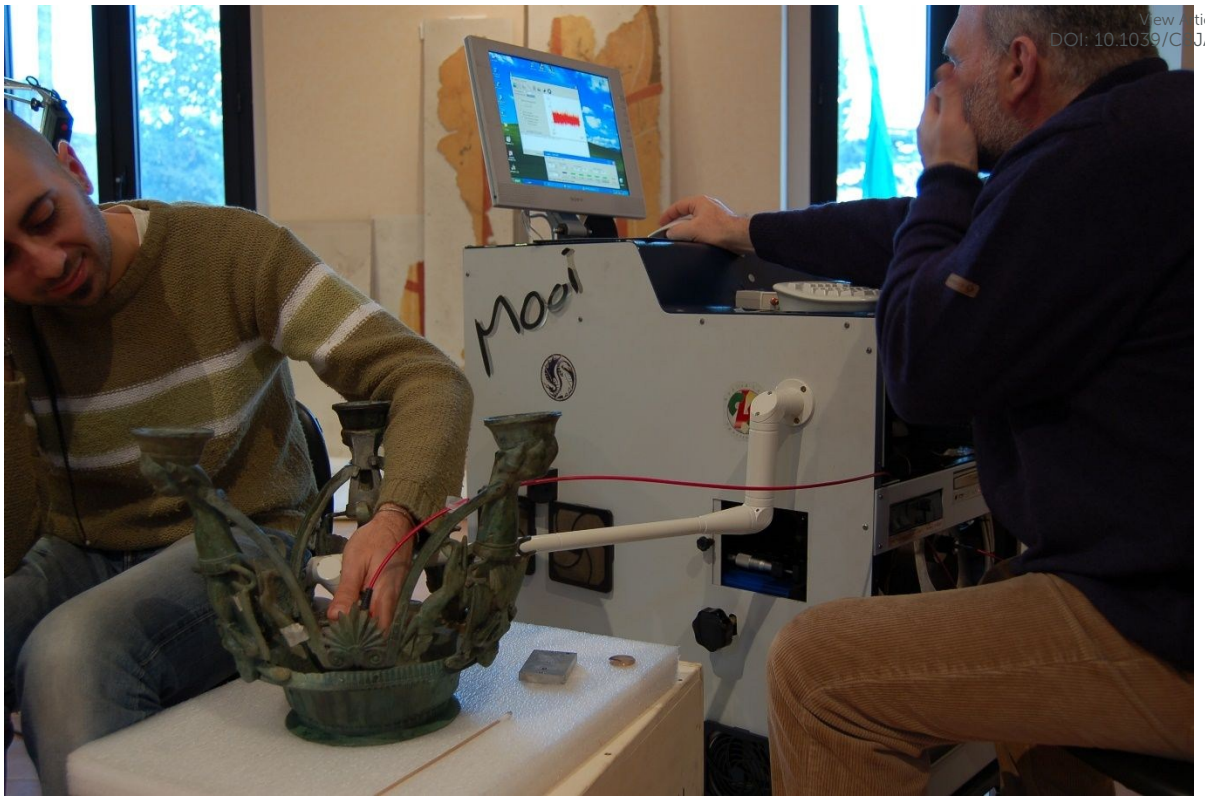

Figure 10 - LIBS measurements on the Trebeništa Crater (ref. [166]).

LIBS was also used by Pardini et al. [167] in 2012, for a preliminary assessment of the validity of XRF quantitative analysis on Roman silver denarii, characterized by a moderate surface patina. Alberghina et al. [168], on the contrary, used micro-XRF for validating LIBS quantitative analysis on bronze alloys. The same authors used LIBS and XRF in 2011 for the study of corrosion process in bronzes [169] and, subsequently, for the study of the materials from the Greek Theater in Taormina [170] and for the stratigraphic analysis of pictorial surfaces [82]. As already mentioned in the section devoted to the applications of LIBS to metals, Agresti et al. in 2016 used LIBS and XRF, together with neutrons and X-Ray Diffraction, for the analysis of three bronze figurines from the collection of the Egyptian Museum of Florence [41,42]. Also Lorenzetti et al. [55] used X-Ray Fluorescence and LIBS for the determination of the alloy of the Pisa Griffin. A comparison of the performances of LIBS, XRF and PIXE techniques for CH and Archaeology studies has been recently published by Lazic et al. [171].

