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Title: SAMPLE TREATMENT AND PREPARATION FOR LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Suggested Reviewers:

Opposed Reviewers:

***Highlights (for review)**

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SAMPLE TREATMENT AND PREPARATION FOR LASER-INDUCED BREAKDOWN SPECTROSCOPY

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1 INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) has been widely investigated in recent decades for different applications ranging from space exploration to biological specimens. The success of LIBS is due to a set of advantages that makes this analytical technique unique such as multi-element analysis, fast response, remote sensing, little to no sample treatment, the attractive cost of the instrumentation, and its ease of use [1,2]. Although LIBS was born as a field technique, the improvement in instrumental capabilities and knowledge on fundamental aspects of laser-induced plasma spectroscopy has allowed for a large expansion into laboratory applications. As a result, LIBS is now competing with other conventional laboratory techniques, still holding some of the advantages mentioned above, but at the same time the analytical performance (i.e., accuracy, repeatability, and reproducibility) should be improved in order to really be competitive with other well-established techniques. As with any ordinary analytical tool, the laboratory setting introduces the possibility of tighter control of LIBS experimental conditions and the use of more sophisticated analysis protocols that may include microscopic techniques, controlled background atmosphere, combination of excitation techniques (i.e. double pulse, plasma supported, fluorescence etc.) and sample treatment [3-5].

In general, LIBS performance may be enhanced using two main approaches: a) improving the plasma emission signal and b) modifying the specimens. Until now the LIBS community has focused its efforts on enhancing the plasma emission, largely avoiding sample treatment, as is demonstrated in several papers [3-6]. One drawback of this approach is that it increases the cost by adding components (e.g., additional lasers, high performance detectors) and calls for specific expertise in the fields of plasma physical chemistry and laser technology. For these reasons this approach, although very interesting, does not meet the requirements of the majority of scientists and operators who want to use LIBS just as they would any other classical analytical tool. However, keeping in mind that enhancement of signal is mainly linked to the number of emitters more than to the plasma parameters, which are generally difficult to control, the main question becomes: how does the laser energy affect material ejection and, in turn, ablation efficiency? Therefore the manipulation of specimens in order to make them more suitable for laser ablation and LIBS is gaining interest for two reasons. First, to decrease the limits of detection (LOD) in already established LIBS applications and second, to expand the capability of LIBS to those applications where heterogeneity and/or matrix effects had limited its use. It is therefore wise to weigh the operational cost of sample treatment against the advantage of applying LIBS analysis instead of another analytical technique, keeping in mind that most conventional analytical techniques inherently require significant manipulation of specimens to achieve good results.

Sample treatment may be approached in different ways. The simplest manipulation concerns mechanical treatment like polishing the surface for improving the reproducibility of the measurements or increasing the roughness to improve the laser coupling. Deeper treatment may include changing the physical state of the specimen or the chemistry of the sample. In these cases, disadvantages may include alteration of the original chemical composition of the specimen, an increase in the analysis time, and destruction of the original specimen. It is clear, therefore, that to treat the sample is to give up one of the most attractive advantages of the LIBS technique, thus the crucial question of this paper: “why use sample preparation in LIBS?”

2 A BRIEF THEORETICAL BACKGROUND

Laser-induced breakdown spectroscopy is based on the optical emission spectroscopy of the plasma produced by laser-matter interaction and so the efficiency of the analytical performance is related to two different aspects: one is directly related to the laser-matter interaction and therefore to the coupling of the laser pulse energy with the physico-chemical properties of the specimen [7]; the other is related to the effects of plasma parameters on the optical emission characteristics of the species in the plasma [8]. Indeed these two aspects are strongly linked, as the plasma itself is the result of excitation by electronic impacts on the particles (i.e., atomic and ionic species) ablated by the laser pulse. It stands to reason that optimizing the energy transfer of the laser pulse to the sample is critical for obtaining a suitable emission spectrum for the chemical analysis. In general, assuming at first approximation that the plasma is optically thin, the emission intensity, I_{ul}, of a line is given by the following equation [9]:

$$I_{ul} = 4\pi G h \nu_{ul} A_{ul} g_u N_u \qquad \text{eq.1}$$

where G is an experimental factor taking into account the probing volume and the instrumental efficiency, ν_{ul} is the frequency of the considered transition, A_{ul} is the spontaneous emission rate, g_u is the degeneracy of the emitting level and N_u is the population number density in the emitting level u.

Although the equilibrium condition in LIBS plasmas requires a deeper discussion [10,11], the Boltzmann distribution may generally be assumed for the emitting species so that eq.1 becomes:

$$I_{ul} = \frac{4\pi G h \nu_{ul} A_{ul} g_u N_0}{Z(T)} \exp\left(-\frac{E_u}{kT}\right) \qquad \text{eq.2}$$

where N_0 is the total number density of the species, T is the excitation temperature and Z(T) and E_u are the partition function and the energy of the emitting level, respectively. From eq. 2 it is clear that the intensity of the emission line depends linearly on the number density of emitters in the plasma and exponentially on the excitation temperature. It is important to underline that in the case of laser-induced plasmas, as a consequence of the expansion, both the temperature and the number density decrease in time until the plasma emission is completely extinguished [12]. The longer the emission persists, the better the detection of the species, and therefore the better the LOD or signal-to-noise ratio. The duration of the emission of ablated material mainly depends on the amount of material sampled with each laser pulse. This is why in LIBS, as well as in other laser ablation based techniques, the ablation process plays a crucial role in the success of an analytical application in terms of LOD, dynamic range, and reproducibility.

Even under optimum ablation conditions, it is important to keep in mind during a LIBS analysis that, because only the small volume under the surface irradiated by the focused laser spot is involved in the ablation (as a consequence of the sampling nature of the laser pulse), only a few hundred nanograms of material can be brought into the plasma phase [6]. On one hand this property is what allows LIBS to have good spatial resolution, while on the other hand it makes LIBS very sensitive to any inhomogeneity of the specimen.

Clearly, adapting a specimen for LIBS measurement could greatly increase the potential of LIBS to achieve the figures of merit that any good analytical tool should have (i.e., sensitivity, accuracy and precision). In the following sections we discuss how sample treatment has been

employed for LIBS in various analytical applications and how proper sample manipulation can improve the analytical performance of LIBS.

3 SOLID SPECIMENS

There are many solid specimen types that require no sample preparation at all, and these have served as model matrices for LIBS analysis, and contributed to the reputation that no sample preparation is required. In most cases it is because they are already in the form of homogeneous solids of sufficient size to withstand the laser shockwave, for example glass [13,14], metals [15-19], and polymers [20-22]. Other materials that consist of homogeneous layers, such as paints, plating, and coatings, can be analysed in a depth profiling experiment or analysis of just the top layer without any sample treatment. For example, a thin Cu layer on Al [23], or toxic elements (Ba, Cd, Cr, and Pb) in the surface layer of painted toys [24]. As an example, in Ref.[25], the authors analyzed layers of house paint for Pb. A strong Pb signal was observed in the underlying wood substrate, which may have been due to absorption of primer, but could also have been due to some paint from the upper layers being ablated at the edges of the LIBS ablation crater. For a more accurate analysis of the substrate or lower layers, a mechanical separation of the layers may be necessary, requiring some sample preparation.

Heterogeneous specimens that do not require fixing may be analyzed without any preparation using a raster scanning pattern or by rotating the specimen during the analysis. If spatial information is desired, each point on the specimen can be treated as a separate analysis (see Section 5.3). If a "bulk" analysis is desired, all the points in the raster scan can be averaged.

However there are many solid specimen types that would benefit from further manipulation in order to: improve durability; and/or enhance sensitivity, repeatability, and/or reproducibility; and/or reduce matrix effects. In some cases without sample preparation the results may be qualitative or suitable for screening, but with sample preparation, excellent quantitative results may be possible. Such solids may require further treatment because of heterogeneity (e.g., soil, rocks, bone), the need to be fixed (e.g., loose powders, biological specimens, see Section 5), the need to remove or dilute the matrix, and/or the need to add an internal standard.

3.1 Reduction of Matrix Effects

3.1.1 Separation

An obvious way to reduce matrix effects is to remove the matrix. However, this is not a trivial procedure for most solid specimens, as it is often an integral part of the material. The difference in solubility of the analyte compared to the matrix may prove useful. For example, soluble salts mixed with sand can be dissolved, the sand removed by filtration or centrifugation, and the salt solution can be prepared for analysis as discussed in Section 4. Minerals of interest can be separated from whole rock by crushing, followed by various separations (e.g., sieving, magnetic, density), and possibly hand-sorting under a microscope. Small grains may need to be fixed (see Section 3.3). Sieving also has the advantage of reducing the "nugget effect", which is when the elemental signature of a few very large particles contributes a bias to the overall (bulk) elemental profile of the powder [26]. Alternatively, petrographic thin or thick sections can be cut from the whole rock and mounted onto glass slides in order to expose mineral grains of interest or fluid

inclusions. For example, LIBS has been used on petrographic sections to determine cation ratios (Na/Ca, Ca/Mg) in fluid inclusions within quartz crystals found in uranium deposits [27].

3.1.2 Dilution

If matrix removal is not possible, dilution of the matrix offers another approach, which can be effective if the analyte concentration is high enough to produce a good signal after dilution, or as a strategy to reduce self-absorption in strongly-emitting emission lines. Matrix dilution can also be useful when using reference standards that are not matrix-matched with the specimens. Good diluents are materials that do not contribute strong matrix effects of their own, and should be free of any analyte or interfering elements. Some diluents may serve a dual purpose as binders for improving pellet cohesion. As an example, a mixture of 80 % KBr, 15 % $CaCO_3$, and 5 % Al_2O_3 was used as a dilution matrix for the analysis of various Pb, Cu, Cr salts [28]. Detection limits for Cu and Cr were at low ppm levels for both LIBS and LA-ICP-MS; however Ca and K emission lines interfered with Pb lines using their LIBS configuration, illustrating the importance of choosing a good diluent with the spectral resolution of one's instrument in mind.

If the matrix cannot be suitably diluted, then matrix-matched calibration standards can be generated using various combinations of sample preparation techniques described in this Solid Specimens section. For example, aliquots of pre-milled sand powder were spiked with internal standard and various concentrations of analyte elements, then dried and either milled and pelletized, or mixed and mounted on adhesive tape [29]. Both methods were effective in calibrating for soil analyses by LIBS, as well as LA-ICP-MS and μXRF. Another interesting approach for creating more closely matrix-matched standards for plants involved creating a "blank" sugar cane matrix material by extracting out nutrient elements from the dried plant tissue with acid. A set of calibration standards were generated by adding back various amounts of the extracted elements to the blank matrix [30].

3.1.3 Internal standard

The use of an internal standard can help reduce matrix effects and help account for sample loss, instrumental fluctuations, and drift. After background subtraction, the analyte signals can be normalized to the signals of the internal standard. With proper selection of an appropriate internal standard, calibration curves may appear more linear, precision and accuracy may improve, and the spectra can be more comparable from one specimen to the next [1,2,31]. The choice of internal standard depends on a number of factors, including the specimen type, instrument configuration, and the emission properties of the internal standard(s) and analyte elements. The ionization state (e.g., I, II, etc.) and intensity of emission lines should be similar for the internal standard and elements of interest, and an internal standard emission line should be present in each spectral range of interest. In some specimens, matrix elements that are already present in a known and fixed amount can be used. For example, Si in float glass [32], Ca in bone and teeth [33], or C in plant-based specimens [34]. In other types of specimens (e.g., soil), the composition may be too variable from specimen to specimen so an internal standard can be added in a known and fixed amount. In that case, the internal standard should be one that is not already present in the specimens (or present in negligible amounts).

If sample preparation is necessary, especially homogenization, then it requires very little additional effort to add diluent and/or internal standard. The internal standard is best added as early in the sample preparation process as possible, so as to account for any losses along the way. It should be noted that there are standard-less, calibration-free LIBS procedures that may also

overcome self-absorption and matrix effects without the need for the above methods, but they generally do not achieve the same accuracy or LOD as can be attained using good sample preparation strategies [35-39].