4 – Specific applications

4.1 LIBS for restoration

LIBS has been frequently proposed and used as a diagnostic tool for monitoring the effectiveness of laser cleaning process for artworks conservation. Tools such as the naked eye of the conservator, or the use of different types of microscopy and spectroscopy can indeed provide good control, but with limited capabilities (i.e. the requirement of experienced operators, the use of off-line instrumentation or even sample

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collection). On the contrary, LIBS can be performed in situ by using pulses from the same cleaning laser, allowing the on-line monitoring of the material removal by recording the corresponding spectra.

On-line monitoring of the restoration process is crucial to define properly the end point of cleaning or to study complex stratigraphies. Here the ability of LIBS to perform depth profile analysis comes in, revealing for example the presence of overpaintings or retouching in successive paint layers [61], the extent of contaminant layers on objects of cultural value [172], or even the presence of chlorine useful to monitor the status of historical buildings [173].

In a pioneering work, Gobernado-Mitre and coworkers [174] evaluated the use of LIBS to monitor the laser cleaning process of limestone from an historical building. The determination of the different chemical composition of the black crust and the underlying limestone proved to be useful in order to avoid surface over-cleaning. The same principle has been applied on painted artworks [175–177,21,61], stained glass [178], marble [179,180,111,115,181], sandstone [178], metals and alloys [182–185].

The instrumental configurations developed for monitoring of the restoration processes are worthy of note more than the specific application. The versatility of LIBS allows indeed designing portable laser cleaning stations for the in-situ restoration in museums and art galleries [176]. Lentjes et al. [186], to overcome the disadvantages of ICCD detectors (high investment costs, ambience sensitivity and complexity), proposed the use a commercial miniature spectrometer applicable for the detection of “spectral fingerprints”, through the analysis of the correlation between the spectra from the ablated material and reference spectra.

At last, also the double pulse LIBS configuration has been applied for restoration purposes. Colao and coworkers [182] reported the use of collinear double pulse LIBS for the laser cleaning of ancient bronzes alloys. In this application, the first pulse was utilized to remove the contamination layer place in the sample surface, while the second was used for quantitative analysis. Fortes et al. [187] developed an orthogonal double pulse LIBS configuration in a re-heating scheme as a diagnostic tool for the restoration of archaeometallurgical samples. Here the second pulse allows the analysis of the material eroded in the cleaning stage, thus avoiding the damage of the sample.

4.2 Underwater LIBS

One of the reasons for the wide application of LIBS lies in the possibility of virtually performing the analysis of any kind of substance (solid, liquid, gaseous or aerosol) in air, in vacuum, in fluids, and even under extreme conditions such as high temperature and pressure environments. This aspect is of particular interest in the analysis of archeological materials, since most of these pieces are found submerged in sea environments. Experts estimate that more than three million shipwrecks currently lie on the sea floors, and of these scientists have explored less than one percent [188].

However, the LIBS analysis of solids in liquids generates phenomena like motions, shaking and splashing, which change laser focusing and generate instability in the plasma. These effects lead to unstable atomic emission, resulting in unsatisfactory figures of merit (i.e., sensitivity, precision and limits of detection) as

compared to solid or gas samples LIBS, and in spectral emission characterized by a broad spectral continuum [189].

Several attempts to improve the sensitivity in liquids using different instrumental developments have been presented. The dual pulse excitations, being the most common approach proposed in the literature for the analysis of submerged solids, has been thoroughly discusses in 2007 by De Giacomo et al., together with the basic aspects of underwater LIBS [189]. Briefly, in the double pulse-LIBS (DP-LIBS) approach the first laser pulse produces a gas bubble whereas the second pulse ablates the sample and re-excites the plasma inside the bubble. In two consecutive works, Lazic et al. examined different processes involved during the laser–water interaction, the dependence of DP-LIBS signal intensity inside liquids on the interpulse delay, and the influence of the optical properties of the vapor bubble induced by the first laser pulse on the formation and detection of the secondary plasma [190,191].