3.2 Homogenization

Homogenization is useful when a bulk characterization is desired. Common ways to homogenize specimens include mixing, milling, fusion, digestion, and leaching. Powders of mixed particle size and/or density should be mixed thoroughly before sampling, unless specific fractions are targeted.

3.2.1 Milling

Milling, or grinding, reduces particle size and increases surface area, in addition to homogenising the sample. The smaller the particle size, the easier the vaporization and atomization in the plasma, which results in a more uniform plasma, and therefore better precision. Smaller particle size also improves digestion, leaching and fusion efficiency, pellet cohesion, coating homogeneity and adhesion onto tape. Different grinding methods include mortar and pestle, knife mills [40], ball mills [28,29], and cryogenic mills [41,42]. In the above-mentioned work ([28], see Section 3.1.2), pellets were made with finely and roughly ball-milled and un-milled powder to evaluate sample preparation methods, with the finely-milled powder yielding the best precision. The milling surfaces (e.g., agate, tungsten carbide, and different grades of stainless steel) should be carefully considered in terms of hardness and elemental composition, as they may contribute some contamination to the sample. For example, W should not be measured when tungsten carbide milling jars and balls are used for milling soil [29].

3.2.2 Fusion

Fusion can be used to create glass disks by fusing a solid or liquid sample with a flux (for example, lithium metaborate and other salts) at extremely high temperatures [43-45]. Fusion dilutes, homogenizes, and fixes the sample into a robust form for analysis by multiple techniques. Some disadvantages of this approach include the loss of volatile elements at high temperature and the large quantities of the flux elements (for example, Li and B), which may cause spectral interferences. One author found heterogeneity within disks by LA-ICP-MS, possibly due the settling of heavier elements during cooling [43]; however many groups continue to have success with the disks [44,45]. For example, better results (mostly the result of reduced matrix effects) were obtained with fusion disks compared to pressed pellets for major elements and a few trace elements in geological samples [45]. However, because a 1064 nm Nd:YAG laser was used, the surface had to be frosted to reduce transparency and increase laser coupling.

3.2.3 Sol gels

Sol gels are homogeneous solids formed from gelling of a colloidal suspension of solid particles in a sol (liquid). The suspension contains a mixture of liquid metal or metalloid alkoxide precursor, water, co-solvent, and a catalyst [46]. The drying steps may or may not involve heat. As with fusion discs, sol gels provide a means of fixing liquid, suspended solid, and colloidal specimens. In one example, solid LIBS calibration standards for Be, Pb and Cr were created using Si, Zr, and Al-based sol gels that were milled with a xerogel binder and pressed into pellets [46]. The most homogeneous and cohesive pellets and the best quality LIBS craters were

obtained with the Zr- and Al-based sol gel pellets (see Figure 1a-f). Shadowgraphy was used to show that small, uniform and controlled particle ejection occurred with the Zr- and Al-based pellets, resulting in better sensitivity and precision. However, the Zr-based pellets exhibited far more matrix peaks than with Al or Si, and the Pb peak was barely detectable (see Figure 1g). Therefore, Al was selected in this case [46].

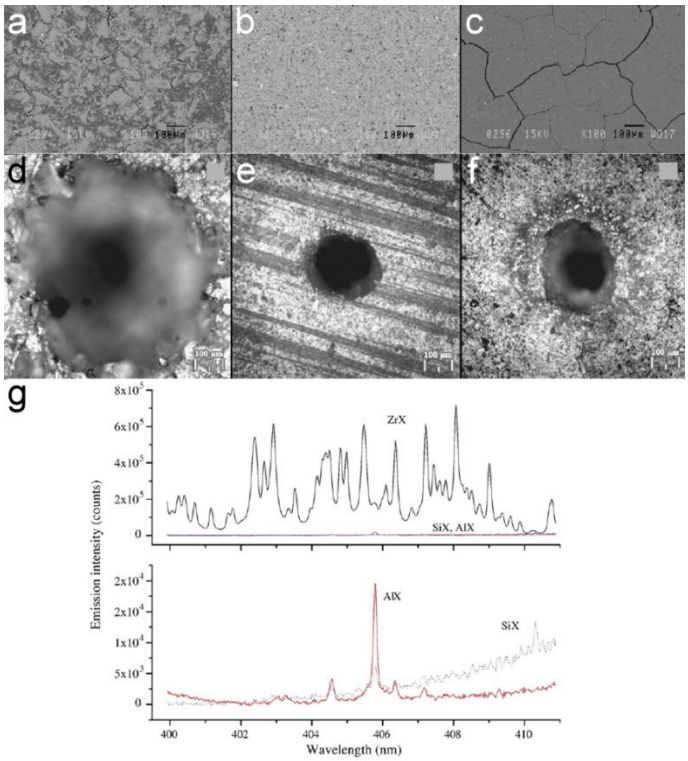

Figure 1.a-c: SEM images, all on the same scale, of pellets pressed from milled sol gel material with xerogel binder (X) (a. SiX, b. ZrX, c. AlX). d-f: Optical photomicrographs, all on the same scale, of the LIBS ablation craters made in the pellets (d. SiX, e. ZrX, f. AlX). g. Overlaid LIBS spectra for each of the pellets (containing 385 ppm Pb). In the lower panel the scale is expanded to show AlX and SiX. From [46], used with permission.

3.2.4 Leaching and digestion

Digestions and leaching are classic methods of preparing solid specimens for elemental analysis, but are time consuming; messy; prone to contamination; require acids, high temperatures and a laboratory; and are often incomplete. Leaching is prone to poor reproducibility. In fact, getting away from digestions was one of the drivers of laser-based analysis methods like LIBS and laser ablation. Micro-milling and micro-wave digestion have improved the process, but many users still prefer to avoid it. Digests and leachates can be treated as liquid samples (see Section 4).