Researchers demonstrated the capability of DP-LIBS to perform underwater analysis of a wide range of materials, from metallic alloys (iron, bronzes and precious alloys) to non-metallic samples (rocks and wood) [192].

The DP approach has also its own limitations, related to the use of two optical paths and their laborious alignment, to the applicability limited to liquid media transparent to the laser pulses and to the poor efficiency of the system beyond 100 bar. The pioneering approach proposed by Beddows and coworkers in 2002, aiming to overcome these problems, is based on a fiber optic cable, which delivers the ablation laser pulse and a buffer gas flow to the sample surface, and collects the emitted light [193]. The buffer gas blowing onto the sample surface offers a quasi-gaseous environment for the plasma, guaranteeing a temporal evolution of the plasma itself similar to that obtain in ambient-air media. Moreover, the displacement of the water due to gas shielding makes the analysis feasible also in non-transparent aqueous media. The instrument was tested in water depths to approximately 180 cm, which is notable, but where the pressure differential respect to water surface was not critical compared to more plausible and deeper sampling sites under water.

The performances of underwater single pulse-LIBS have been further improved by the use of long-pulse laser excitations, after Sakka et al. [194] demonstrated that a good signal quality can be obtained working with a pulse of 150 ns duration as opposed to pulses of <20 ns duration. The mechanisms involved during long-pulse irradiation are surely different from those that take place during double-pulse irradiation, even if still little is known about them.

Regarding the application of underwater LIBS analysis to archeological investigations, the first paper dealing with this topic dates back to 2005, when Lazic and coworkers presented a dual pulse system for the examination of different classes of materials potentially found in undersea archaeological parks (i.e. iron, copper-based alloys, precious alloys, marble and wood) [123]. Samples were analyzed in the laboratory after immersion in simulated sea water (20 mm the height of water column above the focal spot). While no

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particularly instrumental set-up was required for this application, the main problems were encountered in the presence of ablated particles, which progressively reduces the water transparency, and in very weak plasma emission intensities from submerged stones.

For archaeologists, the possibility of performing in-situ elemental analysis is of great interest when the submersed artifacts are not immediately recognizable due to their high corrosion degree or to low visibility conditions. Laserna and coworkers from the University of Malaga constitute the most active group in this field, with four publications focused on in situ and stand-off submarine LIBS analysis of solid samples. In 2012 they presented an instrument consisted of a main unit for laser-fiber coupling and signal detection, and of an underwater probe, interconnected by means of a 40 m long umbilical cord [195]. Both the laser beam and the signal are transmitted through the same fiber optic cable (45 m long), whereas a coaxial gas flux creates a solid–gas interface and improves the ablation efficiency. Metallic archaeological samples were analyzed underwater at 30 m in the Mediterranean Sea by a professional diver able to operate the hand-held probe.

The technological evolution of this instrument, based on the multi pulse transmission through the optical fiber cable, was presented in 2015 [124]. Multi pulse LIBS opens the possibility to increase the laser beam energy transmitted while avoiding the damage of the fiber, and operating in a collinear configuration it uses a single laser source [196]. This configuration was tested for the identification of archeological assets in two real shipwrecks, and to the discrimination of submersed objects having different nature (bronze-alloys, metallic pieces, ceramics and marbles) through LDA classification [197,124]. In the last case, from the initial emission spectrum of 2048 data points, only 10 spectral variables were considered for discriminant analysis, and the resulting model allowed the identification of all considered samples.

The same research group investigated the potential of a stand-off LIBS instrument to work in an underwater open-path environment, thus removing the need to work with a qualified diver [198]. Samples were analyzed at distances up to 80 cm from the sensor at a solid–water interface, using a double pulse collinear configuration. Important parameters, such as the effect of water temperature and the influence of path length on LIBS signal were investigated.