3.3 Fixing

Specimens may need to be fixed for a variety of reasons. For example, to keep them in a specific orientation (e.g., crystal faces of minerals, specimens that have been previously analysed, mapped, or imaged by other techniques); for ease of handling, storage, and transport of delicate or flexible specimens; to arrange multiple specimens and standards into one mount of uniform

height; for ease of polishing; so that the specimens may be re-analysed or analysed by other techniques (e.g., LA-ICP-MS, XRF, EPMA, SIMS); and/or so that the specimen can withstand the high energy laser pulses of LIBS without being disturbed or displaced (e.g., powders) [47]. A number of methods exist, depending on the specimen type and requirements. For example, fusion and sol gels (already discussed above, see Sections 3.2.2 and3.2.3, respectively), pelletisation, epoxy-mounting, and adhesive-mounting.

3.3.1 Pellets

Powders may be pressed into pellets in a dye, as was done for many of the examples given in the Milling section above (see Section 3.2.1). Milling may be required before pressing because the pellet should be homogeneous on a scale that is much smaller than the diameter of the LIBS spot (unless a raster scan will be used). Figure 2a shows an example of a pellet made with milled sediment powder pressed without a binder (using the method described in reference [48]), and some examples of ablation craters and raster lines.

Some powders will not form a cohesive pellet, even when finely milled, so a binder must be added. The binder can also serve as a diluent if desired, and its properties should be similar to those of a good diluent (see Section 3.1.2) while improving pellet cohesion. A number of binders were investigated (KBr, poly(vinyl alcohol), starch, Ag, Al) for use in pellets of various concentrations of Mg [49]. KBr provided the highest ablated mass and signal enhancement for the Mg emission lines, followed by starch, while Al and Ag provided the lowest. PVA provided the best quality crater, with KBr providing the next best. Therefore KBr was recommended [49], though starch and PVA may also be good choices for other applications. Pellets are also commonly used for plant material, as will be discussed in Section 5.

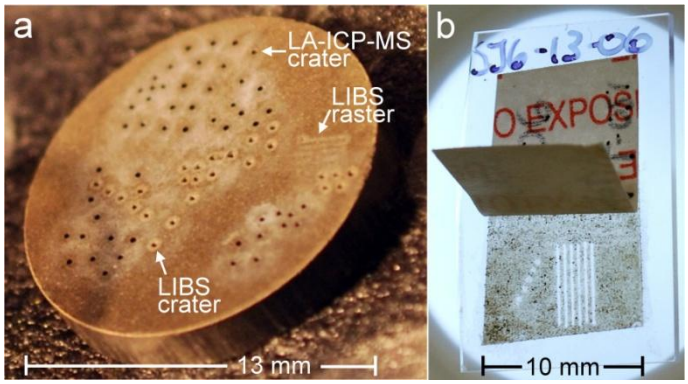

Figure 2. a. A pellet pressed from milled sediment powder. Ablation craters from multiple laser shots (LIBS and LA-ICP-MS) and rasters can be seen. b. A thin layer of soil mounted onto double-sided tape on a piece of a glass slide. Soil was removed effectively by single laser shots and rasters.

3.3.2 Epoxy mounts

Epoxy resin embedding is commonly used in both biological and earth science applications for analysis by LA-ICP-MS, EPMA, SEM, TEM, and SIMS. The biggest advantage is fixing delicate specimens for easier handling (e.g., cutting, polishing, storage, and transport). One of the few examples used for LIBS analysis of solid specimens was the investigation of the composition of growth layers in stalagmite sections [50]. Changes in elemental composition were clearly visible as the scan proceeded across the layers (see Figure 3). Epoxy embedding for biological samples will be discussed further in Section 5.3.

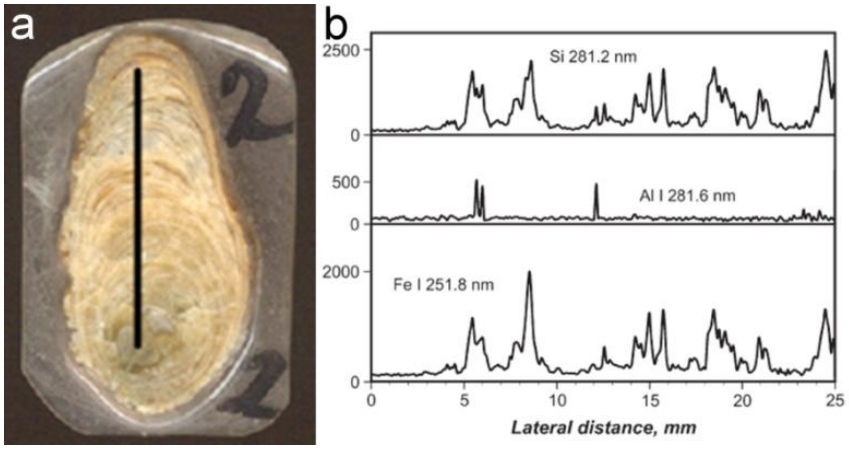

Figure 3. a. A section of a stalagmite with the black line indicating the location of the LIBS raster analysis. b. Signal intensity profiles along the stalagmite for some minor elements. From [50], used with permission.

3.3.3 Adhesives

A simple approach consists of placing specimens, or spreading a thin layer of powder, onto the adhesive surface of a ribbon, tape, or thin layer of glue. Figure 2b shows an example of soil fixed onto double-sided tape, and how the laser removal is localised and quite complete. Depending on the type of adhesive used, the fixation may or may not be permanent. Various other strategies mentioned earlier can be employed in conjunction with the tape-mounting. For example, one group sieved, spiked, and thoroughly mixed soil samples before spreading onto double-sided adhesive tape mounted on a glass cover slip [29]. Analysis by LIBS (and LA-ICP-MS) yielded nearly identical analytical figures of merit to those obtained using pellets made from milled sub-samples of the same specimens. Blank tape was also analysed to determine characteristic tape (background) emissions to monitor [29]. Another group compared tape-mounting to pellets for diluted iron ore, with similar results [51]. Besides tape, an interesting example of adhesive fixing was the collection of various size fractions of airborne particulates from steel-making onto greased aluminum foil substrates for LIBS analysis of toxic elements [52].

4 LIQUID SPECIMENS

Compared to solids, the direct LIBS analysis of liquids, either in the bulk or on the surface of liquids, presents several inherent drawbacks, such as surface ripples, splashing, and shorter plasma duration. The consequences on LIBS analytical performance are often dramatic, especially with respect to measurement repeatability and sensitivity [53-57]. There are basically two strategies for overcoming these difficulties. The first approach consists of finding a more appropriate experimental configuration, such as the used of laminar flows and jets [58-60], droplet and aerosol analysis [60-62], or the use of a double-pulse configuration [55,61,63,64]. The second is to transform the liquid specimen into a solid or “a quasi solid” sample in order to benefit from the advantages of a solid target. This section will focus on liquid-to-solid sample preparation methods used for improving LIBS performance and will review some of the main protocols that have been proposed in the literature. Nanoparticle enhancement of liquids will be discussed in Section 6.3.

4.1 Freezing

The simplest method for transforming a liquid into a solid sample is to freeze it. For example, a comparison was made between a liquid analyzed without sample preparation and the same liquid sample prepared with the following protocol: dilution, agitation (for consistency), then freezing for 30 seconds in liquid nitrogen [65]. Figure 4 illustrates the enhancement obtained in the overall signal (a 6-fold increase in intensity), as well as in the sensitivity of magnesium quantification (a 3.5-fold increase in the slope of the Mg calibration curve).The authors explained this improvement as: better coupling between the laser pulse and the "solid" sample components, which resulted in an increase in the ablation rate and also in higher plasma temperatures and electron densities in ice as compared to liquid water. Another group demonstrated the feasibility of quantitative analysis of sodium and aluminum in aqueous solutions with a quick freezing procedure using liquid nitrogen [66]. Additional advantages of this sample preparation procedure were: a) no pre-enrichment of the solution was required; b) frozen samples were much easier to handle than liquid samples, making possible quantitative analysis with detection limits of the order of a few ppm; and c) no sophisticated fibre-coupling arrangements or alignment procedures were necessary. For the same reasons, a third group recently used this freezing method on treated and untreated sewage [67].

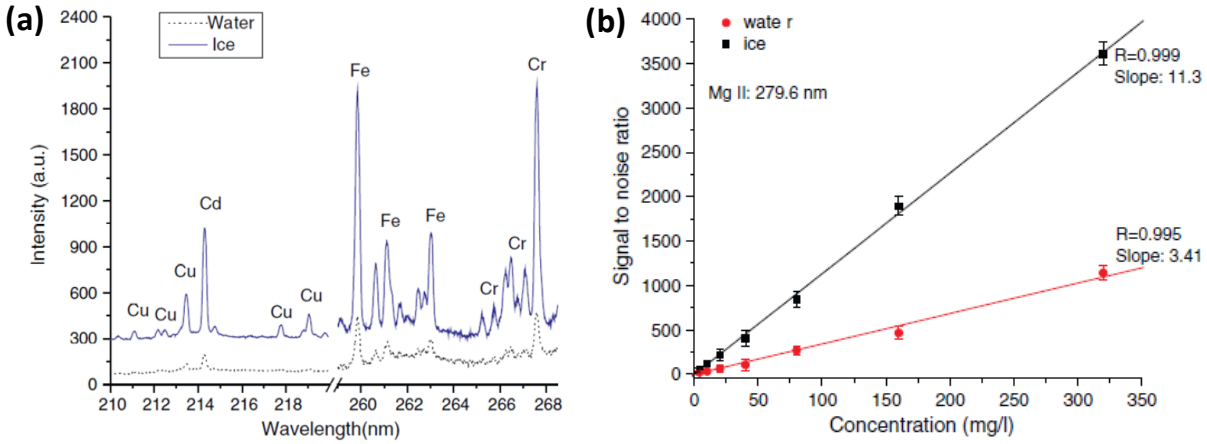

Figure 4.a) Typical LIBS spectra from a 100 ppm multi-element sample obtained from an ice target (dotted line) and a liquid one (solid line). b) A plot of signal-to-noise ratio versus concentration for the Mg II 279.6 nm line obtained from an ice target (black line) and a liquid one (red line). From [65], used with permission.

4.2 Substrate absorption

A simple method that can be used for liquid analysis in a solid matrix configuration consists of using an absorbent substrate. A small volume of solution is deposited onto a porous solid substrate and dried under ambient conditions. The preparation time is only a few minutes, which allows this protocol to be applied on-site. It also has the advantages of significantly improving analytical performance (higher sensitivity due to a better laser-to-solid interaction, little to no matrix effects, and the possibility of applying an internal standard normalization) and ppb-scale LOD can be obtained, if necessary, by repeating the absorption procedure. However the choice of substrate is of strong importance since it must be adapted to the type of liquid to avoid any contamination.

The use of polycarbonate membrane filters has been reported in the literature for the analysis of colloids of heavy metals in water [68]. In this paper, the authors compared different experimental

procedures, such as liquid jet and substrate absorption, demonstrating significant improvements in LOD and measurement reproducibility in the latter case. For quantification of lanthanide elements (Sm, Eu and Gd) in aqueous solution, another group used filter paper as the substrate [69]. A 40 µl aliquot of the solution was transferred drop-wise to the filter paper and was dried with a hot air blower. With this preparation protocol, the authors achieved ppm-scale LODs for these elements. This protocol was also demonstrated for viscous liquids in the analysis of oil standards containing a large number of heavy metals [70]. The oils (approximately 0.6 g) were added drop-wise to filter papers and left for 15 min to spread evenly throughout before analysis. The immersion of a filter paper has also been proposed. For example, a 5 minute immersion in a solution of deionised water containing Ca and Mg provided a more uniform distribution of elements, both on the surface and within the paper, compared to a drop-wise transfer [71]. Another group proposed the immersion of a wood slice (commercially available) in aqueous solutions containing heavy metals [72]. The wood slice was dipped into the aqueous solution for 2 min (enough time to absorb the solution but avoid pre-concentration), taken out and placed on the table for 1 min, and mounted on the sample stage and immediately analysed. The same authors have shown a significant gain in sensitivity using this protocol with an accumulation of 1000 laser pulses, resulting in a lead detection limit of 30 ppb [73].