5 - New developments and perspective

5.1 Micro-LIBS analysis and 3D compositional mapping

The high spatial resolution of the LIBS technique (< 10 μm lateral resolution, < 1 μm in depth resolution) can be fruitfully exploited for obtaining 3D compositional maps of Cultural Heritage objects. The first application of LIBS mapping in Cultural Heritage was presented by Corsi et al. in year 2000, on a Roman fresco (II century A.D.) from St. Albans (UK) [60]. More recently, the coupling of the laser with an optical microscope [199] has paved the road to LIBS-based microanalysis also in Cultural Heritage and Archaeology; Pagnotta et al. in 2017 studied an ancient Roman mortar (5th century A.D.), using different statistical approaches for the determination of the chemical composition of the binder and aggregate fraction in the compositional maps.

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A similar study on a set of mortars, suitable characterized by the occurrence of volcanic rock fragments with a relevant range in grain size, revealed in 2018 the potentiality of the method to provide compositional and spatial distribution data on aggregate grains and hydraulic phases [128]. Pagnotta et al. in 2018 also proposed the use of the remains of thin-section realization ('negative face') for the surface mapping of Neolithic potsherds, demonstrating that the combination of these images with algorithms derived from image processing techniques may return interesting information and supporting data to in-depth investigate pottery components detected by optical microscopy observation [106]. The capability of performing fast quantitative analysis of the LIBS spectra obtained from 3D mapping was shown by the same group in 2018 [108].

In 2018, Senesi et al. obtained a full microscale three dimensional (3D) compositional imaging of weathered limestone from Castello Svevo in Bari (Italy). The analysis allowed the creation of 'virtual thin-sections' (VTS) of the samples, from which the extent of the alteration processes occurred at the limestone surface was estimated [129] (see figure 11).

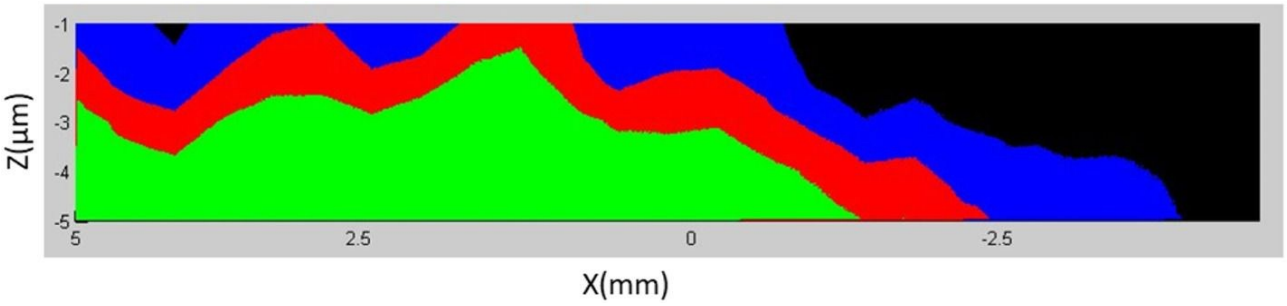

Figure 11 - Virtual Thin Section of the black crust on the limestone surface from Castello Svevo in Bari, Italy (ref. [129]), showing the change of mineralogical composition in the transition from the black crust layer (black) to the limestone underneath (green).