4.3 Liquid-to-solid matrix conversion

Different preparation methods for converting liquid solutions into solid-matrix samples have been reported in the literature. For the determination of Cr, Pb, Cd and Zn in aqueous solutions, calcium oxide (CaO) was added to form calcium hydroxide ($Ca(OH)_2$), and the precipitate was pressed into pellets [56]. The transformation of liquid oil into a solid tablet has been used by more than one group [74,75]. The procedure involved distillation at 350 °C at atmospheric pressure, followed by vacuum distillation at 550 °C. The resulting solid paste of the residue was heated to 150 °C and the molten material was poured into a special stainless steel mould [74]. Another protocol was developed for converting a heavy residue (liquid petroleum crude oil) into a solid asphaltene tablet [76]. Heavy residues were mixed with n-heptane, heated to 90 °C with continuous stirring, and then slowly cooled down at room temperature to improve precipitation of the asphaltene. The mixture was then filtered and the insoluble material was washed and dried before being converted into pellets using a hydraulic press.

Simple and fast liquid-to-solid conversion methods have also been reported in the literature. One example is the analysis of microdroplets dried on an aluminum metallic substrate [62]. The authors named this approach Surface-Enhanced LIBS and demonstrated a significant emission enhancement compared to the direct analysis of microdroplets suspended from the tip of a microsyringe (see Figure 5). Another fast protocol was based on metal precipitation and membrane separation [77]. In the case of suspended solid in liquids, simple filtration followed by drying of the residue has been used [78].

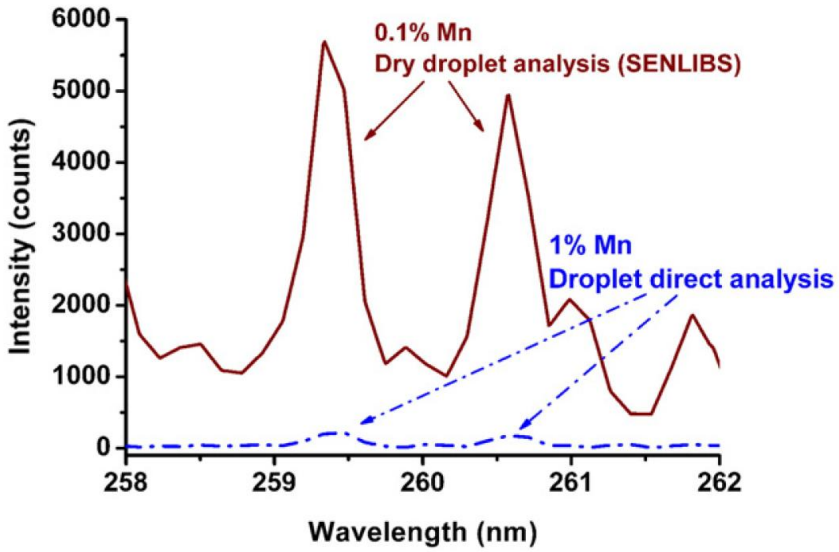

Figure 5. Comparison of LIBS spectra obtained using direct analysis of microdroplets (dash-dot line) and Surface-Enhanced LIBS on aluminum substrate (solid line). From [62], used with permission.

4.4 Liquid layer on solid matrix

In the case of viscous liquids, an alternative indirect method was proposed [79,80]. The authors coated a thin film (~10 μm) of gel-like viscous liquid onto the clean, polished surface of a pure Al target by smearing approximately 2 mL with a glass slide. The resulting LIBS plasma had similar properties to a metallic plasma (i.e., a temperature in the range of 15 000K) and was composed of a mixture of species from the Al target and the viscous liquid. Using this preparation method, the authors demonstrated good analytical performance, with LODs in the range of hundreds of ppb for metals and negligible matrix effects. This indirect method can be applied to a large range of gel-like liquids as long as their viscosity is sufficient for the formation of a uniform thin film on the metallic surface. It has been applied to the analysis of oils [80,81] and, more recently, sunscreen samples [82].

Another thin-coating procedure known as "spin-on-glass" was proposed for the LIBS analysis of slurry samples in order to reduce water content [83]. It involved spreading a liquid on a glass slide using double-sided tape and placing the slide in a spin-coater. By adjusting the rotation speed it was possible to control the coating thickness, sample distribution on the substrate, and moisture removal. The authors demonstrated that the use of this protocol resulted in an improvement in measurement reproducibility and sensitivity over analysis in liquid form.

5 BIOLOGICAL SPECIMENS.

In recent years, the application of LIBS to biology and medicine has grown tremendously [84-86]. This subject is very rich in terms of applications, in part because of the diverse nature of biological specimens, which range from solid or "quasi" solid matrices (e.g., teeth, bones, sea shells) to soft tissue materials (e.g., plants, organs, human skin, vegetables) to liquids (e.g., blood, urine, semen). With the exception of a few specific types of specimens [87-89] or applications [90-92], sample preparation is generally a necessary step for biological applications for several reasons. First, biological materials are generally less "tough" in their texture than

minerals or metals and a matrix transformation can be employed to improve the laser-ablation efficiency and, therefore, the LIBS signal to noise ratio. This is particularly critical when working with soft tissue specimens. Second, biological specimens are generally rather inhomogeneous and a homogenisation procedure needs to be performed in many cases to improve the reproducibility of results. Finally, it is sometimes necessary to fix the specimen simply to ensure its preservation. One point that should be emphasized concerns the preparation protocol, which must be free of any contamination, especially since the elements of interest are in most cases rather common mineral elements, such as Ca, Na, Mg or K.

The preparation of biological specimens is often very similar to solid or liquid preparation methods. For example, many studies used pellets (see Section 3.3.1), mostly for dried plants and vegetables [30,42,93-99], but also for animal tissue [100-102], bacteria [103,104], urinary calculi [105] and milk [106]. This protocol is by far the most commonly used for quantitative biological analysis, since it also allows calibration samples to be prepared relatively easily [30,33,107]. Another example is the freezing procedure (see Section 4.1), which is used for most animal or human soft tissue specimens [108,109]. The last example is the use of a liquid-to-solid matrix conversion for bio-liquids [110-116]. Due to the overlap with solid and liquid preparation protocols already described, this Section will focus mostly on protocols specific to biological specimens. Nanoparticle enhancement of plant material will be discussed in Section 6.3.

5.1 Bacteria

Bacterial pathogens are probably the type of biological specimens that have been the most studied in LIBS. Different sample preparation methods can be found in the literature, such as the use of solid pellets [103,104], or liquid drops deposited and dried on solid substrates like glass slides [113], Petri dishes [117,118], silver filters [116,119], or cellulose filters [112]. Another fairly common method involves analyzing bacteria on an agar-like substrate [120-124]. For example, bacteria were incubated for 24 h, and then thinly smeared onto a 0.7% nutrient-free agar plate [120,121]. The advantages of using such a substrate are as follows: this substrate provided a large, flat area; the bacteria stays hydrated for many hours; the optical emission from this agar does not contribute to the LIBS spectra of the bacteria; the low signal obtained from ablation on blank agar provided a convenient method for determining when the laser had missed the bacteria target; and this straight-forward sample preparation method can also be applied to other liquid (e.g., water, sputum, blood) or mucoid specimens [123]. A similar protocol was used with a bovine blood agar plate, in which bacteria were incubated overnight [125]. In order to spread the colonies over the entire plate surface they used a sterile glass hockey stick. In another paper, the same group proposed a protocol to inoculate bacteria onto different food samples, such as ground beef, lettuce, bologna, eggs, and chicken [126]. Bacterial cultures from an isolated colony were incubated in a soy broth and diluted in autoclaved deionised water for inoculation onto food surfaces. LIBS analysis was performed directly on the food.

5.2 Proteins

Non-invasive detection of cancers can be done through screening of blood for specific protein biomarkers. A novel technique called Tag-LIBS has been developed, in which tags are made by attaching specific antibodies, via avidin-biotin complexing, to nano- and microparticles that are subsequently measured by LIBS [127,128]. When the target antigen is present in a complex

sample matrix, such as blood, it binds with the tag particles via specific antibody-antigen interactions. These particles can be separated from the sample matrix either magnetically (e.g., for magnetite particles) or by microfiltration (e.g., for silicon oxide or titanium dioxide particles), and analysed by LIBS. This method has been employed for the detection of a widely used epithelial ovarian cancer (EOC) biomarker, CA 125, for the diagnosis and monitoring of EOC in human blood specimens. Both titanium dioxide and iron oxide particles were used in a multiplex approach: since both had specific antibodies attached, any CA 125 present in the blood would bind to both, creating a two-element tag (Fe and Ti). Under magnetic separation, only the TiO_2 particles that were bound to the Fe_3O_4 particles via CA 125 would be retained. Washing, agitation, and filtration steps removed non-specific binding, leaving only the two-element tags on the filter, which was dried before LIBS analysis. Femtosecond (fs)-LIBS was used to measure Ti and Fe. A 5-fold improvement over the most sensitive commercially available methods and an estimated near single molecule per particle efficiency was achieved with this method, indicating that it can be used for sensitive detection of ovarian cancer biomarker CA125 in human blood plasma.

Another method for proteins is the dissolution of pure powder in D_2O, followed by freezing to prevent splashing. With the help of spectral deconvolution, this method was applied to the determination of the hydrogen content of bovine serum albumen [129].

5.3 Mapping and space-resolved measurements

Due to their heterogeneous nature, biological tissues are ideal candidates for space-resolved measurements. An approach using LIBS for elemental mapping of biological soft tissues has been proposed [130,131]. Its feasibility was demonstrated by studying the kidney bio-distribution of Gadolinium-based nanoparticles administered intravenously to small animals. In this protocol, the sampled kidneys were frozen at -20 °C, then sliced to a thickness of 150 µm and deposited onto a solid substrate. In order to avoid any signal from the substrate a pure polyethylene microscope slide was used. A more advanced preparation protocol was recently published, in which the organ was fixed in an epoxy resin [132-134]. In this protocol, organ samples were dehydrated in a series of ethanol solutions of increasing concentration, ending with propylene oxide. The samples were then embedded in EPON (1:1 mixture of diglycidyl ether and dodecenylsuccinic anhydride) and prepared using a microtome before LIBS measurements. As shown in Figure 6, the latter protocol significantly improved the LIBS imaging performance, especially with respect to the spatial resolution. Indeed the use of epoxy-embedded specimens offered better ablation control compared with fresh tissue, thus increasing the spatial resolution (typically 100 µm for fresh tissue and 10 µm for EPON-embedded tissue). In addition, quantitative analysis becomes possible, since the resin facilitates the preparation of calibration samples.

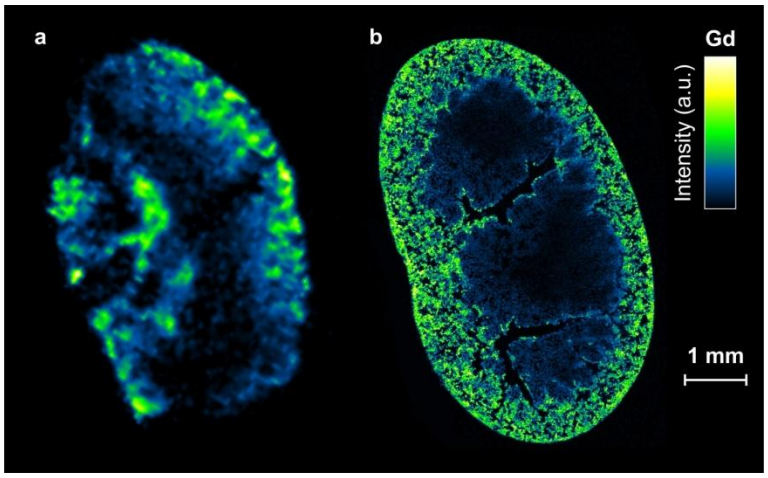

Figure 6.Gadolinium biodistributions in a coronal murine kidney section, 4 hours after nanoparticle administration. a) A 100x100 pixel LIBS map performed on a fresh organ slice of 150 µm thickness with a spatial resolution of 100 µm. Modified from [130], used with permission. b) A 600x410 pixel image obtained from an epoxy-embedded kidney with a resolution of 12 µm.