An interesting development of the micro-LIBS technique has been its integration with Laser Ablation ICP Mass Spectrometry (LA-ICP-MS), firstly proposed by Meissner et al. in 2004 [200]. In 2008, Novotny et al. used micro-LIBS and LA-ICP-MS separately, for elemental, large area 3D mapping of granite [201]. In general, LA-ICP-MS is more performant with respect to LIBS for what concerns limits of detection, trueness and precision. However, MS techniques suffer from the interferences that might make difficult the determination of some elements (H, N, O, Si, Se, As, S), which are, instead, measurable by LIBS. Tandem LIBS/LA-ICP-MS have been successfully applied to archaeological objects by Syta et al. [90] on cross-sections of mediaeval Nubian objects, for the study and discrimination of Egyptian blue vs. lapis-lazuli. It is worth to note, however, that the sequential acquisition of LIBS and mass spectra has been preferred by Kokkinaki et al. against simultaneous application of the two methods, for optimizing mass resolution and minimizing the surface damage of the samples, in case of low ablation threshold materials [202]. On the other hand, the micro-destructivity of both LIBS and LA-ICP-MS techniques clearly limits the possibility of obtaining 3D elemental maps of the same regions on the sample, when a sequential approach is applied.

5.2 Surface- and Nanoparticle-Enhanced LIBS

One of the main advantages of LIBS is the absence of a sample preparation step for the analysis. Most of the proposed techniques for the enhancement of LIBS performances aim to maintain this condition, focusing on the implementation of high-power sources, tunable lasers or high-resolution detectors.

A technique recently introduced by De Giacomo et. al. [203] leads to a minimal sample pretreatment, based on the deposition of metallic nanoparticles on the sample surface. A review was recently published by Dell'Aglio et. al. [204], discussing in depth the mechanisms behind the Nanoparticle Enhanced LIBS (NELIBS), its advantages and limits.

It has been demonstrated how the deposition of metallic nanoparticles (NPs) on a sample can strongly influence the interaction between the laser radiation and the sample surface, depending on the dimension, the concentration and the nature of the NPs.

Assuming a suitable deposition of noble metal nanoparticles and a laser pulse of nanosecond duration, a general explanation of the involved phenomenon can be given as follows.

Upon irradiation, most of the energy delivered by the laser pulse is deposited on the nanoparticles, inducing a coherent and collective oscillation of the electrons on the surface of the NPs. This amplifies the electric field localized on the surface and in the gaps between the NPs, causing an increase in the intensity of the incident laser radiation. This phenomenon causes some electrons to be extracted from the surface of the conductive NPs, inducing a faster breakdown of both the NPs and the sample.

In addition, if the incident laser radiation is resonant with the surface plasmon of the NPs deposited on the samples, another phenomenon takes place. The pulse energy is absorbed by the NPs that are immediately heated as well as the surrounding region. The heat is then transferred to the sample, inducing a localized vaporization and a very efficient plasma excitation, while the damage to the sample surface is confined and of the same order of the NP diameter.

In their works, De Giacomo et. al. [205,206,149,207,208,203] extensively demonstrated how NELIBS can be applied to a variety of samples, using a Nd:YAG laser operating at 1064 nm with pulses in the nanosecond regime and gold or silver NPs.

The best results have been obtained with the analysis of metallic samples (i.e. a pure titanium target) where an enhancement factor, the ratio between the NELIBS and the LIBS emission line intensity, of up to 100 has been registered. In this case the NPs are simply deposited dropwise on the cleaned sample surface and dried before performing the analysis.

Alternatively, it has been shown how, if the NPs are deposited on a dielectric support such as glass, Teflon or silicon, a substrate for the analysis of liquid samples can be obtained. A drop of the liquid sample is deposited on the dried NPs and the solvent evaporated. This allowed for the detection of sub-ppm analytes and significantly improved the technique's LOD limits.

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Furthermore, NELIBS allowed for the enhancement of also molecular bands. In this case, an enhancement factor of about 10 was obtained and a longer persistence of plasma emission was registered when compared to conventional LIBS analyses.

Being a novel technique, NELIBS has not yet been tested for Cultural Heritage applications. Nevertheless, it has proven to be a highly versatile technique, suitable for the analysis of samples of different nature.

The most obvious field of application would be in the study of metallic and precious artifacts. Due to the well proven capability of NELIBS of highly enhancing the LODs of trace elements in alloys and gemstones and the reduced damage dealt to the sample surface, it can be a valuable tool in the identification and the investigation of artifacts, coins, jewelry, etc.