Many other space-resolved studies can be found in the literature, mainly on plants [34,135-138] and calcified tissues [33,139,140]. However, due to the nature of the specimens and sometimes also to the application requirements, these preparation protocols simply consisted of rinsing the specimen with deionised water.

6 NANOPARTICLE ENHANCED LIBS (NELIBS)

Recently the use of nanoparticles in sample preparation has been proposed for improving the sensitivity of LIBS. Indeed the deposition of nanoparticles on a flat surface allows for the exploitation of plasmonic resonance induced field enhancement for improving the ablation and plasma excitation. Although the potential of this technique still requires further investigation, the effect of nanoparticles on LIBS signals is significant. Enhancements of LIBS LODs have been reported in the case of metals and several substrate types for which LIBS does not always give good results. Some examples of nanoparticle enhanced LIBS (NELIBS) applications are discussed below.

6.1 Metals

Besides the signal enhancement, another advantage is that deep sample manipulation is not required. The sample preparation required is basically to deposit a 1 µl drop of colloidal suspension of nanoparticles on the metallic specimen surface. If the nanoparticle surface concentration reaches a certain value (generally on the order of 10^3 mg/cm^2 in the case of 20 nm diameter nanoparticles), the inter-particle distance becomes effective for allowing constructive interference of the plasmonic oscillation. Under this condition the incident laser electromagnetic field is strongly enhanced to several orders of magnitude allowing electrons to escape by electron emission field. The main effect is that several seed electrons are instantaneously produced, allowing multi-point plasma ignition and, in turn, a more efficient ablation. In the case of

metallic samples, an enhancement of the signal up to 2 orders of magnitude has been observed [141,142].

6.2 Glass substrates

Nanoparticles can even be exploited for LIBS analysis of glass with minimal damage. As with the metal substrates, nanoparticles can be deposited on the specimen surface by drying a drop of a colloidal solution. In this case, however, a higher concentration of nanoparticles is required on the surface. Because the glass is not conductive, the initial electron ejection does not directly involve the glass substrate, which preserves it from laser ablation effects and cracking; the irradiation and subsequent explosion of nanoparticles involve the glass substrate layers adjacent to the nanoparticles transferring the glass material into the laser induced plasma. This technique, thanks to the "secondary" ablation of the glass, allows LIBS analysis of glass without any visible damage [De Giacomo et al, in preparation].

6.3 Liquid solutions and fresh specimens

Nanoparticles can also be used to furnish a suitable matrix for liquid solutions and fresh specimens (e.g., tissue, leaves, and vegetables). In the case of liquid solutions, nanoparticles are deposited on an inert substrate (Teflon, silicon etc.) in order to form a thin matrix where a drop of sample solution is loaded on and then dried. Figure 7 is an example of the detection of silver in an aqueous solution of $AgNO_3$, with and without nanoparticle enhancement. It is interesting that with this technique it is possible to quantify sub-ppb concentrations of silver in a 1 µl drop, while with conventional LIBS the LOD is on the order of hundreds of ppb. The same technique has been applied to a protein solution for the detection of Li after a dialysis process and, even in this case, a strong enhancement of the signal was noted. This is significant because proteins are generally a difficult specimen type for LIBS analysis as a consequence of the strong quenching effect of this kind of organic specimen on plasma parameters.
Similar effects may be observed in fresh leaves [143] and tissue, where the nanoparticle enhancement decreases the ablation threshold and feeds the plasma with lower ionization energy species (i.e., the metal atoms that constitute the nanoparticle itself) [144].

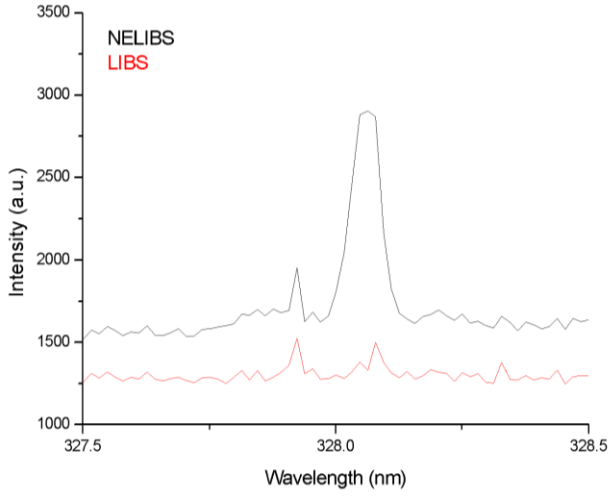

Figure 7. Emission signal of Ag I from 1 µl of 5 x 10^{-7} M solution of AgNO3 by LIBS (red line) and NELIBS (black line). Laser irradiance was 0.8 $W.cm^{-2}$. 1 µl of 0.03 mg/mL 10 nm gold nanoparticles was used for NELIBS.

7 CONCLUSION

There is an array of sample preparation methods, for a variety of specimen types, with various levels of difficulty. Some are borrowed from other analysis techniques and others are novel and designed specifically for LIBS. The use of sample preparation methods has various advantages, from ease of manipulation to improvement of the quality of the LIBS data.

All other "gold standard" analytical techniques, including ICP and XRF, rely on rigorous sample preparation protocols. Sample preparation for LIBS may be the "elephant in the room"; not considering sample preparation for LIBS may be one of the main reasons that LIBS is still not considered a mature technique despite more than 50 years of successful applications. Ironically, many LIBS papers in which extensive sample treatment is used to gain excellent results continue to list "no sample preparation required" in the introduction as an advantage of LIBS.

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