There are many advantages in using NELIBS when studying transparent means, such as glass, and gemstones. First of all, a transparent or translucent sample can make difficult an optimal focusing of the laser beam on the surface, where a layer of NPs is more easily visible. Moreover, glasses and gemstones usually have high breakdown thresholds that, in turn, require a much higher pulse energy to produce a sufficiently energetic plasma and this can lead to an excessive damage of the sample. Due the effect of the NPs, a lower energy is required to generate the plasma, resulting in a more “gentle” ablation, thus preserving the integrity of the sample.

A recent work by Poggialini et. al. [209] illustrated the possibility of using green-synthetized silver NPs for NELIBS with a low power and mobile instrument. Trace elements in copper samples were analyzed with enhancement factors of about 4 and LODs in the order of ppm. This demonstrated the possibility of using a cost-effective alternative to commercially available NPs for NELIBS analyses. The possibility to use this approach also for in situ analyses makes it more suitable and appealing for CH applications.

One of the criticalities of NELIBS application in Cultural Heritage would be the contamination of the sample. While the NPs are removed from the measurement spot by the laser pulse, it is not uncommon that the area where the NPs are deposited is larger than the ablated area, leaving an amount of metallic NPs on the sample surface. This could lead to a series of oxidation and contamination processes that are not acceptable with CH artifacts that are, usually, one-of-a-kind. However, due to the very simple method of sample preparation (i.e. dropwise evaporation of a colloidal solution), no chemical reaction is involved in the NPs deposition. This suggests that the remaining nanoparticles could be removed from the sample surface with wet swabs.

Surface Enhanced LIBS (SENLIBS) is another method for improving the performances of the technique [210]. In this case, a liquid sample is deposited and dried on a suitable solid surface, generally a metal sheet. Opposed to NELIBS for liquid samples, where the laser pulse interacts with the surface plasmon of the NPs, in SENLIBS a dense and hot plasma is generated on the substrate surface and engulfs the dried droplets, enhancing the LIBS signal.

The applicability of SENLIBS to exclusively liquid samples may restrict its use in CH, where the vast majority of the samples are solid. There are, however, some cases in which SENLIBS can be seen as a valuable addition to more conventional techniques.

A work by Campanella et. al. [211] demonstrated how SENLIBS can be combined with HPLC-DAD analyses in order to obtain information on the inorganic fraction of an extract in addition to the organic fraction data. In their work, a series of textiles samples from both reference standards and historical tapestries, were subjected to an extraction process. While the organic dyes are analyzed by LC techniques, the part of the extract containing the inorganic mordant is usually discarded. In this work, microdroplets of the extract were deposited on various substrates and analyzed by LIBS. This allowed for an easy discrimination of the mordant and, in turn, of the dye.

6 – Conclusions

LIBS applications to Cultural Heritage and Archaeology are, as we have seen, a small niche in the slightly larger niche that LIBS occupies in the scene of the current analytical techniques. However, when applied correctly, the technique has demonstrated to give interesting results, providing answers to the mean problems in the field, which are authentication, dating and conservation. The future of LIBS in Cultural Heritage and Archaeology laboratory studies mainly relies on the development of cheaper and more performant micro-LIBS systems, possibly coupled to mass spectrometers and on the full comprehension and consequent exploitation of the nanoparticle LIBS enhancement, which might lead to a drastic reduction of the destructivity of the technique. The results recently obtained on precious stones and glasses seem very promising. On the other hand, in situ application will benefit of the realization of truly portable LIBS/XRF and LIBS/Raman instrumentation, for complementing the positive features of the technique and compensating its weaknesses.

Conflicts of interest

There are no conflicts to declare.

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List of acronyms and abbreviations

3D: Three Dimensional
AAS: Atomic Absorption Spectrometry
A.D.: Anno Domini
B.C.: Before Christ
CF-LIBS: Calibration-Free LIBS
CH: Cultural Heritage
DAD: Diode Array Detector
DP: Double Pulse
DT: Differential Thermal
ED-XRF: Energy Dispersive X-Ray Fluorescence
EDX: Energy Dispersive X-Ray
HLPC: High Performance Liquid Chromatography
ICP: Inductively Coupled Plasma
FT-IR: Fourier Transform Infrared
LA: Laser Ablation
LASER: Light Amplification by Stimulated Emission of Radiation
LC: Liquid Chromatography
LDA: Linear Discriminant Analysis
LIBS: Laser-Induced Breakdown Spectroscopy
LIF: Laser-Induced Fluorescence
LOD: Limit of Detection
MS: Mass Spectrometry
MO: Microscope Observation
NELIBS: Nanoparticle Enhanced LIBS
NP: Nanoparticle
OCT: Optical Coherence Tomography
Modì: Mobile Dual-Pulse Instrument
PCA: Principal Component Analysis
PIXE: Particle Induced X-Ray Emission
PLS-DA: Partial Least Squares Discriminant Analysis
REE: Rare Earth Elements
SENLIBS: Surface-Enhanced LIBS
SEM: Scanning Electron Microscope
SIMCA: Soft Independent Modelling of Class Analogy
SOM: Self Organizing Maps
TGA: Thermal Gravimetric Analysis
UV: Ultraviolet
VIS: Visible
XRD: X-Ray Diffraction
XRF: X-Ray Fluorescence
YAG: Yttrium Aluminium Garnet

Table of Applications of LIBS in CH

Chapter	Material	Application	References
2.1	Bronze	Authentication	[44]
		Classification	[32] [34]
		Composition	[33] [34] [43] [45] [48] [49] [50] [55] [56] [57]
	Gold	Composition	[47]
	Gold/Copper	Stratigraphy	[36]
	Copper	Stratigraphy	[37] [38]
		Classification	[31]
		Composition	[31]
	Iron	Classification	[32]
2.2	Paintings	Composition	[58] [59] [61] [62] [63] [64]
	Fresco	Mapping	[60]
	Wall paintings	Composition	[70] [88]
	Pottery	Composition	[71]
	Enamel	Composition	[72]
	Polymers	Composition	[73]
	Binders	Composition	[74]
	Pigments	Mapping	[90]
2.3	Pottery	Depth profiling	[92] [93]
		Composition	[94] [95] [98] [100]
		Provenience	[103]
		Firing temperature	[104]
		Authentication	[105]
		Mapping	[106] [107]) [108]
	Marble	Laser cleaning	[109] [110] [111] [112] [114] [115] [116]
		Provenience	[117] [118] [119] [120]
	Limestone	Provenience	[121]
2.4	Teeth	Nutrition	[134] [138]
		Composition	[135]
	Bones	Conservation	[136]
		Nutrition	[137] [138] [139]
	Foxing	Distribution	[140]
	Wood	Composition	[141]
2.5	Glass	Composition	[142] [144]
		Classification	[143] [144]
		Conservation	[139] [140]
	Precious stones	Composition	[147] [149]
		Classification	[148] [150]
3.1	Pigments	Composition	[158]
	Pigments	Mapping	[155]
3.2	Bronze	Classification	[165]
		Composition	[166] [168] [55] [41] [42]
		Corrosion	[169]
	Silver	Composition	[167]
	Pigments	Composition	[82]

	Rocks	Composition	[170]
4.1	Construction materials	Diagnostic	[173]
		Cleaning	[174] [178]
	Metal	Cleaning	[182–185] [187]
	Paintings	Cleaning	[175–177]
	Glass	Cleaning	[178]
	Marble	Cleaning	[179,180,111,115,181]
4.2	Metal/Marble/Wood	Classification	[123]
	Metal	Composition	[195]
	Metal/Pottery/Marble	Classification	[197,124]
5.1	Fresco	2D Mapping	[60]
	Mortar	2D Mapping	[199] [128]
	Pottery	2D Mapping	[106]
	Building materials	3D Mapping	[129]
	Rocks	3D Mapping	[201]
	Pigments	Classification	[90]
5.2	Dyes	Classification	[211]

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